Rocky Mountain Conference on Magnetic Resonance

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Article 1

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40th Rocky Mountain Conference on Analytical Chemistry

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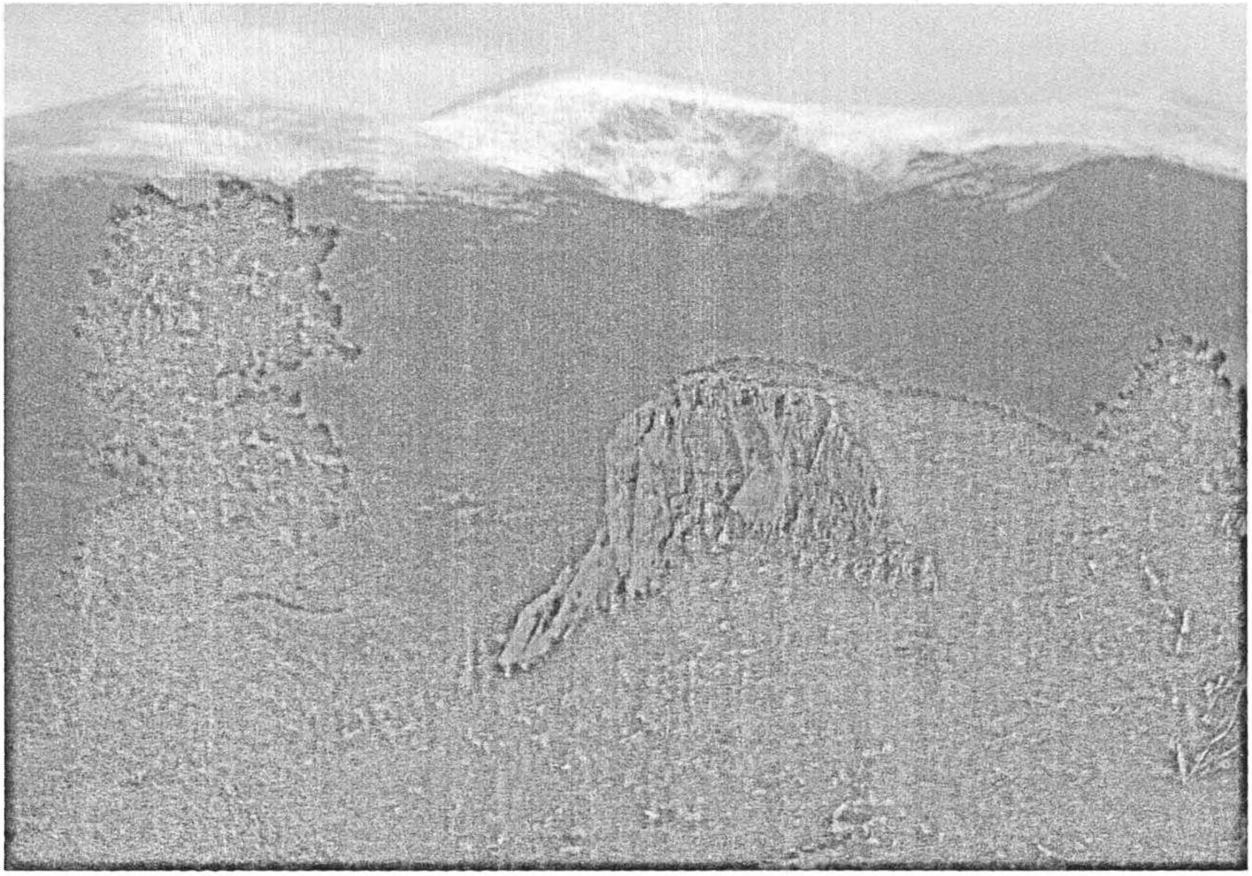
40TH ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY



FINAL PROGRAM AND ABSTRACTS

July 25-Aug. 1,1998

HYATT REGENCY DENVER
1750 WELTON STREET
DENVER, COLORADO

SPONSORED BY:

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

SYMPOSIA SCHEDULE

Room	Sunday 7/26/98		Monday 7/27/98		Tuesday 7/28/98		Wednesday 7/29/98		Thursday 7/30/98	
	am	pm	am	pm	am	pm	am	pm	am	pm
Grand Ballroom			EPR	EPR	EPR	EPR	EPR	EPR	EPR	
Grand Foyer			EPR Posters	EPR Posters	EPR Posters	EPR Posters	EPR Posters	EPR Posters	EPR Posters	
Moulin Rouge			NMR	NMR	NMR	NMR	NMR	NMR	NMR	
Florentine			NMR Posters	NMR Posters	NMR Posters	NMR Posters	NMR Posters	NMR Posters	NMR Posters	
3rd Floor Foyer			NMR Posters	NMR Posters	NMR Posters	NMR Posters	NMR Posters	NMR Posters	NMR Posters	
Far East				Environ. Chem.	Environ. Chem.	Environ. Chem.	Pharm.	Pharm.		
Royal			Electro. Chem.	Electro. Chem.	Pharm.	Pharm.	Mass Spec	Mass Spec		
Gold			Speaker Prep.	Speaker Prep.	Speaker Prep.	Speaker Prep.	Speaker Prep.	Speaker Prep.	Speaker Prep.	
Pavilion			Lumin.	Lumin.	Atomic	Atomic	ICP-MS	ICP-MS		
Parisienne			Radio-chem.	Radio-chem.	Radio-chem.	Radio-chem.			Environ. Sampl.	Environ. Sampl.
Vista						Laser & Material			Comp. Oper.	Comp. Oper.
Imperial Ballroom	Exhibits setup	Exhibits setup	Exhibits	Exhibits	Exhibits	Exhibits	Exhibits			
Imperial Foyer			General Posters	General Posters	General Posters	General Posters	General Posters	General Posters		

Room locations may be found on the map on the back cover of this program.

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Symposia Schedule:

Abstracts start after page 36. 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.

SHORT COURSE SCHEDULE

	Thursday 7/30/98	
	AM	PM
ENVIROMENTAL SAMPLING	X	X
COMPUTER OPERATIONS	X	X

CONFERENCE LOCATION

Technical sessions and the exhibition for the 40JH Rocky Mountain Conference on Analytical Chemistry will be held in the Hyatt Regency Denver Hotel, 1750 Welton Street, Denver, Colorado 80202.

SYMPOSIA ORGANIZERS

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ORGANIZERS OF THE 40TH ROCKY MOUNTAIN CONFERENCE

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Web Site: rockychem.com

UPCOMING CONFERENCE DATES

August 1-5,1999 Hyatt Regency Denver

REGISTRATION

Admission to all technical sessions, vendor sponsored users groups and the exhibition is by the name badge for the 40TH Rocky Mountain Conference. The deadline for **receipt** of the pre-registration form and full remittance of the conference fees is July 15, 1998. Conference fees are payable by check (denominated in $US, only drawn on a U.S. Bank) made payable to the Rocky Mountain Conference. Visa and Mastercard are accepted, as well.

REGISTRATION FEES -1998

(See back pages for Registration Form)

REGISTRATION FEES (U.S. $ draw on U.S. bank)	**Preregistration** (payment recd, by 7/15/98)	**On Site**
Regular (entire conference and exhibition)	$105.00	$125.00
One Day (specify day: M, T, W, R) includes exhibition	$60.00	$ 75.00
Retired / Unemployed	$30.00	$ 40.00
Full Time Student - Regular (includes exhibition)*	$30.00	$ 40.00
Student - One Day (specify day: M, T, W, R) includes exhibition*	$20.00	$25.00
Additional Vendor (beyond 3)	$50.00	$ 50.00
Exhibition Only (non-vendor)	$15.00	$ 15.00
Environmental Sampling Short Course	$225.00	$275.00
Basic Computer Operations and Management	$225.00	$275.00

*Legible copy of student ID must accompany registration form.
REFUNDS: Requests for refunds of conference fees must be **received** by July 25, 1998.

REGISTRATION TIMES

On-site registration for the 40TH Rocky Mountain Conference will be held in the Imperial Ballroom Foyer of the Hyatt Regency Denver during the following hours:

Sunday, July 26	4:00 p.m. - 8:00 p.m.
Monday, July 27	7:30 a.m. - 3:30 p.m.
Tuesday, July 28	7:30 a.m. - 3:30 p.m.
Wednesday, July 29	7:30 a.m. - 3:30 p.m.
Thursday, July 30	8:00 a.m. - 12:00 p.m.

ACCOMMODATION FOR DISABILITIES

If you have a disability and may require accommodations in order to fully participate in this activity, please contact the registration desk We ask your cooperation in notifying us as soon as possible of your need for accommodation. While every effort will be made to meet attendees' needs, we cannot guarantee the availability of accommodations in response to requests received after July 15, 1998.

SOCIAL PROGRAM AT THE HYATT REGENCY DENVER

SCHEDULE OF EVENTS

Sunday, July 26	Registration Mixer	4:00 p.m. - 8:00 p.m.
Monday, July 27	Exhibition	10:00 a.m. - 5:00 p.m.
Monday, July 27	General Posters	3:00 p.m. - 5:00 p.m.
Monday, July 27	Conference Reception	5:00 p.m. - 7:00 p.m.
Tuesday, July 28	Exhibition	9:00 a.m. - 5:00 p.m.
Wednesday, July 29	Exhibition	9:00 a.m. - 2:00 p.m.

REGISTRATION NIGHT MIXER

A cash bar will be open in the Imperial Ballroom Foyer of the Hyatt Regency Denver on Sunday evening, July 26, from 4:00 - 8:00 p.m. Plan to meet other conference attendees and beat the Monday rush to pick up your conference badge and final program.

CONFERENCE RECEPTION

On Monday evening, July 27, from 5:00 to 7:00 p.m., all attendees are cordially invited to join us for cocktails and hors d'oeuvres at the Hyatt Regency in the Imperial Ballroom. The exhibition will be open this evening and submissions from the General Poster session will be available for viewing.

HOTEL ACCOMMODATIONS

(See back pages for Reservation Form)

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 $120 per night (single or double), plus applicable tax.** Please identify yourself as a Rocky Mountain Conference attendee when making reservations to receive this discounted rate. Please see the Hyatt hotel reservation form in the back of this program for more information. Return this form directly to the hotel. **The conference and associated social functions for the conference will be held at the Hyatt Regency Denver.**

Reservations must be received by the hotel prior to **July 3,1998** and before the group reservations block is filled to assure your room accommodations. Reservations requested beyond the cut off date are subject to availability. Rooms may still be available after the cutoff date but not necessarily at the above rate. All reservations are subject to appropriate state, local, and room tax.

TRAVEL SERVICES

Arrangement for air travel and other local travel can be made though **Twin Peaks Travel** the official travel agency of the conference. They may be contacted at (800) 894-8651 (Ask for Jody or Beth). Special discounts have been arranged for conference travelers.

VISITOR INFORMATION

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

MESSAGE CENTER

Incoming telephone messages for conferees will be posted on the Conference Message Board, near the conference registration booth. The telephone number s (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.

JOIN THE ROCKY MOUNTAIN CONFERENCE

The Rocky Mountain Conference Organizing Committee is looking for volunteers! We are looking for additional Symposium Chairpersons and organizing committee staff. Money is available to support new symposia for start-up costs. Please contact Steven Hughes (303) 415-2073 if you are interested in helping make a great conference even better.

SHORT COURSES

(Sponsored by the 40th Rocky Mountain Conference)

Environmental Sampling to Meet Regulatory Compliance **July 30, 1998**
(8:30 AM to 4:30 PM)
Fee: $225 preregistration $275 on-site
Faculty: John R. Dick

The course presents sample management techniques for environmental and /or regulatory compliance sampling. The exploration of this topic shows six major areas to be discussed. In Project Planning: Sample and Analysis plans, DQO Development, Lab Selection, Laboratory Contracting, and Costs will be investigated. The pros and cons of field sampling by the client or a subcontractor will come to light in Sample Collection. In Laboratory Analysis the importance of Audits, Standard Operating Procedures and Method Selection will be shown. The pitfalls in Sample Transportation will cover: RAD Screening On-site, Packaging, Shipping, Return of Unused Samples, and Lab-Generated Waste. The section on Receipt of Analytical Data will guide you step by step through Data Verification, Data Validation and Data Quality Assessment. The final section on Record Management and Reporting demonstrates *"the job is not complete until the paperwork is done."* The overall philosophy of the course is to allow you to control quality and spend the least amount of time and money on your sampling and analysis.

Basic Computer Operations and Management **July 30, 1998**
(8:30 AM to 4:30 PM)
Fee: $225 preregistration $275 on-site
Faculty: Richard Archambeau

Alternate course title: *What to do until the computer repair person arrives!!* This course addresses the importance of understanding the hardware in your computer. Beginning with a fundamental discussion of the functions and practices that are essential to the operation of your computer, the course will expand to cover items such as basic hardware, internal architecture, trouble shooting, minor repairs, parts replacement, and system upgrades. An in-depth description covering the importance of regular backups and how to make this as painless as possible is presented. Attendees will learn how to develop better computer practices essential to improved performance.

For short course information contact:
John R. Dick, PhD
JR Dick & Associates
9160 Sugarloaf Rd
Boulder CO 80302

EXHIBITORS FOR THE 1998 ROCKY MOUNTAIN CONFERENCE

The following exhibitors will be in attendance,
(as of July 10,1998)

Allen Scientific Glass
1752-55th St
Boulder, CO 80301

Bruker Instruments Inc.
Fortune Dr.
Manning Park
Billerica, MA 80211

Doty Scientific Inc.
700 Clemson Rd.
Columbia, SC 29229

Finnigan/ ThermoQuest
355 river Oaks Pkwy
San Jose, CA 95134

JEOL
11 Dearborn Rd.
Peabody, MA 1960

MR Resources, Inc.
158RMain St.
P.O. Box 880
Gardner, MA 01440

Oxford Instruments Inc
BOA Baker Ave. Ext.
Concord, MA 01742

Perkin-Elmer
761 Main Ave.
Norwalk, CT **06859-0235**

Resonance Research
778 Praderia Cr.
Freemont, CA **94539** **Shimadzu**
9282 S. Princeton St.
Highlands Ranch, CO **80126**

Tekmar-Dohrmann
7143 E. Kemper
Cincinnati, OH **45249**

Thermo-Jarrell Ash
27 Forge Parkway
Franklin, MA **2038**

Varian Associates Inc.
811 Hansen Way
Palo Alto, CA **94304**

VG Elemental
1812 Mapleton Ave.
Boulder, CO **80304**

Waters Corporation
41239 Madrid Drive
Parker **80139,** CO **80139**

Wilmad Glass
PO Box **688**
Buena, NJ **08310**

EXHIBIT INFORMATION FOR THE 1998 ROCKY MOUNTAIN CONFERENCE

Exhibit Hours:

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

VENDOR WORKSHOPS

Vendor workshops to be announced at exhibitor booths.

Notes:

Notes:

40TH ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY TECHNICAL PROGRAM

SYMPOSIUM ON ATOMIC AND INORGANIC-MASS SPECTROMETRY

Organized by Howard E. Taylor

Tuesday, July 28,1998

Morning Session: Atomic Spectrometry, Session I, Howard E. Taylor, Presiding

10:00 **Introduction,** H.E. Taylor

10:10 1. **KEYNOTE LECTURE** — ***ATOMIC SPECTROSCOPY: PROGRESS AND PROSPECTS,*** Akbar Montaser, George Washington University

10:55 Break

11:15 2. ***DETERMINATION OF WEAR AND ADDITIVE ELEMENTS IN OILS BY ICP-AES WITH A CID ARRAY DETECTOR,*** Bulman, F.D. and G.N. Coleman, G.R. Dulude, R.W. Pascucci and R.L. Stux, Thermo Jarrell Ash Corp.

11:45 3. ***ION AND ATOM ABSORPTION MEASUREMENTS IN AN AXIAL INDUCTIVELY COUPLED PLASMA,*** C. E. Hensman and G.D. Rayson, New Mexico State University

Afternoon Session: Atomic Spectrometry, Session II

1:30 4. ***A PSEUDO-FLOW INJECTION SYSTEM FOR THE ANALYSIS OF MAJOR AND TRACE METALS BY AXIAL ICP-AES,*** R.C. Antweiler and H. E. Taylor, U.S. Geological Survey

2:00 5. ***SOLID STATE DETECTORS IN ATOMIC SPECTROSCOPY: PART I,*** R.L. Hergenreder, Perkin Elmer Corp.

2:30 6. ***SOLID STATE DETECTORS IN ATOMIC SPECTROSCOPY: PART II,*** R.L. Hergenreder, Perkin Elmer Corp.

3:00 Break

3:30 ***7. A NEW VIEW OF CCD DETECTORS FOR SIMULTANEOUS ICP-AES,*** M. Cole, D. Shrader and G. Russell, Varian Corp.

4:00 8. ***REAL TIME ANALYSIS OF METALS IN STACK GASES USING ARGON/AIR ICP OPTICAL EMISSION SPECTROMETRY,*** G.A. Meyer and G.N. Coleman, Thermo Jarrell Ash Corp.

4:30 9. ***THE USE OF COLD-VAPOR ATOMIC FLUORESECENCE SPECTROMETRY FOR THE DETERMINATION OF TRACE MERCURY CONCENTRATIONS IN SACRAMENTO RIVER WATERS AND SEDIMENTS,*** D.A. Roth, H. E. Taylor, R.A. Antweiler, D.B. Peart, P. Dileanis and C.N. Alpers, U.S. Geological Survey

Wednesday, July 29,1998

Morning Session: ICP/MS, Session I, Howard E. Taylor, Presiding

9:00 ***Introduction,*** H. E. Taylor

9:05 10. ***MICRONEBULIZERS AND AEROSOL DIAGNOSTIC METHODS IN ICP MASS SPECTROMETRY: WHAT ARE THE NEEDS ?,*** A. Montaser, J. A. McLean, M.G. Minnich and L.A. Iascone, George Washington University.

9:40 11. ***DESIGN PHILOSOPHIES AND PERFORMANCE CHARACTERISTICS OF A NEW HIGH RESOLUTION ICP-MS WITH OPTIONAL MULTICOLLECTION CAPABILITY,*** M.K. Donais, P. Marriot, D. Koller, VG Elemental.

10:10 Break

10:30 12. ***TIME OF FLIGHT INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY IN THE REAL WORLD: SOLVING REAL ANALYTICAL PROBLEMS AND BREAKING THROUGH BARRIERS,*** L. Allen and S. Georgitis, LECO Corp.

11:00 13. ***THE OPTIMIZATION OF ICP-MS WITH A HYDROGEN CONTAINING PLASMA,*** U. Carmi, Analytical Lab, Nuclear Research Center - Negev, Israel and H.E. Taylor, U.S. Geological Survey.

11:30 14. ***HIGH VOLUME, HIGH PRODUCTIVITY ANALYSIS OF TRACE METALS IN DIFFICULT MATRICES BY ICP-MS USING EPA METHOD 6020,*** S. Wilbur, Hewlett-Packard Co.

Afternoon Session: ICP/MS, Session II

1:30 15. ***THE ESTABLISHMENT OF A RARE-EARTH STANDARD REFERENCE MATERIAL,*** R.C. Antweiler, H.E. Taylor, P. Verplanck, D.K. Nordstrom, T.L Brinton, D.A. Roth, D.B. Peart and A. Meier, U.S. Geological Survey.

2:00 16. ***IMPROVED SAMPLING TECHNIQUES FOR THE DETERMINATION OF LOW-LEVEL TRACE ELEMENT CONCENTRATIONS IN GROUND WATER,*** T. Ivahnenko and Z. Szabo, U.S. Geological Survey.

2:30 17. ***ICP-MS STUDIES OF COPPER ISOTOPE EXCHANGE IN RHUS Vernicifera laccase,*** C. Miller and J.A. Dunn, John Carroll University

3:00 Break

3:30 18. ***LASER ABLATION ICP-MS: A NEW PERSPECTIVE,*** T.G. Howe, CETAC Technologies.

4:00 19. ***A STATISTICAL ANALYSIS OF ELEMENTAL CONCENTRATIONS MEASURED IN HBR USING THE ICP/MS TECHNIQUE,*** J.O. Proctor and G.W. Johnson, Matheson Gas Products.

4:30 20. ***DETERMINATION OF FOUR ARSENICALS IN NATURAL WATER SAMPLES BY HPLC-HYDRIDE GENERATION-ICPMS,*** J.R. Garbarino, U.S. Geological Survey

SYMPOSIUM ON ELECTROCHEMISTRY

Organized by C. Michael Elliott

Monday, July 27,1998

Morning Session

8:30 21. *THE STRUCTURAL CHARACTERIZATION, ELECTROCHEMICAL REACTIVITY AND RESPONSE STABILITY OF HYDROGENATED GLASSY CARBON ELECTRODES.* Qingvun Chen, and Greg M. Swain, Department of Chemistry & Biochemistry, Utah State University, Logan, UT 84322-0300.

8:55 22 *EFFECTS OF* ***SI0***$_2$ *OVERLAYERS ON ELECTRON TRANSFER AT N-SI ELECTRODES,* Markus D. Groner. and Carl A. Koval, University of Colorado, Dept. of Chemistry, CB 215, Boulder, CO 80303.

9:20 23. *THE EFFECTS OF SURFACE PRETREATMENT OF BORON DOPED DIAMOND THIN FILM ELECTRODES,* Michael C. Granger, and Greg M. Swain, Utah State University, Department of Chemistry and Biochemistry, Logan, UT 84322-0300.

9:45 24. *NEW APPROACHES TO LITHIUM BATTERY CATHODE MATERIALS,* Kevin White. Eiichi Shoji, and Daniel A. Buttry, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.

10: 10 25. *WHERE DOES ELECTRON TRANSFER OCCUR AT LIQUID-LIQUID INTERFACES? RECYCLING AN OLD (BUT GOOD) MECHANISTIC TOOL,* Carl A. Koval. and Heather Oswald, Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215.

10:35 Break

10:45 26. *MECHANISTIC INSIGHTS INTO A THIOL-DISULFIDE REDOX PROCESS PROVIDED BY ELECTROCHEMICAL SIMULATION,* Eiichi Shoji. and Daniel A. Buttry, Dept. of Chemistry, University of Wyoming, Laramie, WY 82071-3838.

11:10 27. *THERMODYNAMIC STUDIES OF ELECTRON TRANSFER AT LIQUID-LIQUID INTERFACES,* Heather C. Oswald. Torri L. Derback, and Carl A. Koval, Department of Chemistry & Biochemistry, Campus Box 215, University of Colorado, Boulder, CO 80302.

11:35 28. *ROTATING RING-DISK ELECTROCHEMICAL STUDY OF ION TRANSPORT IN POLY(PYRROLE)/POLY (STYRENESULFONATE) CONDUCTING POLYMER FILMS,* Corey A. Salzer. and C. Michael Elliott, Colorado State University, Department of Chemistry, Box #102, Ft. Collins, CO 80523.

Afternoon Session

1:30 29. *AMPEROMETRIC DETECTION COUPLED WITH FLOW INJECTION ANALYSIS USING BORON-DOPED DIAMOND THIN FILM ELECTRODES,* Jishou Xu. and Greg M. Swain, Utah State University, Department of Chemistry and Biochemistry, Logan, UT 84322-0300.

1:55 30. *HYDRODYNAMICALLY ASSISTED MINIATURIZED ELECTROCHEMICAL DETECTORS FOR HEAVY METALS,* Michael T. Carter. Eric D. Cravens, and Ross C. Thomas, Eltron Research, Inc., 5660 Airport Blvd., #105, Boulder, CO 80301-2340.

2:20 31. *In situ* *NMR ANALYSIS OF CHARGE CARRIERS IN POLYMER ELECTROLYTES,* R. E. Gerald. II, R. J. Klingler, Jerome W. Rathke, Giselle Sandi, and Klaus Woelk, Chemical Technology and Chemistry Divisions, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439-4837.

2:45 32 *INTERFACIAL CAPILLARY ELECTROPHORESIS AT ELECTRODE SURFACES,* Guoying Chen. Christine Thetford, Lorna Hunter, Rich Martoglio, Shauna Hiley, and Daniel A. Buttry, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.

3:10 33. *FABRICATION AND ANALYSIS OF NOVEL FACILITATED TRANSPORT MEMBRANES,* David T. Mitchell. Brinda B. Lakshmi, and Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

3:35 Break

3:45 34. *ELECTROCHEMICAL AFM STUDIES OF GLASSY CARBON AND BORON-DOPED DIAMOND THIN-FILM SURFACES DURING ANODIC POLARIZATION,* Jian Wang, and Greg M. Swain, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300.

4:10 35. ***RATE CAPABILITY OF NANOSTRUCTURED V_2O_5 ELECTRODES PREPARED VIA THE TEMPLATE METHOD USING A SOL-GEL PRECURSOR,*** Charles J. Patrissi. and Charles R. Martin, Department of Chemistry, Colorado State University, Ft. Collins, CO 80523.

4:35 36. ***RUTHENIUM (II) POLYPYRIDINE BASED ELECTROCHEMILUMINESCENT POLYMERS,*** Corey J. Bloom. C M . Elliott, Francois Pichot, and Lonn S. Rider, Department of Chemistry, Colorado State University, Ft. Collins, CO 80523-1872.

5:00 37. ***pH-SWITCHABLE PERMSELECTIVE GOLD NANOTUBULAR MEMBRANES,*** Kshama B. Jiarge. and Charles R. Martin, Department of Chemistry, Colorado State University, Ft. Collins, CO 80523.

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

Organized by Maria W. Tikkanen
Financial Support provided by Finnigan MAT

Monday, July 27,1998

Afternoon Session: Edward T. Furlong, Presiding

1:20 ***Opening remarks***

1:30 INVITED SPEAKER IN ENVIRONMENTAL MASS SPECTROMETRY
Sponsored by Finnigan MAT.
38. ***DO YOU KNOW WHAT'S IN YOUR DRINKING WATER - IDENTIFICATION OF NEW DISINFECTION BY-PRODUCTS (DBPS).*** Susan Richardson, US Environmental Protection Agency, 960 College Station Road, Athens, GA, 30605

2:30 39. ***OVERVIEW OF A VAILABLE METHODS FOR DISINFECTION BY-PRODUCTS MEASUREMENTS,*** Kenan Ozekin, American Water Works Association Research Foundation, ***6666*** W. Quincy Avenue, Denver, CO 80235. (tentative)

2:50 40. ***THE ANALYSIS OF SEMI-VOLA TILE ORGANIC COMPOUNDS WITH EXTERNAL IONIZA TION ION TRAP GC-MS.*** James B. Edwards, John D. Ragsdale III, and Steven T. Fannin, Finnigan Corporation, 2215 Grand Avenue Parkway, Austin TX 78728.

3:10 41. ***POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN RESERVOIRS SEDIMENTS: GEOCHRONOLOGICAL INDICATORS OF URBANIZATION*** Edward T. Furlong(l). Peter C. VanMetre (2), Edward.C. Callender (3), and Mary C. Olson (1). U.S. Geological Survey, (1) 5293 Ward Road, Arvada, CO 80002, (2) 8011 Cameron Road, Austin, TX 78754, and (3) 2201 Sunrise Valley Drive, MS 432, Reston, VA 20192

3:30 Break

3:50 42. ***QUALITATIVE AND QUANTITATIVE ANALYSIS OF PESTICIDES ON AN ION-TRAP MASS SPECTROMETER.*** Dieter M. Drexler, Sibylle M. Wilbert, Fredrick Q. Bramble, and Stephen C. Werness, ThermoQuest Finnigan, 355 River Oaks Parkway, San Jose, CA 95134.

4:10 43. ***METABOLITE STRUCTURE ELUCIDATION BY USE OF ADVANCED FEATURES OF AN ION-TRAP MASS SPECTROMETER.*** Stephen C. Werness, Steven R. McGown and Raymond C. M. Lau, BASF, Agricultural Products Center 26 Davis Drive, Reasearch Triangle Park, N.C., 27709.

Tuesday, July 28,1998

Morning Session: Maria W. Tikkanen, Presiding

8:30 **Opening remarks**

8:35 ***INVITED SPEAKER IN ENVIRONMENTAL CHEMISTRY***
44. ***TRACE METALS PERSISTENT, ORGANIC POLLUTANTS AND MARINE MAMMALS.*** Paul Becker, NIST, Charleston Laboratory, 219 Fort Johnson, Charleston, S.C. 29412.

9:35 45. ***ZINC PRECIPITATION RUNOFF FROM THERMAL-SPRAYED STRUCTURES.*** S. Matthes, S. Cramer, B. Covino, Jr., G. Holcomb, S. Bullard, Albany Research Center, U.S. Department of Energy, Albany, Oregon 97321-2198.

9:55 46. ***MTBE IN DRINKING WATER RESERVOIRS-MARINE ENGINE EMISSIONS?*** M.W. Tikkanen, R. G. Sykes, R. Hunsinger, R. Berger, and M. Wallis, East Bay Municipal Utility District, 375 11th Street, Oakland, CA 94607.

10:15 Break

10:35 47. ***ATOMIC FORCE MICROSCOPY FOR PHYSICAL AND CHEMICAL CHARACTERIZATION OF NANOMETRIC ENVIRONMENTAL PARTICULATES.*** Kathryn A. Ramires-Aguilar, Amy E. Michel, David

W. Lehmpuhl, John W. Birks, and Kathy L. Rowlen, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215.

10:55 48. ***CHROMIUM SPECIATION USING AN AUTOMATED LIQUID HANDLING SYSTEM WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRIC DETECTION*** Mary Kate Donais, Rob Henry, Tom Rettberg, VG Elemental, 27 Forge Parkway, Franklin, MA 02038.

11:15 49. ***STRATEGIES FOR REVERSIBLE DETECTION OF HYPERGOLIC FUELS IN AIR*** Michael T. Carte , and Jimmy R. Smith, Eltron Research, Inc., 5600 Airport Blvd., #105, Boulder, CO 80301-2340.

11:35 To be announced

Afternoon Session: Maria Tikkanen, Presiding

1:30 50. ***MULTIELEMENT BINDING OF HEAVY METALS BY PLANT MATERIALS.*** Gary Rayson, and Patrick A. Williams, New Mexico State University, Box 30001, MSC 3C, Las Cruces, N.M., 88003.

1:55 51. ***WHOLE BODY ROTENONE RESIDUE DETERMINATION IN THE BROWN TREE SNAKE (BOIGA IRREGULARIS).*** Richard E. Mauldin, John J. Johnston, and Carol A. Furcolow, National Wildlife Research Center, 3350 Eastbrook Drive, Fort Collins, CO 80525.

2:15 52. ***HOW AUTOMATING EPA-SW 846 METHOD 3050B FOR SOILS, SEDIMENTS AND SLUDGES CAN SAVE YOUR LABORATORY TIME AND MONEY.*** Robert L. Lockerman, Greg Leblanc and Gus Obleada, CEM Corporation, P.O.Box 200, Matthews, NC 28106.

2:35 53. ***MODIFIED CLAYS FOR ABATEMENT OF NOx FROM HIGH TEMPERATURE PROCESSES.*** Antonio S. Lara and Alba Yadira Corral, New Mexico State University, Box 30001, MSC 3C, Las Cruces, N.M. 88003.

2:55 Break

3:15 54. ***DETERMINATION OF SUBMICROGRAM-PER-LITER CONCENTRATIONS OF CAFFEINE IN SURFACE- AND GROUND-WATER SAMPLES BY SOLID-PHASE EXTRACTION AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY*** Paul P. Soliven. Mark R. Burkhardt, Stephen L. Werner, and Deborah G. Vaught, United States Geological Survey, National Water Quality Laboratory, MS 407, Denver Federal Center, Denver, CO 80225-0046

3:35 55. ***APPLICATION OF THE DUH-HAYMET-HENDERSON CLOSURE OF THE OZ EQUATION TO THE INTERPRETATION OF INTERACTION-INDUCED RAMAN LIGHT SCATTERING OF BINARY SUPERCRITICAL FLUID MIXTURES***-Frank G. Baglin. Susan K.Murray, Jill Daugherty and Wayne Stanbery, Chemical Physics Program, University of Nevada, Reno Nv. 89557

3:55 56. ***OXIDATION OF SELF-ASSEMBLED DECANETHIOL MONOLAYERS.*** Matthew M. Ferris. Kathy L. Rowlen, Karen L. Norrod, Department of Chemistry and Biochemistyr, University of Colorado, Boulder, Colorado 80309

Program for 21^{st} International EPR Symposium

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Sunday, July 26, 1998 - Open House at the University of Denver

5:45 pm Meet in hotel lobby for bus transportation.

- Bruker will present a brief overview of highlights of their exhibit.
- A buffet supper will be provided, compliments of Bruker.
- There will be demonstrations and exhibits of our spectrometers.

Monday, July 27,1998

Session I, New Spin-Labeling Methods, P. Fajer presiding

8:30 Opening Remarks and Welcome, Sandra S. Eaton

8:35 ***Presentation of International EPR Society Young Investigator Award to Alex Smirnov***

8:40 57. ***MONITORING STRUCTURAL CONFORMATIONS IN PROTEINS AND MEMBRANES WITH HIGH RESOLUTION AT 95 GHZ,*** A. I. Smirnov. R. B. Clarkson, and R. L. Belford, University of Illinois.

9:10 58. ***MOLECULAR DISTANCES FROM DIPOLAR COUPLED SPIN-LABELS,*** E. J. Hustedt and A. H. Beth, Vanderbilt University.

9:40 59. ***TIME-DOMAIN MEASUREMENTS OF METAL-NITROXYL DISTANCES,*** S. S. Eaton and G. R. Eaton, University of Denver.

10:05 Break

10:35 60. ***TOWARDS SOLVING THE PUZZLE OF LENS a-CRYSTALLIN STRUCTURAL INSIGHT FROM SITE-DIRECTED SPIN LABELING STUDIES,*** H. S. Mchaourab. Medical College of Wisconsin.

11:05 61. ***INTERNAL DYNAMICS OF NUCLEIC ACIDS STUDIED BY EPR-ACTIVE PROBES,*** B. H. Robinson. T. Okonogi, C. Mailer, S. C. Alley, A. W. Reese, and P. P. Hopkins, University of Washington.

11:35 62. ***IDENTIFICATION OF CALCIUM-DEPENDENT CHANGES IN THE ROTATIONAL DYNAMICS OF THE INTERDOMAIN CENTRAL HELIX IN CALMODULIN DETECTED BY SPIN-LABEL EPR SPECTROSCOPY,*** Z. Qin, **D.** H. Yin, R. F. Weaver, and T. C. Squier. University of Kansas.

12:00 Lunch

Session II, New Spin-Labeling Methods, P. Fajer presiding

1:30 63. ***REVERSE CORRELATION IN THE HYDRATION BETWEEN LIPID HEAD GROUP AND ACYL CHAIR REGIONS,*** M. Ge and J. H. Freed, Cornell University.

2:00 64. ***LIPID-PROTEIN INTERACTION IN R-3-HYDROXYBUTYRATE DEHYDROGENASE AS STUDIED BY ESR SPECTROSCOPY,*** **D.** Chelius, J. Moeller, S. Hahn, A. R. Marks, J. O. McIntyre, S. Fleisher, J. G. Wise, and W. E. Trommer. University of Kaiserslautern, Germany, Mount Sinai School of Medicine and Vanderbilt University.

2:30 65. ***LETS TALK TOAC,*** G. L. Millhauser. C. Toniolo, D. J. Anderson, and J. McNulty, University of California - Santa Cruz and University of Padova, Italy.

3:00 Break

3:30 66. ***SITE DIRECTED SPIN LABELING STUDY OF THE STRUCTURE OF COLICIN E1,*** L. Salwinski and W. L. Hubbell, University of California Los Angeles

4:00 67. ***DYNAMICS AND ORIENTATION OF MYOSIN REGULATORY DOMAIN,*** B. Hambly and P. G. Fajer. University of Sydney, Australia, and National High Magnetic Field Laboratory, Florida.

4:30 68. ***SPIN-LABELS REVEAL THE MECHANISMS OF MUSCLE CONTRACTION AND RELAXATION,*** D, D. Thomas. University of Minnesota Medical School.

5:00 Conference Mixer and Instrument Exhibit

Tuesday, July 28,1998

Session III, Joint NMR/EPR session, L. Frydman, presiding

8:30 69. *MAGIC ANGLE SPINNING IN NMR AND EPR,* H. W. Spiess. Max Planck Institute, Germany.

9:05 70. *EXPLOITATION OF THE FREE EVOLUTION PERIODS IN PULSE EPR EXPERIMENTS.* J. J. Shane and A. Schweiger, ETH-Zurich, Switzerland.

9:40 71. *PULSED ENDOR IN UNORIENTED SAMPLES: HOW TO INCREASE RESOLUTION AND GAIN THE MULTIPLEX ADVANTAGE,* M. K. Bowman and A. M. Tyryshkin, Pacific Northwest National Laboratory.

10:15 Break

10:45 72. *ENDOR OF METALLOENZYMES: TO THE LIGANDS AND BEYOND,* B. M. Hoffman. Northwestern University.

11:20 73. ***HIGH FIELD (140 GHz/5T) ELECTRON PARAMAGNETIC RESONANCE AND DYNAMIC NUCLEAR POLARIZATION,*** M. Bennati, C. Farrar, D. Hall, S. Inati, M. Rosay, V. Weiss, K. Kreischer, and R. G. Griffin. M.I.T.

12:00 Lunch

Session IV, B. M. Hoffman, presiding

1:30 74. K_3CrO* ***A PROPOSED STANDARD FOR g-FACTOR AND FIELD CALIBRATIONS IN HIGH FIELD EPR SPECTROSCOPY,*** B. Cage. L.-C. Brunei, and N. S. Dalai, Florida State University.

2:00 75. *HETEROGENEOUS DNP EFFECT IN AQUEOUS CARBON-BASED CHAR SUSPENSIONS,* B. M. Odintsov. R. L. Belford, P. J. Ceroke, Z. Sh. Idiyatullin, R. S. Kashaev, V. S. Rukhlov, A. N. Temnikov, and R. B. Clarkson, University of Illinois, Zavoisky Physical-Technical Institute, Kazan, and State Technological University, Kazan.

2:20 76. *ELECTRON PARAMAGNETIC RESONANCE OF A1 CENTERS IN 6H-S1C,* G. J. Gerardi. C. F. Young, and E. H. Poindexter, William Paterson University and Army Research Laboratory.

2:40 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, M-Z)

A 77. *NOTRE DAME RADIATION CHEMISTRY DATA CENTER. 1998 STATUS REPORT,* K. P. Madden. Notre Dame Radiation Laboratory.

B 78. *AN in situ RADIOLYSIS EPR STUDY OF SELF-RECOMBINATION RATE CONSTANTS FOR HYDROXYMETHYL AND 2-HYDROXY-2-METHYLPROPYL RADICALS IN WATER,* S. P. Mezyk and K. P. Madden. Notre Dame Radiation Laboratory.

A 79. *HIGH FIELD ESR AND MAGNETIZATION STUDIES IN SALTS OF* C_{60} *AND* C_{60} *DERIVATIVES WITH TDAE,* A. L. Maniero. L.-C. Brunei, L. Pasimeni, and R. P. Guertin, National High Magnetic Field Laboratory, University of Padova, Italy and Tufts University.

B 80. *EPR DETECTION BY TIME-LOCKED SUB-SAMPLING,* J. S. Hyde, H. S. Mchaourab. T. G. Camenisch, J. J. Ratke, R. W. Cox, and W. Froncisz, Medical College of Wisconsin.

A 81. ***DAP-SL: A NOVEL, NON-LABILE SPIN LABELED AMINO ACID,*** J. C. McNulty. D. Thompson, D. J. Anderson, S. Kent, and G. L. Millhauser, University of California - Santa Cruz and Gryphon Sciences.

B 82. *INVESTIGATION OF THE HAMMERHEAD RIBOZYME BY CW Q-BAND ENDOR SPECTROSCOPY,* S. R. Morrissey. T. E. Horton, T. Wasowicz, and V. J. DeRose, Texas A&M University.

A 83. *TOWARDS DEVELOPMENT OF TARGETED NITROXIDES: UPTAKE OF TEMPOCHOLINE BY BABY HAMSTER KIDNEY CELLS,* J. A. Cianfrogna, and R. Morse. Illinois State University.

B 84. *SIMULATION OF STRAIN IN EPR SPECTRA USING THE METHOD OF GRADIENTS,* M. J. Nilges. R. L. Belford, and L. C. Francesconi, University of Illinois and Hunter College - CCNY.

A 85. *MAGNETIC FIELD GRADIENT AT SOLID-LIQUID INTERFACE IN AQUEOUS CHAR SUSPENSIONS,* B. M. Odintsov. R. L. Belford, P. J. Ceroke, and R. B. Clarkson, University of Illinois and Zavoisky Physical-Technical Institute, Kazan.

B 86. *DISTANCE LIMITATIONS AND NITROXIDE PROBE PAIR INTERACTIONS IN HELICAL DNA -AN*

EPR APPLICATION TO BULGE DYNAMICS, T. M. Okonogi. A. W. Reese, S. C. Alley, E. A. Harwood, P. B. Hopkins, and B. H. Robinson, University of Washington.

A 87. ***PROBING LOCAL STRUCTURE AND MOBILITY AT A BURIED SITE IN HUMAN CARBONIC ANHYDRASE II: A COMPARISON BETWEEN TWO DIFFERENT SPIN LABELS,*** R. Owenius. P. Hammarstrom, M. Lindgren, M. Huber, M. Svensson, L.-G. Martensson, and U. Carlsson, Linkoping University, Sweden and Free University Berlin, Germany.

B 88. ***^{55}Mn PULSED ENDOR DEMONSTRATES THAT THE PHOTOSYSTEM II "SPLIT" EPR SIGNAL ARISES FROM A MAGNETICALLY-COUPLED MANGANO-TYROSYL COMPLEX,*** J. M. Peloquin. K. A. Campbell, and R. D. Britt, University of California, Davis.

A 89. ***AN EPR STUDY OF INTERACTIONS BETWEEN SPIN-LABELED VARIANTS OF HUMAN CARBONIC ANHYDRASE II AND GROEL,*** M. Persson. P. Hammarstrom, M. Svensson, U. Carlsson, M. Lindgren, and B.-H. Jonsson, Linkoping University, Sweden and Umea University, Sweden.

B 90. ***A NEW TYPE OF LOW TEMPERATURE INTEGER SPIN Q-BAND EPR SPECTROMETER FOR METALLOPROTEINS,*** D. T. Petasis and M. P. Hendrich, Carnegie Mellon University.

A 91. ***INFLUENCE OF PROTEIN METAL-SITE OCCUPANCY AND SUBUNIT CONTENT ON THE DYNAMICS OF THE ELECTRON TRANSFER PROCESS IN PHOTOSYNTHETIC BACTERIAL REACTION CENTERS: TRANSIENT Q- AND W-BAND EPR STUDY,*** Q. G. Poluektov. L. M. Utschig, J. Tang, M. C. Thurnauer, U. Heinen, and G. Kothe, Argonne National Laboratory and University of Freiburg, Germany.

B 92. ***ELECTRON SPIN ECHO SIGNAL AMPLITUDES: COMPARISON OF MEASURED AND CALCULATED ECHOES,*** G. A. Rinard, R. W. Quine. S. S. Eaton, and G. R. Eaton, University of Denver.

A 93. ***SPIN STATES OF MANGANESE IONS IN MANGANESE-DOPED YTTRIUM ORTHOALUMINATE, R.*** R. Rahimov. A. L. Wilkerson, W. Lindsay, N. Noginova, G, B. Loutts, M. A. Noginov, and H. R. Ries, Norfolk State University.

B 94. ***STRUCTURAL VARIATION BETWEEN THE LOW AND HIGH pH FORMS OF SULFITE OXIDASE,*** A. Raitsimring. A. Pacheco, and J. H. Enemark, University of Arizona.

A 95. ***PULSED EPR OF INCLUSION COMPLEXES AND METALS IN ZEOLITES,*** E. J. Reijerse. B. M. Weckhuysen, D. E. de Vos, and R. A. Schoonheydt, University of Nijmegen Toernooiveld, the Netherlands and University of Leuven Kardinaal Mercierlaan, Belgium.

B 96. ***NOVEL SMALL-SIZE RESONATORS FOR PULSED EPR,*** A. V. Koptioug, E. J. Reijerse. P. J. van Kan, and A. A. K. Klaassen, University of Aberdeen, United Kingdom and University of Nijmegen Toernooiveld, the Netherlands.

A 97. ***EPR SPECTROSCOPY OF BIOLOGICAL IRON-SULFUR CLUSTERS WITH SPIN ADMIXED S=3/2 GROUND STATES,*** W. R. Hagen, W. A. M. van der Berg, W. M. A. M. van Dongen, E. J. Reijerse. and P. J. van Kan, Agricultural University, the Netherlands and University of Nijmegen Toernooiveld, the Netherlands.

B 98. ***CROSSED-LOOP RESONATOR FOR CRYOGENIC APPLICATIONS.*** G. A. Rinard. University of Denver.

A 99. ***FREQUENCY DEPENDENCE OF EPR SIGNAL INTENSITY.*** G. A. Rinard. R. W. Quine, S. S. Eaton, and G. R. Eaton, University of Denver.

B 100. ***PREDICTION OF SPIN LABEL ORIENTATION IN THE CRYSTAL STRUCTURE OF PROTEINS,*** K, L. Sale. K. A. Sharp, and P. G. Fajer, Florida State University and University of Pennsylvania.

A 101. ***COMPACT EPR RESONATOR FOR PERPENDICULAR AND PARALLEL ORIENTATION OF LONGITUDINAL AQUEOUS SAMPLES,*** A. Sienkiewicz. P. G. Fajer, M. Jaworski, R. E. Hansen, and C. P. Scholes, SUNY-Albany, National High Magnetic Field Laboratory, Update Instruments, and Institute of Physics, Poland.

B 102. ***ESEEM STUDIES ON SUBSTRATE-GENERATED TRYPTOPHAN TRYPTOPHYL N-SEMIQUINONE IN METHYL AMINE DEHYDROGENASE,*** V. L. Davidson, J. L. McCracken, and V. Singh. University of Mississippi Medical Center and Michigan State University.

A 103. ***BINDING OF A LIPOPHILIC MRI CONTRAST AGENT TO BOVINE SERUM ALBUMIN AS STUDIED BY HF (95 GHz) EPR,*** T. I. Smirnova. A. I. Smirnov, R. L. Belford, and R. B. Clarkson, University of Illinois.

B 104. ***LOW FREQUENCY FOURIER TRANSFORM EPR IMAGING,*** A. Sotgiu. G. Placidi, J. A. Brivati, M. Alecci, and L. Testa, Universita dell'Aquila, Italy.

A 105. ***RESONANT COUPLING OF LOW FREQUENCY EPR RESONATORS,*** R. Diodata, M. Alecci, J. A. Brivati, and A. Sotgiu. Universita dell'Aquila, Italy.

B 106. ***COMPARISON OF EFFECTS OF TRANSMEMBRANE ALPHA-HELICAL PEPTIDES WITH DIFFERENT HYDROPHOBIC SURFACE ROUGHNESS ON MOLECULAR ORGANIZATION AND DYNAMICS OF 1-PALMITOYL-2-OLEOPHOSPHTIDYLCHOLINE BILAYERS,*** W. K. Subczyncki. J. S. Hyde, and A. Kusumi, Medical College of Wisconsin, Jagiellonian University, Poland, and Nagoya University, Japan.

A 107. ***THE EXTRACELLULAR NON-HAEM PEROXIDASE FROM THERMOMONOSPORA FUSCA BD25: AN EPR CHARACTERIZATION,*** D. A. Svistunenko. A. Rob, A. Ball, J. Torres, C. E. Cooper, M. C. R. Symons, and M. T. Wilson, University of Essex, England.

B 108. ***SYNTHESIS AND APPLICATION OF NOVEL BIFUNCTIONAL SPIN LABELS,*** R. M. Losel, R. Philipp, T. Kalai, K. Hideg, and W. E. Trommer. University of Kaiserslautern, Germany and University of Pecs, Hungary.

A 109. ***PHOTOSYSTEM II MEMBRANES AND REACTION CENTER INTERMEDIATES OF Y_z' WITH ITS ENVIRONMENT IN ACETATE TREATED CORES,*** M. D. Valentin. P. Dorlet, G. T. Babcock, and J. L. McCracken, Michigan State University and CEN Saclay, France.

B 110. ***HIGH-FREQUENCY ENDOR IN NON-ORIENTED NITROXIDES,*** J. van Tol and P. Wyder, Grenoble High Magnetic Field Laboratory, France and Florida State University.

A 111. A ***NEW HIGH-FREQUENCY TRANSIENT EPR SPECTROMETER,*** J. van Tol and L.-C. Brunei, Grenoble High Magnetic Field Laboratory, France and Florida State University.

B 112. ***CHARACTERIZATION OF FE(III)-TETRAPHENYLPORPHYRIN WITH FLUOROPHENYL SUBSTITUENTS BY EPR AND UV-VIS SPECTROSCOPIES,*** E. A. Vidoto. O. R. Nascimento, Y. Iamamoto, K. J. Ciuffi, and D. G. de Abreu, Institute de Fisica Sao Carlos, Brazil.

A 113. ***ARE CYANIDES BENT IN TRANSITION METAL CYANIDES?,*** N. V. Vugman. J. A. C. Neto, and N. M. Pinhal, Universidade Federal do Rio de Janeiro, Brazil.

B 114. ***REDOX STATE-INDUCED ROTAMER REDISTRIBUTION IN THE AMINO ACID TYROSINE,*** M. S. Perry and K. Warncke. Emory University.

A 115. ***EFFECTS OF FUMONISIN B1 ON LIPID PEROXIDATION IN MEMBRANES,*** J.-J. Yin. M. J. Smith, R. M. Eppley, S. W. Page, and J. A. Sphon, U. S. Food and Drug Administration.

B 116. ***NMR AND EPR STUDIES ON THE REACTIONS OF VANADATE AND THIOL COMPOUNDS,*** B Zhang. A. D. Keramidas, C. R. Roberts, and D. C. Crans, Colorado State University and Syntex-Roche.

A 117. ***EVALUATION OF INTERSPIN DISTANCES DETERMINED BY TIME-DOMAIN EPR OF SPIN-LABELED MYOGLOBIN MUTANTS,*** Y. Zhou. B. Bowler, S. S. Eaton, and G. R. Eaton, University of Denver.

Tuesday evening - EPR Symposium dinner. All attendees are invited, see information on http://www.du.edu/~seaton/eprsym.html

Wednesday, July 29, 1998

Session VI, Biological Radicals, J. Pilbrow presiding

8:30 118. ***EVALUATION OF DEPMPO AS AN IN VIVO SPIN TRAPPING AGENT: A COMPARISON WITH DMPO,*** K. J. Liu. M. Miyake, and H. M. Swartz, Dartmouth Medical School.

8:50 119. ***DIRECT ESR AND SPIN-TRAPPING STUDY OF THE ONE-ELECTRON REDUCTION OF THE CARCINOGEN 4-NITROQUINOLINE N-OXIDE,*** Y. C. Fann. C. A. Metosh-Disckey, M. B. Kadiiska, A. Sygula, G. W. Winston, and R. P. Mason, NIEHS, Louisiana State University, and North Carolina State University.

9:15 120. ***RADICAL PAIR SEPARATION AND REACTIVITY IN BIRADICAL-CONDUCTED ENZYME CATALYSIS,*** S.-C. Ke, G. R. Bishop, J. C. Schmitt, and K. Warncke. Emory University.

9:45 Break

10:45 121. ***THE FATE OF THE OXIDIZING TYROSYL RADICAL IN THE PRESENCE OF GLUTATHIONE AND ASCORBATE: IMPLICATIONS FOR THE RADICAL SINKHYPOTHESIS***, B. E. Sturgeon. H. J. Sipe, Jr., D. P. Barr, J. T. Corbett, J. G. Martinez, and R. P. Mason, NIEHS.

11:10 122. ***NITRIC OXIDE TRAPPING OF THE TYROSYL RADICAL FORMED BY THE ACTION OF PERACETIC ACID ON CATALASE LEADS TO NITROTYROSINE FORMATION,*** R. P. Mason. S. W. Heinzerling, R. P. Glover, and M. R. Gunther, NIEHS.

11:35 123. ***EPR INVESTIGATION OF THE INTRACELLULAR DRUG DYNAMICS AND DISTRIBUTION IN THE PROCESS OF PROGRAMMED CELL DEATH,*** N. Y. Rapoport and A. I. Smirnov, University of Utah and University of Illinois.

12:00 Lunch

Session VII, EPR Imaging, B. Gaffney presiding

1:30 124. ***CHALLENGES OF 3- AND 4-DIMENSIONAL IN VIVO SPECTRAL-SPATIAL EPR IMAGING AT***

RADIOFREQUENCJES WITH NARROW-LINE SPIN PROBES, H. J. Halpern. G. V. R. Chandramouli, B. B. Williams, E. D. Barth, and V. Galtsev, University of Chicago.

2:00 125. ***PULSED IN VIVO RF EPR IMAGING: WHOLE BODY 3D IMAGES OF MURINE MODELS,*** ML Afeworki. N. Devasahayam, D. Coffin, J. Cook, R. Tschudin, S. Subramanian, J. B. Mitchell, M. C. Krishna, J. H. A. Larsen, and K. Golman, National Cancer Institute, NIH and Nycomed Innovations, Sweden.

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, A-L)

C 126. ***PULSED IN VIVO RF EPR IMAGING: WHOLE BODY 3D IMAGES OF MURINE MODELS,*** M, Afeworki. N. Devasahayam, D. Coffin, J. Cook, R. Tschudin, S. Subramanian, J. H. A-Larsen, K. Golman, J. B. Mitchell, and M. C. Krishna, NCI and Nycomed Innovations, Sweden.

D 127. ***AN EPR STUDY OF SOLUBLE POLYPYRROLE,*** M. K. Ahn. C. M. Brodbeck, J. Y. Lee, and C. Y. Kim, Indiana State University, Loyola University, Argonne National Laboratory, and Korea Institute of Science and Technology, Korea.

C 128. ***CW EPR STUDIES OF TRICHOGIN PEPTIDE CONFORMATIONS,*** D. J. Anderson. P. Hanson, J. C. McNulty, V. Monaco, G. L. Millhauser, and C. Toniolo, University of California - Santa Cruz and University of Padova, Italy.

C 129. ***FORMATION OF A CUPRIC FERROCYANIDE-LIKE COMPLEX UPON ADDITION OF FERRICYANIDE TO MEMBRANE FRACTIONS LOADED WITH pMMO FROM M. album BG8,*** H. Yuan, M. L. P. Collins, and W. E. Antholine. Medical College of Wisconsin, and University of Wisconsin-Milwaukee.

D 130. ***MATRIX LINE IN PULSED ELECTRON-NUCLEAR DOUBLE RESONANCE SPECTRA,*** A. V. Astashkin and A. Kawamori, University of Arizona and Kwansei Gakuin University, Japan.

C 131. ***ESEEM STUDIES ON MULTICOPPER PROTEIN FET3,*** C. P. Aznar. J. L. McCracken, D. J. Kosman, K. Hassett, and D. Yuan, Michigan State University, SUNY-Buffalo, and John Hopkins University.

D 132. ***DYNAMICS OF REGULATORY LIGHT CHAIN OF MYOSIN,*** B. Baumann. B. Hambly, K. Hideg, and P. G. Fajer, University of Sydney, Australia, University of Pecs, and National High Magnetic Field Laboratory.

C 133. ***SPIN-ROTATION QUANTUM EFFECTS ON THE EPR LINESHAPES OF $*CH_3$ AND $*CD_3$ RADICALS ISOLATED IN ARGON MATRIX,*** T. Yamada, K. Komaguchi, M. Shiotani, A. R. Sornes, A. Lund, and N. P. Benetis. Hiroshima University, Japan, University of Oslo, Norway, and Linkoping University, Sweden.

D 134. ***DARK GENESIS OF A BIRADICAL INTERMEDIATE IN DNA PHOTOLYASE CATALYSIS,*** G. R. Bishop and K. Warncke, Emory University.

C 135. ***ENDOR AND ESEEM STUDIES OF REACTION INTERMEDIATES IN CLOSTRIDIUM THERMOACETICUM PYRUVATE: FERREDOXIN OXIDOREDUCTASE,*** V. F. Bouchev and J. L. McCracken, Michigan State University.

D 136. ***PARALLEL POLARIZATION EPR STUDIES OF THE S_rSTATE OF THE PHOTOSYSTEM II OXYGEN-EVOLVING COMPLEX,*** K. A. Campbell. W. Gregor, D. Pham, R. J. Debus, J. M. Peloquin, and R. D. Britt, University of California - Davis and University of California-Riverside.

C 137. ***ELECTRON SPIN-ECHO ENVELOPE MODULATION SPECTROSCOPIC STUDIES OF POLYCRYSTALLINE Cu(II)-INSULIN,*** M. J. Colaneri. J. Vitali, and J. Peisach, SUNY - Westbury, University of Texas - Austin, and Albert Einstein College of Medicine.

D 138. ***SPECTRAL-SPATIAL IMAGING USING RADIOFREQUENCY TIME DOMAIN EPR,*** J. Cook. S. Subramanian, M. Afeworki, D. Devasahayam, D. Coffin, R. Tschudin, J. H. A. Larsen, K. Golman, J. B. Mitchell, and M. C. Krishna, NCI and Nycomed Innovation, Sweden.

C 139. ***EPR CHARACTERIZATION OF CHLOROCATECHOL 1,2-DIOXYGENASE: A NON-HEME IRON DIOXYGENASE,*** A. J. da Costa-Filho. A. P. U. de Araujo, and O. R. Nascimento, University of Sao Paulo, Brazil.

D 140. ***SOLID STATE AND SOLUTION CHEMISTRY OF BIS(ACETYLACETONATE) OXOVANADIUM(IV), VO(ACAC)j AND ITS DERIVATIVES,*** K. Cryer. S. S. Amin, B. Zhang, S. S. Eaton, O. P. Anderson, S. M. Miller, and D. C. Crans, Colorado State University and University of Denver.

C 141. ***HIGH-SENSITIVITY EPR OF Mn_{12}-ACETATE,*** N. S. Dalai. B. Cage, T. Hathaway, S. Hill, T. Stalcup, and J. S. Brooks, Florida State University and Montana State University.

D 142. ***HYPERFINE COUPLINGS OF PYRROLE NITROGENS IN NITROSYLATED HEME,*** S. A. Dikanov. D. C. Doetschman, D. G. Gilbert, and J. A. Smieja, SUNY-Binghamton, Institute of Chemical Kinetics and Combustion, Novosibirsk, and Gonzaga University.

C 143. ***SUBSTRATE AFFECTS THE GEOMETRY OF NITRIC OXIDE-HEME BINDING IN ACTIVE SITE OF NEURONAL NITRIC OXIDE SYNTHASE,*** S. A. Dikanov. D. C. Doetschman, D. J. Stuehr, and L. Huang, SUNY-Binghamton, Institute of Kinetics and Combustion, Novosibirsk, and Cleveland Research Institute.

D 144. ***EFFECT OF SOLVENT METHYL GROUPS ON SPIN ECHO DEPHASING FOR CR(V) AND VANADYL COMPLEXES,*** G. R. Eaton and S. S. Eaton. University of Denver.

C 145. ***COMPARISON OF MEMBRANE FLUIDITY OF WILD-TYPE AND COLD-SENSITIVE STRAINS*** *OF* ***LISTERIA MONOCYTOGENES,*** M. R. Edgcomb. S. Sirimanne, P. Drouin, B. Wilkinson, and R. Morse, Illinois State University.

D 146. ***HIGH-FREQUENCY SPIN LABEL EPR STUDIES OF NON-AXIAL LIPID ORDERING IN MEMBRANES WITH CHOLESTEROL,*** B. J. Gaffney and D. Marsh, Florida State University and Max Planck Institute, Germany.

C 147. ***FIELD DISTRIBUTIONS IN LOOP GAP RESONATORS DESIGNED TO OPERATE AT RADIOFREQUENCIES: RESULTS FROM HFSS MODELS AND COMPARISON WITH MEASUREMENTS,*** V. Galtsev. E. D. Barth, and H. J. Halpern, University of Chicago.

D 148. ***STRUCTURAL STUDY OF THE SQUARE PYRAMIDAL TO TRIGONAL BIPYRAMIDAL DISTORTION OF VANADYL COMPLEXES BY^{51} VESE-ENDOR,*** C. Grant. R. D. Britt, and C. R. Cornman, University of California - Davis, and North Carolina State University.

C 149. ***IN VIVO PHARMAKOKINETICS OF A NOVEL, STABLE NITRIC OXIDE SPIN TRAPPING ADDUCT, DTCS.*** H. J. Halpern. E. D. Barth, G. V. R. Chandramouli, V. Galtsev, B. B. Williams, and G. M. Rosen, University of Chicago and University of Maryland.

D 150. ***PULSED EPR STUDIES OF THE RADICALS FORMED BY ^-IRRADIATION OF MALONIC ACID AND METHYL MALONIC ACID,*** J. R. Harbridge. S. S. Eaton, and G. R. Eaton, University of Denver.

C 151. ***HIGH-FIELD ESR STUDIES OF THE DOPED SPIN-PEIERLS SYSTEM Cu^nfieO^*** A. K. Hassan. L. A. Pardi, G. B. Martins, G. Cao, and L.-C. Brunei, National High Magnetic Field Laboratory.

D 152. ***RADICAL REACTANT-ACTIVE SITE INTERACTIONS IN ETHANOLAMINE DEAMINASE,*** S.-C. Ke and K. Warncke, Emory University.

C 153. ***HIGH-FIELD EPR (326 GHZ) AND ENDOR (9 GHZ) STUDIES OF CAROTENOID - SOLID LEWIS ACID INTERACTIONS,*** T. A. Konovalova, L. D. Kispert. P. J. Bratt, L.-C. Brunei, and J. Krzystek, University of Alabama, University of Florida, and Florida State University.

D 154. ***A HIGH POWER 250 GHz DNP/EPR SPECTROMETER,*** K. E. Kreischer. C. T. Farrar, M. L. Bennati, R. G. Griffin, and R. J. Temkin, MIT.

C 155. ***MULTI-FREQUENCY EPR ANALYSIS OF DIPOLAR AND EXCHANGE INTERACTIONS BETWEEN MANGANESE AND TYROSINE IN THE $S_2Y_z^m$ STATE OF PHOTOSYSTEM II,*** K. V. Lakshmi S. S. Eaton, G. R. Eaton, H. A. Frank, and G. W. Brudvig, Yale University, University of Denver, and University of Connecticut.

D 156. ***A PHYSICALLY BASED PREDICTIVE MODEL FOR THE GENERATION OF PARAMAGNETIC CENTERS AT THE Si/SiO_2 BOUNDARY OF MOS TRANSISTORS,*** P. M. Lenahan and J. F. Conley, Pennsylvania State University and Dynamics Research Corporation.

C 157. ***ESR STUDIES OF THE ROLE OF ZEOLITE STRUCTURES IN SELECTIVE CATALYTIC REDUCTION. PART III. MOTIONAL DYNAMICS OF $N0_2$ ON VARIOUS ZEOLITES,*** H. Li. H. Yahiro, K. Komagoji, M. Shiotani, E. Sagstuen, and A. Lund, Hiroshima University, Japan and Linkoping University, Sweden.

D 158. ***MODELING OF PHASE-MEMORY RELAXATION INDUCED BY SURROUNDING NUCLEI IN SPIN-LABELED MUTANTS OF HUMAN CARBONIC ANHYDRASE II,*** M. Lindgren. M. Huber, P. Hammarstrom, M. Svensson, U. Carlsson, G. R. Eaton, and S. S. Eaton, Linkoping University, Sweden, Free University, Berlin, and University of Denver.

C 159. ***CHARACTERIZATION AND SCREENING OF SPIN TRAPS FOR APPLICATION IN VIVO,*** K. J. Liu and Y. Kotake, Dartmouth Medical School and Oklahoma Medical Research Foundation.

D 160. ***ELECTRON SPIN ECHO ENVELOPE MODULATION (ESEEM) STUDIES OF ACTIVE STIE STRUCTURE IN CHLOROPLAST F1-ATP SYNTHASE USING AN OXOVANADIUMP ROBE,*** R. Lobrutto. H.-C. Chiou, S. Myrgren, W. Chen, and W. D. Frasch, Arizona State University.

C 161. ***HIGH-FIELD EPR STUDIES OF SEVERAL MANGANESE(II)-CONTAINING COMPOUNDS,*** L. M. Jones, L. G. Schultz, R. H. Flamion, K. M. Key, and W. B. Lynch. University of Evansville.

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

Thursday, July 30,1998

Session IX, High Spin and High-Field EPR, M. K. Bowman presiding

8:30 162. ***HIGH-FREQUENCY AND -FIELD EPR SPECTROSCOPY OF CR(II) ION,*** J. Krzystek. T. Telser, L. Pardi, and L.-C. Brunei, National High Magnetic Field Laboratory and Roosevelt University.

8:55 163. ***MODELLING EPR SPECTRA DUE TO HIGH SPIN TRANSITION METAL IONS IN GLASSES,*** J Pilbrow. Monash University, Australia.

9:20 164. ***HIGH FIELD EPR OF PHOTOSYNTHETIC REACTION CENTERS,*** P. J. Bratt, A. Angerhofer. J. Krzystek, M. Rohrer, and L.-C. Brunei, University of Florida and National High Magnetic Field Laboratory.

9:45 165. ***PULSED ENDOR AT 140 GHZ AND ITS APPLICATION TO THE RNR TYROSYL RADICAL FROM E. COLI,*** M. Bennati. C. T. Farrar, G. J. Gerfen, J. Bryant, P. Riggs-Gelasco, J. Stubbe, and R. G. Griffin, MIT.

10:10 Break

10:30 166. ***CW AND PULSED EPR STUDIES OF THE BINUCLEAR FE(III)ZN(II) AND FE(III)MN(II) CENTRES IN RED KIDNEY BEAN AND SWEET POTATO PURPLE ACID PHOSPHATASE,*** G. R. Hanson. C. L. Boutchard, L. Carrington, C. J. Noble, S. E. Hamilton, J. de Jersey, L. R. Gahan, and J. R. Pilbrow, University of Queensland, Australia and Monash University, Australia.

10:55 167. ***STUDIES OF LIPOXYGENASE AND OTHER METALLOPROTEINS BY EMR AT 94 GHZ,*** B. J. Gaffney. H. J. Silverstone, G. G. Maresch, and R. T. Weber, Florida State University, Johns Hopkins University, and Bruker Instruments.

11:25 168. ***MM-WAVE EPR OF METALLO-PROTEINS,*** E. J. Reijerse. P. J. van Dam, A. Priem, and W. R. Hagen, University of Nijmegen, the Netherlands.

11:55 Closing Remarks - Gareth R. Eaton

12:00 Lunch

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

GENERAL POSTER SYMPOSIUM

Organized by Mary E. Cast

Authors will be available at their respective posters 5:30 to 6:30 PM Monday, July 27.

(Posters are listed aphabetically by presenting author)

169. ***CONFORMATIONAL ANALYSIS OF PESTICIDES WITH STACKED GC DETECTORS,*** by Rollen J. Anderson. Jessie Butler, and Fausto Pigozzo, E. E. Instruments, 2215 Grand Avenue Parkway, Austin, TX 78728.

170. ***GREEN CHEMISTRY FOR THE 21ST CENTURY.*** F.G. Baglin. R. Jones, L. Tingley and T. Palmer, Materials Technology Limited, Reno Nv. and The Dept. of Chemistry, University of Nevada, Reno, Nevada, 89557

171. ***GLOVEBOX DECONTAMINATION TECHNOLOGY COMPARISON*** by Michael E. Cournoyer. Reanna Aguino, and Doris Quintana, MS G740, NMT-1, Los Alamos National Laboratory, Los Alamos, NM 87545

172. ***ENHANCED METHOD DEVELOPMENT USING SOLID PROBE MASS SPECTROMETRY AND GC-MS/MS,*** by James B. Edwards. John D. Ragsdale III, And Steven T. Fannin, Finnigan Corporation, 2215 Grand Avenue Parkway, Austin, TX 78728.

173. ***ANALYTICAL TANDEM MASS SPECTROMETRY WITH A BENCHTOP EXTERNAL SOURCE ION TRAP MASS SPECTROMETER FOR THE ANALYSIS OF THC AND METABOLITES IN BLOOD,*** by Steven T. Fannin. Wilmo Andollo, James M. Stephens, John D. Ragsdale III, Finnigan Corporation, 2215 Grand Avenue Parkway, Austin, TX 78728.

174. ***APPLYING ADVANCED SIMULTANEOUS THERMAL ANALYSIS TECHNIQUES FOR MORE EFFECTIVE MATERIALS CHARACTERIZATION,*** by Bob Fidler. J. B. Henderson, E. Post, NETZSCH Instruments, Inc., 37 Industrial Blvd. - Section D, Paoli, PA 19301.

175. ***HIGH SENSITIVITY EVOLVED GAS ANALYSIS VIA COUPLED THERMAL ANALYSIS -SPECTROSCOPIC TECHNIQUES,*** by Bob Fidler. J. B. Henderson, E. Post, NETZSCH Instruments, Inc., 37 Industrial Blvd. - Section D, Paoli, PA 19301.

176. ***SPE CLEANUP AND LC-UV DETECTION OF EPHEDRINE ALKALOIDS IN HERBAL PRODUCTS,*** by Jeffrey A. Hurlbut*. Justin R. Carr*; Emma R. Singleton[1], Kent C. Faul[1], Mark R. Madson[1], Joseph M. Storey[1] and Terri L. Thomas[1]; ^Chemistry Department, Metropolitan State College of Denver, P.O. Box 173362, Denver, CO 80217; [1]Food and Drug Administration, Denver Federal Center, P.O. Box 25087, Denver, CO 80225.

177. ***SIMULTANEOUS DETERMINATION OF RESIDUES OF CHLORAMPHENICOL, FLORFENICOL AND THIAMPHENICOL IN MILK,*** by Allen P. Pfenning. Mark R. Madson, Jose E. Roybal, Sherri B. Turnipseed and Steve A. Gonzales, U. S. Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Bldg. 20, Denver, CO 80225.

178. ***GEL PERMEATION CHROMATOGRAPHY AND ^{13}C AND ^{93}NB NMR OF SOL-GEL ALKOXIDE PRECURSORS TO TITANATE-AND NIOBATE-DIELECTRIC MATERIALS,*** by J. Qi. J. Hang, and J. J. Fitzgerald, Department of Chemistry, South Dakota State University, Brookings, SD 57007.

179. ***PHOTOCHEMICAL REACTION: APPLICATION OF LIQUID CHROMATOGRAPHIC POST-COLUMN PHOTOLYSIS TO THE ENHANCED FLUORIMETRIC DETECTION OF A VERMECTINS,*** by Jose E. Roybal. Steve A. Gonzales, Allen P. Pfenning and Sherri B. Turnipseed, U. S. Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Bldg. 20, Denver, CO 80225.

180. ***THE DETERMINATION OF IODIDE IN GROUND WATER AND SOIL BY ION CHROMATOGRAPHY,*** by H. L. Tucker. R. W. Flack, Lockheed Martin Energy Systems Inc., Analytical Services Organization, Box 2009, MS 8189, Oak Ridge, TN 37831-8189.

181. ***ATMOSPHERIC PRESSURE CHEMICAL IONIZATION LC/MS ANALYSIS OF AVERMECTIN RESIDUES,*** by Sherri B. Turnipseed. Jose E. Roybal, Heidi S. Rupp, Steve A. Gonzales, Allen P. Pfenning, U. S. Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Bldg. 20, Denver, CO 80225.

182. ***DEVELOPMENT OF AN ANALYSIS SYSTEM FOR LOW-RANK COAL USING LASER-INDUCED BREAKDOWN SPECTROSCOPY,*** by Fiona J. Wallis. Bruce L. Chadwick, Richard J. S. Morrison, CRC New Technologies for Power Generation from Low-Rank Coal, 8/677 Springvale Rd., Mulgrave, Victoria 3170, AUSTRALIA.

183. ***USE OF NMR TO CHARACTERIZE INHOMOGENEOUS SOLIDS.*** Naira M. da Silva.' Maria Ines B. Tavares' and E.O. Stejskal[2], 'Instituto de Macromoleculas Prof. Eloisa Mano, Universidade Federal do Rio de Janeiro, Brazil, CEP21945-970.[2]Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204

207. ***A REVERSED PHASE HPLC/MS/MS ASSAY FOR THE SIMULTANEOUS QUANTITATION OF RWJ-51204 AND ITS ACTIVE METABOLITE (RWJ-52407) IN HUMAN PLASMA and URINE.*** Desai-Krieger. V.V. Scott, and R. J. Stubbs. The R. W. Johnson Pharmaceutical Research Institute, Bioanalytical Drug Metabolism Department, Welsh & McKean Roads, Spring House, PA 19477.

LASERS AND MATERIAL CHEMISTRY

Organized by Ellen Fisher

Tuesday, July 28,1998

Morning session: Ellen Fisher presiding

9:00 184. ***THE INFLUENCE OF SURFACE ROUGHNESS ON THE MOLECULAR ORIENTATION IN ULTRA-THIN FILMS.*** Garth J. Simpson, Kathy L. Rowlen, Department of Chemistry, Colorado State University, Fort Collins, CO.

9:20 185. ***SURFACE REACTIVITY OF CF2 RADICALS MEASURED USING LASER-INDUCED FLUORESCENCE AND CHF3 PLASMA MOLECULAR BEAMS.*** Nathan E. Capps, Neil M. Mackie, Ellen R. Fisher, Department of Chemistry, Colorado State University, Fort Collins, CO.

9:40 186. ***AZO-DYE CHEMISTRY ON SILICON AND QUARTZ SUBSTRATES.*** Sayling Wong, Garth Simpson, Kathy L. Rowlen, Department of Chemistry, Colorado State University, Fort Collins, CO.

10:00 187. ***VELOCITY DISTRIBUTIONS OF RADICALS IN PLASMA MOLECULAR BEAMS.*** Patrick R. McCurdy, Ellen R. Fisher, Department of Chemistry, Colorado State University, Fort Collins, CO.

10:20 Break

10:35 188. ***DYE COVERAGE EFFECTS ON NANOCRYSTALLINE TIO2 SOLAR CELLS.*** Akiko Fillinger, Bruce A. Parkinson, Department of Chemistry, Colorado State University, Fort Collins, CO.

10:55 189. ***SOLVATION DYNAMICS OF WATER AT THE SURFACE OF ZIRCONIUM OXIDE NANOPARTICLES.*** Debi Pant, Nancy E. Levinger, Department of Chemistry, Colorado State University, Fort Collins, CO.

11:15 190. ***POLAR SOLVATION DYNAMICS NEAR THE LIQUID-LIQUID INTERFACE OF AEROSOL-OT REVERSE MICELLES.*** Ruth E. Riter, Dale M. Willard, Eric P. Undiks, Joel R. Kimmel, Nancy E. Levinger, Department of Chemistry, Colorado State University, Fort Collins, CO.

LUMINESCENCE SYMPOSIUM

Organized by: Robert J. Hurtubise, DeLyle Eastwood, and James R. Gord

Monday, July 27,1998

Morning: Robert J. Hurtubise, Presiding

8:30 ***Opening Remarks***

8:35 191. ***DETERMINATION OF BENZO(A)PYRENE-DNA ADDUCTS BY SOLID-MATRIX PHOSPHORESCENCE,*** by Ming Li and R.J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.

8:55 192. ***QUANTIFYING HOMOCYSTEINE AND OTHER THIOLS IN PLASMA WITH DERIVATIZATION FOLLOWED BY CAPILLARY ELECTROPHORESIS AND LASER-INDUCED FLUORESCENCE,*** by Christopher J. Smith. Shuenae A. Smith, Daphne B. Moffett, Patricia W. Mueller, James Grainger, and Donald G. Patterson, Jr., Centers for Disease Control and Prevention, 4770 Buford Highway, MS F-17, Atlanta, GA 30341.

9:15 193. ***STUDIES OF GROUNDWATER MIGRATION USING CAPILLARY ELECTROPHORESIS/LASER-INDUCED FLUORESCENCE DETECTION,*** by John W. Farley (1), Andrew H. Grange, Patrick L. Ferguson, William C. Brumley (2), and Joseph R. Donnelly (3); (1) Department of Physics, University of Nevada-Las Vegas, Las Vegas, NV 89154; (2) U.S. EPA, NERL, CRD-LV Las Vegas, NV 89193-3478; (3) Lockheed-Martin Services Group.

9:35 194. ***CHARACTERIZING SINGLE FLUORESCENT MOLECULES IN MICROCAPILLARIES BY THEIR ELECTROPHORETIC MOBILITIES,*** by Alan Van Orden and Richard A. Keller, Chemical Science and Technology Division, CST-1, MS M888, Los Alamos National Laboratory, Los Alamos, NM 87545.

9:55 195. ***EU(III) LUMINESCENCE FOR THE INVESTIGATION OF METAL-ION BINDING TO PLANT TISSUES,*** by Timothy L. Danielson and Gary D. Rayson. Department of Chemistry and Biochemistry, Box 30001, MSC 3C, New Mexico State University, Las Cruces, NM 88003.

10:15 Break

10:40 196. ***DRYING CONDITIONS FOR THE FORMATION OF GLUCOSE AND SUCROSE GLASSES IN SOLID-MATRIX LUMINESCENCE,*** by Kristen D. Seeley and Robert J. Hurtubise, University of Wyoming, Laramie, WY 82071-3838.

11:00 197. ***SOLID-PHASE MICROEXTRACTION AND SOLID-MATRIX LUMINESCENCE OF COMPLEX MIXTURES OF POLYAROMATIC HYDROCARBONS,*** by Amanda H. Ackerman and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838

11:20 198. ***THE STUDY OF OXYGEN QUENCHING IN A CONTROLLED ENVIRONMENT,*** by Patricia B. Coleman. Ford Motor Company, PO Box 2053, Mail Drop 3083/SRL, Dearborn, MI 48121-2053.

Afternoon Session: Jim Gord and DeLyle Eastwood, CO-chairs
DeLyle Eastwood, presiding

1:30 ***Opening Remarks***

1:35 199. ***ADVANCES IN THE DESIGN AND APPLICATIONS OF SENSORS BASED ON LUMINESCENT TRANSITION METAL COMPLEXES,*** by J.N. Demas. Wenying Xu, and Kristi Kneas, Department of Chemistry, University of Virginia, Charlottesville, VA 22901; B.A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807.

1:55 200. ***CHARACTERIZING AVIATION FUELS AT HIGH TEMPERATURE AND PRESSURE,*** by James R. Gord and Christopher E. Bunker, Propulsion Sciences & Advanced Concepts Divisions, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433-7103; Keith D. Grinstead, Jr., Innovative Scientific Solutions, Inc., 2786 Indian Ripple Road, Dayton, OH 45440-3638.

2:15 201. ***ASYNCHRONOUS OPTICAL SAMPLING WITH MODELOCKED TI:SAPPHIRE LASERS,*** by Keith D. Grinstead. Jr. and Gregory J. Fiechtner, Innovative Scientific Solutions, Inc., 2786 Indian Ripple Road, Dayton, OH 45440-3638; James R. Gord and Christopher E. Bunker, Propulsion Sciences & Advanced Concepts Division, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433-7103.

2:35 202. ***THE IMPACT OF FUEL ADDITIVES ON THE DETERMINATION OF WATER IN AVIATION FUEL,*** by Matthew R. Rabe. James R. Gord, and Christopher E. Bunker, Propulsion Sciences & Advanced Concepts Division, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433-7103.

2:55 Break

James R. Gord, presiding

3:15 203. *STUDIES OF BROWNING PATTERNS IN LAMINATED EVA ENCAPSULANTS UNDER ACCELERATED EXPOSURES,* by S.H. Glick and F.J. Pern, National Center for Photovoltaics, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401.

3:35 204. *A NEW MODEL FOR THE DETERMINATION OF SURFACE ISOTHERMS USING A LIFETIME PARTITIONING PROTOCOL WITH A NEW LUMINESCENT TRANSITION METAL PROBE,* by Matthew Marlow. B. Patrick Sullivan, and John Bowen, Chemistry Department, University of Wyoming, Laramie, WY 82071-3838.

3:55 205. *DINITRAMIDE, NITROCYANAMIDE, AND DICYANAMIDE: SPECTROSCOPIC AND PHOTOCHEMICAL STUDIES OF THEIR SALTS AND THEIR RE1 TRI- AND PENTACARBONYL COMPLEXES,* by Kevin J. Seward. Scott A. Trammel, and B. Patrick Sullivan, Chemistry Department, University of Wyoming, Laramie, WY 82071-3838.

4:15 206. *FEMTOGRAM DETECTION OF SUSPECTED CARCINOGENS BY HPLC-PEROXYOXALATE CHEMILUMINESCENCE,* by Janet G. Gilliland. Hauser Laboratories, Inc., 4750 Nautilus Court South, Boulder, CO 80301-3240.

SYMPOSIUM ON MASS SPECTROMETRY

Organized by Joseph A. Zirrolli

To be announced.

208. *PETRIFIED FOREST NATIONAL PARK UPPER TRIASSIC TRACE FOSSILS YIELD BIOCHEMICAL EVIDENCE OF PHYLOGENETIC LINK TO MODERN BEES (HYMENOPTERA, APOIDEA),* Paul T. Kay[1]; J. David King[2] and Stephen T. Hasiotis[3], independent, Denver, CO; [2]USGS, Denver, CO; [3]University of Colorado, Boulder, CO.

SYMPOSIUM ON NMR SPECTROSCOPY

NMR Abstracts available at http://www.cchem.berkeley.edu/~jargrp/rmc.html
Organized by L. Frydman, C. Grey, J. Hanna, J. Reimer, S. Sinton, R. Wind and J. Yesinowski

Monday, July 27

Morning:

SESSION I: BIO- AND OTHER MACROMOLECULAR SYSTEMS, Gina Hoatson, Presiding

8:25 ***Welcoming Remarks,*** Robert Wind

8:30 209. ***C-13 NMR STUDY OF THE INCLUSION OF STEREO AND REGIO DEFECTS IN THE CRYSTALLINE REGIONS OF ISOTACTIC POLYPROPYLENE.*** **D.L. VanderHart[a)].** H. Feng[a)], M.R. Nyden[b)], R.G. Alamo[c)], M-H. Kim[c)], L. Mandelkern[d)], E. Perez[e)] and S. Mansel[c)], [a)]Polymers Division, NIST, Gaithersburg, MD, 20899, [b)]Fire Science Division, NIST, [c)]Department of Chemical Engineering, Florida A&M University-Florida State University, Tallahassee, FL 32310, [d)]Florida State University, Tallahassee, FL 32310, [e)]Instituto de Ciencia y Tecnologia de Polimeros, 28006, Madrid

9:00 210. ***SUDDEN AND ADIABATIC EXPERIMENTS: APPLICATIONS TO SOLID-STATE NMR.*** **Beat Meier.** Matthias Ernst, Robbie Iuliucci, Melanie Nijman, and Rene Verel, University of Nijmegen, NSR Center, Nijmegen, The Netherlands, and Laboratorium fur Physilalische Chemie, ETH-Zentrum, 8092 Zurich, Switzerland.

9:30 211. ***VARIABLE DIRECTOR NMR STUDIES OF ALIGNMENT AND DYNAMICS IN SYNTHETIC LIQUID CRYSTALLINE POLYMERS,*** Dan McElheny, Veronica Frydman, Min Zhou and **Lucio Frydman.** Department of Chemistry (M/C 111), University of Illinois at Chicago, 845 W. Taylor Street, Chicago, IL 60607-7061.

10:00 Break

10:30 212. ***RESONANCE ASSIGNMENT AND STRUCTURE DETERMINATION OF ISOTOPICALLY ENRICHED PROTEINS BY SOLID-STATE NMR.*** **Mei Hong.** Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA

11:00 213. ***FAST MAGIC ANGLE SPINNING NMR STUDIES OF POLYMER BLENDS AND INTERFACES.*** **Peter A. Mirau.** Sharon A. Heffner and Sujatha Vathyam, Bell Laboratories, Lucent Technologies, 600 Mountain Ave., Murray Hill, NJ, 07974

11:30 214. ***STRUCTURE OF b-AMYLOID FIBRIL MEASURED BY DIPOLAR RECOUPLING NMR*** R. E. Botto, **D. M. Gregory.** T. L. S. Benzinger #, D. G. Lynn # and S. C. Meredith #, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439 and Departments of Chemistry and Pathology#, University of Chicago, Chicago, IL 60637.

Monday Afternoon, July 27

SESSION II:POSTER SESSION A, Jeff Reimer, Presiding

1:30-3:00 Odd-numbered posters will be presented

SESSION III: NEW TECHNIQUES AND APPLICATIONS A, Steve Sinton, Presiding

3:30 215. ***SURFACE NEAR NMR WITH THE MOUSE.*** P. Blumler. G. Zimmer, A. Guthausen, U. Schmitz, and B. Blumich, Magnetic Resonance Center MARC, RWTH Aachen, Germany

4:00 216. ***MAGNETIC RESONANCE ELASTOGRAPHY: "PALPATION" BY IMAGING.*** R.L. Ehman. A.J. Lawrence, M.A. Dresner, G.H. Rose, A. Manduca, J.P. Felmlee, Mayo Clinic and Foundation, Rochester, MN, 55905, USA.

4:30 217. ***ALBATROSS: NUISANCE OR FRIEND?.*** Daniel P. Weitekamp. and Leonard J. Mueller, A.A. Noyes Laboratory of Chemical Physics, 127-72, California Institute of Technology, Pasadena CA 91125.

Tuesday, July 28

SESSION IV: JOINT NMR/EPR SESSION, Lucio Frydman, Presiding

8:30 218. ***MAGIC ANGLE SPINNING IN NMR AND EPR.*** H.W. Spiess. Max-Planck-Institut fur Polymerforschung, Postfach 3148, D-55021 Mainz, Germany

9:05 219. ***EXPLOITATION OF THE FREE EVOLUTION PERIODS IN PULSE EPR EXPERIMENTS.*** J.J. Shane and A. Schweiger, ETH-Zurich, Switzerland.

9:40 220. ***PULSED ENDOR IN UNORIENTED SAMPLES: HOW TO INCREASE RESOLUTION AND GAIN THE MULTIPLEX ADVANTAGE.*** M.K. Bowman and A.M. Tyryshkin, Pacific Northwest National Laboratory, Richland, WA 99352.

10:15 Break

10:45 221. ***ENDOR OF METALLOENZYMES: TO THE LIGANDS AND BEYOND.*** B.M. Hoffman. Northwestern University.

11:20 222. ***HIGH FIELD (140 GHZ/5T) EPR AND DYNAMIC NUCLEAR POLARIZATION M.*** Bennati, C. Farrar, D. Hall, S. Inati, M. Rosay, V. Weis, K. Kreischer and R.G. Griffin. Francis Bitter Magnet Laboratory, and Dept. of Chemistry, MIT, Cambridge, MA 02139

Afternoon:

SESSION V: POSTER SESSION B, Jeff Reimer, Presiding

1:30-3:00 Even-numbered posters will be presented

SESSION VI: NEW TECHNIQUES AND APPLICATIONS B, Steve Sinton, Presiding

3:30 223. ***BANDWIDTH EXTENSION USING NOISE SPECTROSCOPY.*** D.-K. Yang and D. B. Zax. Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853-1301 USA

4:00 224. ***ADIABATIC FOLLOWING.*** Lorenz Mitschang and Ann E. McDermott, Columbia University, Department of Chemistry, 3000 Broadway, NY, NY 10027

4:30 225. ***QUADRUPOLE ECHO DOUBLE RESONANCE AND SOLID ECHO DOUBLE RESONANCE NMR.*** Yong Ba. Chris A. Tulk, Chris I. Ratcliffe and John A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Canada K1A 0R6

Tuesday Evening, July 28

SESSION VII: VENDOR POSTER SESSION, Jeff Reimer, Presiding

7:30-9:00 pm

Wednesday, July 29

Morning Session:

SESSION VIII: **ROBERT** W. **VAUGHAN MEMORIAL SESSION**
Robert Wind, Presiding

8:30 226. **R**.W. **VAUGHAN PLENARY LECTURE:** ***FLOQUET THEORY AND MAGIC ANGLE SPINNING.*** **Shimon Vega.** Chemical Physics Department, Weizmann Institute of Science, Rehovot 76100, Israel

9:30 227. ***SOLID STATE NMR STUDIES OF BIOMOLECULAR RECOGNITION*** J.R. Long[a], J. Dindot[b], W. Shaw[b,c], A.A. Campbell[c], P.S. Stayton[a], and G.P. Drobny[b]. [a]Department of Bioengineering and [b] Department of Chemistry, University of Washington, Seattle WA 98195, [c] Pacific Northwest National Laboratory, Richland WA 99352

10:10 Break

10:40 228. ***REDOR NMR OF HETEROGENEOUS POLYMER BLENDS.*** J. Schaefer. Department of Chemistry, Washington University, St Louis, MO 63130

11:20 229. ***THREE-DIMENSIONAL STRUCTURES OF ZEOLITE-SORBATE COMPLEXES FROM SOLID STATE NMR.*** **C.A. Fyfe.** A. Diaz, A. Lewis, H. Grondey, G.T. Kokotailo and J-M. Chezeau, Chemistry Department., University of British Columbia, Vancouver, B.C., Canada

Afternoon:

SESSION IX: INORGANIC MATERIALS, John Hanna, Presiding

1:30 230. ***SOLID-STATE NMR STUDIES OF SPIN INTERACTIONS, PHASE TRANSTIONS, AND TRANSFORMATIONS IN INORGANIC MATERIALS FROM POWDERS AND SINGLE CRYSTALS.*** H.J. Jakobsen. H. Bildsoe, J. Skibsted, and T. Vosegaard, Instrument Centre for Solid-State NMR Spectroscopy, Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

2:00 231. ***HOMOGENEITY, HETEROGENEITY, AND DYNAMICS IN OXIDE GLASSES AND LIQUIDS: NEW VIEWS FROM 3QMAS AND HIGH-TEMPERATURE NMR.*** J. F. Stebbins. T. Schaller and S. Wang, Dept. of Geological and Environmental Sciences, Stanford University, Stanford CA 94305-2115, USA

2:30 232. ***NQR DETECTION: SEEING MORE OF WHAT IS THERE.*** J. B. Miller. A. **N.** Garroway, and **B.** H. Suits, Naval Research Laboratory, Chemistry Division, Code 6122, Washington, DC 20375; Michigan Technological University, Physics Department, Houghton, MI 49931

3:00 Break

3:30 233. ***ORIENTATION OF THE QUADRUPOLE AND DIPOLE TENSORS OF HYDROXYL GROUPS BY 170 QUADRUPOLE SEPARATED LOCAL FIELD NMR.*** E.R.H van Eck and M.E. Smith, School of Physical Sciences, University of Kent at Canterbury, Canterbury, Kent, CT2 7NR, United Kingdom.

4:00 234. ***SOLID-STATE 93Nb NMR OF NIOBIUM B-SITE CHEMICAL ENVIRONMENTS AND ORDERING IN PMN AND PMN/PT FERROELECTRICS.*** J.J. Fitzgerald. J. Huang, S. Prasad, P. Zhao and J. S. Shore, Department of Chemistry, South Dakota State University, Brookings, SD 57007

4:30 235. ***IN SITU HETEROGENEOUS CATALYSIS STUDIES BY THE GRASSHOPPER METHOD.*** David Keejer, Jincheng Xiong, Herman Lock, Ting Tao and Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

Thursday, July 30

Morning:

SESSION X: COMPUTING THE NMR PARAMETERS, Clare Grey, Presiding

8:30 236. ***THE NMR CHEMICAL SHIFT: INTRA-AND INTERMOLECULAR EFFECTS.*** Angel C. de Dios. and Ann E. Walling, Department of Chemistry, Georgetown University, 37th and **"O"** Sts., NW Washington, DC, USA, 20057

9:00 237. ***THE INTERPRETATION OF GAUGE-INCLUDING ATOMIC ORBITAL (GIAO) CALCULATIONS OF NMR SHIELDING TENSORS USING NATURAL CHEMICAL SHIELDING (NCS) ANALYSIS.*** F. A. Weinhold, J. A. Bohmann and T. C. Farrar. Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, WI 53706

9:30 238. ***UNDERSTANDING INTERMOLECULAR 129Xe CHEMICAL SHIFTS. APPLICATIONS TO COMPETITIVE ADSORPTION IN ZEOLITES.*** Cynthia J. Jameson. Department of Chemistry, University of Illinois at Chicago, Chicago IL 60607-7061.

10:00 Break

SESSION XI: PROBING THE NMR PARAMETERS, Clare Grey, Presiding

10:30 239. ***DEVELOPMENT OF AN ISOLATED FLOW VT MAS NMR PROBE.*** Paul K. Isbester and **Eric J. Munson.** Department of Chemistry, Smith Hall, University of Minnesota, Minneapolis, Minnesota 55455.

11:00 240. ***ERROR-TOLERANT RF LITZ COILS FOR MICROSCOPY.*** F. David Doty, Cory Hauck, **George Entzminger.** and Andy Yang, Doty Scientific, Inc., 700 Clemson Rd, Columbia, SC 29229

11:**30** 241. ***TOROID CAVITY NMR DETECTOR: APPLICATION TO ELECTROCHEMICAL SYSTEMS.*** R.E. Gerald II, R.J. Klingler, J.W. Rathke, and G. Sandi, Chemical Technology and Chemistry Divisions, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois 60439-4837, USA K. Woelk, Inst. Phys. Chem., University of Bonn, Wegelerstr. 12, D-53115 Bonn, Germany

12:00 **Concluding Remarks,** Robert Wind.

SYMPOSIUM ON NMR
POSTER SESSIONS

Session A: odd-numbered posters will be presented
Session B: even-numbered posters will be presented

The posters are numbered in alphabetical order of the presenting author

242. ***MATRIX ENDOR DETERMINATION OF THE MAGNETIC INTERACTION RANGE BETWEEN AN UNPAIRED ELECTRON SPIN AND NUCLEAR SPINS IN PMR-15 POLYIMIDE RESIN.*** Myong K. Ahn* Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809

243. ^{23}***NA MQMAS INVESTIGATIONS OF SODIUM ULTRAPHOSPHATE GLASSES.*** Todd M. Alam* Carol Click, Timothy J. Boyle and Richard K. Brow(b), Sandia National Laboratories, Albuquerque, NM 87185,(b)University of Missouri-Rolla, Rolla MO 65409

244. ***QUANTITATIVE ANALYSIS OF***^{27}***Al MQMAS NMR SPECTRA OF MICROPOROUS MATERIALS.*** C. Fernandez, L. Delevoye, A. Bailly*, J.P. Amoureux, LDSMM, URA801, Universite of Lille, *59655* Villeneuve d'Ascq, France

245. ***POLARIZATION ENHANCEMENT IN ORGANIC MOLECULES VIA HYPERPOLARIZED SUPERCRITICAL XENON.*** John J. Balbach*, Brian T. Saam, Mark S. Conradi, Washington University, Physics Dept. CB1105, One Brookings Drive, St. Louis, MO 63130-4899

246. ***APPLICATION OF MAGIC ECHOES' TO OVERCOME THE DEAD-TIME IN LOW RESOLUTION NMR MEASUREMENTS.*** G. Bennett* and K. Packer, Physical Chemistry, University of Nottingham, University Park, Nottingham, UK

247. ***AN EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE OLEFINIC CARBON CHEMICAL SHIELDING TENSORS IN Pt(0) AND Pt(II) COMPLEXES.*** Guy M. Bernard*, Robert W. Schurko, Roderick E. Wasylishen (Department of Chemistry, Dalhousie University, Halifax, NS B3H 4J3) and Gang Wu (Present address: Department of Chemistry, Queen's University, Kingston, ON K7L 3N6)

248. ***HIGH-RESOLUTION VARIABLE-TEMPERATURE 19F MAS NMR SPECTROSCOPY OF VINYLIDENE FLUORIDE BASED FLUOROPOLYMERS.*** Jennifer Brandt*, Paul K. Isbester, Eric J. Munson, Department of Chemistry, Smith Hall, University of Minnesota, Minneapolis, Minnesota *55455,* and Thomas A. Kestner, 3M Speciality Adhesives and Chemicals Div., 3M Center Bldg. 236-2B-11, St. Paul, MN. 55144-1000

249. ***A SOLUTE'S VIEW OF A LIQUID CRYSTAL.*** Raymond Syvitski and Elliott Burnell* Department of Chemistry, 2036 Main Mall, University of British Columbia, Vancouver, B.C., V6T 1Z1 Canada, and C.A. de Lange, Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127-129,1018 WS Amsterdam, The Netherlands

250. ***SOLID-STATE NMR CHARACTERIZATION OF FEP FILMS FROM THE HUBBLE SPACE TELESCOPE.*** Cato*, J. Dever, K. de Groh, M.P. Espe, ^Department of Chemistry, University of Akron, Akron Ohio 44325, NASA Lewis Research Center, Cleveland Ohio 44135.

251. ***^{15}N SOLID STATE NMR INVESTIGATION OF NORBORNENE-TERMINATED ADDITION POLYIMIDE CURE AND HYDROLYSIS REACTIONS.*** David B. Curliss* Air Force Research Laboratory, Wright-Patterson AFB, Ohio, Brett Cowans, School of Chemical Engineering, Purdue University, West Lafayette, Indiana

252. ***THE CONTRIBUTION OF BACKBONE DYNAMICS TO ENTROPY CHANGES OCCURRING ON OXIDATION OF CYTOCHROME B5: CAN REDOX LINKED CHANGES IN HYDROGEN BOND NETWORKS MODULATE REDUCTION POTENTIALS?*** Bindi Dangi*, Department of Pharmaceutical Sciences, School of Pharmacy, University of Maryland, 20 N. Pine St., Baltimore, MD 21201, Jeffrey I. Blankman, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, Cary J. Miller Department of hemistry and Biochemistry, University of Maryland, College Park, MD 20742 Current address: i-Stat Corporation, Kanata, ON, Canada, K2L 1T9, Brian F. Volkman Nuclear Magnetic Resonance Facility at Madison, University of Wisconsin-Madison, WI 53706 R. D. Guiles, Department of Pharmaceutical Sciences, School of Pharmacy, University of Maryland, 20 N. Pine St., Baltimore, MD 21201, and The Medical Biotechnology Center, An Institute of the Maryland Biotechnology Institutes, 725 W. Lombard St., Baltimore, MD, 21201

253. ***HOST FRAMEWORK FLEXIBILITY AND FREEDOM OF MOTION OF GUEST MOLECULES IN SUPRAMOLECULAR HOST-GUEST COMPLEXES.*** Shawn McCleskey, Phillip Smith, and James J. Dechter*, Department of Chemistry, University of Central Oklahoma, Edmond, OK 73034

254. ***COMPUTER ANALYSIS OF SINGLE CRYSTAL NMR DATA.*** M.J.T. Ditty*, C.W. Kirby, W.P.Power, Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, Department of Chemistry University of Waterloo, Waterloo, ON, N2L 3G1, Canada.

255. ***INVESTIGATION OF PARTIAL OXIDATION CATALYSIS BY SOLID-STATE NMR.*** Michelle C. Douskey* Bin Chen*, Eric J. Munson; Department of Chemistry, University of Minnesota, Minneapolis, MN 55455

256. ***4-SPIN SPIN-DIFFUSION MECHANISM IN ^{19}F2-D NMR EXPERIMENTS OF OXYFLUORIDES.*** Lin-Shu Du* and Clare P. Grey, SUNY at Stony Brook, Department of Chemistry, Stony Brook, NY 11794-3400,USA, Malcolm H. Levitt, Physical Chemistry Division, Stockholm University, S-10691 Stockholm, Sweden.

257. ***HETERONUCLEAR-CORRELATION EXPERIMENTS FOR CHEMICAL AND STRUCTURAL INVESTIGATIONS OF ALUMINOBOROSILICATE GLASS SYSTEMS.*** James M. Egan *, Karl T. Mueller, Mary Strzelecki, Pennsylvania State University, Chemistry Department, 152 Davey Laboratory, University Park, PA 16802

258. ***^{17}O MQ MAS NMR STUDIES OF ZEOLITES IN THE HIGH FIELD.*** C. Fernandez*, J.P. Amoureux, D. Freude(b), D. Michel(b), F. Bauer(b), H. Ernst(b), U.T. Pingel(b), LDSMM, URA801, Universite of Lille, 59655 Villeneuve d'Ascq (b)Abteilung Grenzflachenphysik, Universitat Leipzig, D-04103 Leipzig, Germany

259. ***REDOR/REAPDOR EXPERIMENTS ON ZEOLITES USING HIGH SPEED CP-MAS PROBEHEAD.*** S. Ganapathy, L. Delevoye, C. Fernandez*, J.P. Amoureux, LDSMM, URA801, Universite of Lille, 59655 Villeneuve d'Ascq, France

260. ***CHARACTERIZATION OF PHOSPHORUS CHEMICAL SHIELDING TENSORS IN A PHOSPHOLE TETRAMER - A COMBINED EXPERIMENTAL AND THEORETICAL STUDY.*** Myrlene Gee*, Gang Wu, Klaus Eichele, Roderick E. Wasylishen, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

261. ***NMR STUDIES OF LITHIUM TRANSITION METAL OXIDE POSITIVE ELECTRODE MATERIALS.*** Becky Gee*, Craig Home, Elton Cairns, Jeffrey Reimer, Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory and Department of Chemical Engineering, 201 Gilman Hall, University of California at Berkeley, Berkeley, CA 94720-1462

262. ***Li-7 NUCLEAR MAGNETIC RELAXATION STUDIES OF METAL OXIDE ELECTRODES FOR Li-ION RECHARGEABLE BATTERIES.*** G.R.Goward* L.F.Nazar and W.P.Power, Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, Department of Chemistry, University of Waterloo, Waterloo, ON, N2L 3G1, Canada.

263. ***SOLID STATE NMR AND Ab Initio INVESTIGATIONS OF THE RELATIONSHIPS BETWEEN ^{17}O QUADRUPOLAR COUPLING PARAMETERS AND STRUCTURE IN ALKALINE EARTH SILICATES.*** Ronald W. Groves*, Karl E. Vermillion, and Philip J. Grandinetti, Ohio State University, Department of Chemistry, Columbus, OH 43210

264. ***APPLICATIONS OF NMR FOR NONDESTRUCTIVE EVALUATION OF NUCLEAR MATERIALS.*** E.S. Growney*, R.E. Gerald II, R.J. Klingler, J.W. Rathke, L.H. Nunez, and S.E. Aumeier, Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois 60439-4873, USA

265. ***'H-^{15}N-^{13}C TRIPLE RESONANCE SOLID-STATE NMR EXPERIMENTS FOR PEPTIDES AND PROTEINS.*** Zhengtian Gu * and Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104

266. ***RECENT DEVELOPMENTS IN q-REDOR AND REAPDOR NMR*** Terry Gullion* Department of Chemistry, West Virginia University, Morgantown, WV 23506

267. ***^{207}PB AND ^{137} BA NMR OF SOLID SOLUTIONS.*** Young-Sik Kye, Bruno Herreros and Gerard S. Harbison*, Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304

268. ***SPECTRAL SIMULATION OF ROTATING SOLIDS BASED ON LANCZOS AND FLOQUET METHODS FOR COUPLED SPIN SYSTEMS UNDERGOING CHEMICAL EXCHANGE BETWEEN MULTIPLE SITES.*** Randall S. Dumont, Paul Hazendonk* and Alex D. Bain, Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1, Canada

269. ***A MULTIFIELD ^{17}O NMR DOR AND DAS STUDY OF SILICEOUS ZEOLITE FERRIERITE.*** Andy P Howes*, Lucy M Bull, Ago Samoson #, Phillip J Grandinettia and Ray Dupree, Physics Department, University of Warwick, Coventry CV4 7AL, U.K, Institute des Materiaux de Nantes, Laboratoire de Chimie des Solides, 2 rue de la Houssinere, B.P. 32229, 44322 Nantes, Cedex 3, France, # Institute of Chemical Physics and Biophysics, Akadeemia Tee 23, Tallinn, Estonia; a Chemistry Department, Ohio State University Columbus, Ohio, USA

270. ***THE Si-29 AND B-11 NMR STUDY OF POLYMER PRECURSOR FOR HIGH TEMPERATURE CERAMICS.*** Sanlin Hu*, Kai Su and Duane Bujalski, Dow Corning Corporation, Midland, Michigan 48686

271. ***SOLID-STATE ^{93}Nb NMR STUDIES OF LEAD NIOBATE INTERMEDIATES AND LEAD MAGNESIUM NIOBATE (PMN).*** J. Huang* P. Zhao, S. Prasad, J. Shore and J.J. Fitzgerald, Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007

272. ***THE USE OF SOLID-STATE NMR TO STUDY PHOTO CATALYTIC REACTIONS ON TITANIUM DIOXIDE SUPPORTED BY POROUS VYCOR GLASS AND OPTICAL FIBERS.*** Son-Jong Hwang*, Charles V. Rice, Sarah Pilkenton and Daniel Raftery, H.C. Brown Laboratory of Chemistry, Purdue University, West Lafayette, IN 47907.

273. ***RELAXATION MEASURMENTS WITH LOW-FIELD, ONE-SIDED NMR.*** J.H Iwamiya* and S.W. Sinton, Advanced Technology Center, Lockheed Martin Missiles & Space, O/H1-34, B/204, 3251 Hanover Street, Palo Alto, CA 94304

274. ***NMR INVESTIGATIONS OF MESOSTRUCTURED ALUMINOPHOSPHATE.*** C. Jagerl*, M.Schulzl, C. Pophal2,W. Heerdegenl, H. Fuess2, 1PATF/ IOQ-HF, Friedrich-Schiller-Universitat, Max-Wien-Platz 1, D-07743 Jena, 2FB Materialwissenschaft, TU Darmstadt, Petersenstr. 20, 64287 Darmstadt

275. ***HOMONUCLEAR CORRELATION SPECTROSCOPY INVOLVING QUADRUPOLAR NUCLEI.*** P. Hartmannl, J.W. Zwanziger2, C. Jagerl*, 1 Friedrich Schiller University Jena, Institute of Optics and Quantumelectronics, Max Wien Platz 1, D-07743 Jena Germany; 2 Indiana University, Department of Chemistry, Bloomington, IN 47405, USA

276. ***STRUCTURE INVESTGATIONS OF $NaPO_3$-Nb_2O_5 GLASSES BY NMR.*** L. Olivierl, S. Barth2, C. Jagerl*, 1 Friedrich Schiller University Jena, Institute of Optics and Quantum Electronics, Max-Wien-Platz 1, D-07743 Jena, Germany; 2 Friedrich Schiller University Jena, Department of Chemistry, August Bebel Str. 2, D-07743 Jena, Germany

277. ***HIGH-PERFORMANCE 4 MM CP/MAS PROBES FOR VARIABLE TEMPERATURE STUDIES IN HIGH-FIELD LIQUID-STATE NMR SPECTROMETERS.*** H.J. Jakobsen* E. Hald, and P. Daugaard, Instrument Centre for Solid-State NMR Spectroscopy, Department of Chemistry; University of Aarhus, DK-8000 Aarhus C, Denmark

278. ***CHARACTERIZATION OF POLYANILINE/DODECYLBENZENE SULFONIC ACID POLYMERIZED FROM AQUEOUS MEDIUM: A SOLIDS NMR STUDY.*** Shifra Kababya*, Michael Appe, Yafit Haba, Gregory I. Titelman and Asher Schmidt; Dept. of Chemistry and Dept. of Chemical Engineering, Technion, Haifa,32000 Israel

279. ***SOLID-STATE NMR STUDIES OF THE VITAMIN B12 FAMILY.*** C.W, Kirby*, J.R. Garbutt, G.R. Goward, and W.P. Power, Guelph-Waterloo, Centre for Graduate Work in Chemistry and Biochemistry, Department of Chemistry, University of Waterloo, Waterloo, ON, N2L 3G1, Canada

280. ***DETERMINATION OF THE FUNCTIONALITY AND FUNCTIONALITY DISTRIBUTION OF POLYETHER POLYOLS BY QUANTITATIVE ^{13}C-NMR SPECTROSCOPY.*** Rene A. Klein*, Jan F. Hernalsteen, Julien Devos, ICI Polyurethanes, International R&D, Analytical Group, Everslaan 45, B-3078, Everberg, Belgium

281. ***ANISOTROPYIN THE P-31, CU-63/65 INDIRECT SPIN-SPIN COUPLING AND P-31 NUCLEAR SHIELDING TENSORS OF LINEAR COPPER(I) PHOSPHINES.*** Scott Kroeker(l)*, Roderick E. Wasylishen(l) and John V. Hanna(2), (1) Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada. (2) CSIRO North Ryde NMR Laboratory, P.O. Box 52, North Ryde-, N.S.W. 2113, Australia.

282. ***SOLID-STATE NMR STUDY OF CESIUM EXCHANGED ZEOLITES.*** Theresa A. Lalain*, Karl T. Mueller, D.E.W. Vaughanl, Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802-6300, USA, lExxon Research and Engineering Company, Route 22 East, Annandale, N.J. 08801, USA

283. ***RIACT MULTIPLE QUANTUM (MQ) MAS NMR SIMULATIONS, MQMAS TRIPLE QUANTUM CP, AND CP MAS NMR EXPERIMENTS OF FLUORIDES.*** Kwang Hun Lim* and Clare P. Grey, Department of Chemistry, SUNY Stony Brook, Stony Brook, NY 11794-3400, USA.

284. ***NMR OF SAMPLES CONTAINING METAL FOILS.*** Herman Lock*, Ting Tao, Jincheng Xiong, David Keeler and Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins CO, USA.

285. ***CROSS POLARIZATION AND DIRECT POLARIZATION TRANSFER TO SURFACE SPECIES USING LASER-POLARIZED XENON.*** Ernesto MacNamara*, Gregory Fisher, Jay Smith, Charles V. Rice, Son-Jong Hwang, and Daniel Raftery, H.C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393

286. ***A THEORETICAL DESCRIPTION OF THE 14N OVERTONE NMR EXPERIMENT IN STATIC AND SPINNING SOLIDS.*** Laura Marinelli* and Lucio Frydman. Department of Chemistry (M/C 111), University of Illinois at Chicago, 845 W. Taylor Street, Chicago, IL 60607-7061

287. ^{129}***Xe NMR STUDIES OF PARTICULATE CARBON BLACKS USED IN POLYMER PROCESSING.*** Kenneth J. McGrath* Code 6120, Naval Research Laboratory, Washington, DC 203755342

288. ***MODELING GLASS STRUCTURE BY COMBINING NMR, NEUTRON DIFFRACTION, AND X-RAY DIFFRACTION DATA.*** J. W. Zwanziger and J. C. McLaughlin*, Dept. of Chemistry, Indiana University, Bloomington, IN 47405

289. ^{31}***P-***^{19}***F REDOR: GENERATING DISTANCE CONSTRAINTS IN THE BACKBONE OF DNA AND RNA.*** Matthew E. Merritt*, John Stringer, Snorri T. Sigurdsson, and Gary P. Drobny, Chemistry Department, University of Washington, Box 351700, Seattle, WA 98195-1700

290. ***MULTINUCLEAR SOLID STATE NMR INVESTIGATIONS OF ALKALI METAL-LOADED ZEOLITES.*** Kelly L. Moran*,[a] Ray Dupree,[a] Paul A. Anderson,[b] Peter D. Barker,[b] Jenny E. Readman,[b] and Peter P. Edwards[b]; [a] Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom; [b] School of Chemistry, University of Birmingham, Birmingham B15 2TT, United Kingdom.

291. ***EXTRACTING DIPOLAR COUPLINGS IN SOLID STATE NMR BY TRANSFORM AND REGULARIZATION METHODS.*** Karl T. Mueller*, David J. Aurentz, and Frederick G. Vogt, Pennsylvania State University, Department of Chemistry, 152 Davey Laboratory, University Park, PA 16802-6300

292. ***STRUCTURAL TRENDS IN TERNARY PHOSPHORUS-SULFIDE-SELENIDE AMORPHOUS MATERIALS.*** Paul F. Mutolo* (1,2) and Hellmut Eckert (2), 1-Department of Chemistry, University of California, Santa Barbara CA 93106 USA; 2-WWU Munster, Institut fur Physikalische Chemie, Schlossplatz 4/7, D-48149 Miinster, Germany.

293. ***SOLID-LIQUID DYNAMIC NUCLEAR POLARIZATION TRANSFER IN AQUOUS CHAR SUSPENSIONS.*** Boris M. Odintsov* (1,3,4), P.J. Ceroke (1,3), and R.B. Clarkson (1,3), 1-Illinois Research EPR Center, Department of Chemistry (2) and Veterinary Clinical Medicine (3), University of Illinois, 190 MSB, 506 S. Matthews, Urbana, IL 61801, USA, 4-Zavoisky Physical-Technical Institute, Kazan, 420029, Russia

294. ***PARTICLE SIZE EFFECT ON TRANSVERSE NMR RELAXATION IN AQUOUS CARBON-BASED CHAR SUSPENSIONS.*** Boris M. Odintsov* (1,3-5), A.N. Temnikov (4), Z.Sh. Idiyatullin (4), R.S. Kashaev (4), R.L. Bedford (1,2), P.J. Ceroke (3), and R.B. Clarkson (1,3), 1-Illinois Research EPR Center, Department of Chemistry (2) and Veterinary Clinical Medicine (3), University of Illinois, 190 MSB, 506 S. Matthews, Urbana, IL 61801, USA, 4-Zavoisky Physical-Technical Institute, 5-State Technological University, Kazan, 420029, Russia

295. ***MOLECULAR DIFFUSION AND DNP ENHANCEMENT IN AQUOUS CHAR SUSPENSIONS.*** Boris M. Odintsov* (1,3-5), A.N. Temnikov (4), Z.Sh. Idiyatullin (4), R.S. Kashaev (4), R.L. Bedford (1,2), P.J. Ceroke (3), and R.B. Clarkson (1,3), 1-Illinois Research EPR Center, Department of Chemistry (2) and Veterinary Clinical Medicine (3), University of Illinois, 190 MSB, 506 S. Matthews, Urbana, IL 61801, USA, 4-Zavoisky Physical-Technical Institute, 5-State Technological University, Kazan, 420029, Russia

296. ***SOLID-STATE*** ^{13}***C NMR AND FTIR STUDIES OF METAL OXALATE PRECURSORS TO ELECTRONIC MATERIALS.*** T.J. Offerdahl* and J.J. Fitzgerald, Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007

297. ***EXPERIMENTAL AND SIMULATED EFFECTS OF INSUFFICIENT DECOUPLING ON DRAWS DEPHASING CURVES.*** Nathan A. Oyler* John A. Stringer, and Gary P. Drobny, Chemistry Department, University of Washington, Box 351700, Seattle, WA 98195-1700

298. ***DIRECT OBSERVATION OF DEFECT SITES IN POLY(LACTIDE) USING*** ^{13} ***C SOLID-STATE NMR SPECTROSCOPY.*** Brian E. Padden*l, Mark T. Zelll, Khalid A.M. Thakurl, Robert T. Kean2, Marc A. Hillmyerl, Eric J. Munsonl; 1Department of Chemistry, University of Minnesota, Minneapolis, MN 55455; 2Cargill Incorporated, Central Research, P.O. Box 5699, Minneapolis, MN, 55440.

299. ***THE Li-6/Li-7 CHEMICAL SHIFT ANISOTROPIES AND QUADRUPOLAR COUPLING CONSTANTS IN ORGANOLITHIUM COMPOUNDS.*** Glenn H. Penner* and Phillis Chang, Department of Chemistry, University of Guelph, Guelph, Ontario, CANADA NIG 2W1

300. ***MEASURING INTERNAL ELECTRIC FIELDS IN PROTEINS WITH SOLID-STATE NMR.*** Alexey Peshkovsky*

Ann E. McDermott, Chemistry Department, Columbia University, New York, NY, 10027

301. ***PHOTOCHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION IN BACTERIAL REACTION CENTERS: MECHANISM AND SIMULATIONS OF THE SOLID-STATE NMR EXPERIMENTS.*** Ann McDermott and Tatyana Polenova*, Chemistry Department, Havemeyer Hall, Columbia University, New York, NY 10027

302. ***MEASUREMENT OF HETERONUCLEAR DIPOLAR INTERACTIONS BETWEEN QUADRUPOLAR AND SPIN-1/2 NUCLEI IN SOLIDS BY MULTIPLE-QUANTUM REDOR NMR.*** Christian Fernandez, David Lang, Jean-Paul Amoureux, Marek Pruski*, University of Science and Technology in Lille and Ames Laboratory, Iowa State University.

303. ***N-15 CHEMICAL SHIFT TENSORS IN NUCLEIC ACID BASES.*** Jian Zhi Hu (1), Julio C. Facelli (3), Donald W. Alderman (1), Ronald J. Pugmire* (1,2), and David M. Grant (1), Departments of Chemistry (1) and Chemical and Fuels Engineering (2), and Center for High Performance Computing (3), University of Utah, Salt Lake City, UT 84112

304. ***DYNAMIC NUCLEAR POLARIZATION AND N-15 NMR SPECTROSCOPY.*** Jian Zhi Hu (1), Mark S. Solum (1), Yi Jiang (1), David M. Grant (1), Robert A. Wind (1,3), Paul D. Ellis (3), and Ronald J. Pugmire* (1-3), Departments of Chemistry (1) and Chemical and Fuels Engineering (2), University of Utah, Salt Lake City, UT 84112, and Environmental and Molecular Sciences Laboratory (3), Pacific Northwest National Laboratory, Richland, WA 99352

305. ***^{13}C SOLID STATE NMR OF GRAMICIDIN A IN A LIPID MEMBRANE.*** Per-Ola Quist*, Department of Physical Chemistry, Umea University, S - 901 87 Umea, Sweden

306. ***THE UNUSUAL PROPERTIES OF SODIUM-SILICON CLATHRATES: ^{23}Na AND ^{29}Si NMR.*** J. He, D.D. Klug, C.I. Ratcliffe*, V.I. Smelyansky and J.S. Tse, Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario, Canada K1A 0R6.

307. ***GAS PHASE MAGNETIC RESONANCE MICROIMAGING STUDIES OF POROUS MATERIALS WITH HYPERPOLARIZED XENON AND THERMALLY POLARIZED GASES.*** I.M. Moudrakovski, C. I. Ratcliffe*, J.A. Ripmeester, Steacie Institute for Molecular Sciences, 100 Sussex Dr., Ottawa, Ontario, Kl A 0R6,Canada

308. ***TOWARDS DYNAMIC NUCLEAR POLARIZATION IN BIOLOGICAL SOLIDS: SIGNAL-ENHANCED SOLID-STATE NMR STUDIES.*** Melanie Rosay* Marc Baldus, Volker Weis and Robert Griffin, Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139.

309. ***METHYLENE-ONLY ^{13}C CP-MAS SPECTRA BY DOUBLE-QUANTUM FILTERED CP.*** Paolo Rossi* and Gerard S. Harbison, Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304

310. ***SOLID STATE NMR, X-RAY DIFFRACTION AND DSC INVESTIGATION OF THE STRUCTURE AND THE SOLID-SOLID PHASE TRANSITION IN 2(2,4-DINITROBENZYL)-3-METHYL PYRIDINE.*** Asher Schmidt* Shifi Kababya, Michael Appel, Mark Botoshansky, Soliman Khatib, and Yoav Eichen. Department of Chemistry and Solid State Institute, Technion, Haifa 32000, Israel.

311. ***NEW EXAMPLES OF ALUMINUM CHEMICAL SHIELDING ANISOTROPY.*** R.W. Schurko* and R.E. Wasylishen, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J3

312. ***CHARACTERIZATION OF SELECTIVE SITE DISTRIBUTION IN MIXED-ALKALI CHABAZITE BY ^Na MQMAS AND ^{7}Li MAS NMR.*** Luis J. Smith*, Anthony K. Cheetham, Hellmut Eckert, Materials Research Laboratory, University of California, Santa Barbara, CA, 93117, and Institut fur Physikalische Chemie, Westfalische Wilhelms - Universitat, SchloBplatz 4/7, 48149 Munster, Germany

313. ***A HIGH EFFICIENCY HFXY 9.7 TESLA CPMAS PROBE*** John A. Stringer*, and Gary P. Drobny, Chemistry Department, University of Washington, Box 351700, Seattle, WA 98195-1700

314. ***NMR INVESTIGATION OF PHOTO-ASSISTED DECOMPOSITION OF TRICHLOROETHYLENE AT THE AIR/SOIL INTERFACE.*** Ting Tao*, Jane J. Yang and Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

315. ***SOLID STATE C-13 AND Si-29 NMR STUDIES OF METHYL-CAPPED SILICA GELS.*** Ting Tao* Herman Lock, Jincheng Xiong and Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

316. ***DETERMINATION OF ^{13}C INDIVIDUAL SPECTRAL DENSITY ANISOTROPIES.*** Samuel J. Varner*, Gina L. Hoatson, Physics Department, Robert L. Void, Applied Science Department, College of William and Mary Williamsburg, VA 23187-8795, USA

317. ***CENTERBAND LINESHAPES OF PROTON MAS SPECTRA CALCULATED WITH AVERAGE HAMILTONIAN THEORY.*** Alexander J. Vega*, DuPont Central Research and Development, Experimental Station, P. O. Box 80356, Wilmington, DE 19880-0356.

318. ***SOLID-STATE NMR STUDIES OF CONFORMATION AND DYNAMICS OF SURFACTANT MOLECULES IN MOLECULARLY ORGANIZED NANOSTRUCTURED MATERIALS.*** Li-Qiong Wang*, Jun Liu, Xiangdong Feng, Glen E. Fryxell, and Gregory J. Exarhos, Pacific Northwest National Laboratories, Richland, WA 99352

319. ***MAS-NMR STUDIES OF MODIFIED ZEOLITE CATALYSTS FOR USE IN ASYMMETRIC REACTIONS.*** Richard P.K. Wells* and Graham J. Hutchings, Department of Chemistry, University of Wales, PO Box 912, Cardiff, UK, CF32 ODY.

320. ***FLOW AND RHEOLOGICAL STUDIES USING TOROID-CAVITY NMR.*** K. Woelk*(l), R. E. Gerald II(2), P. Trautner(l), B. L. J. Zwank(l), J. Bargon (1), R. J. Klingler(2), and J. W. Rathke(2). (1) Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstr. 12, D-53115 Bonn, Germany; (2) Chemical Technology Division, Argonne National Laboratory 9700 South Cass Avenue, Argonne IL 60439, USA

321. ***SOLID STATE NMR STUDIES OF SELECTIVE CATALYTIC REDUCTION OF NO OVER ZEOLITE CATALYSTS.*** Jianjun Wu*, and Sarah C. Larsen, Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, USA

322. ***A NEW MAGIC ANGLE HOPPING EXPERIMENT WITH BALANCED REFOCUSING FOR OBTAINING ONE-DIMENSIONAL HIGH RESOLUTION NMR SPECTRA OF SOLIDS.*** Jincheng Xiong*, Dave Keeler, Herman Lock and Gary Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

323. ***A STUDY OF RELATIONSHIP BETWEEN STRUCTURE AND O-17 ELECTRIC FIELD GRADIENT PARAMETERS IN SOME ALUMINOSILICATES.*** Erdem K. Yildirim*, Simon Kitchin(l), Kelly Moran(l), Michael B. Henderson , Dave M Hamilton, Phillip Grandinetti a, and Ray Dupree(l), (l)Physics Deparment, University of Warwick, Coventry, CV4 7AL, UK, Department of Earth Science, University of Manchester, Manchester M13 9PL,UK, aChemistry Department, Ohio State University, Colombus, Ohio,USA.

324. ***PROCESSING INFLUENCES ON POLYANILINE BY SOLID-STATE NMR.*** Tanya L. Young*, Dali Yang", Benjamin R. Mattes", Matthew P. Espe, University of Akron, Akron, Ohio 44325, "Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

325. ***MULTINUCLEAR NMR AS A PROBE IN NANOCOMPOSITES.*** R. Santos, D.-K. Yang, H. Hegemann and D. B. Zax*, Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853-1301 USA

326. ***INVESTIGATING POLYMORPHISM IN CRYSTALLINE ORGANIC COMPOUNDS USING SOLID-STATE NMR SPECTROSCOPY.*** Mark T. Zell1* Brian E. Padden1, David J.W. Grant2, Eric J. Munson1, Departments of Chemistry 1 and Pharmaceutics2, University of Minnesota, 207 Pleasant St. SE1, and 308 Harvard St. SE2, Minneapolis, MN 55455.

327. ***ONE-AND TWO-DIMENSIONAL SOLID-STATE NIOBIUM-93 NMR SPECTROSCOPY.*** P. Zhao*, S. Prasad, J. Huang, J. J. Fitzgerald, and J. Shore, Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007

SYMPOSIUM ON PHARMACEUTICAL ANALYSIS

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

Tuesday, July 28,1998:

Morning Session: Michael Cutrera presiding

9:30 328. ***FOURIER TRANSFORM RAMAN SPECTROSCOPY IN THE PHARMACEUTICAL INDUSTRY.*** Bonnie L. Leimer, Roel Ferwerda, Nicolet Instrument Corporation, San Jose, CA.

10:15 329. ***VALIDATING YOUR FT-IR: UNDERSTANDING THE VALIDATION PROCESS AND THE SYSTEM TESTS.*** Bonnie L. Leimer, Nicolet Instrument Corporation, San Jose, CA.

11:10 330. ***ORALLY DELIVERED IMMUNOCONTRACEPTIVE VACCINE FOR RUMINANTS.*** Jerome C. Hurley, U.S.D.A., National Wildlife Research Center, Fort Collins, CO.

Afternoon Session: Robert K. Lantz presiding

1:30 331. ***ADVANCES IN LC/MS TECHNIQUES IN CHEMICAL ANALYSIS.*** John MacKay, Andrew Braillesford, Beverly Kenney, Michael Swartz, Waters Corporation, Milford, MA.

2:45 332. ***AUTOMATED PREPARATIVE CHROMATOGRAPHY WITH MASS SPECTROMETER AS THE TRAFFIC COP.*** John MacKay, Andrew Braillesford, Michael Swartz, Waters Corporation, Milford, MA.

4:00 333. ***"MR SANDMAN, SEND ME A PEAK! MAKE IT NARROW AND WITHOUT MYSTIQUE!" AN OVERVIEW OF OPTIMIZING THE COLUMN (DIMENSION AND CHEMISTRY) AND SAMPLE CLEANUP STRATEGIES FOR YOUR LC/MS.*** John MacKay, Dorothy Phillips, Katie Sousa, Water Corporation, Milford, MA.

Wednesday, July 29,1998:

Morning Session: Michael Cutrera presiding

8:30 334. ***IMPROVE PEAK SHAPE, RESOLUTION AND ANALYSIS TIME-LOOK BEYOND C8 AND C18.*** Marilyn A. Stadalius, Maureen J. Joseph, Julia F. Vasta-russel, Carl L. Zimmerman, MAC-MOD Analytical, Inc., Chadds Ford, PA.

9:45 335. ***RAPID RESOLUTION CHROMATOGRAPHYn PRACTICALITIES AND PITFALLS.*** Marilyn A. Stadalius, Maureen J. Joseph, Julia F. Vasta-Russel, Patrick J. Barthel, MAC-MOD Analytical, Inc., **Chadds Ford,** PA.

11:00 336. ***VALIDATED HPLC METHODS n TO TWEAK OR NOT TO TWEAK.*** Marilyn A. Stadalius, Maureen J. Joseph, Julia F. Vasta-Russel, Carl L. Zimmerman, MAC-MOD Analytical, Inc., Chadds Ford, **PA.**

Afternoon Session: Patricia L. Sulik presiding

1:30 337. ***HIGH THROUGHPUT PROTEIN CHARACTERISATION: PROTEOMICS FROM 2D GELS TO PROTEIN STRUCTURE.*** PE/PerSeptive Biosystems.

2:15 338. ***PROTEIN CHARACTERISATION AND DETERMINATION OF POST TRANSLATIONAL MODIFICATIONS.*** PE/Sciex.

3:00 Break

3:15 339. ***MASS SPECTROMETRIC ANALYSIS OF FREE RADICAL DERIVED EICOSANOIDS FROM PLASMA MEMBRANE PHOSPHOLIPIDS.*** Tatsuji Nakamura, Robert C. Murphy, National Jewish Medical **and Research** Center, Denver, CO.

3:40 340. ***COMPLIMENTARY STRENGTHS OF MALDI-TOF AND ESI-TRIPLE QUADRUPOLE MASS SPECTROMETERS IN PROTEIN ANALYSIS AND IN PROTEOME STUDIES.*** Katheryn **Resing, Dept. Chem.** & Biochem., University of Colorado Boulder, Boulder, CO.

SYMPOSIUM ON RADIOCHEMISTRY

Organized by Ann Mullin

Monday, July 27,1998

Morning session: Richard Graham, U.S. Environmental Protection Agency, presiding

8:10 ***Welcoming Remarks,*** Ann Mullin U.S. Geological Survey

8:15 341. ***SAMPLE PREPARATION USING EXTRACTION CHROMATOGRAPHY*** **Lawrence Jassin, Eichrom** Industries, Inc., 8205 S. Cass Avenue, Suite 107, Darien, IL 60561.

8:45 342. ***EXPERIENCE WITH EXTRACTION CHROMATOGRAPHIC RESIN AT THE QUANTERRA RICHLAND LABORATORY*** Mathias Lardy, Jackie Waddell, and Roxie Ross, Quanterra, Inc. 2800 George Washington Way, Richland, WA 99352.

9:15 343. ***RADIUM IN GROUNDWATER ASSOCIATED WITH A COAL STORAGE PILE, SAVANNAH RIVER SITE, SOUTH CAROLINA*** M.E. Denham, D.M. Beals, and W.G. Winn, Westinghouse Savannah River Company, Savannah River Site, Aiken, SC 29808.

9:45 Break

10:00 344. ***COMPARISON OF RESULTS OF TWO APPROACHES TO DETERMINING RADIUM-224 CONCENTRATION BY GAMMA SPECTROSCOPY*** Zoltan Szabo, V.T. de Paul, U.S. Geological Survey, 810 Bear Tavern Road, West Trenton, NJ 08628, T.F. Kraemer, U.S. Geological Survey, 12201 Sunrise Valley Drive, Reston, VA 20192, and Bahman Parsa, New Jersey DHHR.

10:30 345. ***NOVEL LIQUID SCINTILLATION COUNTER FOR MEASURING ALPHA, BETA, AND GAMMA EMITTERS IN THE FIELD*** M.P. Neary, J. Fields and J.E. Noakes, University of Georgia, Center for Applied Isotope Studies, 120 Riverbend Road, Athens, GA 30605.

11:00 346. ***MARLAP(MULTI-AGENCY RADIATION LABORATORY POTOCOLS MANUAL)*** John Griggs, U.S. Environmental Protection Agency, NAREL, 540 South Morris Ave., Montgomery, AL 36115-2601.

Afternoon session:

Karen Schoendaller, Accu-Labs Research Inc., presiding

11:00 347. ***AN EVALUATION OF GROSS-ALPHA AND GROSS-BETA RADIOACTIVITY IN WATER FROM THE SNAKE RIVER PLAIN AQUIFER AT THE IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY, IDAHO*** Leroy L. Knobel, Roy C. Bartholomay, and Linda Williams, U.S. Geological Survey, WRD, INEEL, MS 1160, Idaho Falls, ID 83403.

1:30 348. ***DERIVATION AND APPLICATION OF RISK-BASED SURFACE CONTAMINATION RELEASE CRITERIA FOR A RADIOLOGICALLY CONTAMINATED BUILDING*** R.V. Graham,1 J.W. Lively,2 and D.M. Smith,3 1U.S. Environmental Protection Agency, 999 18th St., Suite 500, Denver, CO 80202-2405, 2MACTEC-ERS, 2597 B3/4 Rd., Grand Junction, CO 81503, 3TMSS, Inc., 73 Spyglass Drive, Grand Junction, CO 80123.

2:00 349. ***USE OF HIGH PRECISION GAMMA-RAY SPECTROMETRY TO ESTIMATE THE AGE OF RADIOBARITE CONTAMINATION AT OILFIELD SITES*** Robert A. Zielinski, James R. Budahn, and James K. Otton, U.S. Geological Survey, Denver Federal Center, Denver, CO 80225.

2:30 Break

Catherine Klusek, DOE Environmental Measurements Laboratory, presiding

2:45 350. ***EFFECT OF RADIOACTIVE-WASTE DISPOSAL AT THE IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY ON SELECTED RADIOCHEMICAL CONSTITUENTS IN WATER FROM THE SNAKE RIVER PLAIN AQUIFER IN THE MAGIC VALLEY STUDY AREA, IDAHO*** Roy C. Bartholomay and LeRoy L. Knobel, U.S. Geological Survey, WRD, INEEL, MS 1160, Idaho Falls, ID 83403.

3:15 351. ***DETERMINATION OF STRONTIUM-90 DISTRIBUTION COEFFICIENTS AT THE IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY*** Molly Pace 1,2, Roy Bartholomay 2, and Jeffery Rosentreter 1,1 Idaho State University and 2U.S. Geological Survey.

3:45 352. ***A CASE STUDY LOOKING AT ISSUES ENCOUNTERED AND RESOLVED AT RAMP, IND.*** R.V. Graham, C. Matson, M.W. Lammering, R. Qullin, U. S. Environmental Protection Agency, 999 18th St., Suite 500, Denver, CO 80202-2405.

4:15 353. ***INTRODUCTION OF EICHROM TEVA, DISC: Tc-99 ANALYSIS*** Anil Thakkar, Lawrence Jassin, Michael Fern, Eichrom Industries and John Sisler.

1

ATOMIC SPECTROSCOPY: PROGRESS AND PROSPECTS Akbar Montaser, J A. McLean, M. G. Minnich, L. A. laconc, and Q. Jin' Department of Chemistry, The George Washington University, Washington, DC 20052, USA

Over the past 60 years, the practice of elemental analysis has dramatically changed. Arc and high-voltage spark spectrometry were extensively utilized m the 1940s for metals analysis. In the 1950s, flame enussion spectrometry was promoted for solution analysis, but flame atomic absorption spectrometry later assumed prominence for the detection of hard to-excite elements. With the arrival of electrothemml atomization in the 1960s, the application of atomic absorption became a commnon practice. With the introduction of practical instnmientation, inductively coupled plasma atomic emission spectrometry (ICPAES) became the standard in the 1970s for simultaneous multielement analysis, especially when the technique was applied to several difficult analytical problems. In the 1980s, ICP mass spectrometry was introduced into the marketplace and eventually became the most powerfid techmque for elemental and isotopic ratio analysis. In general, ICP spectroscopies have had a major impact on elemental analyses because they offer rapid multielement determinations over a wide concentration range and down to part-per-trillion levels.[1,2] No doubt, no other technique has achieved such a rapid acceptance by the analytical chemistry community and related fields such as the semiconductor, environmental, biological, metallurgical, geological, and agricultural sciences. In this presentafion, we address recent developments in elemental analysis, with an emphasis on sample preparation, sample introduction, plasma generation, and new instrumentation for both low- and high-resolution ICP spectrometry. We will also examine future prospects of analytical spectro9metry, and present a roadmap for what remains to be done to realize a perfect method for elemental analysis.

1. A. Montaser, ***Ed.; Inductively Coupled Plasma Mass Spectrometry,*** Wiley-***VCR:*** New York, 1998, 964 pages.
2. A. Montaser and D. W. Golightly, Eds.; ***Inducfively Coupled Plasmas in Analytical Atomic Spectrometry,*** 2nd Ed.; Wiley-VCH: New York, 1992,1017 pages.

2

DETERMINATION OF WEAR AND ADDITIVE ELEMENTS IN OILS BY ICP-AES WITH ACID ARRAY DETECTOR, Bulman, F.D. and G.N. Coleman, G.R. Dulude, R.W. Pascucci and R.L. Stux, Thermo Jarrell Ash Corp.

No Abstract Available.

3

ION AND ATOM ABSORPTION MEASUREMENTS IN AN AXIAL INDUCTIVELY COUPLED PLASMA, Carl E. Hensman and Gary D. Rayson. Department of Chemistry and Biochemistry, Box 30001, MSC 3C, New Mexico State University, Las Cruces, NM 88003

Recently this laboratory has described an instrumental configuration which addresses the difficulties of the determination of trace metals in line-rich, refractory sample matrices. Prior applications of spectral line sources enabled the detection of parts per billion (ppb) concentrations of numerous metals in samples containing as much as 1000 ppm uranium with no significant interference. Unfortunately, the detection of some elements was problematic using this technique. This limitation was attributed to both the first ionization potential and molecular bond strengths of these metals. With the incorporation of a continuum source (i.e., a Xe-arc lamp), the instrument now allows for the determination of both ions and atoms by absorption spectroscopy. This configuration was successful in determining these problematic metals to sub-parts per million (subppm). The development of the current instrumentation and its analytical figures of merit will be discussed.

4

A PSEUDO-FLOW INJECTION SYSTEM FOR THE ANALYSIS OF MAJOR AND TRACE METALS BY AXIAL ICPAES, Ronald C. Antweiler and Howard E. Taylor, U.S. Geological Survey, 3215 Marine St., Boulder, CO 803u-i.

A pseudo-flow injection system for the analysis of major and trace metals on a Varian Liberty 150 AX Turbo Axial ICPAES instrument using a Varian SPS-5 sample preparation system was developed. The purpose was to simulate real flow injection, with its concomitant savings of analysis time and sample, but without the necessity of purchasing and setting up such a system. To implement the pseudo-flow injection system, the instment's commercial software had to be "fooled" by making the autosampler advance to a new sample position well before the previous sample had arrived at the plasma for detection. By coordinating the length of time it actually took for the undispensed sample to arrive at the plasma and for the instrument to stabilize and make a measurement, with the length of time the autosampler spent moving between samples and sipping, a considerable savings of both analysis time and sample volume could be accomplished. Under normal operating conditions for the analysis of one element, 100 seconds and about 4 mL of sample are required for each analysis; by incorporating the pseudo-flow injection scheme, we achieved levels of 20 seconds per sample and less than 1 niL used. We examined the potential for "carry-over" from one sample to another and the stability (reproducibility) of the readings, both within a given undispensed sample and between the same samples analyzed at different times. Even under the most severe constraints we devised for water samples (high concentration samples followed by blanks or low concentration samples), the length of time between samples was only 40 seconds, with only 1.5 mL of sample used. The pseudo-flow injection system we developed is most effective when the number of analytes is small (one or two, to a maximum of three) and the number of samples to be analyzed is large. We found that the typical settings under normal operating conditions of the instrument gave us comparable results to the pseudo-flow injection system when more than three analytes were required. These experiments, while conducted on a specific instrument, can be applied to other analytical techniques as well, and afford the analyst much of the luxury of a "real" flow injection system without the additional expense and instrumentation required for this.

5

SOLID STATE DETECTORS IN ATOMIC SPECTROSCOPY: PART I. Randy L. Hergenroder. 761 Main Ave M/S H67, Norwalk, CT, 06859

Solid State detectors have recently become more common place in Atomic Spectroscopy instrumentation. The reason for this is the improved performance of newer solid state detectors. The use of solid state detectors in atomic absorption spectroscopy and ICP optical emission spectroscopy will be presented. Comparisons will be made with traditional Photo-Multiplier Tubes. The important parameters for the detection of light in AA and ICP will be discussed.

6

SOLID STATE DETECTORS IN ATOMIC SPECTROSCOPY: PART II. Randy L. Hergenroder. 761 Main Ave M/S H67, Norwalk, CT, 06859

Solid State detectors have recently become more common place in Atomic Spectroscopy instrumentation. The second part of this presentation will discuss solid state detectors in both atomic absorption and atomic emission instruments. The advantages solid sate detectors bring to real world analysis will be covered.

7

A NEW VIEW OF CCD DETECTORS FOR SIMULTANEOUS ICP-AES, M. Cole, D. Shrader and G. Russell, Varian Corp.

No Abstract Available.

8

REAL TIME ANALYSIS OF METALS IN STACK GASES USING ARGON/AIR ICP OPTICAL EMISSION SPECTROMETRY, G.A. Meyer and G.N. Coleman, Thermo Jarrell Ash Corp.

No Abstract Available.

9

USE OF COLD-VAPOR ATONUC FLUORESCENCE SPECTROSCOPY FOR MEASUREMENT OF TRACE INORGANIC MERCURY IN WATER AND SEDMMNT FROM THE SACRAMENTO RIVER, D.A. Roth, J. Domagalski, P. Dileanis, D.B. Peart, H.E. Taylor, PC. Antweiler, and C.N. Alpers, U.S. Geological Survey, 3215 Marine St., Boulder, Colorado 80303,

Ultra-sensitive techniques are required to detemline mercury concentrations in natural water samples, even in systems that have been contaminated in the past. Cold-Vapor Atomic Fluorescence Spectroscopy was used to determine mercury concentrations on aqueous and suspended sediment samples from the Sacramento River System, which has been contaminated from past mining practices. This method provides the necessary sensitivity to quantitatively determine spatial and temporal mercury concentration trends. Results from colloidal suspended sediment analyses indicate it as the primary mode of Hg transport and show how Hg is distributed about the sediment. The concentration and distribution of inorganic Hg was measured in samples collected at selected sites on the Sacramento River from below Shasta Dam to Freeport, CA at 6 separate times from July 1996 to May 1997. Dissolved (<O.005 u,m) Hg concentrations remained relatively constant during the study, ranging from below detection limit (<0.4 ng/L) to 2.2 ng/L. Total Hg (dissolved plus colloidal suspended sediment) concentrations ranged from below detection limit to 81 ng/L, demostrating that suspended sediment plays an important role in downriver Hg transport. Sequential extractions of colloidal suspended sediment generally indicate that the greatest amount of Hg associated with the sediment was distributed in the "residual" (mineral) phase with a significant quantity also occurring in the "oxidizable" phase. Only a minor amount of Hg was in the "reducible" phase. Dissolved Hg loading remained constant or increased slightly in the downstream direction through the study area, whereas total inorganic Hg load increased significantly downstream. Analysis of temporal variations generally showed that total Hg loading was positively correlated to discharge.

10

MICRONEBULIZERS AND AEROSOL DIAGNOSTICS IN ICP MASS SPECTROMETRY: WHAT ARE THE NEEDS Akbar Montaser, J. A. M. G. Minnich, and L. A. lacone, Department of Cheniistry, The George Washington University, Washington, DC 20052, USA

In inductively coupled plasma (ICP) spectrometrim test solutions are typically introduced into the plasma in the form of an aerosol. This presentation addresses recent issues related to the production and diagnostic studies of aerosol for microscale sample mtroducuon. We discuss the development of novel micronebulizers that are simple, low-cost devices, based on the high-efficiency nebulizer (HEN), for the direct injection of microliter quantities of test solutions mto the plasma. One new device, the direct injection HEN (DIHEN), was constructed to combine the simplicity, low cost, and aerosol characteristics of the HEN with the well documented advantages of the direct injection nebulizer (DIN). The utihty of the DIHEN for the analysis of small volume biological samples is reported. Novel techniques for aerosol diagnostics such as optical patternator and rainbow refractometry, are also discussed along with key parameters for aerosol characterization, and existing challenges in micronebulization. The aim is to examine the fate of sample droplets, from the pomt of production to the sampling site in the plasma

1. A. Montaser, Ed.; *Inductively Coupled Plasma Mass Spectrometry,* Wiley-VCH: New York, 1998, 964 pages.
2. A. Montaser and D. W. Golightly, Eds.; *Inductively Coupled Plasmas in Analytical Atomic Spectrometry,* 2nd Ed.; Wiley-VCH: New York 1992,1017 pages.

11

DESIGN PHILOSOPHIES AND PERFORMANCE CHARACTERISTTCS OF A NEW HIGH RESOLUTION ICP-MS WITH OPTIONAL MULTICOLLECTION CAPABILITY. Mary Kate Donais. Phil Marriott, Dagmar Koller, VG Elemental, 27 Forge Parkway, Franklin, MA 02038.

Since its introduction in 1989, high resolution ICP-MS (HR ICP-MS) has proven itself to be powerful analytical too] for trace element determinations. HR ICP-MS has permited the separation of analytes of interest from molecular interferences (e.g. As from ArCl, V from OCI) and has provided improved sensitivity when compared to unit mass resolution ICP-MS devices. Some of the historical limitations to this technique have included; size of the instrumentation, lack of automation, slow analysis speed, need for highly trained operators and mediocre isotope ratio precisions. With the advent of multicollector ICP-MS instrumentation, the analyst was introduced to a new technique for performing rapid, high precision isotope ratio measurements without the limitations common to either conventional ICP mass spectrometers or to thermal ionization mass spectrometers (TIMS).

Until very recently, carrying out both high resolution and multicollection measurements on a single instrument was not possible. This presentation will describe the design challenges associated with producing a single instrument to fulfill both tasks and will review the performance characteristics of such an instrument. The system in question, the VG Axiom, is a fully automated, compact HR ICP-MS with optional multicollection capability. The Axiom is about the same size as a VG PlasmaQuad 2 and provides a level of performance sufficient to produce resolving powers greater than 10,000 and limits of detection well below the 0.001 ppt level. Radiochemical applications of this system will be discussed.

12

TIME OF FLIGHT INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY IN THE REAL WORLD: SOLVING REAL ANALYTICAL PROBLEMS AND BREAKING THROUGH BARRIERS.

Lloyd Allen and Stuart Georgitis. LECO Corporation, 3000 Lakeview Avenue, St. Joseph Ml, 49085.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is clearly the dominant analytical technique for trace and ultratrace elemental analysis. Currently several different types of ICP-MS instruments are commercially available including quadrupole and high resolution magnetic sector devices. These systems have successfully provided part per trillion and sub part per trillion level detection limits for some time now. However due to the sequential nature of these systems several limitations have become apparent. For example, under fixed acquisition conditions, the more isotopes the analyst wishes to examine, the longer time the analysis will require. This limitation becomes especially problematic when dealing with small volume samples or transient based sample introduction systems when multielement analysis is required. As well isotopic ratio performance of a sequential system is limited by fluctuations in the ICP and sample iritroducfion system. The focus of this presentation will be on recent work using an axial Time of Flight (TOF) ICP-MS instrument. TOF eliminates the need to scan or peak hop over the Isotopes of interest and can acquire complete elemental mass spectra at a rate up to 30 KHz. This characteristic allows for simultaneous multielement analysis of small volume samples and samples which yield transient signals. Results will be presented from a variety of sample introduction techniques including laser ablation, discrete solution analysis and micronebuuzation techniques.

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THE OPTIMIZATION OF ICP-MS USING A HYDROGEN CONTAINING PLASMA.

U. Camii, Nuclear Research Center-Negev, Israel and H.E. Taylor, U.S. Geological Survey, 3215 Marine St., Boulder, CO

The use of inductively coupled plasma-mass spectrometry for analytical purposes involves precise instnunental optimization. Metalloid elements, such as As, are best measured if they are introduced into the plasma in their hydride form. The combination of ICP-MS with a hydride generator is one of the most sensitive ways to analyze these types of elements. The excess hydrogen which is evolved during the hydride generation process may cause interference within the plasma. This "quenching effect' is attributed to additional energy dissipation paths (such as vibrational and rotational excitation) which are introduced by the diatomic hydrogen. In the present work, the effect on the ICP-MS plasma was studied by introducing controlled amounts of hydrogen. Measurements of both As and In spectral intensities were made. Arsenic was chosen as an indicator element because of its metalloid hydride-foming properties and its relatively high ionization potential. In was selected as an element for study because its properties were similar to those of other elements of interest. With hydrogen present the optimization of the ICP-MS changed significantly. The new set of optimized conditions resulted in higher As intensities. It was also observed that measured As signals were relatively insensitive to small variations in the total hydrogen concentration, when present at levels anticipated to be generated by the hydride formation process. The effects of hydrogen on In intensities will also be shown and discussed.

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HIGH VOLUME, HIGH PRODUCTIVITY ANALYSIS OF TRACE METALS IN DIFFICULT MATRICES BY ICP-MS USING EPA METHOD 6020. Steve Wilbur. Hewlett-Packard Company, 15815 SE 37th Street, Bellevue, WA 9800 -

ICP-MS has the unique capability of eliminating the necessity for both the ICP-AES and GFAA instruments for the analysis of trace metals in environmental samples. By combining the multi-element capability of the ICP-OES with the sensitivity of GFAA into a single analysis with a single sample preparation. ICP-MS has proved to be an efficient, cost-effective alternative to earlier, multi-technique elemental analysis procedures. Additionally, by careful optimization of the entire process of ICP-MS analysis, significant reductions in overall analysis time can be had, greatly increasing the capacity and profitability of the ICP-MS laboratory. In order to achieve the highest possible productivity, a number of potential obstacles must be overcome. These fall into one of three major categories: 1) Sample Handling, 2) Sample Analysis, and 3) Data Handling. Opportunities for improving performance in each of these categories will be discussed.

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THE ESTABLISHMENT OF A RARE-EARTH STANDARD REFERENCE WATER SAMPLE, Ronald C. Antweiler. Howard E. Taylor, Phillip Verplanck, D. Kirk Nordstrom, Terry 1. Brinton, David A. Roth, Dale B. Peart and Allan L. Meier, U.S. Geological Survey, 3215 Marine St., Boulder, CO 80303.

Although several Standard Rock Reference Materials exist for the determination of trace concentrations of rare-earth elements, to date there are no standard reference water samples for these elements. Accordingly, the U. S. Geological Survey recently created two standard reference water samples specifically for rare-earth elements. The two samples were collected from acid mine drainages, one from the Paradise Portal in the San Juan Mountains of southwestern Colorado, and the other from Spring Creek draining Iron Mountain in northern California. About 50 L of each of these waters were filtered through 0.1 *u*m tangential ultrafiltration plates, acidified with *1%* ultrapure nitric acid and separated into 250 mL polyethylene and Teflon bottles. Two bottles of each of these were shipped to 21 different water quality laboratories throughout the world for analysis using a combination of techniques, including inductively coupled plasma mass-spectrometry (ICPMS), neutron activation analysis and isotope dilution determinations.

Our laboratory analyzed these waters using ICPMS. Rare-earth elements were corrected for oxide interferences, and two elements (neodymium and erbium) also were analyzed by isotope dilution mass spectrometry. The results of these analyses are evaluated, along with statistical interpretation of the data from all the participating laboratories. Because the rigor necessary for true certification was not possible, the values of these standards are not "certified". The agreement between many laboratories world'wide, however, gives the "Most Probable Value" data considerable credence, leading to the establishment of the first rare-earth standard for water samples.

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IMPROVED SAMPLING TECHNIQUES FOR THE DETERMINATION OF LOW-LEVEL TRACE-ELEMENT CONCENTRATIONS IN GROUND WATER. Tamara Ivahnenko and Zoltan Szabo, U.S. Geological Survey, 8 10 Bear Tavern Rd. West Trenton, NJ 08628.

Proposed U.S. Envirom-nental Protection Agency maximum contamination levels (MCL's) for trace elements in drinking water are lower than current MCL'S. Although analysis of water samples for dissolved trace elements by inductively coupled plasma-mass spectrometry can result in precise measurements at levels of 1 [tg/L (microgram per liter) or less, conventional field methods for sampling ground water are inadequate to achieve accuracy at this level. Steps implemented by the U.S. Geological Survey to address this problem in New Jersey include (1) well-purging methods that minimize turbidity (low flow rates (2-6 liters per minute) and purging of three or more casing volumes) and require monitoring turbidity in the field, (2) use of standardized equipment-cleaning techniques before collection of each sample and routine collection of equipment blanks, and (3) collection and processing of samples using powderless, vinyl gloves within a portable, enclosed chamber. The magnitude and frequency of detection for most trace elements in pump equipment blanks have decreased since implementation of the improved cleaning techniques, except for the routine presence of Fe, Mn, Ni, and Cr derived from the stainless-steel pump. Drawbacks of the method are that (1) equipment preparation and sample collection are more time-consuming; (2) sample integrity for analyses of Fe, Mn, Ni and Cr are still compromised; and (3) sample-to-sample variability for individual wells, although reduced, may still occur as a result of mobilization of particulates or colloids during pumping. The use of the new sampling and analytical techniques has enabled verification that the concentrations of most trace elements in sampled shallow ground water, are less than 1 *\xg/L.*

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ICP-MS STUDIES OF COPPER ISOTOPE EXCHANGE IN RHUS VERNICIFERA LACCASE. Catherine Miller, Julie A. Dunn, Department of Chemistry, John Carroll University, University Heights, OH 44118.

Laccase contains four copper ions, one In the type I site, and three in the type 2/ type 3 cluster site. The trinuclear cluster is the site of oxygen reduction. Site spcific metal replacement using copper isotopes within the trinuclear cluster site have allowed investigation of substrate binding and well as metal transport and exchange. Isotope counting was first measured using EPR to analyze the ml = -312 transition of a Cu(acac)$_2$ complex to determine the 63Cu/65Cu ratios. This shows that exchange with free copper during the preparation of laocase derivatives does not compromise the mixed-isotope derivatives ICP-MS was used to monitor the change In the 63Cu/650u ratio of various derivatives of the enzyme as well as incubations of the holoprotein with a large excess of copper (I). Analysis shows an average of one copper exchange. Implications of exchange and conditions which favor exchange will be discussed.

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LASER ABLATION ICP-MS: A NEW PERSPECTIVE. Ted G. Howe. CETAC Technologies, 5600 South 42 Street, Omaha, NE 68107.

Laser ablation has become the prominent sample introduction system for the direct analysis of solids. Quantitative analyses of many different sample types are possible using LA-ICPMS and many will be described. A new generation of UV laser systems will also be described, including enhancements specifically designed for geological samples. Time resolved data collection and elemental distribution of elements in coatings will be presented. Novel use of the flat-top beam profile aids in drilling truly flat craters for the analysis of mineral thin-sections, and other optically sensitive samples.

19

A STATISTICAL ANALYSIS OF ELEMENTAL CONCENTRATIONS MEASURED IN HBr USING THE ICP/MS TECHNIQUE. Jude O. Proctor and Greg W. Johnson, Matheson Gas Products, 1861 Lefthand Circle, Longmont, Colorado 80501.

Matheson Gas Products (MGP) endeavors to provide the best quality hydrogen bromide in the specialty gas industry. Several quality assurance tests have been developed for MGP hydrogen bromide, with trace metal composition included on the highest purity grade. Statistical methods currently used to estimate lower limits of detection (LLD) and lower limits of quantitation (LLQ) for elements in test solutions resulting from $HBr_{(ganh)}$ sampling will be reviewed. LLD and LLQ estimates are based on the SEMI method CIO-94; a general description of Method Detection Limit (MDL) determination, For analysis of HBr, concentrations for sixty-five elements are typically determined on the sample solutions; two by flame atomic absorption, eight by ICP/OES, and sixty by ICP/N4S; with a five element overlap between OES and MS. Metals sampling procedures for $HBr_{(ganh)}$ will be described. The presentation will center on a statistical treatment of data obtained using the ICP/MS technique; used to corroborate the LLD and LLQ calculations. The data resulted from a recent analysis on twelve HBr hydrolysis samples and six corresponding reagent blanks.

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DETERMINATION OF FOUR ARSENICALS IN NATURAL-WATER SAMPLES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY/HYDRIDE GENERATION/INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY Mark R. Burkhardt and John R. Garbarino.
U.S. Geological Survey, National Water Quality Laboratory, MS 407, Box 25046 Federal Center,
Denver, Colorado 80225-0046.

Four arsenicals — arsenite, arsenate, dimethylarsinate, and monomethylarsonate — were measured in laboratory reagent-, surface-, and ground-water samples using direct injection high-performance liquid chromatography / hydride generation / inductively coupled plasma-mass spectrometry. The arsenicals were separated on an anion exchange column, converted to arsine in a post-column hydride generator using L-cysteine as the arsenate pre-reduction catalyst, and detected by inductively coupled plasma-mass spectrometry. Analysis time was approximately 7 minutes using a phosphate buffer mobile phase. Method detection limits for a 200-microliter injection volume are 0. 10, 0. 25, 0.25, and 0. 10 *ug/L* (microgram per liter) for arsenite, dimethylarsinate, monomethylarsonate, and arsenate, respectively. Analytical variability ranged from 5 to 10 percent at a concentration of 0.5 ug/L for all arsenicals. Results for total arsenic and individual arsenic specie concentrations in 24 natural-water samples are compared to interlaboratory results using other documented methods. Concentrations for the arsenicals in surface- and ground-water samples used in the comparison ranged from < 0.10 to 900 *ug/L*. Results for reference materials and field-spike recoveries support the accuracy of the method and identify potential matrix-induced interferences.

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THE STRUCTURAL CHARACTERIZATION ELECTROCHEMICAL REACTIVITY AND RESPONSE STABILITY OF HYDROGENATED GLASSY CARBON ELECTRODES. Qingyun Chen and Greg M. Swain, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300

Glassy carbon electrodes were chemically modified by exposure to a hydrogen microwave plasma. This treatment produces a surface that is non-polar, relative oxygen free, and "diamond-like". Structural characterization of the surface by static SIMS indicates the presence of "alkane-like" functional groups terminating the surface ($C_x,H_{2x\pm1}$) which form by the reaction of the glassy carbon edge plane sites with atomic hydrogen. The hydrogenated surfaces exhibit low and stable background currents due to the absence of electroactive carbon-oxygen functionalities. Rapid electrode reaction kinetics are observed for $Fe(CN)_6^{"3/"4}$ and $Ru(NH_3)_6^{+2/+3}$, while slower rates are observed for dopamine, 4-methylcatechol, and particularly $Fe^{+2/+3}$. Stable responses for over three months have been recorded. Structural characterization data from AFM, Raman spectroscopy, XPS and SIMS will be presented as will some of the basic electrochemical properties of these modified surfaces, as they compare with polished glassy carbon. Finally, recent flow injection analysis results using hydrogenated glassy carbon will be highlighted.

22

EFFECTS OF SiO_2 OVERLAYERS ON ELECTRON TRANSFER AT n-Si ELECTRODES. Markus D. Groner and Carl A. Koval, University of Colorado, Department of Chemistry and Biochemistry, CB 215, Boulder, CO 80303, (303) 492-8957.

Thin insulating layers on semiconductor surfaces are interesting for reasons ranging from studying fundamental aspects such as tunneling to practical applications in electronic device fabrication. SiO_2 films ranging from 4 to 20 monolayers were grown on n-Si electrodes using a novel binary reaction sequence technique developed by Klaus, Sneh, and George. (Science, vol. 278, pp. 1934-6,1997) This method allows for atomic layer controlled growth at room temperature, creating very smooth SiO_2 films. The effects of these insulating layers on electron transfer at Si / liquid and Si / solid interface were investigated. Impedance studies and IV measurements were done to determine the effects of different oxide layer thicknesses on the rate of electron transfer from n-Si electrodes into methanol solutions containing benzyl viologen$^{2+/+}$ as the redox couple and 1 M LiCl as the electrolyte. Solid state measurements were performed by vapor depositing gold onto the Si/SiO_2 electrodes. Preliminary results indicate that the SiG_2 slows down the electron transfer but has very few defects which can trap charge carriers.

23

THE EFFECTS OF SURFACE PRETREATMENT OF BORON DOPED DIAMOND THIN FILM ELECTRODES Michael C. Granger, and Greg M. Swain, Utah State University, Department of Chemistry and Biochemistry, Logan, UT 84322-0300

Conventional sp^{2}carbon electrodes typically require pretreatment to activate the surface for electron transfer. Conunon pretreatments include mechanical polishing, laser irradiation, vacuum heat treatment, and electrochemical polarization. Boron-doped diamond electrodes often require no activation to obtain reversible to quasi-reversible electron transfer kinetics for one-electron, outer sphere redox couples. At high dopant concentrations (>10^{20} cm"^{3}), the reversibuity of these couples is not a function of the E° value. In contrast, inner sphere couples undergo very sluggish electron transfer kinetics (AE$_p$ values may be as large as IV). The presentation will address two points: (1) the effect that anodic polarization has on the heterogeneous electron transfer rate constant for $K_3Fe(CN)_6$, K_2IrCl_6, $Cl_3Ru(NH_3)_6$, $Fe^{+2/+3}$, dopamine, ascorbic acid, and methyl viologen, and (2) how this particular treatment compares to other commonly used pretreatments.

24

NEW APPROACHES TO LITHIUM BATTERY CATHODE MATERIALS, Kevin White, Eiichi Shoji and Daniel A. Buttry, Department of Chemistry, University of Wyoming, Laramie, NW 82071-3838

Li cation intercalation in the oxide systems used for cathodes in Li secondary batteries comprises one of the important rate limiting steps in the overall discharge process. We are investigating new approaches to manipulating the structure of these oxide materials with the goal of understanding how structure influences the intercalation rate. Recent progress toward that goal will be discussed for the vanadium pentoxide system.

25

WHERE DOES ELECTRON TRANSFER OCCUR AT LIQUID-LIQUID INTERFACES? RECYCLING AN OLD (BUT GOOD) MECHANISNC TOOL. Carl A. Koval and Heather Oswald. Dept. of Chemistry and Biochemistry, Univ. of Colorado, Boulder, CO 80309-0215.

Electron transfer (ET) between redox active species confined in immiscible phases (usually water and a nonpolar organic liquid) must occur at the interface between the two liquids (for reasons of solubility) and over short distances (due to electronic coupling). At the liquid-liquid interface (LLI) the composition of the solvent varies dramatically over short distances from nearly pure water to nearly pure organic. But where in this boundary region does ET occur and how is the position of reaction affected by the nature of the reactants, solvents, electrolyte ions, etc? This presentation will discuss preliminary attempts to address these questions by analyzing the products of reactions between $Cr(H_20)_6^{2+}$ ions in the aqueous phase and hyprophobic ferricenium ions in nitrile phases.

26

MECHANISTIC INSIGHTS INTO A THIOL-DISULFIDE REDOX PROCESS PROVIDED BY ELECTROCHEMICAL SIMULATION, Eiichi Shoji and Daniel A. Buttry, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838

Thiol-disulfide redox processes are complicated by a variety of chemical steps that accompany the redox process, including dimerization to produce disulfide following oxidation of the thiol, cleavage of the S-S bond following reduction of the disulfide, and various proton transfer steps that can couple to the transfer of electrons. In this contribution, we describe the use of electrochemical simulations to study these processes for 2,5dimercapto-l,3,4-

thiadiazole, which has been extensively studied recently due to the possibility of its use in secondary Li battery cathodes. The important of proton transfers on the thermodynamics and kinetics of the redox steps will be discussed.

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THERMODYNAMIC STUDIES OF ELECTRON TRANSFER AT LIQUID-LIQUID INTERFACES.

Heather C. Oswald. Torri L. Derback, and Carl A. Koval, Dept. of Chemistry & Biochemistry, C. B. 215, Univ. of Colorado, Boulder, CO 80309. (303)-492-8957.

Liquid-liquid interfaces (LLIS) are of interest because of their relevancy to biological systems and their applicability in hazardous waste remediation. We are studying the thermodynamics of electron transfer reactions (ETRs) at LLIs. A generic ETR at a LLI is ML_6^{3+}(w) + R_n-$\mathrm{FER}_{(o)}$ <=> ML_6^{2+}(w) + R_n-$\mathrm{FER}^{+}_{(0)}$. The position of equilibrium for this ETR is governed by the sum of AQW^ and E°'$_{rxn}$- AQW^ is the Galvani potential difference which is determined by the electrolyte ions, their concentrations, and the two solvents. In our studies, we are evaluating the position of equilibrium electrochemically for reactions of aqueous aquo- and amine complexes with alkylated ferrocene derivatives that are soluble in nonpolar solvents. The relative contributions of AQW^ and E°$_{rxn}$ to the position of equilibrium for ETRs at LLIs will be presented.

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ROTATING RING-DISK ELECTROCHEMICAL STUDY OF ION TRANSPORT IN POLY (PYRROLE)/ POLY(STYRENESULFONATE) CONDUCTING POLYMER FILMS.

Corey A. Salzer and C. Michael Elliott, Department of Chemistry, Colorado State University, Ft. Collins, CO 80523

It is often reported that ion transport is the limiting factor in electrochemical redox switching of conducting polymer films. An understanding of which process (anion or cation transport) occurs in a particular film and the effects of various film parameters on the transport characteristics is important in developing systematically customizable conducting polymer materials. Our research utilizes rotating ring-disk electrochemical (RRDE) methods for specific and quantitative study of the ion transport processes occurring in a composite conducting polymer film. With a film grown onto thOdisk of an RRDE, we are able to monitor at the ring, specific ion motion in a composite poly (pyrrole) film. We have applied this to a study of film preference to different cations and have also looked for both cation and anion transport in identical films under various conditions.

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AMPEROMETRIC DETECTION COUPLED WITH FLOW INJECTION ANALYSIS USING BORON-DOPED DIAMOND THIN FILM ELECTRODES

Jishou Xu and Greg Swain, Dept. of Chem. and Biochem., Utah State Univ., Logan, Utah 84322-0300

The use of boron-doped diamond thin films in electroanalysis is a new field of research. Electrochemical applications require stable, active, chemically robust and economical electrodes. Diamond thin film electrodes, fabricated by chemical vapor deposition methods, provide electrochemists with an entirely new type of carbon electrode that meets these requirements for a wide range of applications. Boron doped diamond thin films have been observed to exhibit several electroanalytically important properties: (I) low and stable background current; (ii) wide working potential window in aqueous electrolyte solutions; (iii) quasi-reversible electron transfer kinetics for some redox systems without any conventional pretreatment; (iv) long term response stability; (v) morphological and microstructure stability at high anodic potentials ; (vi) resistance to the adsorption of polar organic molecules and (vii) resistance to fouling in aqueous media. The presentation will focus on flow injection analysis studies of several environmentally and biologically important molecules using diamond-based amperometric detectors. Comparisons will be made between the detector figures of merit for diamond and glassy carbon.

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HYDRODYNAMICALLY ASSISTED MINIATURIZED ELECTROCHEMICAL DETECTORS FOR HEAVY METALS.

Michael T. Carter, Eric D. Cravens and Ross C.

Thomas,EltronResearch,lnc.,566OAirportBlvd.,#105,Boulder,CO 80301-2340.

We report on recent progress involving fabrication of heavy metal electrochemical detection devices. We are currently developing heavy metal detectors which use enhanced mass transfer conditions to lower detection limits, increase analysis speed and sample throughput for anodic stripping voltammetry (ASV) of Pb, Hg, Cd, Zn and other heavy metals. Acidic conditions and the presence of a large NO_3 background were examined because they are commonly encountered at remediation sites including abandoned mining operations and waste from nuclear fuel reprocessing facilities. Proton and NO_3 are both reducible at common metallic electrode materials and were expected to interfere with detection. A practical heavy metal monitor would need to function without sample pretreatment to be truly flexible and affordable. The electrochemical detectors functioned over a wide range of ionic strength, *u*M to M $NaNO_3$, and solution pH ($I < pH < 7$). ASV detection of Pb and Hg were achieved at ppb detection levels in the presence of these interferents and dissolved oxygen, which is also electroactive at potentials of interest in this work. In addition to reporting on the performance of these devices, we will discuss simple, inexpensive methods used during this program to rapidly prototype miniaturized chemical sensors.

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IN SITU NMR ANALYSIS OF CHARGE CARRIERS IN POLYMER ELECTROLYTES, Rex E. Gerald II, Robert J. Klingler, Jerome W. Rathke, 'Giselle Sandi, and 'Klaus Woelk, Chemical Technology and 'Chemistry Divisions, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois 60439-4837, USA 'Inst. Phys. Chem., University of Bonn, Wegelerstr. 12, D-53115 Bonn, Germany

A toroid cavity/electrochemical cell NMR probe and a rotating frame microscopy technique were combined to investigate physical and chemical processes in batteries. The formation and subsequent time evolution of a depletion zone adjacent to the working electrode was monitored by recording radial concentration profiles of the charge carriers. The NMR imaging approach used to obtain the radial concentration profiles provides full chemical shift resolution. Therefore, the concentrations and radial distributions of chemical products from redox side reactions were monitored simultaneously. The radial path taken by the charge carriers in the electrochemical cell produced minimal distortion of the NMR images, which were recorded during cell operation. Fluorine-19 nuclear spin relaxation caused by molecular fluctuations of triflate anions was recorded as a function of radial position from the working electrode across the concentration gradient in a polymer electrolyte. The radial dependence of spin-lattice relaxation rates indicated a variation in the morphology of the polymer near the working electrode. This work is supported by the U. S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38.

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INTERFACIAL CAPILLARY ELECTROPHORESIS AT ELECTRODE SURFACES Christine Thetford, Loma Hunter, Rich Martoglio, Shauna Hiley, Guoying Chen and Daniel A. Buttry, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3 83 8

Chemical analysis of the near surface region at electrodes can be a powerful tool both for understanding chemical processes at electrode surfaces and for developing analytical chemical schemes that couple electrochemically controlled surface capture and release with the separation and detection power of capillary electrophoresis (CE). An attractive approach for such analytical schemes involves using self-assembly at electrode surfaces to enable capture and preconcentration of analytes via some type of biorecognition interaction, followed by electrochemically controlled desorption of the analyte and detection via CE. This contribution describes recent progress toward that goal.

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FABRICATION AND ANALYSIS OF NOVEL FACILITATED TRANSPORT MEMBRANES. David T. Ntchell, Brinda B. Lakshni, and Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins, Colorado, 80523

Facilitated transport involves the incorporation of a carrier agent in a membrane. The agent complexes with the solute of interest and increases the flux of that solute across the Membrane. The Martin group has recently developed a novel type of facilitated transport membrane which we call a sandwich membrane because of its layered construction (see Lakshmi, B. B.; Martin, C. R. *Nature* 1997, 388, 758). The membrane is composed of two layers of polypyrrole which sandwich the carrier agent, apoenzyme, between them. These membranes have proven to be effective in separating molecules as similar as enantiomers. Synthesis of the sandwich membrane can be divided into three main steps: electropolymerization of pyrrole from aqueous solution, pervaporative loading of the carrier agent, and growth of a capping layer of polypyrrole from acetonitrile. Each of these steps has been examined in detail and with a variety of techniques (scanning electron microscopy, single and competing molecule permeation experiments, enzyme assays), to determine which layer or layers of the membrane produce the facilitation. These studies suggested that the facilitation arose from entrapped carrier molecule in the acetonitrile-grown polypyrrole layer. Single layer membranes have been constructed in this fashion which showed enhanced selectivities compared to the sandwich type.

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ELECTROCHEMICAL AFM STUDIES OF GLASSY CARBON AND BORON-DOPED DIAMOND THIN-FILM SURFACES DURING ANODIC POLARIZATION Jian Wang and Greg M. Swain, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300

Anodic polarization of glassy carbon and polycrystalline, boron-doped diamond thin-film electrode surfaces was accomplished by potential cycling in 0.1 M H_2SO_4. Electrochemical atomic force microscopy (ECAFM) results reveal that the glassy carbon surface undergoes significant morphological and n-dcrostructural damage with increasing numbers of potential cycles out to +2.0 V vs. SCE. The nominal surface roughness increases by an order of magnitude after the passage of current densities on the order of 20 mA/cm^2, and a thick layer of graphitic oxide fon-ns. On the contrary, potential cycles out to +2.5 V vs. SCE, or greater, and anodic current densities of 20 mA/cm^2 produce no observable morphological or microstructural changes on diamond. The microstructure of both electrodes was determined by Raman microprobe spectroscopy. The morphological and microstructurai stability of diamond are important electrode characteristics particularly when considering the use of this new electrode material for amperometric detection schemes and electrosynthesis. ECAFM results will be presented for both electrodes. The effect of the polarization on the electron transfer kinetics for several aqueous-based redox systems will be discussed.

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RATE CAPABILITY OF NANOSTRUCTURED V_20_5 ELECTRODES PREPARED VIA THE TEMPLATE METHOD USING A SOL-GEL PRECURSOR. Charles J. Patrissi and Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

Critical parameters that affect the capacity of lithium and lithium-ion batteries at high discharge current are the size and shape of the Li-insertion material particles in the electrode(s). Long dffusion distances within the particles and high current density can cause concentration polarization because Li diffusion within these insertion materials is slow. Concentration polarization results in a premature voltage drop and a loss of electrode and/or battery capacity. We prepared nanostructured electrodes of V_2O_5 using the template synthesis method in order to study the effect of decreased Li diffusion distance and increased insertion material surface area on electrode rate capability. These electrodes consist of nanometer diameter fibrils of polycrystalline V_2O_5 that are approximately 4 *\xm* in length and protrude from a current collector like the bristles of a brush. One advantage of this morphology is a high surface area of V_20_5 which ensures a low current density and minimal voltage drop through the V_2O_5 nanowires. In addition, the short distance for Li diffusion (radius of the fibrils) reduces the effects of concentration polarization at high current.

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RUTHENIUM (II) POLYPYRIDINE BASED ELECTROCHEMILUMINESCENT POLYMERS

Corey **J.** Bloom, C. M. Elliott, Francois Pichot, Lonn S. Rider

Thin layer polymers composed of Ru(II) trisbipyridine complexes have been shown to have conductive and electrochemiluminescent properties. By applying a voltage across a film of this polymer, a disproportionation reaction occurs, producing the oxidized species at the anode and the reduced species at the cathode. Electron transport through the polymer occurs by electron hopping between ruthenium sites. At steady-state, time independent gradients of the oxidized and reduced species exist within the polymer. Where these two species meet, a portion of the product yields Ru(II) in the excited state, which subsequently emits a photon as it returns to the ground state. A solid state device based on this system has been constructed, with a thin film of the polymer "sandwiched" between an indium/tin oxide anode and a gold mesh cathode. While such a device yields an external quantum efficiency of up to 1%, efforts are being made to optimize its performance. The goal is a stable, high efficiency light emitting device which operates with low power consumption.

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pH-SWITCHABLE PERMSELECTIVE GOLD NANOTUBULAR MEMBRANES Kshama B. Jiarge and Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

Gold nanotubular membranes were fabricated using an electroless deposition procedure and polycarbonate membrane as the template. The inside walls of the gold nanotubules were modified with thiols with different terminal groups. The two thiols used were 2-aminoethanethiol hydrochloride(AET) and 2-mercaptopropionicacid (MPA). At low pH, arnino group in the AET modified membrane, is protonated to -NH_3^+ and the membrane shows anion permselectivity. At a higher pH the same membrane did not show any permselectivity as the -NH_3^+ is deprotonated to give rise to the neutral -NH_2 group. Similarly, the MPA modified gold tubules showed cation permselectivity at ligher pH, as the terminal group is -COO", and at a lower pH, did not show any permselectivity as there is a neutral COOH terminal group. This was demonstrated by measuring the membrane potential that is developed when when a concentration cell is setup using different solutions of KC1. The permselectivity was also observed in permeation experiments where anions and cations were excluded from cation anion perselective membranes respectively. Thus, pH-switchable permselective gold nanotubular membranes were fabricated.

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DO YOU KNOW WHAT'S IN YOUR DRINKING WATER? Susan D. Richardson, U. S. Environmental Protection Agency, 960 College Station Rd., Athens, GA 30605

Due to concern over the potential adverse health effects of trihalomethanes (THMS) and other chlorinated by-products in chlorinated drinking water, alternative disinfection methods are being explored. Ozone, chlorine dioxide, and chloramines are currently popular alternatives to chlorine, as they kill microorganisms effectively, but do not produce appreciable levels of THMS, which are regulated by the U.S. Environmental Protection Agency (EPA). Although these alternative disinfectants are widely used in the U.S., there is little information on the DBPs they produce. Are they safer or more harmful than those formed by chlorine?

To answer this question and to ultimately determine if there are harmful DBPs that should be minimized, our laboratory has been carrying out comprehensive studies aimed at identifying all detectable disinfection by-products (DBPS) from these alternative disinfectants. To identify these new DBPS, we are using GC/MS (EI and CI, low and high resolution), GCAR, and LC/MS. Using these techniques, we have identified many DBPs from ozone, chlorine dioxide, chloramine, and chlorine, many of which have never been reported previously. A comparison of DBPs identified to-date will be presented.

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OVERVIEW OF AVAILABLE METHODS FOR DISINFECTION BYPRODUCTS MEASUREMENTS, Denan Ozelein

No Abstract Available.

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THE ANALYSIS OF SEMI-VOLATILE ORGANIC COMPOUNDS WITH EXTERNAL IONIZATION ION TRAP GC-MS, James B. Edwards, John D. Ragsdale III, and Steven T. Fannin, Finnigan Corporation, 2215 Grand Avenue Parkway, Austin, TX 78728.

Solid waste and wastewater analysis, under the guidelines of the United States Environmental Protection Agency (USEPA), continues to be a part of the environmental testing required by a variety of federal, state, and local regulatory agencies. USEPA method 8270 is the method used for semi-volatile organic compound analysis of a growing list of specified compounds of a variety of classes: phenols, pesticides, polynuclear aromatic hydrocarbons, nitrosamines, haloalkanes, and phthalates, among others. The challenge facing the environmental laboratory community is the accurate yet rapid analysis of samples of this type is an increasingly competitive marketplace.

The Finnigan GCQ *Plus,* a benchtop quadrupole ion trap mass spectrometer with an external ion source, has been evaluated for its use as an instrument for this type of analysis. The system was evaluated against method specific criteria in the following areas: mass spectrometer tuning, initial and continuing calibration, and initial demonstration of instrument performance by validation and detection limit studies. The Finnigan GCQ *Plus* has been shown to be capable of compliance with the analytical instrumentation requirements of USEPA method 8270, with performance meeting and /or exceeding established performance guidelines.

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POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN RESERVOIR SEDIMENT: GEOCHRONOLOGICAL INDICATORS OF URBANIZATION Edward T. Furlong (1), Peter C. VanMetre (2), Edward. C. Callender (3), and Mary C. Olson (1). U.S. Geological Survey: (1) Box 25046, MS 407, Federal Center, Denver, CO 80225; (2) 8011 Cameron Road, Austin, TX 78754; and (3) 2201 Sunrise Valley Drive, MS 432, Reston, VA 20192.

Sediment accumulation in reservoirs can provide a chronology of the transport and deposition of polycyclic aromatic hydrocarbons (PAH) in the reservoir watershed. When compared to lakes and estuaries, the greater sediment accumulation rates often measured in reservoirs can provide a historical record of greater resolution. The authors determined PAH accumulation chronologies in cores from several reservoirs in urban, nonindustrial settings and found that each reservoir reflects specific PAH input histories, particularly the expansion of human influence in each watershed. Overall, changes in combustion-derived PAH accumulation follow urban development in the watershed, with contemporary accumulation rates of about 600 ng-cm^-yr"^{1}. The ratio of phenanthrene to anthracene can be used to estimate relative PAH contributions from atmospheric, combustion-derived sources (ratio=9 to 20) and coal or petroleum (ratio=l to 5). In reservoir sediment, the average whole-core ratio ranged from 2.8 to 4.3, suggesting greater PAH contributions from uncombusted coal and petroleum. In 154 streambed sediments collected as part of a national water-quality assessment, the phenanthrene to anthracene ratio averaged 2.8, confirming that uncombusted coal and petroleum dominate PAH distributions in fluvial sediment from many watersheds.

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QUALITATIVE AND QUANTITATIVE ANALYSIS OF PESTICIDES ON AN ION-TRAP MASS SPECTROMETER. <u>Dieter M. Drexler</u>. Sibylle M. Wilbert, Frederick Q. Bramble, and Stephen C. Werness. ThermoQuest Finnigan, 355 River Oaks Parkway, San Jose, CA 95134.

The development of new pesticides as well as the monitoring of released pesticides in the environment requires highly sensitive and very selective detection methods. A detection method for pesticides in complex matrixes suitable to be coupled with HPLC separations is atmospheric pressure ionization mass spectrometry (API-MS). Sensitive LC-MS and LC-MS/MS methods permit the selective quantitation of pesticides. The qualitative analysis of pesticides such as metabolite identification is carried by LC-MS(n), resulting in in-depth structural information. Applications of the quantitative analysis of pesticides in complex matrices by LC-MS/MS as well as metabolite identification by LC-MS(n) will be presented.

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METABOLITE STRUCTURE ELUCIDATION BY THE USE OF ADVANCED FEATURES OF AN ION TRAP MS, Stephen C. Werness, Steven R. McGown, and Raymond C.M. Lau, BASF Agricultural Products Center, Research Triangle Park, NC, 27709.

Metabolite structural elucidation is greatly enhanced by the use of a Finnigan LCQ ion trap mass spectrometer. The use of data dependent MS n product ion trapping significantly shortens the time needed for a MS study of a metabolite. Data will be shown from our most frequently used LC/MS/MS scheme that uses data dependent selection of the largest m/z species to be the parent for the next MS stage, automatically to MS^5. The spectra from this sequential MS/MS product ion experiment yield a large amount of the information required for understanding of the structural data in just one LC/MS injection. Interpretation of the spectra is often easier and faster since most include only a few product ions (with intact isotope distribution) for each stage of MS/MS. For many compounds, MS^4, MS^5, and MS^6 experiments yield the key conclusive evidence of structural similarity to the active ingredient. One of the most powerful tools allows user selection of the parent m/z for any MS" stage. Data will, also, be shown from the LCQ that confirmed the identity of a compound when the parent m/z was less than 1 % of the TIC and barely discernible.

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TRACE METALS, PERSISTENT ORGANIC POLLUTANTS, AND MARINE MAMMALS, Paul R. Becker. National Institute of Standards and Technology, 219 Fort Johnson Road, Charleston, South Carolina 29412

It has been recognized for several decades that, compared to terrestrial species, many marine mammals accumulate lipophilic persistent organic pollutants (e.g., chlorinated pesticides and PCBs) and many trace metals (e.g., mercury, cadmium, and selenium) to high levels. In some cases, high tissue concentrations have been implicated in the decline in the health of some populations of seals (Baltic Sea) and whales (St. Lawrence Estuary). In addition, mass die-offs of marine mammals in the late 1980's and early 1990's, although due to biological disease agents, have raised questions about the role of anthropogenic contaminants in lowering disease resistance and have stimulated the development of research to address these questions. Through increased efforts over the last decade to determine baseline levels of chlorinated hydrocarbons and trace metals in marine mammals, some species-specific and geographic patterns have begun to emerge. Emphasis has recently shifted away from baseline measurements and to investigating the metabolism of these substances, elucidating toxic action, and evaluating animal health through broad-based investigations that combine isomer-specific chemistry with histopathology, immunopathology, and physiological measures. Thus, the contribution of analytical chemistry to evaluating contaminant effects in marine mammals should increase substantially.

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ZINC PRECIPITATION RUNOFF FROM THERMAL-SPRAYED STRUCTURES. S. Matthes. S. Cramer, B. Covino, Jr., G. Holcomb, S. Bullard, Albany Research Center, U.S. Department of Energy, Albany, Oregon 97321-2198.

Thermal-sprayed zinc coatings on concrete are increasingly being used in marine and coastal environments and in areas where road deicing salts are employed as anodes to cathodically protect the steel rebar in reinforced concrete bridges from corrosion damage. Thermal-sprayed coatings on steel are also used to provide long-term, low maintenance corrosion protection for steel structures. Atmospheric corrosion of the zinc coating produces a corrosion film susceptible to acid-base reactions with the acidic constituents of the environment. Such reactions increase the release of zinc ions in precipitation runoff from the structures. Experiments designed to measure chemical composition of precipitation runoff were conducted for periods ranging from 18 to 33 months providing the opportunity to examine seasonal effects of environmental chemistry. Precipitation runoff results are presented from zinc surfaces exposed to a polluted environment, an unpolluted rural environment, and an unpolluted coastal environment. Similar results are presented for thermal-sprayed zinc coatings exposed to the rural and coastal environments. The results can be used to estimate the effects of environmental chemistry on precipitation runoff from thermal-sprayed structures and on the rate of delivery of zinc into the environment.

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MTBE IN DRINKING WATER RESERVOIRS - MARINE ENGINE EMISSIONS? M.W. Tikkanen. R. G. Sykes, R. Hunsinger, R. Berger, and M. Wallis, East Bay Municipal Utility District, 375 Eleventh Street, Oakland, CA 94607.

Contamination of drinking water supplies, both ground water and surface, by the gasoline additive methyl tertiary butyl ether (MTBE) has drawn much public attention recently. In California, ground water wells and surface water reservoirs are being monitored for MTBE contamination. East Bay Municipal Utility District has been monitoring MBTE in its drinking water reservoirs, which include reservoirs where motorized recreational activity is permitted. Occurrence of MTBE, and other BTEX compounds, in these reservoirs has been correlated with marine engine usage. Results from these occurrence studies will be detailed. Preliminary results from a study comparing emissions to water from 4-stroke and 2-stroke engines will be discussed.

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ATOMIC FORCE MICROSCOPY FOR PHYSICAL AND CHEMICAL CHARACTERIZATION OF NANOMETRIC ENVIRONMENTAL PARTICULATES. Kathryn A. Rwnirez-Aguilar. Amy E. Michel, David W. Lehmpuhl, John W. Birks, and Kathy L. Rowlen, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215. please

Atomic, force microscopy (AFM) is a powerful technique for studying the microscopic and nanoscopic world because of its ability to produce high-resolution, three-dimensional images under a wide variety of sample conditions. This research focuses on analysis of reactions between solid particulates and reactive gases utilizing AFM. In particular, emphasis is placed on the use of solid-gas phase reactions for chemical characterization of nanometric particulates of unknown composition. One application of this technique is in the field of atmospheric aerosols, where many questions remain unanswered concerning aerosol formation, transport, agglomeration, and deposition. Simultaneous analysis of size and chemical information using AFM will be possible for particulates as small as 1 nm including ultrafine atmospheric aerosols (<0.1 p,m) for which simultaneous analysis using current techniques is not possible.

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CHROMRUM SPECIATION USING AN AUTOMATED LIQUID HANDLING SYSTEM WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRIC DETECTION Mary Kate Donais. Rob Henry, Tom Rettberg, VG Elemental, 27 Forge Parkway, Franklin, MA 02038

The speciation of inorganic chromium in environmental samples is necessary to accurately assess pollution levels. Of the two chromium oxidation states, Cr(VI) is a known carcinogen, while Cr(III) is an essential element. A total chromium measurement cannot be used to determine environmental impact due to the considerable difference in toxicity of these two elemental forms.

An automated liquid handling system, the PrepLab, can be used with an inductively coupled plasma mass spectrometer to quantify Cr(III) and Cr(VI) in liquid samples. An autosampler is used to introduce discrete sample volumes into an ion exchange column. The Cr(IIII) and Cr(VI) species are separated on-line and are introduced directly into the VG PlasmaQuad 3 ICP-MS for detection. The chromatographic data are collected in time resolved analysis mode with the capability of simultaneous multiple-isotopic detection.

Data will be presented for environmental samples such as waters. Increased sample throughput through the use of automation will be discussed, as well as short- and long-term stability.

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STRATEGIES FOR REVERSIBLE DETECTION OF HYPERGOLIC FUELS IN AIR.

Michael T. Carter and Jimmy R. Smith, Eltron Research, Inc., 5660 Airport Blvd., #105, Boulder, CO 80301-2340.

We report on recent progress in trace detection of hydrazines in air using fiber optic sensors. The sensors exploit acid-base chemistry of certain triphenylmethane dyes with hydrazine (Hz), monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) to achieve reversible and extremely sensitive detection of these compounds. Sensors are currently employing a multimode silica core optical fiber in the evanescent wave mode. The cladding is partially removed and replaced with an hydrazine-sensitive coating. Reversible detection of trace hydrazine at 1 0 ppb or less is routinely achieved with these sensors. They continue to function for up to six months in on-going long term studies. Saturation of response to Hz took 5 -7 min. The dynamic range of the sensor was approximately 0- 6 ppm. However, meaningful measurements could be made at the 10 ppb analyte level in less than 30 s. Effects of interferences such as ammonia, sulfur dioxide and moisture were characterized. The sensor responded to moisture, but without loss of sensitivity. The sensor responded to basic interferences such as NH, and methylamine, but only to 14% to 30% of the analyte response for comparable concentrations. Potential acidic interferences such as SO, were not detected, even at concentrations as high as 1 ppm.

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MULTIELEMENT BINDING OF HEAVY METALS BY PLANT MATERIALS,

Gary D. Rayson and Patrick A. Williams, Department of Chemistry and Biochemistry, New Mexico State University, Box 30001 MSC 3C, Las Cruces, NM 88003

Because of the ability of organisms to bind metal ions with capacity and selectivity, the use of living and non-living biomaterials for heavy-metal remediation has been extensively investigated in recent years. However, the primary characteristic of biomaterials (i.e., the presence of multiple binding sites, or a chemical heterogeneity of sites on the surface) has made it impossible to make predictions regarding the binding behavior of a metal ion under different chemical environments and in the presence of concomitant metal ions. One approach to this difficulty is to obtain information on the binding affinities and capacities of each site type, or their distribution. Because of the major advantage of the convenient and accurate determination of equilibrium capacities, frontal affinity chromatography has been chosen as a supplementary technique to study metal-biomaterial interactions in the presence of potentially competing metal ions. Specifically, the competive binding of Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} to an immobilized biomaterial derived from the plant *Datura innoxia* has been investigated. The removal of these metals from mixed-metal solutions will be discussed in terms of both their their direct binding and the subsequent stripping by 1.0 M acid solutions.

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WHOLE-BODY ROTENONE RESIDUE DETERMINATION IN THE BROWN TREE SNAKE (BOIGA IRREGULARIS).

Richard E. Mauldin. John J. Johnston, and Carol A. Furcolow. National Wildlife Research Center, 3350 Eastbrook Drive, Fort Collins, Colorado 80525.

The brown tree snake (Boiga irregularis) is an introduced pest species on Guam, and is responsible for substantial economic loss due to power outages and agricultural damage, as well as the extirpation of several bird species. Rotenone, a commonly used insecticide/piscicide, was investigated as a potential chemical control agent. To evaluate possible secondary hazards associated with rotenone use, it was necessary to quantify rotenone residues in dosed snakes. An analytical method was developed to determine whole body residues ranging from 0.21 to 250 \xg g"' in snakes. Homogenous 2 g samples of cryogenically pulverized snakes were extracted with ethyl acetate followed by cleanup using silica and florisil solid phase extraction columns. Tissues fortified to 4.82 and 241 \xg g"' yielded analyte recoveries of 87.8% and 88.1 %, respectively. The method limit of detection was 0.207 \xg mL"'.

Linearity was validated from 0.05 - 0.25 jxg mL'**Mr**^{2} = 0.9920) and from 0.250 to 250 \xg mL''^{1}(r^2= 0.9999). The method was simple, rugged, and reliable.

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HOW AUTOMATING EPA-SW846 METHOD 3050B FORSOILS, SEDIMENTS AND SLUDGES CAN SAVE YOUR LABORATORY TIME AND MONEY.

Robert L. Lockerman. Greg Leblanc, and Gus Obleada, CEM Corporation, POB 200 Matthews, NC 28106

On June 13,1997, the USEPA promulgated Method 3050B as a portion of Update III to the Third Edition of SW846 Methods. This alternate method to 3050 permits the use heating devices such as microwave digestion systems and block digesters to perform sample preparation for trace metals analysis.

Method 3050B provides a strong acid leach for the preparation of solid samples such as soils, sludges and sediments. Two separate acid digestion procedures are specified, one for FAAS or ICP-AES and another for GFAAS or ICP-MS. Open vessel heating of larger samples can be performed, which is important when working with non homogenous samples or trying to improve detection limits.

Microwave digestion systems offer the advantage of pre-programmed heating sequences and automated reagent addition. Using this precise control and automation, microwave systems can reduce the time of digestion as well as the technician tasks necessary for sample preparation. This presentation will focus on the use of Method 3050B as well as how to program the CEM STAR Microwave Digestion System to fully automate the preparation prior to analysis.

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MODIFIED CLAYS FOR ABATEMENT OF NOx FROM HIGH TEMPERATURE PROCESSES,

Antonio S. Sara and Alba Yadira Corral, Department of Chemistry and Biochemistry, New Mexico State University, Box 30001 MSC 3C, Las Cruces, NM 88003

Toxic nitrogen oxide, NOx, pollutant levels from industry's high temperature combustion processes must be reduced. Fuel-fired power-plants contribute to this problem. Present short-term solutions use methods that lower combustion temperatures to reduce NOx production. Unfortunately, this method also reduces energy output. The problem is further compounded because lower temperatures mean more inefficiency and so levels of unreacted compounds and incompletely combusted products, especially toxic CO, escalate. What is needed is a long-term solution to reduce the NOx emission levels without sacrificing energy output and also simultaneously reduce CO levels. Selective catalytic reduction, SCR, of NOx provides the solution. Modified synthetic zeolites have shown that these SCR materials can reduce NOx concentration levels with as much as 85% at 450-550 °C. However, the industrial combustion effluent volume is staggering so that catalysts must be inexpensive and readily available in large quantities. Natural and abundant clays are logical alternatives since their chemistries approximate those of zeolites and meet the stated requirements. Cu(II)-modified clays have reduced NOx levels 39-89% at temperatures that range from 200-600 °C with NH as the reducing agent. Some natural clays were effective without chemical modification. The gases that are monitored for SCR are CO, N0$_2$, C0$_2$, 0$_2$, and hydrocarbons collectively. The instrument is an ECOM-AC Plus analyzer.

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DETERMINATION OF SUBMICROGRAM-PER-LITER CONCENTRATIONS OF CAFFEINE IN SURFACE-AND GROUND-WATER SAMPLES BY SOLID-PHASE EXTRACTION AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

Paul P. Soliven. Mark R. Burkhardt, Stephen L. Werner, and Deborah G. Vaught, U.S. Geological Survey, National Water Quality Laboratory, MS 407, Box 25046 Federal Center, Denver, Colorado 80225-0046.

A method for determining caffeine at submicrogram-per-liter concentrations in surface- and ground-water samples has been developed. Caffeine is extracted from a 1-L water sample using a 0.5-g graphitized carbon-based solid-phase cartridge, eluted from the cartridge using methylene chloride and methanol (80% / 20% v/v), and analyzed by high-performance liquid chromatography with photodiode-array detection. The single operator method detection limit (n = 7) in organic-free water samples was calculated as 0.02 \xg/L. Mean recovery and relative standard deviation in organic-free water samples fortified at 0.04 \xgfL was 93 ± 13 percent. The mean recovery for laboratory reagent spikes fortified at 0.5 \ig/L was 84 ± 4 percent. Environmental concentrations of caffeine measured in surface-water samples ranged from 0.003 to 1.44 \xgIL and in ground-water samples ranged from 0.01 to 0.08 (ag/L.

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APPLICATION OF THE DUH-HAYMET-HENDERSON CLOSURE OF THE OZ EQUATION TO THE INTERPRETATION OF INTERACTION-INDUCED RAMAN LIGHT SCATTERING OF BINARY SUPERCRITICAL FLUID MIXTURES-Frank G. Baglin. Susan K.Murray, Jill Daugherty and Wayne Stanbery, Chemical Physics Program, University of Nevada, Reno Nv. 89557

There has been recent interest in the development of better approximations for the thermodynamic and correlation properties of fluids. For practical calculations, such as P,T and D (density) surfaces, semi-empirical closures seem most practicable. Of the semi-empirical techniques, the Duh-Haymet-Henderson (DHH) bridge function has been particularly successful. In the following we apply this bridge function for the Ornstein-Zernicke (OZ) integral equation to molecular binary mixtures. We test the density dependent DHH closure on 10 mole% mixtures of CH4 in 90 mole% C02 or CO using only Lennard-Jones parameters for these substances and evaluate the T_c values for the mixtures. These results are calibrated against the OZ results for pure C02 where T_c is known.
Most importantly however, we will relate the calculated OZ local solution densities to the anisotropic interaction-induced Raman light scattering (iiRLS) signal (from the methane sensor molecule) to demonstrate that the the local methane-solvent density minus the local solvent-solvent density and the iiRLS signal are correlated with each other.

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OXIDATION OF SELF-ASSEMBLED DECANETHIOL MONOLAYERS. Matthew M. Ferris. Kathy L. Rowlen, Karen L. Norrod, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309.

Surface enhanced Raman scattering (SERS) has been demonstrated to be a useful spectroscopic technique capable of studying submonolayer coverages of analyte species. The major limitation of SERS is the reproducibility of the SERS substrates which is due to contamination with carbonaceous species. The well known interaction of alkanethiols with Ag and Au surfaces results in the removal of carbonaceous contaminants by self-assembly of alkanethiols on SERS substrates. Oxidation of decanethiol monolayers has been observed upon exposure with both LTV light and ozone. Each of these oxidation methods result in a semi-stable and weakly adsorbed species which can be displaced by analyte species for SERS analysis. Ag surfaces cleaned by these methods have shown increased enhancement factors as well as reduced background levels for various analytes. Evidence suggests the active species in both oxidation methods is ozone.

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MONITORING STRUCTURAL CONFORMATIONS IN PROTEINS AND MEMBRANES WITH HIGH RESOLUTION EPR at 95 GHZ. Alex 1. Smirnov. R. B. Clarkson, and R. L. Belford. Illinois EPR Research Center, Colleges of Medicine, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Structural organization and conformational changes play important roles in biochemistry of membranes and proteins. Many of these transformations occur on a millisecond and sub-millisecond time scale through several intermediate steps that could co-exist at any particular moment. Magnetic resonance methods (both NMR and EPR) can resolve the coexisting states if the interconversion rate, I/x, is comparable with the frequency separation, A v, between the signals corresponding to the states in absence of interconversion: *x* A v>l 0. For many proteins, conversion between the native (N) and unfolded (U) states occurs within 1 msec; therefore, the difference in the effective resonance frequencies v of the N and U states should be A v = | v_N - v_v | > 10 kHz in order to observe those states simultaneously. In site-directed spin-labeling EPR experiments at conventional frequencies (X-band), the shift between spectral lines corresponding to different conformational states could be anywhere within 0.1-5 G range; however, it is often comparable with the line width, which is of the order of a few Gauss. This and some other problems are naturally solved with HF EPR at frequencies of 95 GHz and higher. Using 95 GHz (W-band) EPR examples we show how this method is used in resolving two co-existing states in protein equilibrium denaturing as well as three states and a distribution of states of spin-labels in a phospholipid bilayer. This work used the resources of the Illinois EPR Research Center (NIH Grant P41 -RRO 1 81 1), an NIH-supported Resource Center.

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MOLECULAR DISTANCES FROM DIPOLAR COUPLED SPIN-LABELS.

Eric L Hustedt and Albert H. Beth, Department of Molecular Physiology and Biophysics, 727 Light Hall, Vanderbilt University, Nashville, TN 37232,

Recent work has demonstrated that both the inter-spin distance and the relative orientation of two immobilized nitroxides can be precisely determined from CW-EPR spectra of the dipolar coupled spin-labels. Spectra of N6-spin-labeled coenzyme NAD-, bound to tetrameric glyceraldehyde-3-phosphate dehydrogenase will be analyzed in detail. The advantages of using multiple microwave frequencies and isotopic substitution (^{15}N for ^{14}N and D for H) will be discussed. Analytical methods for measuring inter-nitroxide distances from CW-EPR spectra in situations where the nitroxides are not immobilized or the nitroxides do not adopt a single unique orientation with respect to each other will be presented.

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TIME DOMAIN MEASUREMENTS OF METAL-NITROXYL DISTANCES,

S. S. Eaton and G. R. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado 80208.

Interaction between a rapidly relaxing electron spin on a transition metal and the more slowly relaxing electron spin of a nitroxyl spin label enhances the relaxation rate of the slowly relaxing spin. In the temperature interval where the metal relaxation rate is comparable to the dipolar splitting between the two paramagnetic centers, there is a characteristic temperature dependence of the nitroxyl phase memory relaxation time, T., measured by electron spin echoes. The changes in T. can be analyzed to determine the distance between the two unpaired electrons. The spin-spin interaction causes an increase in the nitroxyl spin-lattice relaxation rate, which also can be analyzed to determine the interspin distance. In both types of experiments analysis of the nitroxyl data relies upon measured values of the relaxation times for the rapidly relaxing center. Examples will be given for high-spin and low-spin FE(III) and for high-spin Co(II).

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TOWARDS SOLVING THE PUZZLE OF LENS a-CRYSTALLIN STRUCTURAL INSIGHT FROM SITE-DIRECTED SPIN LABELING STUDIES.

Hassane S. Mchaourab, Biophysics Research Institute, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, WI 53226

Small heat-shock proteins (SHSP) and lens a-crystallin show sequence similarity focused exclusively in a stretch of 80 amino acids referred to as the a-crystallin domain. The presence of this domain is associated with a complex and dynamic oligomeric structure and the ability of these proteins to function as molecular chaperones. Therefore, it has been proposed that the a-crystallin domain is a building block of a common structural framework in these proteins. We report the use of site-directed spin labeling (SDSL) to study structure and subunit interactions along the sequence of this domain in aA-crystallin. Nitroxide scanning was used to assign sequence-specific secondary structure and solvent accessibility. A predominately antiparallel (3-pleated sheet structure is observed with a solvent accessibility profile that reflects aspects of the quaternary structure. The local supersecondary structure motifs were determined using spatial proximities between nitroxides located on neighboring (3-strands in the primary sequence. One of the strands, spanning the most conserved region, is located at an interface in the oligomeric structure as inferred from spin-spin interactions between identical residues on different subunits. The extent to which this interface is conserved in heat-shock protein 27 (HSP27) and in a more distant bacterial SHSP was also examined. The systematic application of SDSL is providing insight into the function of SHSP, their dynamic structure, and evolutionary relationships within the family.

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INTERNAL DYNAMICS OF NUCLEIC ACIDS STUDIED BY EPR-ACTIVE PROBES. Bruce H. Robinson, Tamara Okonogi, Colin Mailer, Steve C. Alley, Annabelle W. Reese, Paul P. Hopkins. Dept. of Chemistry, P.O. Box 351700, University of Washington, Seattle WA. 98195

To monitor the, internal dynamics of nucleic acids we have developed a series of EPR active spin probes designed to substitute site-specifically for bases in nucleic acids. We have measured CW-EPR spectra at 9 and 94 GHz and pulsed-ELDOR spectra at 9 GHz. Complete analysis of the CW-EPR data required that the uniform rotational modes of motion and the internal modes of the DNA be included in line-shape simulations. Both the amplitudes and the rates of the internal modes of the dynamics had to be included. The results are consistent with the predictions of the weakly bending rod model, originally developed to emulate duplex DNA dynamics. As a result we can monitor both internal bending and twisting of duplex DNA. This system has been used to study dynamics in duplex DNA as a function of base sequence. We have found that different dinucleotide sequences do show different flexibility, with $d(ApT)_n$ sequences being the most flexible and $d(ApA)_n$ sequences being the least flexible. Local sequence-dependent differences in flexibility give rise to dynamics that couple throughout the DNA. Pulsed ELDOR spectra were analyzed by relaxation theory, again taking into account both the uniform, global motion and the internal motions of the duplex DNA, and the results supported the CW-EPR interpretations.
[We gratefully acknowledge the NIEHS, the UIERC and the NBFML for their assistance in this project]

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IDENTIFICATION OF CALCIUM-DEPENDENT CHANGES IN THE ROTATIONAL DYNAMICS OF THE INTERDOMAIN CENTRAL HELIX IN CALMODULIN DETECTED BY SPIN-LABEL EPR SPECTROSCOPY. Zhihai Qin, Daniel H. Yin, Robert F. Weaver, and Thomas C. Squier. Department of Biochemistry, Cell and Molecular Biology. University of Kansas, Lawrence, KS 66045-2106.

Calcium-dependent changes in the conformation of the interdomain central helix connecting the two opposing globular domains in calmodulin (CaM) were detected using spin-label EPR spectroscopy. Single cysteines were separately inserted into the interdomain central helix with no loss of function, and these sites were individually labeled with the spin label methanethiosulfonate (MTSSL). In all cases, two motional populations were resolved, indicating the presence of two common conformations that are in slow exchange. The spectral contribution associated with the mobile component progressively increases at positions located toward the center of the interdomain linker, indicating increased conformational heterogeneity. Calcium activation acts to stabilize the relative contribution of the immobile component indicating that calcium binding is associated with a direct structural coupling between the opposing globular domains in CaM through the interdomain central helix. These results are discussed in terms of the possible stabilization of protein secondary structural elements in the interdomain central helix upon calcium activation of CaM.

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REVERSE CORRELATION IN THE HYDRATION BETWEEN LIPID HEAD GROUP AND ACYL CHAIN REGIONS. Mingtao Ge and Jack H. Freed, Baker Laboratory of Chemistry, Cornell University, Ithaca, NY 14853

The z- component of the A- tensor, A_{zz}, of a spin label is sensitive to polarity in the immediate environment of the nitroxide radical. A_{zz} values of a series of chain labeled phosphatidylcholines (PC), 5PC, 10PC, 16PC, head group labeled PC, and head group labeled sphingomyelin (SM), in a variety of dispersions of pure lipids, such as DPPC and SM and lipid mixtures with and without cholesterol were measured with cw EPR spectra and least squares fitting. It was found that there is a reverse correlation in polarity between the head group and acyl chain regions. That is, the larger (smaller) the A_{zz}'s for head group spin labels, the smaller (larger) for chain spin labels, which is in agreement with our previous observation of a reverse correlation in polarity between the head group and acyl chain regions for macroscopically oriented vs. dispersed PC bilayers. Incorporation of peptides gramicidin A or carbobenzoxy-D-Phe-L-Phe-Gly into DPPC bilayers are shown to have opposite effects on the hydration of bilayers. The reverse correlation between hydration in the head groups and acyl chains is also evident here. The significance of the effects of the two peptides on lipid phase structure and lipid membrane fusion are discussed.

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LIPID-PROTEIN INTERACTION IN R-3-HYDROXYBUTYRATE DEHYDROGENASE AS STUDIED BY ESR SPECTROSCOPY. Dirk Chelius[a], Johannes Moeller[a], Silvia Hahn[a], Andrew R. Marks[b], J. Oliver McIntyre[c], Sidney Fleischer[0], John G. Wise and Wolfgang E. Trommer[a]. a)Department of Chemistry, University of Kaiserslautern, D-67653 Kaiserslautern, Germany, b)Brookdale Center, Mount Sinai School of Medicine, New York, NY 10029, USA and c)Department of Molecular Biology, Vanderbilt University, Nashville, TN 37235, USA

R-3-Hydroxybutyratc dehydrogenase (BDH) is a lipid-requiring mitochondrial enzyme bound to the matrix face of the mitochondrial inner membrane with a specific and absolute requirement of phosphatidylcholine (PC) for function. PC is required for tight and functional binding of the coenzyme NAD to BDH and, *vice versa,* complex formation with NAD in binary and ternary complexes enhances the interaction of the enzyme with PC. PC bound to BDH was also found to be in rapid exchange with the bulk lipid on the ESR time scale. NAD^+ derivatives spin-labeled at N^6 or C8 are enzymatically active and have been successfully employed with BDH in these as well as in related studies. Investigations were hampered, however, by a slow reduction of the spin label by at least one reactive cysteine SH group of BDH. Although chemical derivatization of these cysteines is accompanied by loss of enzymatic activity, they appear not to be involved in catalysis.

The enzyme from human heart was recently expressed both in insect cells and in *E. coli.* The molecular mechanism of the lipid dependence is now being investigated by site-specific spin labeling of various mutants via spin-spin interaction with spin-labeled NAD. In these mutants, alanine as well as serine substitute for the reactive native SH groups.

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LET'S TALK TOAC. Glenn L. Millhauser, Claudio Toniolo', D. Joe Anderson and Joe McNulty,
Department of Chemistry and Biochemistry, Univeristy of California, Santa Cruz CA 95064 and
'Biopolymer Research Center, CNR, Department of Organic Chemistry, University of Padova, Italy

TOAC is a novel amino acid with a nitroxide ring rigiqly attached to the alpha carbon of the polypeptide backbone. TOAC has been incorporated into model helix forming peptides and antibiotics. In double label experiments, dipolar interactions provide accurate internitroxide measurements out to greater than 10A. These experiments are yielding previously unseen geometric details on folding and conformational fluctuations. We will present recent results on various helical peptides. Strategies for labeling proteins will also be discussed.

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SITE DIRECTED SPIN LABELING STUDY OF THE STRUCTURE OF COLICIN E1. Lukasz Salwinski§ and Wayne L. Hubbell. Jules Stein Eye Institute and Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095 (^present address: Molecular Biology Institute, University of California, Los Angeles 90095)

In order to study the structure of the pore-forming domain of a bacterial toxin, colicin E1, more than 80 single cysteine mutants were prepared and subsequently modified with a sulfhydryl-specific methanethiosulfonate spin label. The electron paramagnetic resonance spectra of the spin labeled protein provided information about colicin structure in both soluble and membrane-bound form.

The results obtained for the water-soluble form of the protein are consistent with the crystallographic data. In particular, the analysis of the periodic properties of the labeled sites within the 402-442 region identified two alpha-helical stretches (406-416 and 428-437) that correspond to helices IV and Vb of the crystal structure.

Dramatic changes of the protein structure were observed upon membrane binding. Incorporation of the residues 402-405 and 417-421 into helix TV leads to formation of a 19 residue long helix localized at the water:lipid interface. Measurement of the immersion depth of residues on the lipid-exposed face of the helix reveals that it spans the membrane with the residue 412 located near the center of the bilayer. The many tertiary interactions detected by the spin labels show that the helix remains in close contact with other parts of the molecule, suggesting the possibility that it may be part of a pore.

The position of the helix in the membrane is affected by pH as well as by modifications of the charges within the D408-R409 par that is localized on the lipid-exposed face of the helix and is believed to form a salt bridge.

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DYNAMICS AND ORIENTATION OF MYOSIN REGULATORY DOMAIN Breft Hambly and Plotr G. Fajer, Department of Pathology, University of Sydney and the National High Magnetic Field Laboratory, Tallahassee, FL 32306

Force Generation results from bending of the myosin head

We have previously shown that spin probes attached to the regulatory domain (via the regulatory light chain) of the myosin head are anisotropic in rigor, but become highly disordered during both relaxation and contraction. These data contrast to spectra obtained from spin probes attached to the catalytic domain. Highly ordered spectra are obtained in rigor and become disordered in relaxation. Contraction spectra can be deconvoluted into an ordered component similar to rigor (- 20% depending on conditions) and a disordered component similar to relaxation. From these data, we proposed that force is generated by the actin-bound myosin head by an active reorientation of the regulatory domain with respect to the catalytic domain, implying the necessity for a hinge between these two domains.

Hinge between catalytic and regulatory domains

The ability of the myosin head to attain various orientations of catalytic and regulatory domains implies segmental flexibility within the head. This segmental dynamics was investigated with STEPR in myosin filaments in which the head is attached to the filament surface via the regulatory domain. The regulatory domain is further divide into two parts: the essential and regulatory light chains (ELC and RLC). As expected, the domain proximal to the filament surface (RLC) was slowest (t_r =100 (as), the central region (ELC) was intermediate t_r = 20 us, and the distal catalytic domain was moving fastest (t_r = 7 us). A mobility difference of this magnitude can be expected if the three domains are joined by a very flexible hinges. Modulation of hinge flexibility (stiffness) might control the coupling of the strain generated in the catalytic domain to the thin filaments and may be a key to a dynamic model for force generation..

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SPIN-LABELS REVEAL THE MECHANISMS OF MUSCLE CONTRACTION AND RELAXATION, David D. Thomas, University of Minnesota Medical School, Minneapolis, MN 55 455

My coworkers and I have used EPR to investigate the molecular motions involved in muscle contraction and relaxation, using spin labels specifically attached to protein and lipid components in muscle fibers and membranes. The catalytic domain of myosin undergoes a disorder-to-order transition upon muscle contraction. The regulatory (light-chain) domain of myosin, farther from actin, shows two distinct angles, differing by 36°, and a substantial shift from one orientation to the other occurs upon contraction. These results reveal a much more complex and dynamic mechanism than previously proposed for muscle contraction. The calcium pump in cardiac muscle, which is responsible for muscle relaxation becomes more mobile (more aggregated) upon phosphorylation of the regulatory protein phospholamban, and phospholamban becomes less mobile (more aggregated). Thus the reciprocal aggregation of these two proteins may be the key to understanding calcium regulation in the heart. Experiments with mutant proteins and site-directed spin-labeling reveal directly the changes in phospholamban structure that accompany its phosphorylation and interaction with the calcium pump.

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MAGIC ANGLE SPINNING IN NMR AND EPR.

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Solid state magnetic resonance spectra are largely broadened due to anisotropic interactions of the spins involved. In NMR this broadening can be removed by MAS because spinning frequencies (several kHz) exceeding these broadenings can mechanically be achieved. Therefore, MAS is a major ingredient of virtually all high-resolution solid state NMR experiments. Due to technical improvements high speed spinning at frequencies between 10 and 35 kHz is possible today. If multiple pulse decoupling or cross polarization is desired, special rotor synchronisation and dipolar recoupling requirements have to be met in order to achieve optimum resolution and sensitivity. Examples of such schemes in 1H- and 13C-NMR will be described and demonstrated by various examples, including multiple quantum NMR spectroscopy. A similar line-narrowing by conventional MAS is unfortunately not possible in EPR-spectroscopy, where spinning speeds in the range of tens of MHz would be required due to the much higher frequencies involved. However, ultra-slow MAS, which is well established in two-dimensional NMR and there involves spinning frequencies of 50- 100 Hz only, can be realized in EPR with high speed spinners now available. Examples of artificially narrowed EPR spectra will be presented.

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EXPLOITATION OF THE FREE EVOLUTION PERIODS IN PULSE EPR EXPERIMENTS.

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Usually, during the time intervals between the microwave pulses in pulse EPR experiments such as the two-pulse echo or the three-pulse stimulated echo experiments (ESEEM), the spin system is allowed to evolve freely or is subjected to RF-irradiation (pulse ENDOR). Here we present some new tools for manipulating the spin system during free evolution periods. Sensitivity improvement by Right Angle Spinning (RAS) is obtained when the sample is rotated along an axis perpendicular to the static magnetic field. It allows one to use higher repetition rates. Anisotropy-resolved EPR is also based on Right Angle Spinning. In this two-dimensional experiment the stimulated-echo-detected EPR signal is measured as a function of the RAS spinning speed, which separates components in the EPR spectra based on their anisotropy. Electron-Zeeman resolved EPR uses the electronic Zeeman term in the spin Hamiltonian to add a dimension representing the electronic g-factor, e.g., the determination of coupling constants at non-canonical orientations. RF-driven ESEEM allows the detection of nuclear transition frequencies even when there are no pseudo-secular terms in the spin Hamiltonian to generate the necessary forbidden transitions, such as for free radicals in solution. In the time-domain Chirp-ENDOR experiment, broadband chirp RF pulses utilize the nuclear polarization created by microwave pulses to effectively create nuclear coherence. The experiments will be illustrated with a number of applications.

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PULSED ENDOR IN UNORIENTED SAMPLES: HOW TO INCREASE RESOLUTION AND GAIN THE MULTIPLEX ADVANTAGE.

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The anisotropy of the EPR spectrum and inhomogeneous broadening of the ENDOR spectrum complicate pulsed ENDOR measurements on unoriented samples of free radicals and metalloproteins. The EPR anisotropy means that determination of the complete ENDOR spectrum requires repeated measurements at positions within the EPR spectrum. The anisotropy of the hyperfine interactions inhomogeneously broaden the ENDOR spectrum so that ENDOR lines from different nuclei often overlap and are difficult to assign. We present new pulsed ENDOR experiments that help with both these problems. An excitation scheme based on split-Hamiltonian theory allows one to obtain the ENDOR spectrum from several points across the entire EPR spectrum simultaneously, thus achieving the multiplex advantage in pulsed ENDOR. An electron nuclear quadruple resonance scheme allows one to correlate ENDOR frequencies from different electron manifolds but the same orientation. This provides information analogous to HYSCORE spectroscopy without the requirement for ESEEM. Examples will be described of applications both in free radicals and in metalloenzymes. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy through Contract No. DE-AC06-76RLO 1830.

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ENDOR OF METALLOENZYMES: TO THE LIGANDS AND BEYOND. B.M. Hoffman*, Northwestern University.

ABSTRACT NOT AVAILABLE

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HIGH FIELD (140 GHZ/5T) EPR AND DYNAMIC NUCLEAR POLARIZATION M. Bennati, C. Farrar, D. Hall, S. Inati, M. Rosay, V. Weis, K. Kreischer and R.G. Griffin*, Francis Bitter Magnet Laboratory, and Dept. of Chemistry, MIT, Cambridge, MA 02139. E-mail: griffin@ccnmr.mit.edu

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 Gunn diode and a gyrotron as microwave sources and radicals and metal ions as paramagnetic polarizing agents. In a water:glycerol frozen solutions the 1H and 13C NMR signal strengths of both the solvent and solute have been enhanced by a factors of -200, which represents a reduction of >100 in sample size requirements or >10,000 in signal acquisition time. These experiments using a water: glycerol: nitroxide system have also been employed to acquire DNP enhanced NMR spectra of large proteins. The mechanism of the DNP enhancements will be discussed in detail. Possibilities for operation at higher frequencies will also be described.

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KjCrO* A PROPOSED STANDARD FOR g-FACTOR AND FIELD CALIBRATIONS IN HIGH FIELD EPR SPECTROSCOPY Brant Cage[1,3], Louis-Claude Brunei[2,3], and Naresh S. Dalai[1,3], department of Chemistry, [2]Department of Physics, [3]Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, Florida State University, Tallahassee FL. 32306.

Currently there is a need for good EPR standards of the g-value, field linearity and calibration in High Field EPR spectroscopy. This presentation will show that K_3CrO_g possesses the qualities required for a good EPR standard. These characteristics are that in its diluted form K_3Cr0_8 has a linewidth of less than 4 Gauss at the highest field investigated (14 T), the chemical composition is well known, and there are no phase transitions from 343 K - 1.4 K. One advantage of K_3Cr0_8 is that the linearity of the field can be established from a well defined hyperfine splitting due to the ^{53}Cr isotope. Another important advantage of K_3Cr0_8 is that with an isotropic g-factor = 1.9712, its signal does not interfere with those of g = 2 systems. In addition, the linewidth of both the concentrated and dilute system have been well investigated at fields of up to 14 Tesla.

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HETEROGENEOUS DNP EFFECT IN AQUEOUS CARBON-BASED CHAR SUSPENSIONS. Boris M. Odintsov[1,3-5], R.L. Belford[1,2], P.J. Ceroke[3], Z. Sh. Idiyatullin[5], R.S. Kashaev[5], V.S. Rukhlov[4], A. N. Temnikov[5] and R. B. Clarkson[u], Illinois Research EPR Center, Department of [2]Cheniistry and [3]Veterinary Clinical Medicine, University of Illinois, 190 MSB, 506 S. Mathews, Urbana, IL 61801, USA, [4]Zavoisky Physical-Technical Institute, [5]State Technological University, Kazan, 420029, Russia

The heterogeneous *H Dynamic Nuclear Polarization (DNP) effect is studied for a system consisting of newly synthesized carbon chars suspended in water. A pulsed *H DNP technique at low magnetic field has been used to study hyperfine interactions, molecular and spin dynamics in inhomogeneous suspensions of carbon based chars. Utilizing the Torrey model, the influence of "cage effects" on DNP enhancement in porous media is discussed. Results suggest that the main DNP processes in char suspensions occur in pore spaces and the short-range nuclearelectronic interactions have a dominant effect on DNP enhancement. Long-range interactions associated with other (nuclear and electron-nuclear) relaxation processes at the renfinder of the surface layer can have small or even negligible effect. Surface properties strongly effect the DNP data in char suspensions. Hydrophilic character of chars is associated with positive DNP enhancement and Fermi contact hyperfine interactions at the solid-liquid interface. Theoretical modeling of the DNP enhancement indicates that chars with developed porous structure and small pore size, low tortuosity, and fast spin-lattice relaxation of solvent molecules in the pore space exhibit large DNP effects in char suspensions. Partial supported provided by the NIH (GM 42208,5160, RBC).

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ELECTRON PARAMAGNETIC RESONANCE OF Al CENTERS IN *6H-SiC.* Gary J. Gerardi William Paterson University, Wayne, NJ 07470, Chris F. Young and Edward H. Poindexter, Army Research Laboratory, Adelphi, MD 20783.

The EPR spectrum of Al-doped 6H-SiC reveals additional Al-related impurity centers not related to the highly anisotropic silicon substitutional center (Al_{si}) attributed to the effective-mass-like Al acceptors at the three inequivalent Si sites in the 6H polytype. While the observed spectral intensities scale with Al doping, the temperature and saturation characteristics of the new resonances differ from those of Alsi. The new Al centers observed near g = 2 are slightly anisotropic but have comparable linewidths to the Al_{Si} center. For highly concentrated Al-doped samples another broad resonance is found near g = 2.22. All of the observed Al-related centers appear to contribute to the free-carrier concentration which indicates that they are acceptor-like centers. Evidence suggests that some of these new resonances are due to Al_c centers.

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NOTRE DAME RADIATION CHEMISTRY DATA CENTER. 1998 STATUS REPORT Keith P. Madden. Radiation Chemistry Data Center, Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556-0579 U.S.A.

The Radiation Chemistry Data Center of the Notre Dame Radiation Laboratory is a chemical information resource supported by the United States Department of Energy. The primary function of RCDC is the collection, compilation, evaluation, and dissemination of quantitative information on radiation chemical systems, focusing on transient reactive intermediates. Since free radicals, ionic species, and excited states are produced by other chemical methods as well as radiation chemistry, complementary data from the photochemical, biological, and electrochemical literature are collected for comparison with radiation chemical results. The nature of the data collected by the center includes, but is not limited to, reaction rate constants, radiation chemical yields, thermochemical reaction parameters, photochemical quantum yields, and experimental spectra (spectrophotometric, magnetic resonance, ion-mass) used to determine the quantitative chemical attributes of these systems. The ultimate aim of this work is the establishment of standard reference values for the properties of these reactive intermediates. This report describes the offerings of the center (our current awareness service and critically evaluated numeric chemical property databases), and gives instructions for electronic access to the center's resources.

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AN IN SITU RADIOLYSIS EPR STUDY OF SELF-RECOMBINATION RATE CONSTANTS FOR HYDROXYMETHYLETHYL AND 2-HYDROXY-2-METHYLPROPYL RADICALS IN WATER. Stephen P. Mezyk and Keith P. Madden. Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556-0579.

Arrhenius parameters for the self-termination of hydroxymethylethyl $C(CH_3)_2OH$] and 2-hydroxy-2methylpropyl [- $CH_2C(CH_3)_2OH$] radicals in dilute aqueous solution were determined using electron pulse radiolysis and time-resolved EPR. Rate constants of 2k[«$C(CH_3)_2OH$] = (1.56 0. 10) x 10^9 and 2k[. $CH_2C(CH_3)_2OH$] = (1.1 8 0.20) x 10^9 dm^3 mol"^{1} s"^{1} for these radicals were measured at 26.4 and 26.6°C respectively. The corresponding activation energies were 18.8 1.2 (5.3-71.7°C) and 15.83 0.92 (8.5-69.8°C) kJ mol^1 for these two reactions. Calculations of the diffusion-controlled rate constants for the reactions of these radicals yield substantially higher rate constants than those measured in this study, showing that radical reactivity dominates the effects of diffusion in the recombination processes of these radicals in water.

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HIGH FIELD ESR AND MAGNETIZATION STUDIES IN SALTS OF C_{60} AND C_{60} DERIVATIVES WITH TDAE A. L. Maniero[1]. L.-C. Brunei[1], L. Pasimeni[2], R. P. Guertin[1'3']; ^IMAR, National High Magnetic Field Laboratory, Tallahassee, FL32310; [2]Dept. diChimicaFisica, Univ. di Padova,l-35100 Padova, Italy;[3] Dept. of physics, Tufts Univ., Medford, MA 02155.

TDAE-C_{60} salts have been extensively investigated after the discovery of ferromagnetic phase transition at Tc= 16 K by several methods. We have applied the HF-ESR technique to freshly prepared and aged powder samples of TDAE-C_{60} together with SQUID magnetization measurements to elucidate the magnetic behavior of the phase transition above Tc. The value of Tc measured by SQUID was 16 K for the freshly prepared sample, confirming previous results, and 5 K for the aged sample. HF-ESR spectra, recorded for both samples in the temperature range of 60 K above Tc, exhibited selective down shift of the resonant fields across the spectrum. The results were qualitatively explained by the theory developed to account for the one-dimensional short-range order effects in magnetic materials. Accordingly, on cooling TDAE-C_{60} salt there is a pretransition change of the properties of the material, characterized by fluctuations of different amplitudes in the spin exchange and dipolar interactions. Our investigation by HF-ESR and SQUID methods was extended to the salts of TDAE and fullerene derivatives. Mono and poly-adducts of C_{60} have been examined. Magnetization measurements of the TDAE -N-methylfulleropyrrolidine salt showed temperature dependent Curie-Weiss susceptibility with an expected spin near 1/2, but no magnetic ordering above T=2 K. On the other hand, the HF-ESR spectrum displayed a downshift in the resonent fields for T<30 K, similar to that observed for TDAE-C611-

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EPR DETECTION BY TIME-LOCKED SUB-SAMPLING. James S. Hyde, Hassane S. Mchaourab. Theodore G. Camenisch, Joseph J. Ratke, Robert W. Cox, and W. Froncisz, Biophysics Research Institute, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, WI 53226

We introduce and demonstrate a new data acquisition method for EPR spectroscopy that permits simultaneous detection of multiple in- and out-of-phase harmonics for both dispersion and absorption. The harmonics are the resonance response to any applied coherent modulation such as the static field or the incidence microwaves. The method, called time-locked sub-sampling, consists of the following steps: i) conversion of the microwave carrier to an intermediate frequency (IF) carrier; (ii) sub-sampling of the IF carrier by an A/D converter four times in *K* IF cycles where *K* is an odd integer greater than one; (iii) dividing the digital words into two streams, odd indexes in one and even in the other, followed by sign inversion of every other word in each stream; (iv) feeding the two streams to a computer for the digital equivalent of phase-sensitive detection (PSD). The system is broadbanded, in the frequency domain, with narrow banding for improved signal-to-noise ratio occurring only at the PSD step. All gains and phases are internally consistent. The method will provide significant improvement in the methodology of EPR modulation spectroscopy including ST-EPR and MQ-EPR. For linear stationary EPR a two-fold improvement in the signal-to-noise ratio is anticipated.

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DAP-SL: A NOVEL, NON-LABILE SPIN LABELED AMINO ACID
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Site-specific spin labeling has evolved into a powerful tool for the determination of both structural and dynamic features of macromolecular systems. The choice of spin label used has considerable impact on the final results. Published work includes a long, flexible spin label (Cys-SL) and a rigidly attached nitroxide (TOAC), each with benefits and limitations. To fit between these extremes, a novel amino acid spin label synthesized in part from 2,2-diaminopropionic acid (DAP) has been incorporated into water-soluble peptide systems previously characterized by both TOAC and Cys-SL. The resulting amino acid is L-chiral, shorter than Cys-SL, and relatively stable with regard to physical and chemical conditions. Doubly-labeled DAP peptides exhibit dipolar couplings and CD spectral features of aqueous [nascent] helices; results of NMR NOESY and TOCSY experiments will also be presented.

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INVESTIGATION OF THE HAMMERHEAD RIBOZYME BY CW Q-BAND ENDOR SPECTROSCOPY

Susan R. Moffissey. Thomas E. Horton, Tomasz Wasowicz, Victoria J. DeRose, Department of Chemistry, Texas A&M University, College Station, TX 77842.

The role of divalent metal ions in the phosphodiester bond cleavage reaction performed by the hammerhead ribozyme is being investigated. In order to study the metal ion-ribozyme interactions, the native Mg^{2+} was replaced by paramagnetic Mn^{2+}. Recent X-band EPR studies have determined the number of Mn^{2+} bound per ribozyme under solution conditions. ENDOR (electron nuclear double resonance) spectroscopy is applied to further investigate the metal ion-ligand interactions. Results will be presented from a cw Q-band ENDOR investigation of the hammerhead ribozyme as well as a series of Mn^{2+}-complexes that model the potential metal-ribozyme interactions.

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TOWARDS DEVELOPMENT OF TARGETED NITROXIDES: UPTAKE OF TEMPOCHOLINE BY BABY HAMSTER KIDNEY CELLS

Julie A. Cianfrogna and Reef (Philip D. II) Morse. Departments of Biology and Chemistry, Illinois State University, Normal, IL 61790-4160

It is now clear that reactive oxygen species, such as superoxide and peroxide, act as signals in the control of cell growth and development Our research is a first step towards understanding how these signal molecules act at the molecular level. Previous studies have shown that TEMPOL between 0.1 and 0. 3 mM accelerates, and at 0.5 mM and above, inhibits growth of baby hamster kidney cells. A charged nitroxide, ZWIT, which does not enter the cell, shows no effect. We predicted that TEMPOCholine would have the same affect on cell growth as the ZWIT, but our data indicates that TEMPOCholine exerts its effects at a much lower concentration than the ZWIT. This implied that TEMPOCholine was being transported into the cell. To calculate TEMPOCholine uptake, BHK cells were incubated in I mM TEMPOCholine. Samples of the media were taken at 0, 24, and 48 hours to determine the amount of TEMPOCholine that had been reduced and taken up by the cells. BHK cells harvested at 48 hours showed no TEMPOCholine signal, but upon addition of FECN (I mM) followed by freezing and thawing, a TEMPOCholine signal appeared (appropriate controls were negative for TEMPOCholine signal). We calculated the intracellular concentration of TEMPOCholine to be 0.125 mM, a sufficient concentration to affect cell growth based on the TEMPOL results. We postulate that the choline moiety of TEMPOCholine may accelerate uptake. We hope to take advantage of this phenomenon to develop targeted nitroxides based on choline derivatives.

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SIMULATION OF STRAIN IN EPR SPECTRA USING THE METHOD OF GRADIENTS.

Mi. Nilcies and R.L. Belford, Illinois EPR Center, University of Illinois, Urbana, 111. 61801, and L.C. Francesconi, Hunter College of the City University of New York, Department of Chemistry, NY, NY 10021.

For *many* metal !on systems the linewidth is nearly completely dominated by strain effects. The EPR spectra of many of these systems are not first-order, so simple M, and M^-dependent linewidth expressions are deemed inappropriate. We have found that an efficient and highly accurate method to calculate strain effects in EPR spectra is the use of exact analytical gradients. Further improvements can be obtained by transforming gradients of the eigenvalues of the spin Hamiltonian transformed to the field domain using the results of the fourth-order frequency perturbation. In addition to g and A strain, this method can be applied to strain in both the nuclear and electric quadrupole tensors. Examples of are both are given.

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MAGNETIC FIELD GRADIENT AT SOLID-LIQUID INTERFACE IN AQUEOUS CHAR SUSPENSIONS. Boris M. Odintsov[1 3 4],' R-L. Belford[1'2], P.J. Ceroke[1 3], and R.B.Clarkson[1'3],. Illinois Research EPR Center, Department of[2] Chemistry and [3]Veterinary Clinical Medicine, University of Illinois, 190 MSB, 506 S. Mathews, Urbana, IL 61801, USA, [4]Zavoisky Physical-Technical Institute, Kazan, 420029, Russia

In accordance with a solution of the magnetostatic boundary value problem, the magnetic field gradient G_z at the solid-liquid interface was estimated for a particular case of paramagnetic microparticles of chars suspended in water. Calculations show that this gradient is at least in part due to the difference in susceptibilities AX between water molecules and solid surface. The static magnetic susceptibility of chars was measured with a SQUID magnetometer system (MPMS, Quantum Design, CA). Measurements were carried out over a temperature range 4 - 3 00 K at 1, 5 T magnetic field. The temperature behavior of static magnetic susceptibility of chars exhibits Curie-Weiss behavior over the whole temperature range. The Weiss constant was found to be positive for all samples, characterizing the overall exchange as antifeffomagnetic. Large paramagnetic magnetic susceptibility was observed at low temperatures. As the temperature increases, the sign of the magnetic susceptibility is changed, and at room temperature the samples are predominantly diamagnetic. At low temperatures AX can lead to a very large magnetic field gradient at the solid-liquid interface, which can influence the EPR line width in char suspensions. The value of G,. increases as particle size decreases. Partial supported provided by the NIH (GM 42208, GM 5163 0, RBC), by U.S. Department of Energy (DE FG22-96 PC 96205) and by Nycomed Innovation.

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DISTANCE LIMITATIONS AND NITROXIDE PROBE PAIR INTERACTIONS IN HELICAL DNA-AN EPR APPLICATION TO BULGE DYNAMICS. Tamara M. Okonogi. Annabelle W. Reese, Stephen C. Alley, Eric A. Harwood, Paul B. Hopkins, and Bruce H. Robinson, Department of Chemistry, Box 351700, University of Washington, Seattle, WA., 98195-3700.

A thymidine modified nitroxide spin label, Q, is incorporated into an oligomer of DNA of specific base sequence using standard phosphoramidite chemistry. The complementary strand is made separately. Q pairs best with 2-aminopurine as its partner on the complementary strand. A base without its partner in the complement strand forms a bulge or mismatch in the duplex DNA. To explore the effects of base pair mismatch on neighboring bases, a set of duplex DNAs (all of length 15 base pairs) is designed in which the bulge position occurs either at the spin label or at the base next to the label. Individual control sequences collectively contain all relevant arrangements of the bulge and the spin probe for a specific DNA sequence. The EPR spectra are analyzed for couplings which result from sequence and dynamical effects. The relationships between couplings and effects are reported. To determine structural information about DNA bending, sets of 14 and 28 base pair duplex DNAs, containing an homogeneous pair of spin labels placed 1,2,3, and 10 base pairs apart, are examined. The spin-spin interactions allow determination of the maximum distance between probes that permits inter-label communication. Distance information provide insight into DNA bends and geometries.

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PROBING LOCAL STRUCTURE AND MOBILITY AT A BURIED SITE IN HUMAN CARBONIC ANHYDRASE II: A COMPARISON BETWEEN TWO DIFFERENT SPINLABELS. Rikard Owenius(1), Per Hammarstrom(2), Mikael Lindgren(1), Martina Huber(u), Magdalena Svensson(2), Lars-Goran Martensson(2), Uno Carlsson(2). (1)IFM-Chemical Physics,(2) EFM- Biochemistry, Linkoping University, S-581 83 Linkoping, Sweden. (3)On leave from: Department of Organic Chemistry, Free University Berlin, 14195 Berlin, Germany.

Spin labels have proven useful to probe the structure and dynamics of proteins. Combined cw and pulsed EPR techniques can be used to compare chemically different spin labels and determine how their chemical nature affects their sensitivity towards the local structure and dynamics. Mutants of human carbonic anhydrase H (HCAII) have previously been investigated by spin-labeling of specifically introduced SH groups. In our recent studies exclusively the spin label N-(I-oxyl-2,2,5,5-tetramethyl-3-pyrrolidinyl)iodoacetamide (IPSL) has been used. Here IPSL was compared with another spin label, (l-oxyl-2,2,5,5-tetramethylpyrroline-3-methyl)methane-thiosulfonate (MTSSL), to elucidate fundamental differences in the characteristics of the labels and possible effects they might have on the stability of the protein. One particular site (L79C) buried in one hydrophobic cluster of HCAII was spin labeled, followed by cw EPR and fluorescence measurements at various stages of unfolding at room temperature. There is a notable difference in the spectral appearance using the different spin labels at different degrees of unfolding. The combined results imply that the structure of the protein and structural changes upon unfolding can depend upon the type of spin label used.

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^{55}*Mn* ***PULSED ENDOR DEMONSTRATES THAT THE PHOTOSYSTEM II "SPLIT" EPR SIGNAL ARISES FROM A MAGNETICALLY-COUPLED MANGANO-TYROSYL COMPLEX***

Jeffrey. M. Peloquin. Kristy A. Campbell, and R. David Britt, Department of Chemistry, University of California, Davis, Davis, CA 95616

Electron spin echo ENDOR spectroscopy demonstrates the presence of ,^{55}Mn nuclear spin transitions associated with the "split" EPR signal photo-generated in acetate-inhibited Photosystem II membranes. This split EPR signal has previously been assigned to the neutral tyrosine radical Y_z\ This new ENDOR result shows the split signal also arises from the PSII Mn cluster, thus proving the existence of a coupled mangano-tyrosyl complex at the core of the oxygen evolving complex. Both the EPR and ENDOR spectra of the split signal can be simulated by introducing exchange (J = -850 MHz) and dipolar (D = 150 MHz) coupling terms between a g=2.0046 tyrosine center and a tetranuclear Mn center, utilizing the same hyperfine and g matrices for the Mn center that successfully simulate both the EPR and ENDOR spectra of the S_2-state multiline signal. In the point dipole limit, the D = 150 MHz value translates to an interspin distance of 8.1 A.

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AN EPR STUDY OF INTERACTIONS BETWEEN SPIN-LABELED VARIANTS OF HUMAN CARBONIC ANHYDRASE II AND GROEL.

Malin Persson. Per Hammarstrom, Magdalena Svensson, Uno Carlsson, Mikael Lindgren(+), Bengt-Harald Jonsson(#). EFM-Biochemistry,(*)IFM-Chemical Physics, Linkoping University, S-581 83 Linkoping, Sweden. (#)Department of Biochemistry, Umea. University, S-901 87 Umea. Sweden

The interaction between variants of human carbonic anhydrase II (HCA II) and GroEL at room temperature was investigated using electron paramagnetic resonance (EPR) spectroscopy in combination with site-directed spin labeling. Considering the difference in the mobility of the spin-label in various positions in HCA II, with and without the presence of GroEL, a number of general conclusions can be made. The interaction with GroEL occurs in outer parts of the HCA II molecule, such as peripheral *B*-strands and the N-terminal domain. HCA II appears to be unfolded to about the same extent as a GuHCl-induced molten-globule intermediate of the enzyme when it binds to GroEL. As a result of the interaction, the rigid and compact hydrophobic core exhibits higher flexibility, which is likely to facilitate rearrangements of misfolded structures during the folding process. The degree of binding to GroEL and accompanying inactivation of the enzyme depend on the stability of the HCA II variant, and nonspecific hydrophobic interactions appear to be most important in stabilizing the GroEL-substrate complex. GroEL efficiently protects HCA II from irreversible aggregation at higher temperatures.

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A NEW TYPE OF LOW TEMPERATURE INTEGER SPIN Q-BAND EPR SPECTROMETBR FOR METALLOPROTIENS, Doros T. Petasis and Michael P. Hendrich, Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213.

Most of the existing Q-band spectrometers employ cylindrical cavities for more intense microwave magnetic fields B, but are so constructed that only one orientation between the external field B and B, is allowed, namely the B Bj orientation, thus limiting the use of the spectrometer to measurements on Kramers systems (half-integer spin). We have designed and built epoxy resin microwave cavities to use as part of an integer spin Q-band (34 GHz) continuous wave (CW) EPR spectrometer operating in the range $2\,K < T < 100\,K$ and geared toward studies on metalloprotein and metalloenzyme samples. The cylindrical cavities operate in the TE_{011} mode with a side wall coupling to the waveguide probe which allows orientation of the cavity where the external field B can be parallel to the microwave field Bj. Such orientation allows observation of EPR transitions in non-Kramers ions (integer spin) which are normally forbidden when B Bj. Rotation of the external magnetic field also permits a B B! orientation for observation of half-integer spin signals without disturbing the sample. The main body of the cavity consists of a brass metallic helix which suppresses unwanted extraneous modes (such as TM_{1n}) and eddy currents. End walls with thin metallic annuli are used instead of solid metal walls, which adequately support the TE_{011} mode but also allow excellent penetration of the modulation field and reduction of eddy currents. Reduction of eddy currents is important for improved sensitivity at low temperatures, especially in metalloprotein applications where signals are weak and improvements in signal-to-noise ratio are essential, by increasing the modulation field at the sample. The performance characteristics of our spectrometer will be discussed and measurements on protein samples will be presented..

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INFLUENCE, OF PROTEIN METAL-SITE OCCUPANCY AND SUBUNIT CONTENT ON THE DYNAMICS OF ELECTRON TRANSFER PROCESS INPHOTOSYNTHETIC BACTERIAL REACTION CENTERS: TRANSIENT Q- AND W-BAND EPR STUDY, Oleia G. Poluektov. Lisa M. Utschig, Jau Tang, Marion C. Thurnauer; Argonne National Laboratory, Chemistry Division, 9700 S.Cass Ave., Argonne, IL 60439-4831 and U. Heinen, Gerd Kothe, Department of Physical Chemistry, University of Freibrug, Albertstr. 21, 79104, Freiburg, Germany

We report on a study of transient spin-polarized EPR spectra from photosynthetic bacterial reaction centers , which were recorded at high magnetic field at 95 GHz and 35 GHz microwave frequencies (W- and Q-band, respectively). The study was performed to investigate the sensitivity of transient spectra to protein metal-site occupancy and subunit content and, as a consequence, to the rate (k_Q) of the electron transfer to the primary quinone acceptor. The W-band spin-polarized spectra were recorded by pulsed Electron Spin Echo technique in which the laser flash was followed by two microwave pulses. Direct time-resolved technique was used for the recording of the Q-band spectra. It was shown that the shape of the W-band spin-polarized spectra of the charge-separated state $P_{865}^{+}Q_{A}$" is sensitive to k_Q. The difference between spin polarized spectra of the reaction centers with different k_Q confirms the predictions of Sequential Electron Transfer Polarization (SETPP) theory. The high spectral resolution of W-band allows for more precise g-tensor and structural determinations. A temperature dependence of the spin polarized spectra of the sample with reduced k_Q was observed. We believe that such observations can provide new information on the activation energy, as well as on the influence of the protein environment on the electron transfer process. The analysis of the temperature dependence of the spin-polarized spectra in the framework of SETP theory is in progress. (Work done at ANL was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-31-109-Eng-38.)

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ELECTRON SPIN ECHO SIGNAL AMPLITUDES: COMPARISON OF MEASURED AND CALCULATED ECHOES. George A. Rinard, Richard W. Quine. Ruiton Song, Sandra S. Eaton, and Gareth R. Eaton. Departments of Engineering and Chemistry and Biochemistry, University of Denver, Denver, CO 80208.

Measured amplitudes of electron spin echoes for the standard irradiated fused quartz sample will be compared with the calculated echo amplitude. Properties of the spin system, the shape of the echo, the width of the spectrum relative to microwave B_1, and the properties of the resonator were considered to estimate the amplitude of the echo at the resonator. The gains and losses of all components or groups of components in the path from the resonator to the echo signal digitizer have been measured to calculate the effective overall gain of the spectrometer system. Agreement of the measured echo amplitude with that calculated is within the uncertainties of the various gain and loss measurements. Similar treatment of noise through the spectrometer system provides basis for focusing efforts to enhance S/N in EPR spectrometers.

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SPIN STATES OF MANGANESE IONS IN MANGANESE-DOPED YTTRIUM ORTHOALUMINATE.

Rakhim R. Rakhimov. Amy L. Wilkerson, Walter Lindsay, Natalia Noginova, George B. Loutts, Mikhail A. Noginov, and Heidi R. Ries; Center for Materials Research, Norfolk State University, Norfolk, VA 23504, USA.

Dynamics of manganese charge states Mn^{2+} and Mn^{4+} in Mn doped yttrium orthoaluminate ($YAI0_3$) have been investigated by electron paramagnetic resonance (EPR) method at 9.5-9.8 and 34 GHz, and optical spectroscopy. Two paramagnetic charge states of manganese with a total electron spin of S = 5/2 (Mn^{2+}) and S = 3/2 (Mn^{4+}) were identified. Parameters of the Spin Hamiltonian were calculated using EPR spectra of polycrystalline samples. In addition to the allowed $AM_s = 1$ transitions, low field forbidden $AM_s = 2$ transitions were observed for both Mn^{4+} and Mn^{2+}, and $AM_s = 3$ transitions for Mn^{2+}. The intensities of forbidden transitions were analyzed and compared to the intensities of allowed transitions. Analytical expressions were derived showing that relative intensities of forbidden transitions increase with the increase of spin relaxation times. Experimental EPR spectra showed that the relative intensity of forbidden transitions increases with a decrease of temperature, and decreases at higher Mn dopant concentration. The effect was explained assuming the increase of spin-lattice relaxation time at low temperature, and the decrease of spin-spin relaxation time at higher dopant concentration. Photo-irradiation of Mn doped $YAIO_3$ single crystals at 488 nm leads to a decrease of Mn^{4+} EPR spectral intensities. This is consistent with the previously suggested optically induced disproportionation reaction ($2Mn^{4+} \longrightarrow Mn^{3+} + Mn^{5+}$) in $YAIO_3$.

This work was supported by the Department of Energy, Grant No. DE-FG01 -94EW11493, and by the National Aeronautics and Space Administration, Grant No. NAG- 1 - 1453.

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STRUCTURAL VARIATION BETWEEN THE LOW AND HIGH pH FORMS OF SULFITE OXIDASE.

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The coordination of a OH group to Mo(V) in the low pH form *(lpH)* of Sulfite Oxidase (SO) has been observed by Bray et al. as a splitting at the g_z and g_x positions of CW EPR spectrum. This splitting is absent in the distinctive high pH form *(hpH)* of the enzyme. Two-pulse, four- pulse and HYSCORE Electron Spin Echo Modulation Spectroscopy (ESEEMS) at two operational frequencies (8.7 and 15.6 GHz) have been utilized to determine whether the difference between these two forms is due to deprotonotation or variation in hyperfine interactions. As a result, we demonstrated that an OH group remains coordinated to Mo(V) in the *hpH* form , although the isotropic constant on the proton is reduced by an order of magnitude in comparison with the l*pH* form. This reduction is explained as a shift of the Mo-H vector to a node of the d_{xy} orbital, where the unpaired electron resides. Additionally, we found that the *hfi* parameters and the orientation of the proton *hfi* tensor in the *hpH* form is not unique. Also, it was shown that the nuclear quadrupole coupling constant of the OD group (in D_2O buffer) is unusually small and equal to 0.09MHz in the *hpH* form, in contrast with a more common value of 0.24 MHz found for the *IpH* form.

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PULSED EPR OF INCLUSION COMPLEXES AND METALS IN ZEOLITES.

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The most active and selective redox catalysts are often found in nature in the form of metallo-enzymes. The active center usually contains a metal ion in unsaturated coordination. It has been demonstrated that in zeolites metal complexes with relatively high catalytical activity can be stabilized [1,2]. In this study we present a 2D-ESEEM study of several Cu complexes in zeolite Y with aminoacids as ligands. In particular the nitrogen ESEEM of a Cu(histidine)$^{2+}$ complex is analyzed in terms of the quadrupole and hyperfine parameters of the remote imidazole nitrogen. The data are compared to Cu(his) interactions reported in inorganic complexes and proteins.
In addition, the structure of several Manganese species stabilized in zeolite A is studied using 1D and 2D ESEEM. The data are interpreted in terms of water coordination and symmetry of the complex. [1] W.J. Mortier, R.A. Schoonheydt, Prog. Solid State Chem. 1985,16,1
[2] D.E. de Vos, P.P. Knops-Gerrits, R.F. Parton, B.M. Weckhuysen, P.A. Jacobs, R.A. Schoonheydt, J. Inclus. Phys. Mol. Recogn. Chem. 1995, 21,185

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NOVEL SMALL-SIZE RESONATORS FOR PULSED EPR, Andrei V. Koptioug[1], Edward J. Reijerse[2]. Paul J. van Kan[2], and Adri A.K. Klaassen[2] (1) Department of Bio-Medical Physics and Bio-Engineering, University of Aberdeen, Foresterhill, Aberdeen AB9 2ZD, United Kingdom, (2)Department of Molecular Spectroscopy, University of Nijmegen Toernooiveld, 6525 ED Nijmegen, The Netherlands

We present a detailed investigation of the microwave Alderman Grant Resonator [1] (AGR) for pulsed EPR applications in the range 2-8 GHz. It is demonstrated that this resonator combines the advantages of two popular resonating structures in EPR, the Bridged Loopgap resonator (BLGR) and the Slotted Tube Resonator (STR). The improved properties include: a high filling factor, a good separation of magnetic and electric field components, and convenient access for light and RF. The manufacturing and tuning of the AGR is described in detail. In addition we show preliminary results obtained on bimodal versions of this resonator as well some new structures based on a crossed loop principle.
[1] D.W. Alderman and D.M. Grant, J. Magn. Reson. 36, 447 (1979).

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EPR SPECTROSCOPY OF BIOLOGICAL IRON-SULFUR CLUSTERS WITH SPIN ADMIXED S=3/2 GROUND STATES, Wilfred R. Hagen[1'2], Willy A.M. van der Berg[1], Walter M.A.M. van Dongen[1], Edward J. Reijerse[2]. and Paul J. van Kan[2]. (1) Department of Biomolecular Sciences, Laboratory of Biochemistry, Agricultural University, Dreijenlaan 3, NL-6703 HA Wageniilgen (2)Department of Molecular Spectroscopy, University of Nijmegen Toernooiveld, 6525 ED Nijmegen, The Netherlands

The ground-state paramagnetism of synthetic cubane clusters, $[Fe_4S_4L_4]^{3}$", can be of three types: pure spin, physical spin mixture, or spin-admixed. The former two types are also abundantly present in biology; a first biological example of the latter has recently been found in the "hybrid-cluster protein" [1]. In this work biological spin-admixed cubanes have been examined in detail regarding EPR and ESEEM parameters, biological significance, and biological distribution.
[1] A.F. Arendsen et al. J. Biol. Inorg. Chem. 1998, 3, 81

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CROSSED-LOOP RESONATOR FOR CRYOGENIC APPLICATIONS. George A. Rinard. Department of Engineering, University of Denver, Denver, CO 802Q8

The design of the crossed-loop resonator previously demonstrated at room temperature (J. Magn. Reson. A 122, 50 and 58 (1996)) has been enhanced to provide remote adjustments so that it can be used in a cryostat for cryogenic EPR applications. An implementation at S-band will be described.

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FREQUENCY DEPENDENCE OF EPR SIGNAL INTENSITY. George A. Rinard. Richard W. Quine, Sandra S. Eaton, and Gareth R. Eaton. Departments of Engineering and Chemistry and Biochemistry, University of Denver, Denver, CO 80208.

To obtain adequate depth penetration into large aqueous samples, including animals, EPR imaging is performed at the lowest feasible frequency - typically between 250 MHz and 2 GHz. The feasibility of imaging physiologically significant signals at these frequencies is dependent upon obtaining adequate signal-to-noise (S/N). A frequently-posed question is "what, in principle, should one expect to be able to achieve with an ideal spectrometer"? Contrary to some prior derivations, it is shown that the sensitivity of EPR measurements is, as expected, the same as for NMR, and that in general comparisons of EPR sensitivity as a function of frequency *w* have been pessimistic by one factor of *w*. The sensitivity of EPR can increase at lower frequency if the sample size is scaled inversely with frequency.

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PREDICTION OF SPIN LABEL ORIENTATION IN THE CRYSTAL STRUCTURE OF PROTEINS, Kenneth L. Sale[1]", Kim A. Sharp* and Piotr G. Fajer[1]*, department of Biological Sciences and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32306, *Department of biochemistry and Biophysics, University of Pennsylvania, Philadelphia, PA 19104

Knowledge of the orientation of a nitroxide spin label within a protein is essential to the interpretation of EPR spectra in terms of the orientation of the labeled protein within a macromolecular complex. Thus, we have developed a strategy for determining, the orientation of the nitroxide probe within a protein via direct modeling of the probe environment. A series of spin labels of varying size and structure were docked to each of several sites within the myosin head crystal structure. The "modified" structure was annealed, and an exhaustive search over conformational space was performed using XPLOR to obtain the most probable orientation of the spin label within the binding, pocket. The predicted conformation was compared to the orientation of the label obtained from the spectra of myosin heads in an ordered system. Good qualitative agreement was obtained for several spin labels with different principal axes geometry.

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COMPACT EPR RESONATOR FOR PERPENDICULAR AND PARALLEL ORIENTATION OF LONGITUDINAL AQUEOUS SAMPLES. Andrzei Sienkiewicz*[&], M. Jaworski[&], Peter G. Fajer°, and Charles P. Scholes[+]; Departments of *Physics and [+]Chemistry , SUNY, 1400 Washington Ave., ALBANY, NY 12222, °NHMFL, 1800 E. Paul Dirac Dr., TALLAHASSEE, FL 32306, institute of Physics, Al. Lotnikow 32, 02-668 WARSAW, POLAND.

Most conventional EPR spectrometers employ rectangular or cylindrical resonators having an intense magnetic component (Bj) oriented perpendicular to the external Zeeman field **(B).** Thus, in order to obtain a high S/N, aqueous longitudinal samples are usually oriented perpendicular to the external magnetic field. In the case of spin-labeled muscle cell protein molecules, the EPR spectra reveal a strong dependence on the orientation of the muscle fiber axis relative to the external magnetic field. We present a novel Dielectric Resonator (DR)-based resonant structure that accommodates longitudinal aqueous samples in both perpendicular and parallel orientations relative to the direction of the external field **B.** The resonant structure consists of two commercially available MuRata-Erie X-band DRs that are separated by a Rexolite spacer. This spacer is used to tune the resonator to the desirable frequency and to provide for the parallel access for longitudinal samples (capillaries). A quartz capillary of 0.6 mm I.D. containing aqueous solution of IASL spin label (6.25 uM) was used for preliminary tests. Depending on the spacing between the DRs, the S/N ratios were ca. 2.1 - 2.6 times smaller for the parallel orientation than for the regular perpendicular sample insertion. These results are in good agreement with the theoretically estimated resonator Q- and filling factors for electric (Ej) and magnetic (B,) components for both sample orientations. In either case, S/N ratios were better for the DR-based structure than for a modified TM_{110} cavity. Preliminary EPR measurements performed on IASL-labeled myosin filaments also revealed better S/N ratios than that obtained with the use of the TE_{102} (perpendicular orientation) and TM_{110} cavities (in either orientation).

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ESEEM STUDIES ON SUBSTRATE-GENERATED TRYPTOPHAN TRYPTOPHYL N-SEMIQUINONE IN METHYL AMINE DEHYDROGENASE. Victor L. Davidson, John L. McCracken and Vinita Singh. Department of Biochemistry, University of Mississippi Medical Center, Jackson, MS 39216, Department of Chemistry, Michigan State University, East Lansing, MI 48824.

MADH is a periplasmic enzyme which catalyzes the oxidative deamination of methylamine to formaldehyde and ammonia. The cofactor (Tryptophan Tryptophyl Quinone, TTQ) is first reduced by methylamine, and then undergoes sequential transfer of two electrons to amicyanin , a blue copper protein, via the formation of aminosemiquinone intermediate. The aim of this project was studying the electronic structure of the semiquinone intermediate and the effect of binding to amicyanin on its electronic structure and spin density distribution. The focus of this study was on the hyperfine couplings arising due to the nitrogens present in the semiquinone. Three-pulse ESEEM spectra of 1=1 ^{14}N-methylaniine-reduced sample show three features at 1.04,1.5 and 4.3 MHz, which are absent in 1= 1/2 ^{15}N-methylamine-reduced sample. This reveals the presence of the substrate nitrogen in the semiquinone and its magnetic interaction with the unpaired electron spin. Multifrequency, three pulse ESEEM studies show distinct contributions from the two indole nitrogens of the TTQ semiquinone. Simulations of the experimental data and a detailed analysis of these data will be presented.

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BINDING OF A LIEPOPHELIC MRI CONTRAST AGENT TO BOVINE SERUM ALBUMIN AS STUDIED BY HF (95 GHz) EPR. Tatyana I. Smirnova. Alex 1. Smirnov, R. L. Belford, and R. B. Clarkson. Illinois EPR Research Center, University of Illinois at Urbana-Champaign.

Rational development of new selective gadolinium paramagnetic contract agents (PCAS) for magnetic resonance imaging (MRI) requires detailed understanding of their interaction with biological macromolecules. Here we demonstrate how high field EPR at 95 GHz can be used to study interaction of a lipophilic PCA, a pentane derivative of Gd-DOTA, with bovine serum albumin (BSA). Typically, at X-band, EPR spectra of Gd(III) chelates in aqueous solution exhibit a single broad resonance line at g =2, difficult to model accurately. Significant narrowing of the Gd(III) signal at 95 GHz allowed us to clearly observe changes in Gd(III) signal upon binding of PCA to BSA. Because of the nature of the ligand, the Gd-DOTAP may bind to BSA in a way similar to fatty acids. To examine this hypothesis, we carried out experiments with binding spin-labeled doxyl stearic acids (DSA) and Gd-DOTAP to BSA. Increase in g-value dispersion at 95 GHz enabled us to observe simultaneously the EPR spectra from Gd-DOTAP and DSA and to study both binding effects and spin-spin interactions. Observed broadening of the signal from 5-DSA located at the entrance of hydrophobic channel is too large to be explained by spin-spin exchange or dipole interactions between free Gd-DOTAP in solution and DSA. We speculate that it is caused by dipole-dipole interaction of DSA with the Gd-complex bound in close proximity to hydrophobic channels. This work used the resources of IERC (NIH P41 -RRO 1811), an NIH-supported Resource Center. T.I.S. acknowledges a postdoctoral NIH fellowship (F32 CA 73156).

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LOW FREQUENCY FOURIER TRANSFORM EPR IMAGING, Antonello Sotgiu. Giuseppe Placidi, John A. Brivati, Mareello Alecci, and Luca Testa, INFM and Dipartimento di Scienze e Tecnologie Biomediche, Universita dell' Aquila, Via Vetoio, 67 100-L'Aquila, Italy

The capability of detecting free radicals in vivo is very important for many biomedical applications. Radio frequency (RF) pulsed Fourier transform (FT) EPR spectroscopy/imaging apparatus at about 300 MHz suitable for very small samples of about 2 ml has been proposed (Bourg et al, JMR 1993). Recently, two-dimensional (2D) in vivo FT-EPR imaging was reported and a RF crossed coil EPR resonator suitable for FT-EPR with large samples (up to 50 ml) was described. We present the performance, in terms of sensitivity and spatial resolution, of a 220 MHz FT-EPR spectrometer suitable for imaging applications. 2D images obtained with a large volume phantom simulating in vivo conditions are presented. The phantom was composed of a small tube (dia 1.5 cm, length 4 cm) filled with de-oxygenate-d lithium phthalocyanine (LiPtc) powder (1.5 g). The tube was inserted at the centre of a cylinder (dia 2.8cm, length 8 cm) containing 47 ml of physiological saline solution. This phantcxn was inserted in the centre of the EPR resonator. Each FID signal was min 5000 points for a total time of 5 u.s and an average of 10000 FIDs was done in 90 s. The SNR of the FIDs measured in absence of the field gradient was estimated in the frequency domain (on the absolute value of the FID FT) and was found to be about 2000.FID signals were acquired in the presence of a variable Gz gradient (from 2 to 10 mT/m) to obtain sensitivity/spatial resolution optimisation. 2D FT-EPR images, in a plane longitudinal to the magnet axis, were obtained by acquiring 16 FIDs in the presence of stationary gradients of 4 mT/m. These FIDs were processed for image reconstruction using a filtered back-projections method. A typical 2D image (62*62 pixels, 32 grey levels, FOV= 1 1 cm) of the LiPtc phantom was obtained. The measured spatial resolution of this image was 2 mm. The use of narrow-line (less dm 50 ***\xT)*** paramagnetic probes and the present FT-EPR apparatus should permit imaging of free radicals in whole rats.

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RESONANT COUPLING OF LOW FREQUENCY EPR RESONATORS, Diodato, Marcello Aleeci, John A. Brivati, and Antonello Sotgiu. INFM and Dipartimento di Scienze e Tecnologie Biomediche, Universita dell' Aquila Via Vetoio 10, 67100-L'Aquila Italy

In CW EPR inductive coupling (IC) with a loop is suitable only with high quality factor (Q) resonators. Wben biological samples are used the Q is greatly reduced and critical coupling is difficult or impossible to achieve. We describe a new resonant inductive coupling (RIC) technique for EPR resonators suitable for samples of high conductivity. A prototype of an RIC has been designed and tested with a 200 MHz loop gap resonator (LGR). The RIC is based on the theory of the resonant coupled circuits (T F E, Radio Engineering, McGraw-HiU, 195 1), where the primary is the resonant loop and the secondary is the LGR. The RIC facilitates optimal coupling because it allows: delivery of the maximum power from the RF source to the load (combined resonant loop and LGR) by capacitive regulation; modification of the power distribution between the resonant loop and the LGR, by adjusting their stand alone frequency difference and the coupling coupling distance. The RIC was tested with a LGR (dia 5 cm, length 7.5 cm) operating at 200 MHz and the results compared to the standard IC method. The RF B, amplitude was measured with the perturbing metal sphere technique. The RF field homogeneity was also measured (LGR length in which the RF intensity has a deviation less than 20 % from its maximum value/total length of the LGR). With the IC, as the loaded Q decreases from 330 to 9, the coupling distance decreases from 15 to 1 mm and the homogeneity decreases from 62 % to 45 %. Using the RIC the loop distance decreases from 25 to 10 mm and the homogeneity remained constant to 52% . These results show that the RIC makes it possible to optimise the coupling coefficient, the RF field amplitude and the homogeneity with very low Q.

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COMPARISON OF EFFECTS OF TRANSMEMBRANE a-HELICAIL PEPTIDES WITH DIFFERENT HYDROPHOBIC SURFACE ROUGHNESS ON MOLECULAR ORGANIZATION AND DYNAMICS OF 1 -PALMITOYL-2-OLEOYLPHOSPHATIDYLCHOLINE BILAYERS. [1,2]Witold K. Subczynski, James S. Hyde, and [3]Akihiro Kusumi. Medical College of Wisconsin, Milwaukee, WI USA; [2]Jagiellonian University, Krakow, Poland; [3]Nagoya University, Nagoya, Japan.

Previously, we investigated how the transmembrane a-helical peptide, Ac-K_2L_2**4K**$_2$-amide (L_{24}) with a smooth hydrophobic surface affects the molecular organization and dynamics of I-palmitoyl-2-oleoylphosphatidylcholine (POPC) membranes (Subczynski et aL, ***Biochemistry*** 37, 3156-64,1998). Presently, we extend our investigations to another transmembrane a-helical peptide, Ac-$K_2(LA)_{12}K_2$-amide ($(LA)_{12}$), which possesses significant roughness of the hydrophobic surface. In both cases, conventional EPR spectra showed that phosphatidylcholine spin labels (n-PCs) detect the existence of a single homogenous environment, indicating that both POPC and $(LA)_{12}$ (POPC and L_{24}) are likely to undergo fast translational diffusion in $(LA)_{12}$-POPC (L_{24}-POPC) membranes of up to 1 0 mol% peptide. Both $(LA)_{12}$ and L_{24} increase the hydrophobicity of the membrane interior, however, the effect of $(LA)_{12}$ is slightly weaker. The effect of 10 mol% (LA) 2 on the order parameter is similar to that of decreasing the temperature by 11 -20°C between 1 0 and 55°C, while the effect of 10 mol% L_{24} is similar to that of decreasing the temperature by ~8°C. L_{24} increases the rotational correlation time and decreases the activation energy for rotational diffusion of 16-PC, while $(LA)_{12}$ increases only the rotational correlation time without affecting the activation energy for rotational diffusion. A possible explanation of these differences is given.

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THE EXTRACELLULAR NON-HAEM PEROXIDASE FROM THERMOMONOSPOR FUSCA BD25: AN EPR CHARACTERISATION. Dimitri A. Svistunenko Abdul Rob, Andrew Ball, Jaume Torres, Chris E. Cooper, Martyn C.R. Symons, Michael T. Wilson. Department of Biological Sciences, Central Campus, University of Essex, Wivenhoe Park, Colchester, Essex C04 3SQ, United Kingdom

The actinomycete Thermomonospora fusca BD25 contains a peroxidase with a high activity over a broad range of temperature and pH and a high stability against denaturing agents. Unusually this peroxidase (PO) is a non-heme enzyme. As prepared PO is characterised by two weak EPR signals, detected at helium temperature, a free radical signal (g = 2.0045) and a broad signal at g=2.056. The peroxidase activity of the purified enzyme was assayed using H_20_2 and 2-4-dichlorophenol (DCP). The intensity of the free radical EPR signal correlated with the peroxidase activity in a variety of enzyme preparations. Furthermore when DCP and H_20_2 were added to PO a significant increase of both the free radical signal and the broad signal at g = 2.05 6 was observed. We associate the increase of the broad signal with the oxidation of the preparation since a similar increase can be achieved by the addition of ferricyanide. The high intensity of the broad signal in the ferricyanide treated PO allowed us to deconvolute the signal into two components using the difference in their relaxation characteristics: one was an EPR signal indicative of a type 2 copper protein and the other an almost symmetrical singlet at g = 2.059. The singlet was assigned to an iron complex with a high degree of symmetry and weakly coordinated ligands. The reasons for this interpretation will be discussed.

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SYNTHESIS AND APPLICATION OF NOVEL BIFUNCTIONAL SPIN LABELS, Ralf M. Losel[a)], Reinhard Philipp[a)], Tamas Kalai[b)], Kalmin Hideg[b)] and Wolfgang E. Trommer[a)] [a)]Department of Chemistry, University of Kaiserslautem, D-67653 Kaiserslautern, Germany [b)]lnstitute of Organic and Medicinal Chemistry, University of Pecs, H-7643 Pecs, P.O. Box 99, Hungary

The synthesis of new bifunctional spin-labeled cross-linking reagents is described. Covalent attachment to papain was achieved via a thiol-specific thiosulfonate residue and, for the second anchor point, via a non-specific photoreactive azido function. The thiosulfonate formed a reversible disulfide linkage, which could be cleaved again reductively by dithiothreitol. The spin label, a pyrroline-l-oxyl radical, was highly immobilized after attachment to papain by both functional groups and showed little if any relative motion with respect to the protein.

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PHOTOSYSTEM II MEMBRANES AND REACTION CENTER INTERACTION OF YZ' WITH ITS ENVIRONMENT IN ACETATE TREATED CORES. Marilena Di Valentin', Pierre Doriet[§], Gerald T. Babcock* and John L. McCracken*, ^Department of Chemistry, Michigan State University, East Lansing, MI 48824 [§]DBCMYSBE Bat 532, CEN Saclay, 91191 Gif-sur-Yvette cedex, France

The photosynthetic oxidation of water to oxygen occurs in photosystem 11 (PSII) at an active site composed of a tetranuclear cluster of manganese ions, a redox active tyrosine, Y_z, and two essential cofactors, calcium and chloride. Recently, several experimental observations have led to the proposal of a metalloradical catalytic cycle in which water oxidation occurs via hydrogen atom abstraction by the tyrosyl radical from water bound to the manganese cluster. This model predicts a close proximity between the radical tyrosine, Y_z\ and the Mn-cluster, and the involvement of the radical in a bifurcated hydrogen bond. Magnetic resonance techniques have been used in this work to probe the interaction of the tyrosyl radical with its environment in PSII samples in which the catalytic cycle is blocked by acetate treatment and the enzyme is trapped in a paramagnetic S_2 Y_z* State. Radical interaction with the metal cluster has been studied via simulations of the EPR spectra obtained for this state. The simulations were based on a radical pair model and included terms for both electron-electron dipolar and exchange interactions. The results show a dominant exchange interaction between the radical and the manganese cluster in these preparations and led to an estimate of 8-9 A for the spin-spin distance. ESEEM spectroscopy and 'H2 0/2H20 exchange were used to study interactions of the S_2 Y_2" state with exchangeable hydrogen nuclei in the site. Two-pulse ESEEM data show features expected for a spin-coupled species in support of our analysis of the continuous wave EPR spectrum. A theoretical treatment of ESEEM for the spin-coupled system using the density matrix formalism has been developed.

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HIGH-FREQUENCY ENDOR IN NON-ORIENTED NITROXIDES, J VAN TOL*. P. WYDER
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One of the most important objectives of ENDOR at high frequencies and high frequencies is the increased orientational selection that one can obtain in powder samples of systems with a small g-anisotropy. Here this is illustrated with cw-^{1}H-ENDOR measurements at 245 and 285 GHz of nitroxides in polystyrene and toluene glasses. The experiments were performed without a cavity and with a limited amount of microwave power (< I mW). For that reason ENDOR signals could only be obtained at relatively low temperatures (< 20K). However this proved to be an advantage as well, because at temperatures small compared to the EPR frequency, only ENDOR signals from the lower electron spin state are obtained. This simplifies the spectra and allows for a direct determination of the sign of the hyperfine splitting. The different nitroxides give distinctly different powder-ENDOR spectra and most of the ^{1}H hyperfine tensors can be deduced from them.

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A NEW HIGH-FREQUENCY TRANSIENT EPR SPECTROMETER, J VAN TOL. L.-C. BRUNEL,
Center for Interdisciplinary Magnetic Resonance, NHMFL, FSU, Tallahassee.

At present we are constructing a new high-field transient EPR spectrometer, with the aim of increasing both the field-resolution as well as the time-resolution in transient EPR experiments. This in order to address open questions in the research fields of photosynthesis, photo-chemistry, and other kinetics processes. The spectrometer will be a multifrequency setup (95-380 GHz) with optimal performance around 360 GHz. A (multiplied) Gunn-diode serves as the millimeter-wave source and an optional Fabry-Perot resonator can be used as cavity.
Optical excitation will be provided in the 1st, 2nd, 3rd, and 4th harmonics of the ND:YAG, as well as in the 420-2000 nm range with a 100 ps ND-YAG pumped OPG.

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CHARACTERIZATION OF Fe (III)-TETRAPHENYLPORPHYRIN WITH FLUOROPHENYL SUBSTITUENTS BY EPR AND UV-Vis SPECTROSCOPIES. Ednalva Aparecida Vidoto. Otaciro Rangel Nascimento, Yassuko lamamoto, Kitia Jorge Ciuffi, Daniela GonValvez de Abreu. Grupo de Biofisica, Instituto de Fisica de Siio Carlos,USP, CP 369,13560-970, Siio Carlos, SP, Brazil. E-mail: nalva@ultra3000.ifsc.sc.usp.br.

There are recently been considerable efforts to isolate and characterize the high valence iron porphyrin complex as an intermediate in synthetic catalytic processes of oxygenation such as hydrocarbon hydroxylation. The interest in these systems is due their capacity to mimetize enzymes such as cytochome P-450, responsible for important reactions, such as the activation of the alkane C-H bond in living organisms. Some iron porphyrins was synthesized with differents axial ligands and differents modifications in the phenyl groups. We have been studied some of these iron porphyrins such as Fe(III) tetraphenylporphyrin (FeTPP), with 5,10,15 and 20 fluoro substitution in phenyl groups. We observed the structural modifications of these porphyrins as a function of the solvents such as dichoromethane (DCM), methanol (MEOH) and the mixture in 1:1 at volume ratio of these solvents. These studies had been made by EPR spectroscopy at low temperature (4K) and UV-Vis spectroscopy at room temperature. These spectroscopic data has been analysed by simulation programs to characterize the structural differences between those porphyrins and to understand the role of the solvents. (Financial Support: FAPESP,CNPQ,CAPES and FINEP)

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ARE CYANIDES BENT IN TRANSITION METAL CYANIDES ? Ney V. Vugman, Jose' A. Coelho Neto and Nelson M. Pinhal, Instituto de Fisica - Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brazil, 21910-240.

Ionizing irradiation on diamagnetic transition metal cyanide complexes leads to interesting non- usual oxidation states and to the opportunity of studying these new complexes via ESR spectroscopy. Questions have been raised concerning the linearity of the metal-cyanide bonds. Symons and co-workers postulated a cyanide bending in divalent cobalt complexes in order to interpret spin densities calculated from the measured nitrogen super-hyperfine interactions. We also found necessary to invoke a cyanide bending in divalent rhodium complexes to understand the measured (CW ESR) super-hyperfine parameters. In this work Electron Spin Echo Envelope Modulation spectroscopy is employed to study the finer details of the nitrogen super-hyperfine interaction in $[Rh(CN)_6]^{4'}$" in KCI host lattice. It is found that equatorial cyanides may occupy several non-equivalent configurations that may be attributed to distinct bending degrees. This bending is temperature dependent and plays a role on the magnetic and quadrupolar aspects of the super-hyperfine interaction.

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REDOX STATE-INDUCED ROTAMER REDISTRIBUTION IN THE AMINO ACID TYROSINE. M. Scott Perry and Kurt Warncke. Department of Physics, Emory University, Atlanta, GA 30322

Redox state-dependent changes in the relative orientation of the phenol side chain and the peptide group in the amino acid tyrosine have been characterized by using X-band electron paramagnetic resonance (EPR) and electron spin echo envelope modulation (ESEEM) spectroscopies. The isotropic hyperfine interaction between the two (3-methylene-H nuclei bonded to C_p and unpaired ~-electron spin density at the ring carbon atom C_1 depends on the dihedral angle, 0, between the phenol ring normal and the Cp-H^ bonds. Thus, EPR and ESEEM lineshapes depend sensitively on 9. EPR spectra from the radical generated by UV photolysis of tyrosine ring-d_4 in rigid polycrystalline basic aqueous media at T<170 K are comparable with those reported previously. These spectra represent equilibrium 0 values that correspond to the diamagnetic state of the phenol ring. After the temperature of the medium is raised to the glass transition region (T_g), and then returned to 170 K, the EPR spectrum maintains the same peak-to-trough width of 18 G, but the central peak feature at g=2.002 is eliminated. Further, in 3-pulse ESEEM,T-summation spectra (,t=450-1352 ns; 8.819 GHz, 3138 G) of the tyrosyl (3-d_2 radical, an intensity shift toward lower frequency is observed within the strongly-coupled (3-^{2}H rn_s=+l/2 feature. The results evince a redox state-induced change in the $C_r C_p$ rotamer distribution, which is revealed by a relaxation of the tyrosyl radical to its true equilibrium 6 values at T_g. EPR and ESEEM simulations indicate an angular shift of A9=10°-20° between the rigid and relaxed radicals. The results suggest that redox-linked rotamer changes are associated with electron/proton and hydrogen transfer reactions mediated by catalytic tyrosine/tyrosyl radical couples in enzymes.

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EFFECTS OF FUMONISIN B_1 ON LIPID PEROXIDATION IN MEMBRANES. Jun-Jie Yin. Mitchell J. Smith, Robert M. Eppley, Samuel W. Page and James A. Sphon. CFSAN, FDA, Washington, DC 20204.

ESR spin-label oximetry has been used to study the effects of fumonisin B_1 (FBj), on O_2, transport in phosphatidylcholine (PC) bilayers. The incorporation of $FB_{(}$ increased the membrane fluidity and permeability; enhanced O_2 transport properties near the surfaces of both saturated and unsaturated lipid bilayers. We also used ESR oximetry and spin trapping techniques to study the effects of FB! on lipid peroxidation in egg yolk phosphatidylcholine bilayers. In addition to conventional incubations, lipid peroxidations were also initiated by Fe'-ions, UV illumination of H_2O_2 or ultrasound irradiation. The rates of lipid peroxidation were estimated by monitoring $[O_2]$ in the aqueous phases of liposomes. Lipid-derived free radicals — generated during the oxidation process — were measured by a spin trapping method. The incorporation FBj made the membranes highly susceptible to oxidation. Our results provide the first evidence that the fumonisins apparently increase the rate of oxidation, promote the production of free radical intermediates and accelerate the chain reaction associated with lipid peroxidation. The disruption of membrane structure, the enlargement of the oxygen diffusion-concentration products, as well as the enhancement effects on membrane permeability, thus provide additional insights into potential mechanisms by which the fumonisins could enhance oxidative stress and cell damage.

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NMR AND EPR STUDIES ON THE REACTIONS OF VANADATE AND THIOL COMPOUNDS,

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The reaction of vanadate with thiol compounds is particularly poorly understood and relevant to interpretations of results probing the insulin-mimetic properties of vanadim compounds. This system is particularly complex because vanadate undergoes hydrolytic, protonation and redox chemistry in the presence of thiols. In the following study the reaction of vanadate with 2-mercaptoethanol has beeb studied as a model reaction for the vanadate-thiol reaction. ^{51}V NMR spectroscopy has been used to characterize the vanadium(V) complex that forms in the solutions; *H NMR and EPR spectroscopy has been used to examine the redox chemistry that takes place under the mild physiological conditions. The reaction is found to be sensitive to substrate, vanadium concentration and pH. The rate law of the mercaptoethanol reaction has been determined at alkaline pH. How the characterization of the model reaction of vanadium(V) with mercaptoethanol can be used to obtain information specific for other biological relevant thiols (cysteine, glutathione and dithiothreitol) will be presented and the results discussed.

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EVALUATION OF INTERSPIN DISTANCES DETERMINED BY TIME-DOMAIN EPR OF SPIN-LABELED METMYOGLOBIN MUTANTS.

Yi Zhou. Bruce Bowler, Sandra S. Eaton, and Gareth R. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado 80208, USA

Site-directed mutagenesis was used to introduce cysteines at selected surface sites on sperin whale myoglobin (val66cys, lys98cys, hisl2cys, and ala53cys). Nitroxyl spin labels were attached to the cysteines. Both high spin and low spin samples of each mutant were prepared and examined. Relaxation times for nitroxyl and heme FE(IH) were measured between 4 and 150 K by a combination of saturation recovery (SR), electron spin echo (ESE) and CW spectroscopy. The iron-nitroxyl interspin distances were experimentally determined by analysis of the SR and ESE data. The interspin distances were calculated using the computer program, Insight, starting from X-ray crystallographic structures, and compared to the EPR experimental results. Results from the high spin vs low spin samples, as well as long distance vs short distance samples will be discussed.

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EVALUATION OF DEPMPO AS AN IN VIVO SPIN TRAPPING AGENT: A COMPARISON WITH DMPO.

Ke Jian Liu. Minoru Miyake, Harold M. Swartz, Department of Radiology, Dartmouth Medical School, Hanover, NH 03755;

Application of the spin trapping technique in intact animals requires an understanding of the stability of the spin traps and their spin adducts in vivo. We have studied the stability and distribution of the spin trap, 5-diethoxyphosphoryl-5-methyl-l-pyrroline-n-oxide (DEPMPO), in vivo in mice using HPLC, and the stability of the spin adduct, $DEPMPO/S0_3$ in vitro and in vivo, and compared the results with those of DMPO. Similar to DMPO, DEPMPO was quickly taken up (< 15 min) after intraperitoneal injection, and distributed evenly in the liver, heart, and blood of the mice. Using a low frequency EPR spectrometer, we were able to observe a spin trapped $SO_3^{\#}$" radical both with DMPO and DEPMPO directly in the intact mouse. DEPMPO had a detectable spin adduct signal at a concentration as low as 2 mM, as compared to 6 mM for DMPO. In vivo the spin adduct $DEPMPO/S0_3$ - was several times more stable than $DMPO/S0_3$ We conclude that DEPMPO is potentially a good candidate for trapping radicals in functioning biological systems, and represents an improvement over the commonly used trap DMPO.

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DIRECT ESR AND SPIN-TRAPPING STUDY OF THE ONE ELCTRON REDUCTION OF THE CARCINOGEN 4-NITROQUINOLINE N-OXIDE. Yang C. Fann§. Caroline A. Metosh-Disckey[$], Maria B. Kadiiskat*, Andrzej Sygule[#], Gary W. Winston* and Ronald P. Masont[1]*, §ITSS, *Free Radical Metabolite Section, Laboratory of Pharmacology and Chemistry, National Institute of Environmental Health Sciences, National Institute of Health, P.O. Box 12233, Research Triangle Park, NC 27709. department of Chemistry and department of Biochemistry, Louisiana State University, Baton Rouge, LA 70803. •Department of Toxicology, North Carolina State University, Box 7633, Raleigh, NC 27695

Many nitroaromatic compounds are known for their potent mutagenicity and carcinogenicity, It has been reported that nitroarenes such as 4-nitroquinoline N-oxide (4-NQO) can undergo univalent reaction to form highly reactive free radical intermediates which may contribute significantly to their ability to attack cellular components such as proteins or DNA. In this study, the anion radical of 4-nitroquinoline N-oxide and its nitroso intermediate were examined by direct ESR. Due to the complicity of these ESR spectra, computer algorithms developed in our laboratory including auto-correlation and auto-simulation were used to analyze hyperfine parameters. In addition, the ESR spin trap technique was used to ascertain the superoxide anion radical catalyzed by 4-NQO or 4-nitropyridine N-oxide and a one-electron transfer enzyme such as cytochrome P450 reductase or xanthine oxidase. No ESR signal was detected when the two-electron transferring enzyme, DT diaphorase, was used, which provided indirect evidence for the oneelectron reduction mechanism in the metabolism of these nitro compounds to free radicals.

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RADICAL PAIR SEPARATION AND REACTIVITY IN BIRADICAL-CONDUCTED ENZYME CATALYSIS Shyue-Chu Ke, G. Reid Bishop, Jennifer C. Schmitt and Kurt Wamcke. Dept. of Physics, Emory University, Atlanta, GA 30322

Ethanolamine deaminase is a vitamin B_{12} coenzyme-dependent enzyme that catalyzes radical-mediated oxidative deamination of ethanolamine. Thetmohomolysis of the B_{12} cobalt-carbon bond creates a low spin Co", 5'-adenosyl radical pair. The 5'-adenosyl radical subsequently abstracts an H-atom from substrate, and substrate radical rearranges to product radical. The molecular mechanisms of radical pair separation and substrate rearrangement steps in the ***Salmonella typhimurium*** enzyme are being addressed by using techniques of pulsed EPR spectroscopy. Enzyme-bound g=2 radical intermediates are formed from substrate 2-aminoethanol and the substrate analogs, L-2-aminopropanol, ethylene glycol and glycerol. X- and Ku-band electron spin echo envelope modulation (ESEEM) studies of the radicals cryo-trapped during steady-state turnover reveal weak coupling to a single conu-non "N nucleus of peptide bond or cofactor adenosine origin. Hyperfine and nuclear quadrupole coupling parameters from ESEEM simulations are being used to correlate spectral differences among substrates with different radical orientations ***in situ*** and with the extent of radical rearrangement. The 2-aminopropanolyl radical is distinguished from the other radicals by a stronger spin-spin coupling with Co^{11} (J=200 MHz ***vs.*** <40 MHz; $P_{satj0\cdot5}$ ratios of >5 at 130 K). The 2-aminopropanolyl and an-tinoethanolyl radicals are known to accumulate in pre- and post-rearranged states, respectively. Therefore, the decoupling is proposed to stabilize against recombination during slow rearrangement steps. Time-resolved pulsed-laser photohomolysis FT-EPR and ESE studies are being used to address this model, and to identify intermediate states in radical pair separation. Supported by NIH DK-52183.

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THE FATE OF THE OXIDIZING TYROSYL RADICAL IN THE PRESENCE OF GLUTATHIONE AND ASCORBATE: IMPLICATIONS FOR THE RADICAL SINK HYPOTHESIS. Bradley E. Sturgeon. Herbert **J.** Sipe, Jr., David P. Barr, Jean T. Corbett, Josd G. Martifiez, and Ronald P. Mason. ***Laboratory ofpharniacology and Chemistry, National Institute ofenvironmental Sciences, National Institutes ofhealth, Research Triangle Park, NC 27709.***

The antioxidant properties of ascorbate have been known for quite some time. Cellular systems contain as much as a millimolar concentration of both ascorbate and glutathione (GSH) with the concentration of GSH oftentimes significantly higher than ascorbate. It has been proposed that GSH and superoxide dismutase (SOD) act in a concerted effort to eliminate biologically generated radicals. The tyrosyl radical (tyr*) generated by horseradish peroxidase in the presence of hydrogen peroxide and tyrosine will react with GSH to form the glutathione thiyl radical (GS*), which can be detected by spin trapping with 5,5-dimethyl-lpyffoline N-oxide (DMPO) to form the DMPO/*SG radical adduct. Under physiological conditions, the GS* can react with the glutathione anion (GS~) to form the disulfide radical anion (GSSG*~). This highly reactive disulfide radical anion will reduce molecular oxygen, forming superoxide. In a concerted effort, SOD will dismutate superoxide, resulting in the elimination of the radical. The GSH chemistry involved is well documented and accounts for the consumption of oxygen by thiol radicals. Nevertheless, the physiological relevance of this GSHISOD concerted effort is questionable. In a tyrosyl radical-generating system containing ascorbate (100 uM) and GSH (8 mM), the ascorbate completely eliminates oxygen consumption and diminishes GS* formation. In the presence of ascorbate, the tyrosyl radical will oxidize ascorbate forming the ascorbate radical. When measuring the ascorbate radical directly using fast-flow ESR, only minor changes in the ascorbate radical ESR signal intensity occur in the presence of GSH. These results indicate that in the presence of physiologic concentrations of ascorbate, GSH is not involved in the detoxification pathway of oxidizing free radicals.

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NITRIC OXIDE TRAPPING OF THE TYROSYL RADICAL FORMED BY THE ACTION OF PERACETIC ACID ON CATALASE LEADS TO NITROTYROSINE FORMATION

Ronald P. Mason. Susan W. Heinzerling, Richard Glover, and Michael R. Gunther, Free Radical Metabolite Section, Laboratory of Pharmacology and Chemistry, National Institute of Environmental Health Sciences, National Institutes of Health, Research Triangle Park, NC, 27709 USA.

The determination of protein nitrotyrosine content has become a frequently used technique for the detection of oxidative tissue damage. Protein nitration has been suggested to be a final product of the production of highly reactive nitrogen oxide intermediates (e.g., peroxynitrite). Catalase forms a tyrosyl radical in its reaction with peracetic acid.[1] In the presence of nitric oxide, the electron spin resonance spectrum of the tyrosyl radical disappears. Western blot analysis of bovine liver catalase (10 uM) after treatment with equimolar nitric oxide and peracetic acid (10-50 uM) revealed nitrotyrosine formation. Nitrotyrosine was formed less effectively when nitrite was substituted for nitric oxide in the reaction, consistent with nitrotyrosine formation through nitrogen dioxide reacting with tyrosyl radical, as proposed by van der Vliet *et al.*[2] Nitrotyrosine formation from tyrosyl radical and nitric oxide was oxygen-independent, and the intensity of the nitrotyrosine bands in the Western blots was clearly greater with nitric oxide than with nitrite, indicating that the reaction of the tyrosyl radical with nitric oxide was a more important source of nitrotyrosine than the reaction with nitrogen dioxide under these conditions. The results provide evidence for tyrosine nitration by the reaction of tyrosyl radical with nitric oxide and/or nitrogen dioxide radicals without involving peroxynitrite.

Ivanchich, A., Jouve, H.M., and Gaillard, J. (1996) J. Am. Chem. Soc. 118,12852-12853
[2]van der Vliet, A., Eiserich, J.P., Halliwell, B., and Cross, C.E. (1 997) J. B iol. Chem. 272, 7617-7625

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EPR INVESTIGATION OF THE INTRACELLULAR DRUG DYNAMICS AND DISTRIBUTION IN THE PROCESS OF A PROGRAMMED CELL DEATH.

Natalya Y. Rapoport and Alex I. Smirnov. Department of Bioengineering, 108 BPR Bldg, University of Utah, Salt Lake City, Utah 84112 and Illinois EPR Research Center, University of Illinois, Urbana EL 61801

A paramagnetic analog of the anti-cancer anthracyclin drug, doxorubicin, named Ruboxyl (Rb) was used to investigate the intracellular dynamics and distribution of the drug in cancerous cells in the process of apoptosis (programmed cell death). The EPR spectra of HL-60 cells incubated with Rb showed the superposition of EPR signals arising from drug molecules differing in mobility and local environment, indicating drug localization in various cell compartments. After one hour of cell incubation with the drug, a broad signal characteristic of highly immobilized, partially ordered drug molecules appeared to dominate the spectrum. However, after five hours of the subsequent cell incubation in a drug-free medium, the EPR spectrum changed, suggesting that some population of highly mobile drug molecules was now present in a hydrophilic environment. This population grew significantly with increasing incubation time on the expense of ordered population, which suggests dramatic changes either in drug localization or in the properties of drug-containing cell compartments. The results of model X-band and W-band EPR experiments on drug-DNA and drug-phospholipid interactions will be presented. Possible mechanisms responsible for the spectral changes we observed will be discussed.

For model experiments, the resourses of IERC (NIH P41 -RRO 1 81 1) were used.

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CHALLENGES OF 3-AND 4-DIMENSIONAL IN VIVO SPECTRAL SPATIAL EPR IMAGING AT RADIOFREQUENCY WITH NARROW LINE SPIN PROBES. H.J. Halpern. G.V.R. Chandramouli, B, B. Williams, E.D. Barth, V. Galtsev, U. Chicago, Chicago, IL 60637

Narrow line trityl spin probes from Nycomed Innovations make possible an order of magnitude improvement in signal to noise, spatial resolution and physiologic sensitivity of ***in vivo*** spectral-spatial EPR imaging (EPRI). The narrow line challenges the stability and homogeneity of conventional systems. These problems are reduced operating at 250 MHZ but are still significant. The minimum linewidth of the symmetric trityl is approximately 25 mG (2.5 uT), 3 parts in 10^4 of the 90 G (9 mT) main magnetic field. The size of the spectral spatial data set in a 3-spatial dimension, 4-dimension spectral spatial image is unweildly: a 256 point by 64 projection by 64 x 64 plane acquisition involves nearly 10^8data points. Full 3-spatial dimensional system challenges acquisition strategy and storage and analytic speeds of computers. We show spectral resolution enhancement by decreasing creasing the main field inhomogeneity to less than 2 mG/cm. We will present spectral spatial images with submillimeter spatial resolution and fraction of a milligauss spectral resolution obtained using a 250 MHZ imaging spectrometer imaging phantoms consisting of few microliter phantoms. Strategies to reduce the number of necessary projections will be discussed. 2-spatial dimension oxygen tension images of a mouse tumor will be presented.

Supported by NIH grant CA69538 and the Nycomed Corporation, Oslo, Norway.

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PULSED IN VIVO RF EPR IMAGING: WHOLE BODY 3D IMAGES OF MURINE MODELS, M. Afeworki, N. Devasahayam, D. Coffin, J. Cook, R. Tschudin, S. Subramanian, J. B. Mitchell, and M.C. Krishna, Radiation Biology Branch, National Cancer Institute, NIH, Bethesda, MD 20892 and J.H. A. Larsen and K. Golman, Nycomed Innovations, Malmo, Sweden.

A time domain pulsed EPR spectrometer operating at 300 MHz was used to detect and image paramagnetic spin probes ***in vivo.*** The animals were housed in volume resonators having loaded Q in the range of 20-30. The dead times were between 300 - 500 ns following pulses of 50-80 ns duration. FIDs of 4 K points were acquired and summed by an averager with a retrigger rate of 4.3 us at 1 GS/s. Two- and three-dimensional images of phantoms with spin probes that have narrow, single EPR linewidths were used to optimize spectrometer conditions. Images were reconstructed by filtered back-projection techniques with static gradients. ***In vivo*** studies were performed on murine objects by both tail vein cannulation and ip injection, of non-toxic, water soluble spin probes (that have single, narrow EPR lines with long T_p T_2) with adequate pharinacologic half-fife. Distinct volumes of spin probe accumulation ***in vivo*** was noted. In addition, timedependent changes in the spin probe content was also observed. Efforts are being made to correlate spin density with the anatomy.

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PULSED IN VIVO RF EPR IMAGING: WHOLE BODY 3D IMAGES OF MURINE MODEL Mobae Afeworki,* Nallathamby Devasahayam,* Debbie Coffin,* John Cook,* Rolf Tschudin,* Sankaran Subramanian,* Jan Henrik.A.-Larsen,' Klaus Golman,' James B. Mitchell,* and Murali C. Krishna,* Radiation Biology Branch, National Cancer Institute, NIH, Bethesda, MD 20892 and 'Nycomed Innovations, Malmo, Sweden.

A time domain pulsed EPR spectrometer operating at 300 MHz was used to detect and image paramagnetic spin probes in vivo. The animals were housed in volume resonators having loaded Q in the range of 20-30. The dead times were between 30Q - 500 ns following pulses of 50-80 ns duration. FIDs of 4 K points were acquired and summed by an averager with a retrigger rate of 4.3 its at I GS/s. Two- and three-dimensional images of phantoms with spin probes that have narrow, single EPR linewidths were used to optimize spectrometer conditions. Images were reconstructed by filtered back-projection techniques with static gradients. ***In vivo*** studies were performed on murine objects by both tail vein cannulation and ip injection, of non-toxic, water soluble spin probes (that have single, narrow EPR lines with long T_2) with adequate pharmacologic half-life. Distinct volumes of spin probe accumulation ***in vivo*** was noted. In addition, time-dependent changes in the spin probe content was also observed. Efforts are being made to correlate spin density with the anatomy.

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AN EPR STUDY OF SOLUBLE POLYPYRROLE. Myong K. Ahn, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809; Charles M. Brodbeck, Department of Physics, Loyola University, Chicago, Illinois 60626; Lennox E. Iton, Materials Sciences Division, Argonne National Laboratory, Argonne, Illinois 60439; and J. Y. Lee and C. Y. Kim, Polymer Materials Laboratory, Korea Institute of Science and Technology, Seoul 130-650, Korea

Doped polypyrroles (ppy) are organic conductors with conductivities up to 100 S/cm, approaching that of metal conductors. Recently C. Y. Kim, et al. (Synthetic Metals 1995, V74, p. 103) synthesized dodecylbenzene sulfonic acid (DBSA) doped ppy that dissolves in chroloform and other organic solvents and can be cast into thin films. We examined the epr activities of such soluble ppy samples. The temperature dependence of the epr intensity, when line width variations were taken into consideration, was inversely proportional to absolute temperature (Curie's Law) in the range of 3.7 - 296 K. At room temperature soluble ppy, both solid and in solution, shows a large epr absorption peak with a symmetric line shape. The fact that the epr absorption intensity varies from sample to sample and seems uncorrelated to conductivity confirms the concept that diamagnetic bipolarons are the dominant charge carriers.

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CW EPR STUDIES OF TRICHOGIN PEPTIDE CONFORMATIONS. D. Joe Anderson, Paul Hanson, Joseph C. McNulty, Vania Monacot, Glenn L. Millhauser, and Claudio Toniolot. Department of Chemistry and Biochemistry, University of California, Santa Cruz CA 95064 and tbiopolymer Research Center, CNR, Department of Organic Chemistry, University of Padova, Italy.

The nitroxide-containing amino acid TOAC is an ideal spectroscopically-active replacement for the C-alpha disubstituted amino acid aminoisobutyric acid (AIB). AIB occurs naturally in many peptides of fungal origin whose structure and dynamics are of interest because of their membrane modifying properties. For this study, several models of one such class of peptides first isolated from Trichoderma longibrachiatum have been synthesized. These trichogin analogues include TOACs in place of any of the three AlBs in the parent sequence. Conventional and half-field CW EPR measurements of the biradicals from this series of peptides provide not only distance information for comparison with structural models, but also a qualitative measure of conformational heterogeneity.

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FORMATION OF A CUPRIC FERROCYANI]DE-LIKE COMPLEX UPON ADDMON OF FERRICYANIDE TO MEMBRANE FRAC'NONS LOADED WITH pMMO FROM M. album BG8. Hua Yuan,[1] Mary Lynne Perille Collins,[2] and William E. Antholine,[1] biophysics Research Institute, Medical College of Wisconsin, 8701 Watertown Plank Rd., Milwaukee, WI 53226, and [2]Dept. of Biological Sciences and Center for Great Lakes Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53201.

Particulate methane monooxygenase, pMMO, catalyzes the oxidation ofmethane to methanol using dioxygen. Recently we showed that one of the EPR-detectable sites is a type 2 site ***(J. Am. Chem. Soc.*** 1 19, 5073-4,1997). The unusual signal observed by us (g» = 2.28, no hyperfine structure) and others ***(J. Am. Chem. Soc.*** 1 1-8 12766-76, 1996) following addition of ferricyanide to membrane fractions has also been observed from type 3 copper of ascorbate oxidase or laccase reacted with ferrocyanide (Sakurai, Inorg. Chim. Acta 195, 255-8,1992; ***Biochem. J*** 284, 681-5,1992). Most likely, upon addition of ferricyanide to samples with high pMMO concentrations, Cu(l+) is oxidized to Cu(2+) and ferrocyanide is formed. Excess ferrocyanide may also be formed from other reducing equivalents in the membrane fraction or cells. Then the isotropic EPR signal, which is similar to the -signal from Cu(2+)Fe(CN)," appears, followed by the unusual EPR signal with g» = 2.28 upon incubation of the sample at -20 °C. One interpretation of the unusual EPR signal is that interstitial sites are filled by low molecular weight molecules like water to give axial metry. The formation of this unusual signal is consistent with, but not proof of, a type 3 or even trinuclear copper However, this signal is, most likely, not from an intrinsic trinuclear site as proposed.

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MATRIX LINE IN PULSED ELECTRON-NUCLEAR DOUBLE RESONANCE SPECTRA. Andrei V. Astashkin[1]* and Asako Kawamori[2]. ^University of Arizona, Department of Chemistry, Tucson, Arizona 85721, USA. [2]Kwansei Gakuin University, Faculty of Science, Uegahara I-I -1 55, Nishinomiya 662, Japan.

There are two basic techniques of pulsed electron-nuclear double resonance (ENDOR) spectroscopy, one due to Mims and the other due to Davies, that are used most often in practical applications. According to the available theory, the ENDOR effect in these techniques becomes smaller for smaller hyperfine interaction (hfi) constants. Nevertheless, in the ENDOR spectra obtained by both methods, quite frequently, the most intense line is that due to the distant matrix protons, that is, nuclei with extremely small hfi. To our knowledge, so far no satisfactory explanation of this fact has been given in the literature. An analysis performed in this work shows that the finite intensity of the matrix line in the Mims and Davies ENDOR spectra is obtained due to the action of the radiofrequency pulse on a large number of the nuclear spins being in resonance simultaneously. The fundamental reason for the matrix line effect is shown to be same as that for the multiplet structure in the EPR spectra of the unpaired electrons interacting with many nuclei simultaneously, i.e., the additivity of the local magnetic fields produced by different nuclei at the position of the unpaired electron. Theoretical expressions describing the matrix ENDOR effect are derived and verified experimentally.

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ESEEM STUDIES ON MULTICOPPER PROTEIN FET3, Constantino P. Aznar, John L. McCracken, Daniel J. Kosman, Richard Hassett and Daniel Yuan, Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, Department of Biochemistry, SUNY, Buffalo, New York 14214 and Department of Biophysics and Biophysical Chemistry, The John Hopkins University, Baltimore, Maryland 21205

FET3, an extracellular membrane-bound protein from yeast Saccharomyces has been suggested as a homologue of ceruloplasn-iin, a multicopper oxidase which plays a role in iron metabolism in mammals. The copper-dependent FET3 catalyses the oxidation of ferrous to ferric ion and reduction of dioxygen to water. Evidence of the existence of type I, II and II copper sites has been provided by absorption and CW-EPR spectroscopy. To gain insight to its ferroxidase activity further characterization of the protein's ligands, particularly at the type I and II copper sites has been undertaken using the technique of Electron Spin Echo Envelope Modulation (ESEEM). Initial results suggest histidyl imidazole and water as metal ligands.

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DYNAMICS OF REGULATORY LIGHT CHAIN OF MYOSIN Bruce Baumann, Bren Hambly, Kalman Hideg and Plotr G. Fajer, Molecular Biophysics Graduate Program FSU, DePartment of Pathology, University of Sydney, Australia Institute of Organic and Medicinal Chemistry, University of Pecs, Hungary and the National High Magnetic Field Laboratory, Tallahassee, FL 32306

Motional dynamics of mutant regulatory light chain (RLC) was measured using saturation transfer EPR in synthetic myosin filaments. A mutant light chain containing a single cysteine (CI54) was expressed in E. coli and labeled in solution with an indane dione spin label. The labeled environment restricts the motional freedom of the label as visualized by molecular modeling (see Sale and Fajer abstract); making it an ideal site for studying protein motion. The labeled protein was exchanged into myosin preserving its functionality as measured by ATPase activity.

Effective rotational correlation times for labeled RLC were significantly shorter than those obtained for labels on neighboring essential light chain and distal motor domain; t_r = 100, 20 and 7 us respectively. These differences reflect the presence of internal flexibility/hinges within the myosin 77 head. The observed flexibility might be modulated by the chemical states of ATPase cycle and provide an additional constraint on force generation models. There is an increasing body of experimental evidence that phosphorylation of the regulatory light chain is an important modulatory mechanism of myosin function e.g. in smooth muscle the phosphorylation is the activating mechanism for muscle contraction. Comparison of the RLC dynamics in the phosphorylated and dephosphorylated myosin reveals changes in rotational correlation time. Changes of motional freedom and associated steric restrictions might well provide a structural mechanism by which phosphorylation regulates ATPase activity.

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SPIN-ROTATION QUANTUM EFFECTS ON THE EPR LINESHAPES OF CH_3 AND CD_3 RADICALS ISOLATED IN ARGON-MATRIX Tomoya Yamada*, Kenji Komaguchi* and Masaru Shiotani*, and Anders R. Somes[+], Anders Lund[x] and Nikolas P. Benetis[x]. ^Hiroshima University, Dept. of Applied Chemistry, Higashi-Hiroshima 739, Japan, "Dept. of Physics, University of Oslo, PO Box 1048, N-0316 Oslo, Norway, [x]Dept. of Physics WK Linkoping University, S-581 83 Sweden.

The experimental EPR lineshapes of the $^{\#}CH_3$ and $^{\#}CD_3$ radicals isolated in argon matrix show very distinctquantum effects at cryogenic He temperatures, up to 40 K. For example, extremely sharp EPR transitions,line splitting and exclusion of lines by the Pauli principle were observed. We could quantitativelysimulate the experimental EPR lineshapes for the above radicals by employing the isolated three-dimensional free-quantum-rotor model for the corresponding symmetric tops. The quantum effects are attributed to the coupling of the nuclear spin degrees of freedom to the rotational motion. The responsible coupling term in the hamiltonian is the anisotropic hyperfine interaction of the methyl radical a-protons/deuterons. In comparison with the two-dimensional 0-proton methyl rotor (A.R. Somes and N.P. Benetis, ***Chem. Phys.*** 226 (1998) 1 5 1), the so-called E-lines are absent here. Instead, line splitting of each of the two central A-lines of the proton spectrum is present at intermediate, to high temperatures. There are different quantum effects present on the EPR lineshapes of the deuteron rotor, e.g. abnormally strong central line, but the spectrum becomes classical within a temperature interval of less than 10 K.

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DARK GENESIS OF A BIRADICAL INTERMEDIATE IN DNA PHOTOLYASE CATALYSIS. G. Reid Bishop and Kurt Wamcke, Department of Physics, Emory University, Atlanta, GA 30322-2430.

The DNA-photolyase [DNPL] enzyme from ***Escherichia coli*** uses reduced anionic flavin adenine dinucleotide [FADH] to cleave thymidine dimers [T<>T] in DNA damaged by short-wavelength UV light. We demonstrate by X-band EPR and electron spin echo envelope modulation [ESEEM] spectroscopies that a novel g=2 EPR signal is generated during anaerobic dark mixing of photoreduced EPR-silent DNPL-FADH with T<>T containing substrate. Comparison of ESEEM from the dark radical with ESEEM from relaxed neutral semiquinone FADH* in DNPL (tau=170-576; 9.10 GHz; 3250 G; T=6 K) reveals common spectral features in the frequency range of 1-10 MHz. However, the 3.4 MHz feature, which dominates FADH* ESEEM spectra, is absent in dark radical samples. These results suggest that photoreduction of FADH' results in a meta-stable activated form of FADH" that is competent to drive radical pair separation with formation of a substrate-dependent biradical in the dark. Two proposals for the identity of the g — 2 EPR signal are (i) T<>T coupled to anionic FAD*" or (ii) T<>T coupled to a modified form of neutral FADH*. The identity of the dark biradical species and the mechanism of its formation are currently being addressed using laser-triggered time-resolved techniques of pulsed-EPR spectroscopy.

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ENDOR AND ESEEM STUDIES OF REACTION INTERMEDIATES IN CLOSTRIDIUM THERMOACETICUM PYRUVATE: FERREDOXIN OXIDOREDUCTASE, Vladimir F. Bouchev and John L. McCracken, Department of Chemistry, Michigan State University, East Lansing, MI 48824

ENDOR and ESEEM studies of species arising from substrate addition to Pyruvate: Ferredoxin Oxidoreductase (PFOR) have been carried out to characterize the paramagnetic reaction intermediates as well as elucidate some aspects of the catalytic mechanism (Menon & Ragsdale, 1997). The EPR spectrum of the PFOR/pyruvate adduct at 4 K displays a sharp line at g = 2.005 attributed to hydroxyethyl thiamine pyrophosphate (HE-TPP) radical superimposed on a complex lineshape characteristic of rhombic [Fe_4S_4] Clusters. The ENDOR spectrum at g = 2.00 reveals hyperfine coupling of two sets of substrate methyl (3-protons. The corresponding values of the proton hyperfine coupling parameters are $A_{iso}^{(1)}$ = 13.75, $B_n^{(1)}$ = 3.60, $B_\pm^{(1)}$ = -1.80 MHz, and $A_{iso}^{(2)}$ = 16.33, $B_n^{(2)}$ = 3.33, $B_\pm^{(2)}$ = -1.67 MHz. The temperature invariance of the proton lineshapes in a large temperature range (4 K to 200 K) indicates that the methyl group is rapidly rotating even at 4 K. The hyperfine couplings are scaled down by a factor of $g_n^{(H)}$ /$g_„^{(D)}$ upon substituting the pyruvate methyl hydrogens with deuterium, thus showing that the radical signal is substrate-derived. A pair of ^{31}P lines at 5.48 and 5.99 MHz is resolved in ENDOR due to isotropic remote hyperfine interaction with HE-TPP phosphorus. Stimulated ESEEM shows weak, complex ^{14}N modulations in the range 0.7-5.0 MHz arising from both HE-TPP nitrogen coupling and the coupling of protein nitrogens [Fe_4S_4]. HE-TPP ^{14}N coupling parameters for the hyperfine and quadrupolar interactions are tentatively estimated through ESEEM simulations to be A_u = 2.36 MHz and A i = 1.36 MHz, e^2qQ =1.9 MHz, asymmetry parameter *r*\ = 0.7. The results of the present investigation confirm that the EPR signal at g = 2.005 is due to a substrate-derived radical - intermediate in the PFOR/pyruvate reaction.

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PARALLEL POLARIZATION EPR STUDIES OF THE SI-STATE OF THE PHOTOSYSTEM]I OXYGEN-EVOLVING COMPLEX, Kristy A. Campbell.* Wolfgang Gregor,* Donna Pham,' Richard J. Debus,' Jeffrey M. Peloquin,* and R. David Brite,* *Department of Chemistry, University of California, Davis, CA 95616, department of Biochemistry, University of California, Riverside, CA 92521

An Si-State parallel polarization 'multiline' EPR signal arising from the oxygen-evolving complex has been detected in spinach PSII membrane and core preparations depleted of the 23 and 17 kda,.extrinsic polypeptides, but retaining the 35-kDa extrinsic protein. This Si-State multline signal, with an effective g value of 12 and at least 18 hyperfine lines, has previoulsy been detected only in PSII preparations from the cyanobacterium Synechocystis sp. PCC 6803 [Campbell, K. A.. Peloquin, J.M., Pham, D. P., Debus, R. J., and BriU, R.D. (1998) J. Am. Chem. Soc. 120, 447-448]. This signal provides direct evidence for the influence of the extrinsic PSII proteins on the magnetic properties of the Mn cluster.

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ELECTRON SPIN-ECHO ENVELOPE MODULATION SPECTROSCOPIC STUDIES OF POLYCRYSTALLINE CU(II) -INSULIN. Michael J. Colaneri*%, Jacqueline Vitali* and Jack Peisach%, *Dept. of Chemistry and Physics, SUNY College at Old Westbury, Old Westbury, NY 11568, #Dept. of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712 and %Dept. of Physiology and Biophysics, Albert Einstein College of Medicine, Bronx, NY 10461

A comparison of ESEEM patterns observed from polycrystalline Cu (II)- Insulin with and without bound Cd(II) ions indicate a dramatic change of the quadrupole coupling parameters of the remote nitrogens of two histidine imidazoles that ligate to copper. In the absence of cadmium, the quadrupole parameters are like those observed from ESEEM studies of type I copper proteins. When Cd(II) ions are allowed to soak into the Cu (II)- Insulin crystals, the quadrupole parameters undergo a change and take on values that are normally found in type 11 copper proteins. Simulations of the Fourier-transformed ESEEM patterns coupled with structure modeling indicate that these changes stem from differences in the hydrogen bonding environments of the imidazole remote nitrogen. In the native Zn(II)- Insulin structure these nitrogens are hydrogen bonded to water molecules. With Cd(II) ions present, an analysis of the ESEEM patterns show that these Imidazole nitrogens form stronger L hydrogen bonds to those glutamates which are responsible for the binding of cadmium.

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SPECTRAL-SPATIAL IMAGING USING RADIOFREQUENCY TIME DOMAIN EPR. JL. Cook*, S. Subramanian*, M. Afeworki* N. Devasahayam* D. Coffin*, R. Tschudin*, JHA Larsen', K. Golman', J. B.

Mitchell* and M.C. Krishna*. Radiation Biology Branch, National Cancer Institute, NIH, Bethesda®, MD 20892 and 'Nycomed Innovation Malmo, Sweden

A radiofrequency EPR spectrometer operating in time domain suitable for in vivo functional imaging studies is described. The spectrometer operates in the frequency range of 280 - 300 MHz affording a penetration of at least 5 cm in biologic tissue. The sensitivity of detection is enhanced by utilizing the signal averaging techniques routinely used in pulsed nuclear magnetic resonance. With excitation pulses amplified to 283 Vpp, dead times in a cylindrical resonator of 25 mm diameter and 55 mm length were in the order of 400 - 600 ns, following which the free induction decays (4 k points/wave form) have been collected using a 1 GHz digitizer/averager. In this configuration, repetition rates in the order of 0. 1 MHz have been utilized to exploit the short phase memory times of paramagnetic species.

Utilizing a non-toxic, water soluble infusible paramgnetic spin probe exhibiting a single narrow EPR signal with an oxygen dependent line width in the range of 30 - 200 mG, 3-dimensional spatial imaging in murine objects (C3H mice) is demonstrated after an iv infusion. The signals were spatially encoded using static gradients. The images were obtained by standard filtered back projection techniques and show a good spatial resolution (< 1 mm). We are in the process of developing spectral-spatial algorithms for time domain pulsed EPR imaging. Results from spectral-spatial imaging experiments on phantom objects containing spin probes with different pO$_2$ levels will be presented.

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EPR CHARACTERIZATION OF CHLOROCATECHOL 1,2-DIOXYGENASE: A NON-HEME IRON DIOXYGENASE.

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The technologic application of the enzyme Chlorocatechol 1,2-Dioxygenase based on its biological function (the cleavage of synthetic aromatic hydrocarbons) is the main reason for its spectroscopic studies. These synthetic hydrocarbons are continuously produced and discharged to the environment by the modern industry. Many of those compounds are resistant to both chemical oxidation and biological degradation. A number of those halogenated hydrocarbons have been shown to be degraded and used as sources of carbon and energy by specialized strains of aerobic and anaerobic bacteria. The catechol dioxygenases are a class of bacterial non-heme iron enzymes that catalyze the addition of both atoms of molecular oxygen to 1,2-dihydroxybenzene (catechol) or other catechol derivatives (like cblorocatechol) with subsequent cleavage of the aromatic ring. The chlorocatechol dioxygenase gene (clca) from P,@eudomonas plasmid pAC27 was subcloned into the expression vector PETCLCA (obtained from the pET28a expression vector), allowing the production of chlorocatechol dioxygenase. EPR measurements of the active enzyme in solution samples were performed at 9.3GHz and liquid Helium temperature. Enzymatic activity assay was performed spectrophotometrically (UV-Vis) by monitoring the change in absorbance at 260nm for the enzyme-substrate complex. The presence of the characteristic high-spin FE(III) ion in a rhomb'lc environment was observed, similar to the results obtained for other catechol dioxygenases. Preliminary spin label and time-resolved EPR experiments are also reported. (Financial Support: FAPESP,CNPq,CAPES)

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SOLID STATE AND SOLUTION CHEMISTRY OF BIS (ACETYLACETONATE) OXOVANADIUM(IV), VO(ACAC) AND DERIVATIVES.*

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Bis(acetylacetonate)oxovanadium(IV) and two derivatives with alkylated acac ligands, VO(Me-acac)$_2$ and VO(Et-acac)$_2$ (Me-acac = 3-methyl-2,4-pentanedione and Et-acac = 3-ethyl-2,4-pentanedione), were studied in aqueous solutions to elucidate structure and stability. The solid-state structure of the VO(Me-acac)$_2$ complex was determined by X-ray diffraction and compared to VO(acac)$_2$ and related complexes. Room temperature EPR spectroscopy was correlated with visible spectroscopy to determine the composition of mixtures resulting upon dissolution in aqueous media. An equilibrium between three species was established. The species were the cis and trans H_2O adducts of $VO(R\text{-}acac)_2$ and the hydrolysis product $[VO(R\text{-}acac)(H_2O)]^+$. Differences in stabilities of the vanadium species were explored as the acac ligand was alkylated. Low temperature EPR results and effects of safts were investigated to further understand solution composition under physiological conditions.

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HIGH-SENSITIVITY EPR OF MN$_{12}$ -ACETATE, N. S. Dalai, B. Cage, T. Hathaway, Chemistry Dept. and NHMFL, Florida State University, Tallahassee, FL 32310, S. Hill, Dept. of Physics, Montana Stcite University, Bozeman, MT 59717, T. Stalcup, J. S. Brooks, Dept. of Physics and NHMFL, Florida State University, Tallahassee, FL 32310.

The energy level diagram of Mn_{12} - Acetate is probed close to the top of the anisotropy barrier using a novel, high-sensitivity, EPR technique. Multiple resonances, and their temperature dependence, are observed from 35 .to 115 GHz, for a single high-quality crystal. The data are of sufficient detail to make extremely accurate comparisons with predictions based on a spin S = 10 Hamiltonian. The gross features of the EPR spectra confirm the strong axial symmetry, and show clear evidence for a significant fourth order term in the Hamiltonian. However, closer examination of the zero-field splittings close to the barrier indicate possible inadequacies of the spin S = 10 model. Several weak EPR transitions persist at low temperatures; we discuss the possibility that these transitions occur as a result of a finite population of levels other than the ground state.

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HYPERFINE COUPLINGS OF PYRROLE NITROGENS IN NITROSYLATED REME. S.A. Dikanov,[a,b] D.C. Doetschman,[a] D.G. Gilbert,[3] J.A. Smieja.[c] [a]Centerfor Pulsed EPR and Photochemistry, Department of chemistry, SUNY-Binghamton University, Binghamton, NY 13902-6016, institute of chemical Kinetics and Combustion, Novosibirsk 630090, Russia, "Department of Chemistry, Gonzaga University, Spokane, WA 99258

Nitric oxide (NO) biosynthesis has important roles in mammalian physiology and pathology. NO is generated on a heme site by a family of enzymes called nitric oxide syntheses (NOSs). This endogenous NO interacts with other heme and nonheme iron proteins performing various cellular inhibition and activation functions. Thus, detailed structural information about the interaction of NO with the metal center, especially heme, is required for understanding the synthesis of endogenous NO and its physiological role. The results of previous investigations show that ESEEM spectra of pyrrole nitrogens are sensitive to the geometry of NO-heme binding. However, their complete analysis is complicated because the quadrupole interaction produces dominant spectral features and information about the hyperfine couplings with all four pyrrole nitrogens is limited. We report on a study of ^{15}N hyperfine couplings in the six-coordinated model complex NO-Fe(^{15}N-TPP)-pyridine using 2D ESEEM spectroscopy. These spectra measured throughout the entire EPR spectrum clearly show the peaks from several types of pyrrole nitrogens with different hyperfine couplings and allow the determination of isotropic and anisotropic parts, as well as the orientation of the hyperfine tensors relative to the g-tensor of the complex.

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SUBSTRATE AFFECTS THE GEOMETRY OF NITRIC OXIDE-HEME BINDING IN THE ACTIVE SITE OF NEURONAL NITRIC OXIDE SYNTHASE, S.A. Dikanov[a,b], D.C. Doetschman,[a] D.J. Stuehr,[c] L. Huang[c], [a]Center for Pulsed EPR and Photochemistty, Department ofchemistry, SUNY-Binghamton University, Binghamton NY 13902-6016, institute of Chemical Kinetics and Combustion, Novosibirsk 630090, [c]Russia, Department of Immunology, The Cleveland Clinic Research Institute, Cleveland, Ohio 44195

Nitric oxide (NO) biosynthesis has important roles in mannnalian physiology and pathology. NO is generated on a heme site by a family of enzymes called nitric oxide syntheses (NOSs). They catalyze a two-step oxidation of L-arginine (L-arg) that initially generates N-hydroxyarginine (argOH), as an enzyme-bound intermediate, and NO plus citruiline as final products. A variety of evidence suggests that the NOS heme plays a central role in the catalysis. The NOS heme iron is ligated to the protein through a cysteine thiolate and can bind a variety molecules as a sixth ligands. Substrate appears to bind directly above the heme and can interact with a ligand bound to the heme such as

NO. The tetrahydrobiopterine cofactor (HB) is also critical for catalytic activity. In the current report, we utilize ESEEM spectroscopy to investigate how substrates (L-arg and arg-OH) and (HB) control the coordination structure of heme Fe-NO complex in the oxygenase domain of neuronal NOS (nNOS). The samples containing L-arg and arg-OH have significantly different multicomponent three-pulse nitrogen ESEEM spectra. Among them three peaks at frequencies -0.4,1.1 and 1.5 MHz which are typical quadrupole frequencies of pyrrole nitrogens can be recognized. These peaks demonstrate completely different orientational dependence of their intensity in these two samples that provides the first evidence of the different geometry of NO binding. The two dimensional ESEEM experiments with these samples, as well as samples prepared using ^{15}N labeled arginines and deuterated buffer, are currently in progress. They will clarify the mechanism of substrate-NO interaction.

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EFFECT OF SOLVENT METHYL GROUPS ON SPIN ECHO DEPHASING FOR CR(V) AND VANADYL COMPLEXES. Gareth R. Eaton and Sandra S. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208

For nitroxyl radicals at 11 to 40 K we observed that two-pulse spin-echo dephasing was dominated by solvent protons and was filster in solvents that contained methyl groups than in solvents that did not contain methyl groups (M. Lindgren et al. J C S. Perkin Trans 2, 2549 (1997)). To test the generality of these effects we have now examined the solvent dependence of T_m below 40 K for complexes of two d^1 transition metals: chromyl bis(I-hydroxy-cyclohexanecarboxylic acid), $CrO(HCA)_2$" aquo vanadyl ion, VO^{2+}, (aq), and vanadyl bis(trifluoroacetylacetonate), $VO(tfac)_2$. For both $CrO(HCA)_2$" and VO^{2+} (aq) T_m was about 4.8 lis at 20 K in 1:1 H_2O:glycerol and >50 u.s in 1:1 D_2O: glycerol-d_8. The large impact of solvent deuteration on T_m confirms the dominant role of protons in echo dephasing for these complexes in protonated solvents. For $CrO(HCA)_2$" and $VO(tfac)_2$ T_m decreased as the solvent was changed from 1: 1 H_2O: glycerol or 9:1 CF_3CH_2OH: ethyleneglycol (no methyl groups) to 9:1 iPrOH:MeOH to 9:1 nPrOH:MeOH, which is similar to the effects of solvent methyls on spin echo dephasing that was observed for nitroxyl radicals. We propose that the effect of solvent methyls on spin echo dephasing is a general effect under conditions where spin echo dephasing is determined by dipolar interaction with surrounding nuclear spins.

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COMPARISON OF MEMBRANE FLUIDITY OF WILD-TYPE AND COLD-SENSITIVE STRAINS OF LISTERIA MONOCYTOGENES Michelle R. Edgcomb, Samanthi Sirimanne*, Pascal Drouin*, Brian Wilkinson*, and Reef (Philip D, II) Morse, Departments of Chemistry and Biology*, Illinois State University, Normal, EL 61790-4160.

Listeria monocytogenes is a food-borne pathogen that proliferates at refrigeration temperatures. This gram-positive bacterium in its virulent form causes a number of human diseases. The organisms' capability of growth at low temperatures is due in part to membrane lipids that impart essential fluidity. The study of the role of 12-methyltetradecanoic (anteiso-C15) fatty acid in membrane fluidity at various growth temperatures becomes crucial to understanding Listetia's fatty acid profile at different environmental temperature,. Direct measurement of membrane lipid motion at different levels in the membrane bilayer is obtained from spectral deconvolution and simulation of the three hyperfine lines obtained from the nitroxides 2N10, 3N10, 4N10, and 5N10 and compared with fatty acid analysis by gas-liquid chromatography of both nonpathogenic and cold sensitive mutants grown at different temperatures. Initial work with 2N10 and 5N10 shows that the membranes of strain SLCC5 3 (nonhemolytic and avirulent) grown at 30°C have no sudden phase changes. The motion of 2N10 is somewhatan isotropic,but the degree of anisotropy remains constant over a temperature range of 5°C to 42°C. In contrast, 5N10, which samples the deep portions of the membranes, shows a distinct population of nitroxides whose motion is strongly restricted. This population decreases with increasing temperature. We conclude that the polar head group region of Listeria membranes are fluid over a wide temperature range and that this may contribute to the thermal adaptability of the organism. However, the vertical and horizontal fluidity profile of the membrane is complex.

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HIGH-FREQUENCY SPIN LABEL EPR STUDIES OF NON-AXIAL LIPID ORDERING IN MEMBRANES WITH CHOLESTEROL Betty J. Gaffhgy* and Derek Marsh[+] ^National High Magnetic Field Lab, Florida State University, 1800 E. Paul Dirac Dr., Tallahassee, FL 32310, USA and [+]Abt. Spektroskopie, Max-Planck-Institut fur biophysikalische Chemie, Am Fassberg 11, D-37077 Gottingen, Germany

The EPR spectra of spin4abelled lipid chains in fully hydrated bflayer membranes of DWC and cholesterol have been studied in the fiquid-ordered phase at a microwave frequency of 94 GHz. At this high frequency, the spectra should be optimally sensitive to lateral chain ordering that is expecte(m formation of in-plane domains. Indeed, the high-frequency EPR spectra from random dispersions of the cholesterol-containing membranes display very little axial averaging of the nitroxide g-tensor anisotropy, for lipids spin labeled toward the carboxyl end of the sn-2 chain. For these labeling positions, anisotropic ^{14}N hyperfine splittings are resolved in the g_{zz} and g_{yy} regions of the non-axial EPR spectra. For positions of labeling further down the lipid chain, the axial averaging of the spectral features systematically decreases. Concomitantly, the time-averaged $<A_{zz}>$ element of the ^{14}N-hyperfine tensor decreases, indicating that the axial rotation at the terminal methyl end of the chains arises from correlated torsional motions about the bonds of the chain backbone, the dynamics of which also give rise to a differential broadening of the ^{14}N-hyperfine manifolds. These results provide an indication of the way in which detergent-insoluble domains containing high cholesterol content may form in cell plasma membranes.

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FIELD DISTRIBUTIONS IN LOOP GAP RESONATORS DESIGNED TO OPERATE AT RADIOFREQUENCIES: RESULTS FROM HFSS MODELS AND COMPARISON WITH MEASUREMENTS. V. Galtsev, E.D. Barth, H.J. Halpern U. Chicago, Chicago, IL

Low-field, low-frequency (200-300 MHZ) EPR spectroscopy and imaging for in vivo study encounters several instrumental challenges .The use of loop-gap resonators (LGR) or lumped component resonators is established in radiofrequency (RF) EPR. Design of LGR can be facilitated by computer simulation of resonator performance, in particular, that of B_x distribution in the resonator. We have used Hewlett-Packard HFSS (High-Frequency Structure Simulator) program solving Maxwell's equations for structure under study in finite element approximation. A comparison of such a simulations with measurements for several LGR manufactured in our laboratory either with or without lossy phantoms (made of fresh meat) representing living system are described. There are significant differences in B_x distributions inside resonators with and without phantoms. The influence of lossy phantoms on absolute values of B, is more significant, in agreement with that what could be predicted from their influence upon loaded Q of resonators. HFSS simulations will be shown to be more consistent with experimental B_l measurements than usually used formulae to predict Q. We will also show the use of HFSS simulations to increase field homogeneity through resonator design modifications for lossy samples.

Supported by NIH grant CA69538

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STRUCTURAL STUDY OF THE SQUARE PYRAMIDAL TO TRIGONAL BIPYRAMIDAL DISTORTION OF VANADYL COMPLEXES BY ^{51}V ESE-ENDOR. Chris Grant[1], R. David Britt[1], Charles R. Cornman[2], 1)Department of Chemistry, Uniersity of California Davis, CA 95616. 2)Department of Chemistry, North Carolina State, University, Raleigh, NC 27695

A series of sterically crowded schiff base ligand complexes of vanadyl (VOII) have bee n investigated by ^{51}V Electron Spin Echo-Electron Nuclear Double Resonance (ESE-ENDOR). These complexes range in geometry from square Pyramidal to trigonal bipyramidal and serve as models for the interaction of the vanadyl ion with protein phosphatases. The technique of ^{51}V ENDOR has been used to investigate ^{51}V nuclear quadrupole coupling parameters which are sensitive to the coordination environment of the vanadium ion, and thus sensitive to the geometry changes within this series of complexes.

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IN VIVO PHARMAKOKINETICS OF A NOVEL, STABLE NITRIC OXIDE SPIN TRAPPING ADDUCT, DTCS. HJ. Halpern, E.D. Barth, G.V.R. Chandramouli, V. Galtsev, B. B. Williams U.Chicago, Chicago, IL. S. Pou, G.M. Rosen U. Maryland, Baltimore, MD

A nitric oxide spin trap was recently reported by Yoshimura, et al.[1], the NO iron complex of N-(dithiocarboxy) sarcosine, DTCS. The complex, is $Fe(DTCS)_2NO$. $Fe(DTCS)_2$ complex is compared with the more commonly used iron complex of N-methyl-D-glucamine dithiocarbamate, $Fe(MGD)_2$. We present kinetic data comparing the pseudo first order rate constants of $Fe(DTCS)_2$ for combination with NO with that of $Fe(MGD)_2$. Preliminary data were derived exposing $Fe(DTCS)_2$ and $Fe(MGD)_2$ to gaseous NO bubbled through the solution and NO released from spermine-NO in solution. Rate constants appear to be similar: 1.7×10^6 M"^{1} sec"^{1} for $Fe(DTCS)_2$ and 1.2×10^6 M"^{1} sec^1 for $FE(MGD)_2$. The in vitro stability of $FE(DTCS)_2$ NO and $FE(MGD)_2$ NO in the presence of superoxide and thiol are compared. $Fe(DTCS)_2NO$ again appears to be somewhat superior to $Fe(MGD)_2NO$ approximately twice as resistant to reduction and oxidation. The kinetics of $FE(DTCS)_2$ NO and $Fe(MGD)_2NO$ in the abdomen of C3H mice were compared. Concentrations of the iron complex refer to the iron concentration with the adduct added in 5 times molar excess. $Fe(DTCS)_2NO$ and $Fe(MGD)_2NO$ was prepared by bubbling the iron complex with NO gas for three and 10 min respectively to obtain maximum signal. Mice were injected IP with 1 ml of 10 mM $Fe(DTCS)_2NO$ or 20 mM $Fe(MGD)_2NO$ to equalize input signal .The $Fe(DTCS)_2NO$ halflife of the abdominal signal was 41 minutes. The halflife of $Fe(MGD)_2NO$ appears to be much shorter.[1] [Yoshimura, T., Fujii, S., Yokoyama, H., and Kamada, H. Chemistry Letters 1995, 309-310] Supported by NIH grant CA69538

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PULSED EPR STUDIES OF THE RADICALS FORMED BY y-IRRADIATION OF MALONIC ACID AND METHYL MALONIC ACID. James R. Harbridize, Sandra S. Eaton, and Gareth R. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208, USA

Pulsed EPR studies as a function of temperature were performed on the radicals formed by y-irradiation of malonic acid and methyl malonic acid powders. The unpaired electron in irradiated malonic acid is coupled to a single proton whereas the unpaired electron in irradiated methyl malonic acid is coupled to a single methyl group. This creates vastly different longitudinal and transverse relaxation processes in these radicals. Using pulsed electron-electron double resonance (ELDOR) the longitudinal relaxation processes for both radicals have been broken down into their individual components. The malonic acid radical exhibits a fast nuclear relaxation process that is attributed to hydrogen bonding in the sample. The methyl malonic acid radical exhibits a fast cross relaxation that is attributed to the modulation of the magnetic,field at the unpaired electron by the freely rotating methyl group. Transverse relaxation times were measured using both 2-pulse ESE and Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences and also show large differences in the relaxation times for both radicals. These differences will be discussed in terms of both intermolecular and intramolecular processes.

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HIGH-FIELD ESR STUDIES OF THE DOPED SPIN-PEIERLS SYSTEM $Cu_uZn_xGeO_3$, Alia K. Hassan, Luca A. Pardi, George B. Martins, Gang Cao, Louis-Claude Brunei, Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, 1800 E. Paul Dirac Dr., Tallahassee, Florida 32310

High-field Electron Spin Resonance measurements were made on powder samples of the Zn doped Spin-Peierls system $Cu_{1\cdot x}$,Zn_xGe0_3 (x=0.00, 0.01, 0.02, 0.03, 0.05) at different frequencies (95,110,190, 220, 330 and 440 GHz) at low temperatures. The spectra of the doped samples show additional resonances relative to the spectra of the pure compound, whose positions are dependent on Zn concentration, frequency and temperature. The analysis of the intensity behavior of these lines with temperature allows us to identify them as originating from transitions within states situated inside the Spin-Peierls gap. A qualitative explanation of the details of the spectra is possible if we assume that these states in the gap are associated with "loose" spins created near the Zn impurities, as recently theoretically predicted [1]. We also observe that the original gap is partially suppressed upon doping. The ESR results presented here are the first observations of these states inside the gap. The behaviors of these excitations with temperature, frequency and doping level offer an insight into the physical properties of the system investigated.

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RADICAL REACTANT-ACTIVE SITE INTERACTIONS IN ETHANOLAMINE DEAMINASE. Shyue-Chu Ke and Kurt Wamcke, Department of Physics, Emory University, Atlanta, GA 30322

Ethanolamine deaminase is a vitamin B_{12} coenzyme-dependent enzyme that catalyzes the radical-mediated oxidative deamination of ethanolamine. Cryo-trapped enzyme-bound radical intermediates formed during, steady-state turnover of the Salmonella typhimurium enzyme with 2-aminoethanol and the substrate analogs, 2-aminopropanol, ethylene glycol and glycerol, have been characterized by using X- and Ku-band electron spin echo envelope modulation (ESEEM) spectroscopy. Three-pulse ESEEM spectra obtained at 6 K from the 2-aminopropanol-generated radical display a 6 line pattern in the frequency range 0.6-5.0 MHz. Resolution of spectral components is higher than in a previous study of this radical [Tan et al., J. Biol. Chem. 261, 3483 (1986)], allowing more accurate description of the coupling. Magnetic field tracking and t-suppression effects among the Amj=±l and Am_r-±2 frequency components demonstrate that the features arise from coupling to a single ^{14}N nucleus. Simulations of multifrequency (9.06,10.32,10.90 GHz) 3-pulse ESEEM data collected at x=263-1430 ns yield the following principle hyperfine.tensor and nuclear quadrupole coupling parameters: A=[-1.08, -0.81, -0.81] MHz; e^2qQ/h=3.05 ±.05 MHz; *r\=0.51* ±.02. The quadrupole parameters suggest that the ^{14}N originates either from a polypeptide bond nitrogen, as suggested by Tan et al., or from coenzyme adenosine ring nitrogen. The aminoethanol- and glycerol-generated radicals exhibit multifrequency ESEEM spectra modified from those of the 2-aminopropanol radical, while ethylene glycol spectra show a novel ^{14}N pattern. ESEEM simulations are being used to correlate the spectral differences with different radical orientations in situ and with the extent of radical rearrangement. Supported by NIH DK-52183.

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HIGH-FEELD EPR (326 GHz) AND ENDOR (9 GHz) STUDIES OF CAROTENOID - SOLID LEWIS ACID INTERACTIONS. Tatyana A. Konovalova,[a] Lowell D. Kispert.[a] Peter J. Bratt,[b] Louis-Claude Brunei[0] and J. Krzystek,[0] (a) Department of Chemistry, the University of Alabama, Tuscaloosa, AL 35487; (b) Department of Chemistry, the University of Florida, Gainesville, FL 32611; (c)NHMFL, Florida State University, Tallahassee, FL 32310.

The 326 GHz EPR spectrum of canthaxanthin adsorbed on silica-alumina measured over a temperature range of 5-80 K at the National High Magnetic Field Laboratory exhibits a single asymmetric unresolved line. Successful computer simulation of the line indicated it to be a result of g anistropy where g_n = 2.0034 and $g_{\pm}$ = 2.0023. This type of g tensor is consistent with the Stone theory for polyacene ~-radical cations which states that the g tensor becomes cylindrically symmetrical with increasing chain length. This also demonstrates that the symmetrical unresolved EPR line at X-band frequency (9 GHz) is due to a carotenoid jt-radical cation with unpaired density distributed over the polyene chain as predicted by RHF/INDO-SP calculations. 9 GHz ENDOR measurements provide strong support for the formation of carotenoid radical cations on activated alumina and silica-alumina as a consequence of electron transfer from the adsorbed carotenoid molecules to the Al^{111} Lewis acid sites and the formation of strong complexes between carotenoid molecules and Lewis acid sites. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Grant DE-FG05-86ER13465.

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A HIGH POWER 250 GHz DNP/EPR SPECTROMETER, Kenneth E. Kreischer. Christian T. Farrar, Marina L. Bennati, Robert G. Griffin, and Richard J. Temkin, Plasma Science and Fusion Center and Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139.

We are presently constructing a high power 250 GHz spectrometer that will be suitable for dynamic nuclear polarization (DNP) and EPR studies. The microwave source for will be a 100 watt (cw), fundamental free-running gyrotron oscillator that will operate in the TE-031 mode. Nonlinear codes indicate that about 150 watts of rf power will be generated by a 12 kV, 40 mA beam, with about one-third of this power lost in the cavity walls due to ohmic heating. An efficiency of 21 % is expected. A quasi-optical mode converter will be used to convert the TE-031 cavity mode into a Gaussian rf output beam about 1 cm in diameter. We will eventually upgrade the gyrotron to second harmonic operation at 500 GHz. We are also building a low power EPR spectrometer that will be operated in both pulsed and cw modes. This heterodyne system will be based on a 83.4 GHz reflection amplifier driving a frequency tripler and will provide at least 2 mW at 250.2 GHz. A 124 GHz Gunn diode, phase-locked to the 250.2 GHz source, and second harmonic mixer will be used to generate an IF frequency of 2.2 GHz. Pulsed mode operation will be accomplished using a low frequency pin switch to gate the reflection amplifier. The advantage of this method is that there is no insertion loss associated with the microwave switching. Both transmission and reflection mode probes are being considered. That latter may be difficult because of the lack of a quasi-optical circulator at 250 GHz. The transmission lines will use either corrugated waveguide or optiguide, and both Fabry-Perot and cylindrical resonators are being considered for holding the sample. We are also acquiring a magnet for the EPR spectrometer with a center field of 8.9 T (375 MHz 1H, 250.2 GHz electron) and a field sweep range of ±1.0 T.

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MULTI-FREQUENCY EPR ANALYSIS OF DIPOLAR AND EXCHANGE INTERACTIONS BETWEEN MANGANESE AND TYROSINE IN THE S_2 Y_z STATE OF PHOTOSYSTEM II <u>K. V. Lakshmi</u>.[A] Sandra S. Eaton[8], Gareth R. Eaton[8], Harry A. Frank[c] & Gary W. Brudvig[A] Departments of Chemistry, Yale University[A], New Haven, CT 06520-8107; University of Denver[8], Denver, CO 80208; University of Connecticut[0], Storrs, CT 06269-4060

Acetate-inhibited photosystem II, upon room temperature illumination, exhibits a 240 G wide X-band EPR signal at 10 K.[1] This EPR signal arises from an interaction between the S_2 state of the Mn_4 cluster and an oxidized tyrosine residue, $Y_z\backslash$[2] In the present study, the exchange and dipolar interactions between the two paramagnetic species are simulated at X- and Q-band frequencies utilizing second-order perturbation theory.[3] The positions and relative intensities of the hyperfine lines in the S = 1/2 S_2-state multiline EPR signal are accurately simulated by including g-anisotropy and four sets of axially symmetric ^{55}Mn hyperfine tensors. These parameters are then used to simulate the dipolar and exchange interactions giving rise to the broad experimental S_2 Y_z* EPR signal at X- and Q-band frequencies. A precise distance determination between the Mn_4 cluster and $Y_z^{\#}$ in the 0_2-evolving complex better enables us to elucidate the direct involvement of Y_z" in water-oxidation chemistry. Supported by NIH GM32715 and GM36442 (Yale) and NIH GM21156 (Denver).

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A PHYSICALLY BASED PREDICTIVE MODEL FOR THE GENERATION OF PARAMAGNETIC CENTERS AT THE Si/SiO$_2$ BOUNDARY OF MOS TRANSISTORS. <u>P.M. Lenahan</u>. Pennsylvania State University, University Park, PA, 16802, and J.F. Conley, Dynamics Research Corporation, Beaverton, Oregon, 97006.

Paramagnetic defects at the Si/Si0$_2$ boundary, P_5 centers, play dominating roles in several instabilities which limit the size, speed, and lifetime of the metal/oxide/silicon (MOS) field effect transistors which dominate virtually all of modem microelectronic technology. P_b centers involve an unpaired electron highly localized in a high p-character orbital of a silicon atom bonded to three other silicon atoms at the Si/SiO$_2$ boundary. Several years ago, we showed that molecular hydrogen reactions with MOS oxide E' centers are closely linked to the generation of P_5 centers. Quite recently we developed a simple statistical mechanics model which accurately predicts the generation of E' centers in MOS devices. Combining our E' generation model and simple reaction thermodynamics we've developed a model which predicts the densities of paramagnetic P_b centers generated in MOS structures. We show that the predictions of the model are in reasonable agreement with experimental results.

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ESR STUDIES OF THE ROLE OF ZEOLITE STRUCTURES IN SELECTIVE CATALYTIC REDUCTION. PART III MOTIONAL DYNAMICS OF NO_2 ON VARIOUS ZEOLITES

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Electron Spin Resonance (ESR) spectroscopy was used to study the effect of zeolite structure on the motional dynamics of NO_2 on the surface of zeolites. The temperature-dependent ESR spectral line shapes were quantitatively analysed using slow-motion-ESR theory. It was observed that the motional dynamics of NO_2, is strongly dependent on the type of zeolite (Beta-type, ZSM-5, Mordenite, L-type and Ferrierite zeolites). The following important observations are made: (1). In similar channel structural zeolites, the diffusion rate of NO_2 is proportional to the channel size, the order of the diffusion rates is Beta-type > ZSM-5 > Ferrierite and L-type > Mordenite; (2). The diffusion of NO_2 is faster in the 3-D structural zeolites (Beta-type, ZSM-5 and Ferrierite) than that in the 1-D zeolites (L-type and Mordenite). The order of NO_2 diffusion rates is quite similar to that of catalytic activities for Selective Catalytic Reduction (SCR).

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MODELING OF PHASE-MEMORY RELAXATION INDUCED BY SURROUNDING NUCLEI IN SPIN-LABELED MUTANTS OF CARBONIC ANHYDRASE II.

(1)Mikael Lindgren, (2)Martina Huber, (3)Per Hammarstrom, (3)Magdalena Svensson, (3)Uno Carlsson, (4)Gareth R. Eaton, (4)Sandra S. Eaton. (1)IFM-Chemical Physics, (3)IFM-Biochemistry, Linkoping University, S-581 83 Linkoping, Sweden. (2)On leave from: Department of Organic Chemistry, Free University Berlin, 14195 Berlin, Germany. (4)Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado, USA 80208.

The effect of the surrounding medium (protein) on the phase memory times (T_M) of spin labels in proteins was measured by pulsed EPR and interpreted using a theoretical model. Glassy solutions of seven spin-labeled mutants, in which the position of the spin label ranges from buried to surface exposed, were studied. T_M values were between 2 and 4 us, depending on the position of the spin label. In deuterated buffer different T_M values, and ESE modulation due to deuterium nuclei were observed, reflecting the accessibility of the spin label. As previously shown, the shape of the ESE decay can report on the nuclear environment surrounding the spin-label (J. Chem. Soc, Perkin Trans. 2, 1997, 2549). A qualitative simulation model to explain the echo shape on the basis of dephasing due to proton flip flops in the vicinity of the label will be presented. The model uses the positions of nuclei determined from crystal structures and/or protein structures modified by force calculations to calculate the effect of the protons on the spin label ESE decay curves.

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CHARACTERIZATION AND SCREENING OF SPIN TRAPS FOR APPLICATION IN VIVO,

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Free radicals have been postulated to have important roles in the development of ischemia-reperfusion damage, cancer, aging, and other types of uncontrolled oxidation. Due to the very reactive nature of these species, however, they are generally very short-lived in vivo. Most of the approaches to detect these species in biological systems use in vitro systems, isolated organs, or in vitro analyses of free radicals generated in vivo. The obstacle which prevents the direct detection of free radical in vivo is the stability of the free radical and their spin adducts. We have initiated a study to characterize and screen several dozens spin traps to search for better traps which could produce more stable spin adducts in biological systems. Specifically, hydrophobicity and cytotoxicity of these spin traps were determined. Biologically relevant spin adducts of these spin traps were synthesized, and their decay rates in mice in vivo and reaction rates with ascorbate ion were determined. We will summarize the results we have obtained so far, and will discuss some of key issues in the future development of the technique of in vivo EPR spin trapping.

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ELECTRON SPIN ECHO ENVELOPE MODULATION (ESEEM) STUDIES OF ACTIVE SITE STRUCTURE IN CHLOROPLAST F1 -ATP SYNTHASE USING AN OXOVANADIUM PROBE.

Russell LoBrutto. Hung-Cheng Chiou, Simon Myrgren, Wei Chen, and Wayne D. Frasch. Department of Plant Biology and Center for the Study of Early Events in Photosynthesis, Arizona State University, Tempe, Arizona, 85287-1601.

ESEEM has been applied to the identification of ligands to and near neighbors of VO^{2+} in the F_r-ATP synthase from spinach, and from Chlamydomonas reinhardtii. The vanadyl cation was substituted for the native Mg^{2+} cation in two distinct sites, to act as a paramagnetic probe for both CW and pulsed EPR. In latent-state F_rATPase from spinach, prepared with VO(ATP) in nucleotide binding site 2, stimulated echo ESEEM spectra revealed the presence of one or more weak (around 0.4 MHz) ^{31}P superhyperfine couplings. These are consistent with a non-coordinating polyphosphate chain which shares the active site with VO^{2+}. VO(ATP) was also introduced into wild-type and mutant ATPases from Chlamydomonas. In addition to the ^{31}P features found in the spinach spectra, the Chlamydomonas spectra (at selected magnetic field settings) showed evidence of a weak ^{14}N coupling, similar to that of an amino nitrogen that coordinates VO^{2+} axially. All of the same features were observed in the lysine 178-to-histidine mutant in site 3. The structural and mechanistic implications of these results are discussed.

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HIGH-FIELD EPR STUDIES OF SEVERAL MANGANESE(II)-CONTAINING COMPOUNDS. Laura M. Jones, Laura G. Schultz, Ryan H. Flamion, Katheryn M. Key and W. Bryan Lynch. Department of Chemistry, University of Evansville, 1800 Lincoln Avenue, Evansville, IN 47722.

We have studied a series of manganese(II)-containing compounds in an effort to determine accurate zero-field splitting (zfs) values. High-field EPR spectra of simple octahedral and tetrahedral complexes (MnL_4X_2 and MnL_2X_2; X = halide, L = picoline, o-phenanthroline or triphenylphosphine oxide) are easily simulated with third-order perturbation theory using the zfs values as fitting parameters. However, a few of these compounds, those with intense transitions at g = 2, show significant deviations from their simulations. These deviations will be interpreted in terms of the large amount of dispersion present in the spectra. Inorganic complexes can serve as models for the interpretation of EPR spectra of manganese(II)-containing proteins. However, interpreting the protein spectra is not as straight-forward as with the inorganic complexes. We will show high-field EPR spectra of several proteins which will be interpreted using a distribution in zfs values, a technique commonly used at low fields. Supported by the Petroleum Research and Research Corporation.

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HIGH-FREQUENCY AND -FIELD EPR SPECTROSCOPY OF CR(II) ION. J. Krzystek[a] J. Telser[b], L. Pardi[a], and L.-C. Brunel[a], [a]National High Magnetic Field Laboratory, Tallahassee, FL 32310, and [b]Roosevelt University, Chicago,]IL 60605.

In our continuing effort to apply high-frequency and -field Electron Paramagnetic Resonance to spin systems hitherto considered 'EPR-silent' we have performed experiments on the Cr(II) ion. In its high-spin form, this d^4 transition metal ion is characterized by spin number S = 2. Experiments in the frequency range of 95-380 GHz and field range of 0-15 T have allowed us to record a complete set of spectra of aqueous Cr^{2+} in frozen solution. The $[Cr(H_2 0)_6]^{2+}$ ion is characterized by an axial zero field splitting tensor with the parameter D = -2.2 cm^{-1}. The relevance of current results to EPR spectroscopy of other high-spin, non-Kramers transition metal ions will be discussed.

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MODELLING EPR SPECTRA DUE TO HIGH SPIN TRANSITION METAL IONS IN GLASSES, John R Pilbrow. Department of Physics, Monash University, Clayton, Victoria, Australia 3168

Modest concentrations of transition metal ions or rare earth ions are found in commercial glasses and are, therefore, natural spin probes for EPR investigations. They may also be incorporated in synthetic glasses. As part of an investigation of spin-lattice relaxation of transition metal ions in glasses it became apparent that the time had come to review strategies for computer simulation of CW-EPR spectra and also for Echo Detected EPR. Important progress in simulating EPR spectra due to glasses has been made in the past, based, however, on distributions of parameters for a single spin Hamiltonian. Past modelling in glasses is frequently characterised by large linewidths[1] and essentially unrealistic high symmetry spin Hamiltonians with large distributions in the spin Hamiltonian parameters[2]. The difficulty is that such an approach does not properly account for the random site-to-site variation which means the sites most likely have C point symmetry and the individual tensors and interaction matrices will not share the same principal axes within a given site and the orientations themselves need to be considered as random variables. It is well recognised that the problems are formidable when dealing with rare earth ions such as Eu^{2+} and Gd^{3+} where S = 7/2. For example, the g = 6 feature for such ions is correctly associated with a particular turning point in the field versus orientation plot. 3 EPR modelling of high spin transition and rare earth ions in glasses will be reviewed and some possible directions for overcon-dng deficiencies in current practice suggested.

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HIGH FIELD EPR OF PHOTOSYNTHETIC REACTION CENTERS. Peter J. Bratt,[3] <u>Alexander</u> erhofer,[a] J. Krzystek,[b] Martin Rohrer,[b] and Louis-Claude Brunei[b], (a)Department of Chemistry, The University of Florida, Gainesville, FL 3261 1; (b) The National High Magnetic Field Laboratory, 1800 E. Paul Dirac Dr., Tallahassee, FL 32310.

We present the full temperature dependence of the g-factor anisotropy of the primary donor radical cafion of plant photosystem I (PS I) and bacterial photosynthetic reaction centers (RC) of ***Rhodobacter sphaeroides*** R26. Both RC types are well resolved at a frequency of 330 GHz and 11.7 Tesla. In comparison to monomeric Chlorophyll (Chl) a and Bacteriochlorophyll (BChl) ***a in vitro*** the g-matrix is more isotropic. The temperature dependence reveals a trend to a more isotropic g-matrix at higher temperatures for PS I while for the bacterial RCs only very little change is observed. The results will be discussed in terms of the electronic structure of the dimer cation.

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PULSED ENDOR AT 140 GHz AND ITS APPLICATION TO THE RNR TYROSYL RADICAL FROM E. COLL <u>M. Bennati</u>. C. T. Farrar, G. J. Gerfen, J. Bryant, P. Riggs-Gelasco, J. Stubbe and R. G. Griffin. Francis Bitter Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

A new spectrometer for pulsed ENDOR at 140 GHz is described. The probe consists of two high-quality resonance circuits for microwave and radio frequencies. Using a cylindrical resonator adapted to allow for RF penetration and IMPATT diodes for power amplification we achieved n/2 microwave pulses of ~ 100 ns. The RF circuit is based on a conventional solid state NMR LC-circuit, but we use variable capacitors to tune and match across the desired frequency scan range. Measured RF n pulse lengths are 7-10 *u*s. The performance of the spectrometer is demonstrated with the ENDOR spectra of the stable tyrosyl radical from the enzyme Ribonucleotide Reductase (RNR) from ***E. Coli.*** The EPR spectrum of the tyrosyl radical displays substantial g-anisotropy at 5 Tesla and permits orientation selective ENDOR. H-Davies-ENDOR was performed at different positions of the EPR line at 10 K and leads to high-resolution spectra especially in the small coupling region (+/- 5 MHz). Comparison with data recorded on the protein in modified buffers and Davies ENDOR simulations permit the unambiguous assignment of the different hyperfine couplings.

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CW AND PULSED EPR STUDIES OF THE BINUCLEAR FE(III)ZN(II) AND FE (III) MN (II) CENTRES IN RED KIDNEY BEAN AND SWEET POTATO PURPLE ACID PHOSPHATASE <u>G.R. Hanson</u>. C.L. Boutchard[1], L. Carrington[2], C.J. Noble[1], S.E. Hamilton[2], J. de Jersey[2], L.R. Gahan[3], J.R. Pilbrow[4], Centre for Magnetic Resonance,[2] Dept. of Biochemistry, and [3]Dept. of Chemistry, The

University of Queensland, Brisbane, QLD Australia, 4072.[4]Dept. Physics, Monash University, Clayton, VIC Australia, 3168.

The refined X-ray crystal structure [1] of the red kidney bean enzyme (RKBPAP) reveals a binuclear Fe-Zn centre in which the Fe and Zn are bridged by a monodentate carboxylate (Aspl64). The ligands to the ferric ion Tyrl67, His325 and Aspl35, His 286, His 323 and Asn201 are ligands to the zinc ion. The three remaining ligands were suggested to arise from a hydroxide ion ligated to the Fe(III), a water molecule coordinated to Zn(II) and a bridging hydroxide ion. Continuous wave and pulsed EPR studies of RKBPAP indicate that these sites are ionizable as the pH dependence of the EPR spectrum of RKBPAP is quite complicated, suggesting the presence of multiple species. Computer simulation of the spectra at pH 4.9 reveals two species with D and E/D values of -2.5 cm"^{1}, 0.145 and -.95 cm^{1}, 0.23 respectively. Two and three pulse ESEEM and HYSCORE spectra of the RKBPAP-phosphate complex at 1.9 K confirm histidine ligation to the FE(III) and secondly, the presence of phosphate close to the binuclear FcZn centre. CW EPR spectra of the sweet potato enzyme at 2.1 and 4.2 K reveals resonances arising from a mononuclear Fe(III)centre which is different from that found in RKBPAP. At higher temperatures (10-35K) the EPR spectra reveal resonances consisunt with a weakly antiferromapetically coupled binuclear Fe(III)-Mn(II) centre.

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STUDIES OF LEPOXYGENASE AND OTHER METALLOPROTEINS BY EMR AT 94 GHZ,

Betty J. Gaffney[1]. Harris J. Silverstone[2], Guenter G. Maresch[3] and Ralph T. Weber[4]
National High Magnetic Field Lab, Florida State University, Tallahassee, [2]Chemistry Department, Johns Hopkins University, Baltimore MD, [3]Bruker Analytische Messtechnik, Germany, [4]Bruker Instruments, USA

The iron center in lipoxygenase is unusually stable in air in the ferrous state and this center cycles between ferrous and ferric during the catalytic cycle. The iron center appears deeply buried within the structure of this 94 kDa protein, yet the enzymatic reaction (oxidation of linoleic or related fatty acids) proceeds at near diffusion-controlled rates. EPR studies at 94 GHz (W-band) and 9.2 GHz (X-band) address the interaction of substrates and inhibitors with the lipoxygenase iron center. Ligands of interest include oxygen (apparent substrate), nitric oxide (inhibitor) and reducing inhibitors. Quantitative evaluation of the spectra includes simulation of S>l/2 spin systems and comparison with reference proteins such as transferrin.

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MM-WAVE EPR OF METALLO-PROTEINS,

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Although the application of conventional EPR methods (CW-EPR at frequencies up to Q-band) in the study of metalloproteins still forms an essential element in the elucidation of the electronic structure of these systems, in recent years the interest in High-Frequency EPR has grown considerably. Since EPR spectrometers up to 95 GHz are now commercially available one can say that the field is developing into a mature methodology. The advantages of high frequency EPR, in particular in the study of high spin systems, do however not stop at 95 GHz. Therefore, the developments are continuing towards higher and higher frequencies.

In this contribution we discuss the development of a multi frequency EPR facility up to 1000 GHz optimized for the study of high spin systems in biochemistry. The facility includes setups based on conventional waveguide technology as well as quasi-optical versions to cover the high frequency range. A field range from 0-15 T can be covered within a few minutes using Bitter magnets.

Several preliminary experiments will be discussed: As a model for biological high-spin systems a sample of metMyoglobin was measured at 130,190, and 285 GHz. The g=5.9 perpendicular line from the S=5/2 ferric heme was detected and its linewidth was compared to data previously obtained at Q-, X-, S- and L-band. The data are fitted in terms of g-strain and D-strain contributions. As a model for biological integer spin systems the S=l signal of Ni(II) in Zn(ethylenediamine)$_{2}$(NO$_{3}$)$_{2}$ was studied at 35 GHz and 130 GHz. An unusual power dependence of the 'double-quantum' line was detected and investigated. In addition the first high frequency EPR experiments on Iron in rubredoxin and a-Alumina are presented. These experiments demonstrate a spectacular simplification of the EPR for S=5/2 systems with intermediate D (0.3-0.5 cm^{-1})

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CONFIRMATIONAL ANALYSIS OF PESTICIDES WITH STACKED GC DETECTORS, Rollen J. Anderson. Jessie Butler, Fausto Pigozzo, C.E. Instruments 2215 Grand Avenue Parkway Austin, TX 78728

Pesticides are important for reducing crop losses due to weeds, insects, and diseases. A wide spectrum of chemicals is utilized requiring the implementation of exhaustive analytical methods while attempting to increase sample throughout. The current suggested multi-residue method (MRM) involves extraction with acetonitrile, partitioning in methylene chloride, concentration, and solvent exchange to hexane. Nitrogen, phosphorous, and sulfur containing pesticides are analyzed on a Nitrogen Phosphorous Detector (NPD) or Flame Photometric Detector (FPD) and chlorinated pesticides on an HALL Electrolytic Conductivity Detector or Electron Capture Detector (ECD). The ECD is a semi-specific detector, responding to compounds with a high electron affinity. Even non-chlorinated analytes like phthalates will respond on the ECD. Since the ECD is a nondestructive detector, the detector may be used in series with another dissimilar detector for confirmational analysis. Combining the ECD with an NPD and FPD gives greater flexibility to analyze for compounds on the Pesticide Analytical Methods (PAM) target list while simultaneously confirming the analysis. The author will address the performance of the stacked ECD/FPD and ECD/NPD for the MRM in various sample matrices proving linearity and sensitivity for several pesticides.

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GREEN CHEMISTRY FOR THE 21ST CENTURY. F.G. Baglin. R. Jones, L. Tingley and T. Palmer, Materials Technology Limited, Reno Nv. and The Dept. of Chemistry, University of Nevada, Reno, Nevada, 89557

Materials Technology Limited applies green chemistry to manufacturing, e.g., shingles, wallboard, friction products and circuit boards. Industrial wastes are primary feedstocks. Our principal technology uses coal-combustion wastes, portland cement and industrial calcium wastes (i.e. acetylene-manufacturing waste calcium hydroxide). Chemically bonded ceramics (CBC) are formed and treated with supercritical carbon dioxide from generating plant flu gas. The calcium/cement components react into calcium carbonates. Carbon is fixed in the final product. Results are measured by mechanical tests and scanning electron microscopy. Various waste fibers may be used as reinforcement ;often, these react in the high pH of cement pore water. Carbonation, however, lowers the pH to about 7, preventing degradation. We have dissolved surface-doped latex into the CBC matrix. We will show various samples at the meeting.

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GLOVEBOX DECONTAMINATION TECHNOLOGY COMPARISON by Michael E. Cournoyer, Reanna Aguino, Doris Quintana, NMT-1, LANL, MS G740, Los Alamos, NM 87545-0000.

Reconfiguration of the CMR Building and TA-55 for mission requirements will require the disposal or recycle of 200-300 gloveboxes or open front hoods, these gloveboxes and open front hoods must be decontaminated to meet discharge limits for LLW. During the course of this project 8 gloveboxes distributed between TA-55 and CMR will be decontaminated for disposal or recycle into other programs. Gloveboxes and open front hoods at CMR have been painted. One of the deliverables on this project is to identify the best method for stripping the paint from large numbers of gloveboxes. The four methods being tested are the following: electropolishing, electroplating paint stripping, dry ice pellets and high pressure water technology. The advantages and disadvantages for each technology will be outlined. Last, cost comparisons between the technologies will be presented.

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ENHANCED METHOD DEVELOPMENT USING SOLID PROBE MASS SPECTROMETRY AND GC-MS/MS, James B. Edwards, John D. Ragsdale III, and Steven T. Fannin, Finnigan Corporation, 2215 Grand Avenue Parkway, Austin, TX 78728

Analytical testing using GC-MS can be roughly divided into three phases: method development, sample analysis, and quality control monitoring. Once a method has been developed that is appropriate for the testing requirements, it is often not re-examined unless the testing requirements change or a problem develops. In either case, it is desired that the method development phase proceed quickly and efficiently, to leave more time for the analysis of samples and subsequent data processing, review, and documentation.

As the capabilities of benchtop GC-MS systems have grown, so too has the potential for longer method development cycles. The development of appropriate analytical conditions, for experiments such as MS/MS, can sometimes involve long GC analyses before the results of new conditions can be examined. This can prolong the process of method development to an unproductive level.

One solution to this situation is the use of Solid Probe Mass Spectrometry as an adjunct to GC-MS analysis. Solid probe analyses are typically completed on the order of 1 to 5 minutes, and new solid probe systems offer the capabilities of probe programming, to replace some level of the separation capabilities of GC. An enhanced method development cycle is described in which conditions are rapidly developed and explored using solid probe analysis and then conditions moved to a GC-MS analysis technique. These techniques can then be used to either shorten method development time, or allow for more method optimization to take place in the same amount of time as required using only GC-MS techniques.

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ANALYTICAL TANDEM MASS SPECFROMETRY WITH A BENCHTOP EXTERNAL SOURCE ION TRAP MASS SPECTROMETER FOR THE ANALYSIS OF THC AND METABOLITES IN BLOOD, Steven T. Fannin, Wilmo Andollo, James M. Stephens, John D. Ragsdale III, Finnigan Corporation 2215 Grand Avenue Parkway, Austin, TX 78728

Tandem Mass Spectrometry (MS/MS) is a powerful analytical technique for the analysis of compounds in complex matrices. MS/MS enhances selectivity by greatly reducing the chemical background, which provides improved S/N (lower detection limits). Further, MS/MS enhances confirmation of identification, providing full product ion spectra of target compounds.

The work performed in our laboratory characterizes and demonstrates MS/MS with electron and chemical ionization techniques on an external source ion trap mass spectrometer (the GCQ Plus, Finnigan, Austin TX) for the analysis of A^9THC and its principal metabolites in blood. For the Electron Capture-Negative Ion Chemical Ionization (EC-NICI) mode perfluorinated derivatizing reagents were used producing highly electronegative derivatives. In this report, negative ion MS/MS data are presented showing full product ion spectra of THC and carboxy-THC, thereby providing confirmation at low detection limits in blood samples. Detection limits and linearity are presented, illustrating the analytical utility of MS\MS for the THC analysis in complex physiological matrices.

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APPLYING ADVANCED SIMULTANEOUS THERMAL ANALYSIS TECHNIQUES FOR MORE EFFECTIVE MATERIALS CHARACTERIZATION, B. Fidler. J.B. Henderson, E. Post, NETZSCH Instruments, Inc., 37 Industrial Blvd. - Section D, Paoli, PA 19301

Thermal analysis is a series of techniques that study the effect of temperature on material properties. Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), and Thermogravimetry (TG) have proven themselves particularly suitable for research and quality control applications in industrial and academic environments. A sample can be characterized more completely if the TG and DTA/DSC results can be assigned to it exactly. This paper vall closely examine the importance of such parameters as decomposition temperatures, temperature stability, and oxidative stability as they impact, for example, decomposition and aging processes, outgassing, and desorption behavior and other characteristics related to material performance.

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HIGH SENSITIVITY EVOLVED GAS ANALYSIS VIA COUPLED THERMAL ANALYSIS - SPECTROSCOPIC TECHNIQUES, B. Fidler. J.B. Henderson, E. Post, NETZSCH Instruments, Inc., 37 Industrial Blvd. - Section D, Paoli, PA 19301

Evolved Gas Analysis (EGA) is becoming increasingly important in connection with thermoanalytical methods such as thermogravimetry (TG) and simultaneous thermal analysis (TG-DTA/DSC). Practical applications of evolved gas analysis include analysis of decomposition and aging processes, additives, residues, outgassing, desorption behavior and more. The most useful coupling methods in thermal analysis are Fourier Transform Infrared Spectroscopy (FTIR) and Mass Spectrometry (MS). This poster will compare and contrast results from various thermoanalytical experiments conducted under a series of defined pressures and gas atmospheres via TG-DSC/DTA closely coupled with both FTIR and MS.

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SPE CLEANUP AND LC-UV DETECTION OF EPHEDRINE ALKALOIDS IN HERBAL PRODUCTS. Jeffrey A. Hurlbut & Justin R. Carr of MSCD- Emma P, Singleton, Kent C. Faul, Mark R. Madson, Joseph M. Storey, & Terri L. Thomas of FDA; Chemistry Department, Metropolitan State College of Denver, P.O. Box 173362, Denver, Colorado 80217

A solid phase extraction (SPE) cleanup and a liquid chromatography method with UV detection is presented for the analysis of up to seven different ephedrine alkaloids in herbal products. The procedure consists of extracting the alkaloids from the herbal product with acidified buffer, isolating the alkaloids on a propyl sulfonic acid SPE column, elution off of the column with a high ionic strength buffer, and LC separation with detection at 255 nm. LC separation is performed by isocratic elution on a YMC phenyl column using 0.1 M sodium acetate - acetic acid (pH = 4. 8) mobile phase containing triethylamine and 2 % acetonitrile. All of the ephedrine alkaloids are completely separated in a 15 min run. The average recovery of five common alkaloids from three different spiked matrices is 90 % with an average RSD of 4.4 % for spikes for each alkaloid between 0.5 and 16 mg/g. The average recovery of ephedrine and pseudoephedrine from six different herbal products is 97 % based on label claims. The results of ruggedness testing as well as the results from a second laboratory validation of the procedure are also presented.

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SIMULTANEOUS DETERMINATION OF RESIDUES OF CHLORAMPHENICOL, FLORFENICOL AND THIAMPHENICOL IN MILK BY GC/ECD. Allen P. Pfenning. Mark R. Madson, Jose E. Roybal, Sherri B. Turnipseed and Steve A. Gonzales, Food and Drug Administration, Animal Drugs Research Center, Denver, CO 80225

A GC method is described for determining residues of chloramphenicol (CAP), florfenicol (FF) and thiamphenicol (TAP) in raw milk. CAP, a broad-spectrum antibiotic, has effective antibacterial properties as well as serious toxic effects on humans. More recently, TAP and FF have been developed and found to be effective antibacterials. The raw milk is extracted with acetonitrile, centrifuged, evaporated, reconstituted in water and passed through a C_{18} SPE column, which is eluted with 60% methanol, the eluate evaporated and derivatized with Sylon BFT. Toluene is then added directly to the sample, followed by the addition of water. After centrifugation the organic layer is carefully removed and the analytes determined by GC with electron capture detection (ECD). Milk was fortified at 5,10, 20, 40 and 80 ng/mL (X = IO ng/mL) of each analyte. Overall recoveries were 92,100, and

104% for CAP, FF and TAP respectively. Overall inter-assay (between day) variability was 6.1, 6.7 and 6.0% for CAP, FF and TAP respectively.

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GEL PERMEATION CHROMATOGRAPHY AND ^{13}C and ^{93}Nb NMR OF SOL-GEL ALKOXIDE PRECURSERS TO TITANATE-AND NIOBATE-DIELECTRIC MATERIALS. J. Qi, J. Huang, and J.J. Fitzgerald, Department of Chemistry, South Dakota State University, Brookings, SD 57007

Gel permeation chromatography (GPC) studies of the solution chemistry of polymeric metal alkoxide sol-gel precursors to electronic materials have been studied using Phenogel 500 A columns with either 2-methoxyethanol (MOE) or ethanol (ET) as the mobile phase. Monometallic, bimetallic and trimetallic alkoxide precursors examined include: Pb(OCH$_2$CH$_2$OCH$_3$)$_2$, Ti(OCH2CH$_2$OCH$_3$)$_2$, lithium niobate-ET, lead titanate-MOE, barium titanate-MOE, magnesium niobate-MOE, and lead magnesium niobate (PMN)-MOE. The alkoxide precursor solutions are shown to contain monomeric, dimeric, trimeric, and oligomer species of relatively low molecular weights. GPC studies (followed by AA of collected fractions) and solution ^{13}C and ^{93}Nb NMR have been used to examine the composition and structure of solution species in many of these systems. For example, LN-ET solutions, containing linear polymeric species based on single crystal X-ray diffraction studies, have been examined at different Nb/Li molar ratios and Nb^{5+} concentrations using both GPC and solution ^{13}C and ^{93}Nb NMR. These investigations have demonstrated the utility of these methods to advance our understanding of the solution chemistry of monometallic and dimetallic Ti^{4+} -alkoxide and Nb^{5+}-alkoxide systems, thereby providing direction for future studies of more complex trimetallic alkoxides such as PMN-MOE.

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PHOTOCHEMICAL REACTION: APPLICATION OF LIQUID CHROMATOGRAPHIC POST-COLUMN PHOTOLYSIS TO THE ENHANCED FLUORIMETRIC DETECTION OF AVERMECTINS. Jose E. Roybal. Steve A. Gonzales, Allen P. Pfenning and Sherri B. Turnipseed, Food and Drug Administration, Animal Drugs Research Center, Denver, CO 80225

A liquid chromatographic system with post-column photochemical derivatization for the detection of several Avermectins is described. Avermectins are classified as anthelmintics (de-wormers). They are gaining in popularity as antiparasitic veterinary drugs in animal husbandry, LC methods designed to monitor or analyze for these drugs have been either by UV (245 nm) or Fluorescence detection after precolumn chemical derivatization. Optimization parameters for the separation and fluorescence response of Eprinomectin, Doramectin and Ivermectin using photochemical derivation are presented. Incorporation of a photochemical reactor, 254nm, (Beam Booster) post-column permitted fluorescence detection without precolumn chemical derivatization and extensive cleanup procedures of reagent by-products. Fluorescence detection is accomplished at an excitation wavelength (EX):365 nm and an emission wavelength (EM): 470 nm (440nm cutoff filter). Evaluation of a variety of reverse phase columns, mobile phases and photochemical reaction parameters (coil lengths, pH, exposure times, mobile phases, etc.) are discussed.

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THE DETERMINATION OF IODIDE IN GROUND WATER AND SOIL BY ION CHROMATOGRAPHY, H L. Tucker. R. W. Flack, Lockheed Martin Energy Systems Inc., Analytical Services Organization, Box 2009, MS 8189, Oak Ridge, TN 37831-8189, USA

The Upper East Fork Poplar Creek (UEFPC) and portions of the Y-12 Plant area have been exposed to actual and potential releases from the Y-12 Plant operations since the mid-1950's. The Y-12 Plant has been actively engaged in the development and manufacture of classified materials throughout its history. Comprehensive analyses of selected soils and waters from the UEFPC and selected Plant areas will allow an assessment of classified chemicals employed at the Y-12 Plant without specification of them. A rapid Ion Chromatographic method, with isocratic separation and micromembrane suppression is discussed within this paper for the analysis of iodide in soils, and floodplain ground waters. This developmental method, which uses Dionex Corporation's new AS-11, 4-mm colunm, will be used for future routine iodide analysis.

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ATMOSPHERIC PRESSURE CHEMICAL IONIZATION LC/MS ANALYSIS OF IVERMECTIN RESIDUES Sherri B. Turnipseed, Jose E. Roybal, Heidi S. Rupp, Steve A. Gonzales, Allen P. Pfenning, Food and Drug Administration, Denver, CO 80225

Avermectins are a class of antibiotic used for the treatment of parasitic diseases in agriculture and possibly aquaculture species. Avermectin residues in edible tissues and milk are usually monitored by analysis with liquid chromatography using fluorescence detection after dehydration of the molecule to forin an aromatic fluorescent moiety. Mass spectral analysis is the prefeffed technique for conformation of suspect residues due to its inherent specificity and sensitivity. Several avermectin residues have been successfully confirmed in food matrices using atmospheric pressure chemical ionization (APCI) LC/MS with negative ion detection. Various factors such as "in source" dissociation, nebulizer temperature, and chromatographic conditions have been optimized. Three to four ions are chosen for selected ion monitoring for each drug residue. The technique has been used for the confimiation of ivermectin and doramectin in salmon tissue at residue (20-40 ppb) levels, and a multiresidue conformation for four avermectins in milk has also been explored. APCI LC/MS can also be used to evaluate the feasibility of detecting avermectins using a post-column photochemical reaction rather than the traditional chemical dehydration.

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DEVELOPMENT OF AN ANALYSIS SYSTEM FOR LOW-RANK COAL USING LASER-INDUCED BREAKDOWN SPECTROSCOPY. Fiona J. Wallis. Bruce L. Chadwick, and Richard J.S. Morrison, CRC New Technologies for Power Generation from Low-Rank Coal, 8/677, Springvale Rd, Mulgrave, Victoria 3170 AUSTRALIA.

The efficiency of coal power generation can be adversely affected by variation in the chemical composition of the coal. Specifically, variation in the concentrations of the inorganic ash-forming components of coal may result in reduced thermal efficiency and service time of the station boilers. Thus, determining the inorganic content of the coal, prior to its utilisation, would allow the implementation of strategies to minimise such problems. Ideally, a time-efficient technique able to be deployed at the coal mine face would be used for such analysis. Such a technique is laser-induced breakdown spectroscopy (LIBS). A laboratory-based LIBS instrument has been developed utilising the fundamental wavelength of a Nd:YAG laser for plasma generation and a spectrometer equipped with an ICCD for subsequent detection of elemental emission. Recent studies undertaken with this instrument have identified all the major inorganic components of Victorian brown coal; including Na, Fe, Ca, Mg, Si and Al. Time-gating of the fluorescence emission was used in these experiments to optimise the detection capabilities of the technique. Initial studies also demonstrate the ability of this instrument to perform quantitative analyses of low-rank coal.

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USE OF NMR TO CHARACTERIZE INHOMOGENEOUS SOLIDS. Naira M. da Silva.' Maria Ines B. Tavares' and E.O. Stejskal[2], Institute de Macromoleculas Prof. Eloisa Mano, Universidade Federal do Rio de Janeiro, Brazil, CEP21945-970. department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204

One of the goals of polymer blending is the creation of miscible blends. The ability to assess accurately the degree of miscibility thus is of great importance to the polymer scientist. This study will use different NMR methods for the characterization of phase separation. In addition to the use of carbon-resolved proton T1Q to characterize spin diffusion between phases with intrinsically different relaxation rates, two-dimensional wideline separation (WISE) may be used to create artificial population differences between phases and enhance the visibility of cross-relaxation between them. The samples to observed are blends of asphalt and ethylene-propylene-diene rubber (EPDM)/atactic polypropylene (aPP), a typical solid-liquid material. The two NMR methods demonstrate that with different time scales involved they see phase separation differently.

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THE INFLUENCE OF SURFACE ROUGHNESS ON ORIENTATION MEASUREMENTS OF ULTRA-THIN FILMS. Garth J. Simpson, Kathy L. Rowlen, Department of Chemistry, University of Colorado at Boulder, Boulder, CO 80309-0215.

Formation of mono- and multi-layer surface films by self-assembly or by Langmuir-Blodgett deposition allows for development of highly oriented films with molecular level control over their physical and optical properties. Consequently, mono- and multi-layer films have been proposed as efficient materials for applications such as nonlinear optics, piezoelectrics, and pyroelectrics. A fundamental issue often neglected in characterizing such films is the role of surface roughness in influencing the macroscopic molecular orientation. In order to quantify roughness effects in the most common orientation measurements made on such films (linear dichroism, second harmonic generation, and sum-frequency generation), a model has been proposed and tested that utilizes fractal descriptions of rough surfaces. Based on calculations from the model, we find that neglect of roughness can lead to large errors (easily in excess of 20o for a typical mono-layer film) in the interpretation of spectroscopic orientation measurements on commonly used substrates such as fused silica.

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SURFACE REACTIVITY OF CF2 RADICALS MEASURED USING LASER-INDUCED FLUORESCENCE AND CHF3 PLASMA MOLECULAR BEAMS. Nathan E. Capps, Neil M. Mackie, and Ellen R. Fisher, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872.

Fluorocarbon discharges have been widely studied because of their ability to promote etching of a variety of substrates and to deposit a wide range of fluorinated polymer films. CF and CF2 radicals are important species in fluorocarbon plasmas and are postulated to contribute both to plasma polymerization and to selective etching of Si and Si02. The surface reactivity of CF2 radicals during the plasma processing of a variety of substrates using the Imaging of Radicals Interacting with Surfaces (IRIS) technique is reported. IRIS combines spatially-resolved laser-induced fluorescence with molecular beam and plasma techniques. The molecular beam source is 100% CHF3 plasma, which is widely used for cleaning applications in industry. This study investigated the surface reactivity of CF2 on silicon, silicon dioxide, silicon nitride, 304 stainless steel, and System 8 Photoresist at ambient temperatures as well as on a heated Si substrate. Preliminary results on CF radicals will also be discussed.

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AZO-DYE CHEMISTRY ON SILICON AND QUARTZ SUBSTRATES. Salying Wong, Garth Simpson, Kathy Rowlen, Department of Chemistry, University of Colorado at Boulder, Boulder, CO 80309-0215.

Azo-dye chemistry has potential applications in optic and optoelectronic fields. These dyes can be reacted with chlorophenyl silanes and alkylbromo silanes to form layers on silicon and quartz surfaces. Depending on the functionality of the terminus of the dye, one could form monolayers or multilayers. FTIR, ARPAS (angle resolved photoacoustic spectroscopy), elipsometry and contact angle measurements were taken to confirm the reaction and to characterize the molecular orientation of the molecules and the thickness of the layers.

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VELOCITY DISTRIBUTIONS OF RADICALS IN PLASMA MOLECULAR BEAMS. Patnck R. McCurdy and Ellen R. Fisher; Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872.

Low-temperature plasmas are used extensively to etch and deposit a wide variety of materials. The underlying chemical mechanisms for these processes remain unclear, however. To fully understand the chemistry of low-temperature plasmas, knowledge of the energy partitioning between species must be acquired. Energetics for plasma radicals are often difficult to obtain. Using spatially- and temporally-resolved laser-induced fluorescence (LIF), we have measured the velocity distributions of radicals in effusive plasma molecular beams as a function of applied rf plasma power. Monte Carlo simulation methods are used to model spatial profiles of radicals in the molecular beam. The model assumes a Gaussian distribution and calculates time-dependent changes in the profiles using Maxwell-Boltzmann distributions. Results for three radicals will bediscussed: NH2 radicals in an NH3 plasma molecular beam; SiJ radicals from a SiH4 plasma; and OH radicals from a TEOS/02 plasma. For NH2 and OH, translational temperature increases with rf power; while for SiH, there is little dependence on rf power. Additional data on velocity profiles for NH2 radicals scattered from a 300 K Si substrate will be presented. Mechanistic implications will be discussed.

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DYE COVERAGE EFFECTS ON NANOCRYSTALLINE TITANIUM DIOXIDE SOLAR CELLS.

Akiko Fillinger and Bruce A. Parkinson, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872.

Nanocrystalline TiO2 has been a popular subject in photoelectrochemistry since Michael Gratzel reported high efficiencies for sensitized porous nanocrystalline TiO2 for a next generation solar cell material (Nature 1991, 353, 737-735). Despite intense investigation, there are still many fundamental questions left concerning the nanoporous Ti02 photochemical cells. One such question is the nature of the dye-semiconductor interface. How are dye molecules attached to the TiO2 surface? What is the binding geometry of the dye molecules? Does the binding geometry have an effect on photon-to-electricity conversion efficiency? In our research group this aspect has been studied by examining dye coverage effects on the photoresponse of Ti02 film, sensitizing with the most commonly used dye, cis-di(thiocyanato)-bis(2,2'-bipyridine-4,4'-dicarboxylate)ruthenium(N3). Studies of the action spectra showed that the enhancement of photoresponse by an increased dye coverage is greater in the longer wavelength region (>550nm) than in the shorter wavelength region considering the lower absorbance of N3 dye in the longer wavelength region. One of the possible explanations for this phenomenon is dye aggregation (which may cause red shifting) in the process of adsorbing onto Ti02 film. Also, the kinetics for dye adsorption and desorption were measured. This information provides clues to the binding of the dye molecules to the Ti02 surface.

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SOLVATION DYNAMICS OF WATER AT THE SURFACE OF ZIRCONIUM OXIDE NANOPARTICLES.

Debi Pant and Nancy E. Levinger, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872.

Time-resolved fluorescence-upconversion spectroscopy has been used to study the polar solvation dynamics of water at the surface of zirconium oxide (Zr02) nanoparticles. The interfacial solvent response displays two subpicosecond diffusive components with the same time constants as observed for the bulk solution. However, the relative amplitudes for the individual relaxation components are significantly different leading to a faster average solvation response for molecules at the Zr02 surface. There is no evidence for relaxation occurring on a longer time scale as might be expected of solvent strongly adsorbed to the nanoparticle surface. Furthermore, the overall Stoke's shift of the absorbed dye's fluorescence spectrum is considerably smaller than the dye in bulk solvent, which implies that the solvation energy is smaller for the dye adsorbed to the Zr02 surface. We attribute the subpicosecond solvent response to the net orientation of water molecules at the nanoparticle surface. These measurements have implications for the electron injection into semiconductors.

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POLAR SOLVATION DYNAMICS NEAR THE LIQUID-LIQUID INTERFACE OF AEROSOL-OT REVERSE MICELLES.

Ruth E. Riter, Dale M. Willard, Eric P. Undiks, Joel R. Kimmel, and Nancy B. Levinger, Department of Chemistry, Colorado State University, Fort Collins, CO 80523 -1872.

Chemical processes such as electron and proton transfer are greatly influenced by the surrounding milieu. Much work has been done in the last 10 years to investigate the solvent effect on these primary reactions. However, the solvent properties at and near interfaces are vastly different than in bulk. To investigate solvation dynamics at liquid-liquid interfaces, we have measured the solvent response of water and formamide in Aerosol-OT (AOT) reverse micelles using ultrafast, time-resolved fluorescence-upconversion spectroscopy. These experiments show that the interaction of water with the AOT head groups eliminates bulk-like water motion. As the volume of the water pool increases, water molecules become free to move, and the solvent response reveals a dynamic relaxation component on a time scale comparable to bulk water motion. Additionally, the Na+ counterion of the AOT head group is responsible for reducing a large fraction of the water motion in these environments. For formamide-AOT reverse micelles, the IR spectra indicate that the intramicellar formamide retains a large degree of hydrogen-bonding character and appears to be less perturbed than the water structure in similar-sized micelles. However, like water in these environments, the motion of formamide is nearly completely frozen. This result suggests that the restrictive nature of the micellar size plays a major role in limiting solvent movement.

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DETERMINATION OF BENZO[A]PYRENE-DNA ADDUCTS BY SOLID-MATRIX PHOSPHORESCENCE.

Ming Li and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071.

Benzo[a]pyrene (B[a]P) is involved in chemical carcinogenesis in which B[a]P covalently binds to DNA to form DNA adducts. Until now, most of the methods for the determination of B[a]P-DNA adducts are either indirect or relatively expensive. Room-temperature solid-matrix phosphorescence (RTSMP) is inexpensive and offers both sensitivity and selectivity for B[a]P-DNA adducts. In this work, DNA adducts were prepared at several different levels of modification using the diol epoxide of B[a]P. The modification levels ranged from 0.00001% to 0.005%. The quantitative aspects of determining B[a]P-DNA adducts were explored by obtaining the SMP intensities of the adducts on Whatman I PS filter paper and 30% TINO,/NaOAc powder mixture as a function of sample size and the limits of detection for the different DNA adduct samples. Both linear ranges and nonlinear ranges were obtained for SMP intensity versus sample size for a given percentage of modified DNA adduct sample. In addition, it was demonstrated that there was a linear relationship between SMP and percentage modification of DNA for the DNA adduct samples that were modified at very low levels. Currently, the best detection limit by SMP is 0.000019% modification, or I adduct per 5 million nucleotides.

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QUANTIFYING HOMOCYSTEINE AND OTHER THIOLS IN PLASMA WITH DERIVATIZATION FOLLOWED BY CAPILLARY ELECTROPHORESIS AND LASER-INDUCED FLUORESCENCE.

Christopher J. Smith, Shuenae A. Smith, Daphne B. Moffett, Pabicia W. Mueller, James Grainger and Donald G. Patterson, Jr., Centers for Disease Control and Prevention, 4770 Buford Highway, MS F-17, Atlanta, GA 30341

Elevated homocysteine (HCYE) levels are an independent risk factor for coronary artery disease. Changes in HCYE levels may arise from dietary modification, vitamin supplements, or the administration of folic acid. To track changes in HCYE levels, several methods have been recently developed. We present a new method which determines total plasma HCYE. After the protein-bound HCYE is reduced to a free form, the total HCYE is dedvatized with a fluorogenic reagent. Separation of the dedvatized plasma is performed using capillary zone electrophoresis. With a confocal optic detector, fluorescence excitabon by a helium/cadmium laser at 325 nm induces analyte emission near 530 nm. We present results using our method, and compare with a mufti-laboratory study using a HPLC method.

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STUDIES OF GROUNDWATER MIGRATION USING CAPILLARY ELECTROPHORESIS/LASER-INDUCED FLUORESCENCE DETECTION.

John W. Farley (1), Andrew H. Grange, Patrick L. Ferguson, William C. Brumley (2), and Joseph R. Donnelly (3). (1) Department of Physics, University of Nevada-Us Vegas, Us Vegas, NV 89154 (2) U.S. EPA, NERL, CRD-LV, Us Vegas, NV 89193-3478; (3) Lockheed-Martin Services Group, Las Vegas, NV.

Capillary electrophoresis (CE) has been applied to the determination of ground water migration based on laser-induced fluorescence (LIF) detection. Detection limits of injected dye in the low ppt ranges have been accomplished with both a spectrofluorometer and with CE/LIF based on the Ar ion laser. The real world problem was the determination of ground water migration between adjacent RCRA and Superfund sites. Fluorescent dyes were injected into wells and were discovered in monitoring wells by extracting pads that adsorbed the dye. The methodology based on CE/LIF exhibits increased specificity over existing methodology due to the separation and unique migration time of the dye (fluorescein). Additional studies were aimed at achieving sub-ppt levels in the water directly using solid-phase extraction and field-amplified injection techniques. We achieved sensitivities of 300 parts per quadrillion.

*This work was performed while A.H.G. held a National Research Council/CRD-LV Senior Research Associateship. NOTICE: The U.S. Environmental Protection Agency (EPA), through the Office of Research and

Development (ORD), prepared this abstract for a proposed oral presentation. It does not necessarily reflect the views of EPA or ORD.

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CHARACTERIZING SINGLE FLUORESCENT MOLECULES IN MICROCAPILLARIES BY THEIR ELECTROPHORETIC MOBILITIES. Alan Van Orden and Richard A. Keller, Chemical Science and Technology Division, CST-1, MS M888, Los Alamos National Laboratory, Los Alamos, NM 87545.

The ability to sequentially detect single fluorescent molecules in solution as they flow through the focal volume of an excitation laser beam represents an important new development in analytical chemistry, with applications in the biomedical sciences that include DNA sequencing, DNA fingerprinting, hybridization analysis, and single molecule identification. Single molecule techniques have great potential to significantly enhance the speed and sensitivity of these assays. However, one of the limitations to these methods is the difficulty associated with identifying different analyte species that are present in a mixture at the single molecule level, due to the small number of photons detected per molecule. This paper will describe a new technique for identifying single molecules in a mixture that takes advantage of the different electrophoretic mobilities of each analyte. We have used fluorescence correlation spectroscopy (FCS) to measure the average transit times of single Rhodamine 6G (R6G) and R6G labeled DCTP molecules as they flow through a capillary electrophoresis system. From analysis of the FCS data, we obtain the electrophoretic mobility of each analyte and their relative concentrations. This technique is highly sensitive and rapid, with analysis times for solution concentrations in the low pM range of only a few seconds.

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EU(III) LUMINESCENCE FOR THE INVESTIGATION OF METAL-ION BINDING TO PLANT TISSUES, Timothy L. Danielson and Gary D. Rayson, Department of Chemistry and Biochemistry, Box 30001, MSC 3C, New Mexico State University, Las Cruces, NM 88003

The necessity of the selective removal of toxic heavy metals down to parts per billion (ppb) levels places greater derhands on the technologies of remediation. A method being considered for the remediation of heavy metals is the complexation of metal ions with plant biomasses. An objective of on-going investigations within our-laboratory is the elucidation of the fundamental chemical interactions governing the binding of metal ions to the plant-based biomaterial. Present work pertains to the binding of lanthanide and actinides to root, stem and leaf tissues of tumbleweeds. The more elaborate cell structure of these tissues will enable the elucidation of a better understanding of the interactions associated with metal uptake. The excitation spectra associated with the $^5D_0$—>$^7F_2$ luminescence transition of EU(III) has been used to examine the binding sites on the plant material. This is characterized by narrow, un-split spectral lines which are species sensitive. The application of this technique to the elucidation of metal ion binding sites on the roots, stems, and leaves of both young and mature tumbleweed plant tissues will be presented and the ramifications of those data on the potential application of higher plants for the direct remediation of lanthanide-contaminated water and soil will be discussed.

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DRYING CONDITIONS FOR THE FORMATION OF GLUCOSE AND SUCROSE GLASSES IN SOLID-MATRIX LUMINESCENCE. Kristen D. Seeley and Robert J. Hurtubise, University of Wyoming, Laramie, WY 82071

In this work, microwave drying was introduced to dry sugar solutions to form clear glasses that contained trace amounts of organic compounds. Both room-temperature fluorescence (RTF) and room-temperature phosphorescence (RTP) were obtained from the lumiphors. The analytical figures of merits of the lurniphors were compared for the glasses with samples dried by a convection oven and a microwave oven. Sucrose, with an organic lumiphor, readily formed a clear glass when the microwave oven was used to dry the sample, but a clear glass could not be formed using the convection oven. Interestingly, the heavy-atom effect was minimal when employing Nal as a heavy-atom salt and drying the sample with the microwave oven. However, a typical limit of detection for a phosphor in a sucrose glass without a heavy-atom salt was 11 pg/mg. Further investigations are being done to enhance the RTF and RTP signals in glucose and sucrose glasses using the microwave oven. Also, pyrene has been used as a probe to study the lumiphor environment in the glasses. For example, pyrene's vibronic modes were studied by varying the amount of methanol used in the preparation of the glasses.

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SOLID-PHASE MICROEXTRACTION AND SOLID-MATRIX LUMINESCENCE OF COMPLEX MIXTURES OF POLYAROMATIC HYDROCARBONS. Amanda H. Ackerman. and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, University Station Box 3838, Laramie, Wyoming 82071.

Solid-phase microextraction was used in conjunction with solid matrix luminescence for the detection of polyaromatic hydrocarbons (PAH) at the sub-ng mL"1 to pg mL"1 levels. Some of the PAH investigated were phenanthrene, 1,2-benzanthracene, benzo[a]pyrene, and coronene. The PAH were extracted onto small circular pieces of Whatman I PS filter paper from aqueous solutions. After drying the filter paper, room-temperature fluorescence and phosphorescence spectra from the adsorbed PAH were easily obtained. Whatman I PS filter paper is a hydrophobic material and can strongly attract PAH dissolved in water. The IPS paper has unique properties that permit room-temperature phosphorescence to be obtained from adsorbed PAH. Using both phosphorescence and fluorescence emission spectra, it was possible to differentiate up to four components in a mixture of PAH extracted onto filter paper.

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THE STUDY OF OXYGEN QUENCHING IN A CONTROLLED ENVIRONMENT, Patricia B Coleman, Ford Motor Company, P.O. Box 2053, Mail Drop 3083/SRL, Dearborn, MI 48121-2053

In order to study the oxygen quenching of luminescence, a controlled environment chamber was designed and built. The environment in the chamber, which fits into the fluorescence spectrometer sample compartment, is totally under computer control. A circulating water bath is used to control the temperature in the chamber, and the atmosphere can be varied depending on the experiment. The oxygen and nitrogen concentration in the chamber can be varied using mass flow controllers, or the chamber can be evacuated or pressurized. These features allow for automated testing of new luminophore polymer matrix combinations under conditions that simulated real world applications. A comparison of the performance of a typical oxygen sensor material to both the mixed gases and pressure/vacuum experiments will be presented in this talk.

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ADVANCES IN THE DESIGN AND APPLICATIONS OF SENSORS BASED ON LUMINESCENT TRANSITION METAL COMPLEXES. J. N. Demas, Wenying Xu, and Kristi Kneas. Department of Chen-fistry, University of Virginia, Charlottesville, VA 22901; B. A. DeC-traff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807.

A variety of inorganic complexes show great promise as molecular probes and luminescence-based sensors. The majority of work uses d^6 systems Ru(II), Re(l), and OS(II) with a-diimine ligands (e.g., 2,2'- bipyridine, 1,10-phenanthroline, and analogues). Central to the rational design of practical systems is an intimate understanding of the interactions between the probe or sensor molecule and the polymer based support or the target. Advances in understanding the interactions of metal complexes and polymeric supports will be discussed using examples from oxygen and pH sensors. We conclude by pointing out that these areas are still in their infancy and that the ultimate goal of a totally rational design of probes, luminescence enhancers, and polymer-supported sensors is as yet an imperfectly realized goal.

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CHARACTERIZING AVIATION FUELS AT HIGH TEMPERATURE AND PRESSURE. James R. Gord and Christopher E. Bunker, Propulsion Sciences & Advanced Concepts Division, Air Force Research Laboratory, Wright-Patterson Air Force Base OH 45433-7103; Keith D. Grinstead, Jr., Innovative Scientific Solutions, Inc., 2786 Indian Ripple Road, Dayton OH 45440-3638

In modern high-performance aircraft, the fuel serves two essential functions: It provides the energy for propulsion and acts as the coolant for on-board heat sources. As a result, the fuel is exposed to temperatures at which oxidative and pyrolytic reactions occur. The ultimate products of these reactions are gums and particles that can severely affect the safe and efficient operation of the aircraft. To improve the thermal stability of the fuel and thereby enhance the capabilities of future high-performance aircraft, a thorough understanding of the chemical and physical processes that occur in fuels at high temperatures and pressures is required. A great deal of interest has been focused on obtaining this understanding; however, many of the techniques employed to date have been applied only to the study of fuel cooled to room temperature following thermal stressing. Characterizing the fuel ***in situ*** while at temperature and pressure during stressing will no doubt yield an improved understanding of the fouling process and provide superior thermal management solutions. This paper describes progress in applying optical spectroscopic methods to the study of the chemical and physical processes that occur in aviation fuels under high-temperature, high-pressure conditions.

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ASYNCHRONOUS OPTICAL SAMPLING WITH MODELOCKED TI:SAPPHIRE LASERS. Keith D. Grinstead. Jr.. and Gregory J. Fiechtner, Innovative Scientific Solutions, Inc., 2786 Indian Ripple Road, Dayton OH 45440-3638; James R. Gord and Christopher E. Bunker, Propulsion Sciences & Advanced Concepts Division, Air Force Research Laboratory, Wright-Patterson Air Force Base OH 45433-7103

Time-resolved studies achieved through pump-probe experiments based on state-of-the-art picosecond- and femtosecond-pulsed lasers sources can reveal detailed chemical kinetics and dynamics on ultrashort time scales. While the pump-probe configuration delivers exceptional temporal and spatial resolution, it suffers from some significant limitations when practiced in a traditional delay-line-based geometry. Time-resolved data acquired with a slow-scanning delay line are subject to baseband noise, and any deviation from perfect delay-line alignment and beam collimation produces erroneous pump-probe signals arising from walk off and blooming effects. Asynchronous Optical Sampling (ASOPS), an alternative pump-probe configuration pioneered by Lytle and Laurendeau (Appl. Spectrosc. 41,1 (1987)), offers solutions to these limitations. The pump-probe delay is realized in the form of a repetitive phase walk out between two modelocked lasers operating at slightly different pulse repetition rates. The details of ASOPS implementation with modelocked Ti:sapphire lasers is discussed. -

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THE IMPACT OF FUEL ADDITIVES ON THE DETERMINATION OF WATER IN AVIATION FUEL. Matthew R. Rabe. James R. Gord, and Christopher E. Bunker, Propulsion Sciences & Advanced Concepts Division, Air Force Research Laboratory, Wright-Patterson Air Force Base OH 45433-7103

Additive packages designed to enhance the thermal stability and, therefore, the cooling capacity of aviation fuel while cleaning engine components as well have recently been developed. JP-8+100, aviation fuel modified with one such additive package, is currently undergoing evaluation in the field at a number of Air Force facilities throughout the United States. While JP-8+100 exhibits improved thermal stability and cleans engines effectively, its detergents and dispersants tend to emulsify water in the fuel and degrade the performance of filter/coalescer units designed to strip this water. Eliminating water is essential since both dissolved and free water contribute to the formation of ice crystals in the fuel system at the low temperatures characteristic of high-altitude operation. In addition, some data suggest that these additive packages may impact analytic techniques for determining water in fuel. This paper describes efforts to assess this impact and to establish a validated technique for determining water in additive-modified aviation fuel. Such a method is critical to the development of filter/coalescer units compatible with fuel additive packages.

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STUDIES OF BROWNING PATTERNS IN LAMINATED EVA ENCAPSULANTS UNDER ACCELERATED EXPOSURES. S. H. Glick and F. J. Pem. National Center for Photovoltaics, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401. (303)-384-6615

Laminated EVA copolymers of commercial formulation(s) used for photovoltaic (PV) encapsulation exhibit yellow-browning discoloration upon photothermal degradation. Field exposure with or without mirror enhanced irradiance produces uniform EVA browning, but accelerated exposure testing (AET) at black panel temperatures of 85'C and 145'C produces non-uniform browning patterns over the c-Si solar cells where the central regions are lighter in discoloration. AET exposures result in an initial increase in fluorescence peak intensities around 420 nm (X.. = 350 nm), due to decreased shielding of photodecomposing UV absorber. The 420 nm peak then decreases as the exposure time increases in concomitance with the appearance of an intense broad peak with a maximum between 525 and 575 nm and a yellow to brown color, as a result of transformation of the original curing-generated chromophores into conjugated polyenes of mixed lengths. Further exposure causes more red shift of the broad peak to 600-650 mn with substantially decreased emission intensity while the EVA turns into very dark brown. When compared to field exposures, the non-uniform browning patterns observed in AET might have resulted from alterations in reaction rates due to factors such as sample temperature, light intensity, and oxygen diffusion and consumption rates. More detailed experiments are underway to explore the mechanisms.

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A NEW MODEL FOR THE DETERMINATION OF SURFACE ISOTHERMS USING A LIFETIME PARTITIONING PROTOCOL WITH A NEW LUMINESCENT TRANSITION NDETAL PROBE. <u>Matthew Marlow</u>. B. Patrick Sullivan, and John Bowen, Chemistry Dept. University of Wyoming Laramie, WY 82071-3838.

A new model for the determination of surface isotherms was developed, with the introduction of a new luminescent transition metal probe, using a lifetime partitioning protocol. A phase modulation technique was employed to determine the partitioning between the surface and solution. The structural nature of the surface with energy gap considerations,were used to explain the increase in lifetime of the probe when adsorbed to the surface. By vaqing colloid concentration and concentration of the probe, isotherms were determined. A binding constant was determined for the variable concentration of the probe, ca. 2000.

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DINITRAMIDE, NITROCYANAMIDE, AND DICYANAMIDE: SPECTROSCOPIC AND PHOTOCHEMICAL STUDIES OF THEIR SALTS AND THEIR Re^{I} TRI-AND PENTACARBONYL COMPLEXES. <u>Kevin J. Seward</u>. Scott A. Trammell, B. Patrick Sullivan, Chemistry Dept., University of Wyoming, P.O. Box 3838, Laraniie, V;Y 82070.

Dinitramide (dn, $N(NO_2)_2$") is a relatively new compound (discovered as Kdn in 1971 and currently being proposed as a smokeless rocket propellant). Its environmental impact is just now being studied; this project will tackle this from a photochemical perspective for this novel species as well as the related nitrocyanwnide (ncn, $N(CN)(NO_2)$") and dicyanamide (dcn, $N(CN)_2$") anions. The purpose of these studies is 1) to characterize these anions spectroscopically, both as salts and via their novel Re complexes (fac-Re(2,2'-bpy)$(CO)_3$L, $Re(CO)_5$L, and ***fac***-$Re(PPh_3)_2(CO)_3$L, where L = dn, ncn, or dcn) and 2) to identify their photochemical products as well as photochemical reaction pathways.

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FEMTOGRAM DETECTION OF SUSPECTED CARCINOGENS BY HPLC-PEROXYOXALATE CHEMILMINESCENCE, <u>Janet G. Gilliland</u>. Hauser Laboratories, Inc., 4750 Nautilus Court South, Boulder, CO 80301-3240.

Levels of detection at least one order of magnitude better than fluorescence were achieved utilizing peroxyoxalate chemiluminescence for detection of selected chemiluminescence sensitizers, as cited by Hanhela and Paul. High performance liquid chromatography with ultraviolet/fluorescence/chemiluminescence analyses in series was performed, with condition optimized for chemiluminescence. Levels of detection in the femtogram range are reported for some compounds. The McPherson Chemiluminescence Detector with spiral flow cell and near-zero dead volume reagent mixing in the flow cell was utilized.

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A REVERSED PHASE HPLC/MS/MS ASSAY FOR THE SIMULTANEOUS QUANTITATION OF RWJ-51204 AND ITS ACTIVE METABOLITE (RWJ-52407) IN HUMAN PLASMA and URINE. D. Desai-Krieger. V.V. Scott, and R. J. Stubbs. The R. W. Johnson Pharmaceutical Research Institute, Bioanalytical Drug Metabolism Department, Welsh & McKean Roads, Spring House, PA 19477.

A reversed phase HPLC/MS/MS assay was developed for RWJ-51204, a pyrido[l,2a]benzimidazole under investigation as a potential anxiolytic. An analog of RWJ-51204, viz. RWJ-51799, which differs only by the presence of an additional fluorine atom on the benzene ring, was used as the internal standard (IS). The active 4^1 hydroxy phenyl metabolite of RWJ-51204 was also chromatographically separated and quantitated. Separation of drug, metabolite and the IS was obtained on a Zorbax SB-C_8 column using a mobile phase consisting of acetonitrile and 0.02 M ammonium acetate buffer, pH=4.0 (50:50). The column temperature was maintained at 60 °C, a flow rate of 1.0 mL/min was employed. Under these conditions RWJ-51204 eluted at 3 minutes preceded by the metabolite at 1.4 minutes and the IS at 2.5 minutes, with baseline separation of the peaks. The pH of plasma (1 mL sample size) and urine samples (500 ***yL*** sample size) was adjusted using 1.0 M Na_2C0_3 and the samples extracted with methyl t-butyl ether. This one step clean up removed any interferences with the drug, metabolite and/or IS peaks from human plasma and urine. The column effluent was analyzed by multiple reaction monitoring using the PE Sciex® API III Plus triple quadrupole mass spectrometer in the positive ion APCI mode. Linear curves were obtained for drug and metabolite in plasma and urine in the 0.01- 2.5 ng/mL range with excellent correlation coefficients, r > 0.995. The assay developed a simple approach for analysis of pyrido[l,2a]benzimidazoles in biological fluids.

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PETRIFIED FOREST NATIONAL PARK UPPER TRIASSIC TRACE FOSSILS YIELD BIOCHEMICAL EVIDENCE OF PHYLOGENETIC LINK TO MODERN BEES (HYMENOPTERA, APOIDEA), Paul T. Kay[1]; J. David King[2] and Stephen T. Hasiotis[3], [1] Independent, Denver, CO; [2] USGS, Denver, CO; [3] University of Colorado, Boulder, CO.

Here we present preliminary organic geochemical results from solvent extractions obtained from six fossil linings and their adjacent permineralized matrices using Electron Impact ionization Gas Chromatography - Mass Spectrometry / Mass Spectrometry, thus demonstrating additional diverse evidence suggestive of Apoidean origin for these approximately 1.5 cm long, flask shaped ichnofossils. Three components identified in the extractables are: a homologous series of three ***straight-chained aliphatic esters*** — C_{14}-C_{14}, C_{14}-C_{16} and C_{14}-C_{18} — seen only in the fossil linings; a homologous series of n-alkanes — C_{14} through C_{34} having no odd/even preference; and total ion chromatograms of numerous isoprenoids. The esters and n-alkanes gave molecular ions, while the isoprenoids fragmented when ionized. Only the esters are significantly interpretable at this time. Interestingly, some terpanes are seen only in the cell linings. We regard the three tetradecyl (C_{14}-) esters with particular significance in that it raises the possibility of ***in situ*** preservation of whole, unaltered, ***de novo*** biomolecules; although diagenetic ring-opening of ***de novo*** macrocyclic lactones catalyzed by ***in vitro*** free radicals within sedimentary porespace water is another interpretation.

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C-73 *NMR STUDY OF THE INCLUSION OF STEREO AND REGIO DEFECTS IN THE CRYSTALLINE REGIONS OF ISOTACTIC POLYPROPYLENE.*

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C-13 CPMAS techniques are used to isolate signals from the crystalline regions and to reveal weak resonances, distinct from those of the backbone, in several i-PP samples. The positions and intensities of these resonances are correlated with known concentrations of various stereochemical and regio defects in the chains; thus, information about the incorporation of defects into the crystalline regions is obtained. Before one can convert defect intensities to defect concentrations, one must be reasonably sure how many distinct defect resonances are produced by a single defect site. Spectral assignments for defect resonances in high resolution NMR are almost irrelevant for this task because a) the defect sites are characterized by fixed conformations versus time-averaged conformations in solution and b) in the crystalline environment, the bond distortions in the vicinity of the defect sites are probably significant. Our efforts in addressing this assignment problem will be discussed. Information regarding the partitioning of chain defects between the crystalline and the non-crystalline regions of iPP is valuable for understanding the dependence of properties on microstructure (in particular, the microstructures of iPP's made with metallocene and Ziegler-Natta catalysts).

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SUDDEN AND ADIABATIC EXPERIMENTS: APPLICATIONS TO SOLID-STATE NMR.

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Numerous NMR experiments require that a matching condition is fulfilled. A well-known example is Hartmann-Hahn cross polarization where the amplitude of the RF fields applied to the two spin species must be matched at the famous Hartmann-Hahn condition. Another example is the rotational-resonance condition, where the MAS spinning speed must be set to be a sub-multiple of the chemical-shift difference of the two nuclei. Sometimes, it is quite painful to fulfil these matching conditions. Adiabatic alternatives to both examples that release considerably the matching conditions and, at the same time, make the polarization transfer more efficient, will be discussed. Applications will focus on macromolecules.

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VARIABLE DIRECTOR NMR STUDIES OF ALIGNMENT AND DYNAMICS IN SYNTHETIC LIQUID CRYSTALLINE POLYMERS.

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Natural abundance NMR was employed to investigate synthetic liquid crystalline polymers, important macromolecules with numerous practical applications as structural materials and optoelectronic devices. These analyses involved a new 13C variable director NMR experiment in which spectra are recorded for different angles between the direction of the ordered macromolecular fluid and the external magnetic field. This separates each peak's isotropic and anisotropic shielding components, and enables the assignment and order characterization of even complex molecular systems. In certain cases, however, variable director spectra show -in addition to the expected shifts- peaks that were significantly broadened by a mechanism that is unaccounted by conventional liquid crystalline NMR models. These broadenings were traced to the slow tumbling of the fluid macromolecules with respect to the NMR time scale, an hypothesis that was validated by spectral simulations. This enables a line shape-based analysis of polymer chain dynamics in ordered polymeric fluids, whose nature will be briefly discussed.

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RESONANCE ASSIGNMENT AND STRUCTURE DETERMINATION OF ISOTOPICALLY ENRICHED PROTEINS BY SOLID-STATE NMR.

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The orientation- and distance- dependent spin interactions exploited in solid-state NMR make it a uniquely suitable tool, for probing detailed local structures of membrane proteins and fibrous proteins that cannot be crystallized or dissolved in solution. However, due to the low spectral resolution and the ensuing difficulty of resonance assignment, it is still rare to obtain many structural parameters in a single solid-state NMR experiment for determining the global structures of proteins. We are employing various magic-angle-spinning multidimensional correlation techniques, including 13C-15N and 13C-13C correlation and 13C-13C double quantum spectroscopy, to test the possibility of assigning the 13C and 15N spectra of an unoriented and partially labeled protein. The first step, assignment of cross peaks to amino acid types, has been achieved for more than half of the residues. The mixing time dependencies of these correlation spectra provide information on some intraresidue and interresidue distances semi-quantitatively. A C7-based homonuclear double-quantum experiment (INADEQUATE) with a wide spectral width (-25 KHz) in the indirect dimension was developed to accommodate the large chemical shift dispersions between the carbonyls and the aliphatic carbons.

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FAST MAGIC ANGLE SPINNING NMR STUDIES OF POLYMER BLENDS AND INTERFACES.

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Fast magic angle spinning proton NMR is used to study polymer blends and the glass-polymer interface. The results show that high resolution spectra are observed for polymers at or above the glass transition temperature, and 2D NMR can be used to identify the intermolecular interactions that cause the molecular level mixing in polymer blends. The same methods are used to measure polymer-surface interactions in high surface area glass-polymer composites. Multiple-quantum proton NMR with fast magic angle sample spinning is used to probe the molecular dynamics of bulk and surface-confined polymers.

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STRUCTURE OF b-AMYLOID FIBRIL MEASURED BY DIPOLAR RECOUPLING NMR.

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Alzheimer's Disease is characterized histopathologically by the deposition of amyloid plaques, especially in areas of neuron loss. The primary component of these plaques is a 39-43 amino acid peptide called b-amyloid (Ab). Efforts toward the elucidation of the structure of Ab have been hindered in the past by the insoluble, non-crystalline nature of Ab fibrils, which renders them unsuitable for standard methods of protein analysis. We have implemented the DRAWS method for measuring interstrand distances between 13C-13C spin pairs Ab peptides. A single 13C-labeled amino acid was incorporated into the peptide for each measurement, allowing distances to be determined in the case of contacts arising solely from intermolecular associations of peptide chains. Using this approach, we have determined distances for several labeled amino acid pairs along the peptide chain, and have elucidated the specific conformation and alignment of the core domain of Ab peptide. We have shown that the core structure of Ab fibrils consists of an extended parallel b-sheet with each amino acid in exact register. Our approach is completely generalizable, and provides a new strategy for characterizing biopolymer self-association. The work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract no. W-31-109-ENG-38.

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SURFACE NEAR NMR WITH THE MOUSE.

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The NMR-MOUSE (Mobile Universal Surface Explorer) is a portable device that allows the investigation material close to the surface (ca. 1 cm) of arbitrarily large objects (G. Eidmann, R. Savelsberg, P. Blumler, and B. Blumich, J. *Magn. Reson.* A **122** (1996) 104). These samples may even contain ferromagnetic parts. So far measurements of NMR-relaxation times and selfdiffusion coefficients were used to characterize properties of polymer and biomedical samples. The NMR-MOUSE consists of strong permanent magnets and a surface coils, yielding a field strength of about 0.4 T (directly at the surface) with a sensitive depth up to 10 mm. The static magnetic and the rf field are very inhomogeneous, which has to be considered for the development of suitable pulse sequences to achieve optimum contrast and measurement times.

Many relaxation measurements were tested to characterize polymer products. Molecular diffusion in liquids can be used for solvent suppression as well as for the calibration of the local gradients. An important feature of the NMR-MOUSE is the simplicity in determination of the anisotropy of relaxation times or selfdiffusion coefficients by simply turning the probe. The NMR-MOUSE is a practical, robust and inexpensive gadget for localized NMR. The development of dedicated hardware and pulse sequences for applications to industrial problems, e.g. quality and process control, is the focus of the ongoing research activities.

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MAGNETIC RESONANCE ELASTOGRAPHY: "PALPATION" BY IMAGING.

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For centuries, palpation has been used as an effective technique for detecting cancer in accessible regions of the body. The sensitivity of this diagnostic method is based on the fact that malignant tumors are often characterized by substantially different mechanical properties than surrounding normal tissue. Unfortunately, small or inaccessible lesions cannot be detected by touch, and conventional diagnostic imaging methods such as ultrasound, computed tomography (CT), and magnetic resonance imaging (MRI) "do not provide information that is in any way analogous. The goal of this research is to develop a method for quantitatively imaging the viscoelastic properties of tissues *in vivo.* A critical component of this technique is a method for *directly observing propagating acoustic waves in tissue, using an NMR imaging sequence with synchronous motion-sensitizing gradients.* This technique can image acoustic shear waves with displacement amplitudes of less than *100 nanometers.* The wave images are processed to yield quantitative maps of viscoelastic properties. Preliminary work has shown that focal tumors can be delineated in resected organ specimens. Early trials with human volunteers have yielded elastographic images of skeletal muscle, breast, and brain, *in vivo.* The findings suggest that the technique has potential to provide a new quantitative tool for characterizing the viscoelastic properties of tissue and biomaterials.

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ALBATROSS: NUISANCE OR FRIEND?.

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The spin Hamiltonian needed to describe nearly all magnetic resonance experiments is an average over rapidly relaxing spatial degrees of freedom. This has been taken to be a Boltzmann average of quantities calculable from the time-independent Hamiltonian describing the system. We show why this approach is conceptually flawed and describe the physics of previously unsuspected, intrinsically dynamic, contributions to the spin Hamiltonian for this ubiquitous situation. Numerical estimates indicate that these new terms are required in order to simulate nuclear magnetic resonance spectra at the

resolution with which they are routinely measured. Statistical analysis of new experiments on the dynamic NMR of methylcyclohexane in solution show that the traditional analysis is untenable, but that the new terms allow a self-consistent description of the data. An approach is outlined in which the underlying spin Hamiltonians for particular molecular eigenstates may be combined with a tractable quantum description of rovibrational relaxation to give the necessary dynamic corrections, which are described by an average Liouvillian born as the result of spatial susceptibility (ALBATROSS).

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MAGIC ANGLE SPINNING IN NMR AND EPR.

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(Abstract Available Under Paper 69.)

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EXPLOITATION OF THE FREE EVOLUTION PERIODS IN PULSE EPR EXPERIMENTS.

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(Abstract Available Under Paper 70.)

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PULSED ENDOR IN UNORIENTED SAMPLES: HOW TO INCREASE RESOLUTION AND GAIN THE MULTIPLEX ADVANTAGE.

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(Abstract Available Under Paper 71.)

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ENDOR OF METALLOENZYMES: TO THE LIGANDS AND BEYOND.

B.M. Hoffman*, Northwestern University.

(Abstract Available Under Paper 72.)

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HIGH FIELD (140 GHZ/ST) EPR AND DYNAMIC NUCLEAR POLARIZATION.

M. Bennati, C. Farrar, D. Hall, S. Inati, M. Rosay, V. Weis, K. Kreischer and R.G. Griffin*, Francis Bitter Magnet Laboratory, and Dept. of Chemistry, MIT, Cambridge, MA 02139. E-mail: griffin@ccnmr.mit.edu

(Abstract Available Under Paper 73.)

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BANDWIDTH EXTENSION USING NOISE SPECTROSCOPY.

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One tempting feature of noise spectroscopy, and of its application to solid state nuclear magnetic resonance, is the claim that the traditional link between the strength of the excitation field and the undistorted spectral bandwidth is effectively broken. Nonetheless, its application to broadline solid state NMR spectroscopy has been limited; typical implementations of noise excitation and detection sequences would appear to require unrealistically short probe- and receiver-recovery times for most very broadline (> 100 kHz) applications. In this presentation, we explain theoretically and demonstrate experimentally that accurate lineshapes can be observed in as challenging an experiment as deuterium solid state NMR spectroscopy, even in the presence of dynamics. Spectral bandwidths in excess of 500 kHz are achieved without substantial (i.e. time-consuming) modifications to either probe or spectrometer, and deuterium powder pattern lineshapes which span 250 kHz are demonstrated to be faithfully reproduced, using rf fields as weak as a few hundred Hz. We believe that these techniques can be further extended to the observation of true absorption spectra several times broader.

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ADIABATIC FOLLOWING.

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Adiabatic pulses are usually derived from the adiabatic condition which states, in term of magnetic resonance, that the reorientation of the effecive field must be slower than the precession of magnetization around the effective field. We have started out from a two-level system that is perturbed by a resonant field of variable frequency and of constant amplitude to derive a new model of adiabatic following. Our approach differs from the conventional one by forcing the spin system to be in a stationary state with respect to the effective field during its reorientation. From this Ansatz a linear relation between the angular velocity, describing the reorientation of the effective field, and the magnitude of the effective field can be derived. This relation allows the formulation of an equation of motion for the frequency of the applied field, whose solutions can be used to construct adiabatic pulses. The proportionality constant of the linear relation derived from our model turns out to be equivalent to the adiabaticity factor of the conventional approach, and to be an adiabatic invariant (constant adiabaticity pulses). Within our model, the adiabatic invariant can be clearly related to the performance of the pulse: its value is (grossly) inverse proportional to the amount of excited (inverted) magnetization.

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QUADRUPOLE ECHO DOUBLE RESONANCE AND SOLID ECHO DOUBLE RESONANCE NMR.

Yong Ba*, Chris A. Tulk, Chris I. Ratcliffe and John A. Ripmeester, Steacie

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It is well known that double resonance NMR experiments, such as SEDOR (Spin Echo Double Resonance) and REDOR (Rotational Echo Double Resonance) experiments, can be applied to obtain heteronuclear dipolar coupling constants and thus internuclear distances. This presentation will discuss two more kinds of double resonance NMR experiments, i.e., Quadrupole Echo Double Resonance (QEDOR) and Solid Echo Double Resonance (SOLEDOR). These experiments are introduced by a theoretical analysis of spin evolution during the pulse sequences, and are demonstrated by deuterium-proton double resonance experiments on polycrystalline glycine selectively deuterated at the amino site. The Quadrupole Echo NMR experiment has been widely used to study local molecular motions. The new QEDOR experiment provides additional information about the molecular environment by probing the heteronuclear dipolar interaction. Thus we will show one application of the QEDOR experiment to study dynamic process occurring during the formation of tetrahydrofuran (THF) clathrate hydrate from hyper-quenched amorphous solid.

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R.W. VAUGHAN PLENARY LECTURE: *FLOQUET THEORY AND MAGIC ANGLE SPINNING.*

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During the last ten years or so Floquet theory has been used to describe a variety of NMR experiments of solids, rotating at the magic angle. Examples of these experiments are rotational resonance (R^2), rf-driven dipolar recoupling (RFDR), cw and variable amplitude cross-polarization magic angle spinning (CPMAS), proton MAS NMR, proton driven spin diffusion and Lee-Goldburg decoupling as well as rotational echo adiabatic passage double resonance (REAPDOR). The Floquet description of the spin systems is in particular helpful when Fourier analysis of the spatial and spin parts of the Hamiltonians can be obtained easily. Then it provides physical insight into these experiments and enables numerical simulations of spectra of coupled multi-spin systems.

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SOLID STATE NMR STUDIES OF BIOMOLECULAR RECOGNITION.

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Recent solid state NMR studies of biomolecular recognition will be described. Proteins play an important role in the biological mechanisms controlling hard tissue development, but the details of molecular recognition at inorganic crystal interfaces are poorly understood. We have applied a recently developed dipolar recoupling solid state NMR technique. Dipolar Recoupling with a Windowless Pulse Sequence (DRAWS), to directly probe the conformation of an acidic peptide adsorbed to hydroxyapatite (HAP) crystals. The phosphorylated hexapeptide DpSpSEEK (N6, pS=phosphorylated serine) was derived from the N-terminus of salivary statherin. Constant composition kinetic experiments demonstrated that like statherin, this the N6 peptide inhibits the growth of HAP seed crystals. DRAWS has been used to measure internuclear diatnces in N6 and other statherin-derived peptides adsorbed onto HAP. The results suggest that these peptides are adsorbed in extended conformations, rather than an in helical conformations as has been postulated. Solid state NMR can thus be used to obtain detailed structural information on proteins and peptides at interfaces. Examples of solid state NMR data obtained from other biomolecular systems will be presented, as time permits.

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REDOR NMR OF HETEROGENEOUS POLYMER BLENDS.

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The dipolar coupling between stable-isotope labels in heteronuclear pairs is measured by rotational-echo double resonance (REDOR) in magic-angle spinning experiments on solids. The REDOR difference, DS = So-S, where S and So are the spectra with and without rotor-synchronized pulses that interfere with the formation of rotational echos, depends only on the rotor period, the total dipolar evolution time (both of which are known), and the dipolar coupling and so determines the distance between labeled nuclei directly. When labels are on different chains in different phases of a polymer blend, REDOR can be used to characterize the structure and dynamics of a buried interface. We will illustrate the application of REDOR to the analysis of such interfaces including: (i) the interface between a polystyrene core and a polyacrylic acid-polyacrylamide shell of a 28-nm diameter amphiphilic particle that complexes hydrophobic and amphiphilic drugs and metabolites; (ii) the surface of a 38-nm diameter polycarbonate domain buried in a polyfluorostyrene matrix; and (iii) the interface between components in a blend of polystyrene and a fith-generation benzyl ether dendrimer.

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THREE-DIMENSIONAL STRUCTURES OF ZEOLITE-SORBATE COMPLEXES FROM SOLID STATE NMR.

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Zeolites are open pore three dimensional aluminosilicate materials widely used as sorbents and catalysts. Their unique molecular sieving properties depend on the interactions between the organic molecules and the channel systems in the framework but it is difficult to obtain detailed structural information by single crystal x-ray diffraction as the materials are microcrystalline with dimensions of a few microns. In the present paper we show that detailed three-dimensional structural information can be obtained from the application of a number of solid state NMR techniques including 13C spin diffusion, CP, REDOR and TEDOR. The validity of the approach is confirmed for one system whose structure is known and one unknown structure is predicted and subsequently confirmed. Direct distance determinations for isolated spin pairs in these systems will be described and the potential of this approach discussed.

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SOLID-STATE NMR STUDIES OF SPIN INTERACTIONS, PHASE TRANSTIONS, AND TRANSFORMATIONS IN INORGANIC MATERIALS FROM POWDERS AND SINGLE CRYSTALS.

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A tour on multinuclear solid-state NMR applications to inorganic materials will be given. Results on the determination of anisotropic interactions for spin-1/2 and quadrupolar nuclei in selected inorganic complexes and salts are presented. Thus, tensors for the anisotropic chemical shielding and quadrupole coupling as well as their relative orientaton, or absolute orientation in the crystal frame, have been obtained from powder or single-crystal NMR methods. Variable temperature MAS NMR results for some of these interactions, for the phase transitions and thermal history of the three phases (alfa, beta, and gamma) in KN03, and for the conversion of the hydrates of some cadmium complexes will be discussed. New probe design for single-crystal and VT MAS NMR will also be presented.

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HOMOGENEITY, HETEROGENEITY, AND DYNAMICS IN OXIDE GLASSES AND LIQUIDS: NEW VIEWS FROM 3QMAS AND HIGH-TEMPERATURE NMR.

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New high-resolution NMR techniques for quadrupolar nuclides are becoming very useful for investigating the structure of oxide glasses, because they (1) often give enhanced separation of peaks from different structural units; and (2) allow peak shapes to be interpreted in terms of real structural disorder, which is a critical issue in any amorphous material. High T NMR studies complement these data with dynamical information. Intermediate-range compositional heterogeneity, or homogeneity, can affectboth. In borosilicate glasses, for example, new 170 3QMAS results have clearly resolved Si-O-Si, Si-O-B, and B-O-B oxygens, and show considerable mixing among the B and Si networks (contrary to some conventional wisdom). In situ, high T MAS has quantified the rate of exchange among B04 and B03 groups, and of Si species, well above the glass transition, and can be most readily interpreted in terms of nano-scale heterogeneity. 170 and 27A1 MAS and 3QMAS spectra of various La- and Y-containing glasses highlight the great disorder caused in the network by these high field strength cations, which promote the formation of A105 and A106 groups and perhaps even of oxygens that are not bound to any tetrahedral cations.

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NQR DETECTION: SEEING MORE OF WHAT IS THERE.

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We have been investigating the use of nuclear quadrupole resonance (NQR) for the detection of explosives in various environments. In these real world applications of magnetic resonance, signals must be excited and detected efficiently with a minimum of interference from outside sources. In this talk we will discuss recent developments in hardware and experiment design that improve NQR signal detection efficiency independent of the pulse sequence, and minimize interference from acoustic ringing and external noise sources. The use of circularly polarized excitation and laboratory frame quadrature detection will be emphasized.

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ORIENTATION OF THE QUADRUPOLE AND DIPOLE TENSORS OF HYDROXYL GROUPS BY 170 QUADRUPOLE SEPARATED LOCAL FIELD NMR.

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Valuable structural information is contained in the orientation and magnitude of tensorial interactions that can be obtained from NMR spectra. Here we present the first 170 2D-quadrupole separated local field experiments on the hydroxyl groups of Mg(OH)2 and Mg(OH)x(OCH3)2-x from which the orientation of the quadrupole tensor within the structure can be obtained. From simulation of the static 170 NMR spectra and CP-dynamics we obtained, e2qQ/h=6.8 MHz, eta=0, diso=20 ppm, and rOH=1.001 A for Mg(0H)2 and e2qQ/h=7.25 MHz, eta=0, diso=-25 ppm, and rOH=0.995 A for the hydroxyl oxygen in Mg(OH)x(0CH3)2-x. Based on differences in the OH distance and in the 170 quadrupole coupling constant it was concluded that the OH bond in Mg(OH)x(OCH3)2-x was more covalent. 170 2D-quadrupole separated local field experiments revealed that the quadrupole and dipole tensors in both samples were collinear. Since the effect of the homonuclear proton dipolar coupling was less prominent in the amorphous sample, as evidenced by differences in CP-dynamics and spectral resolution in the dipolar dimension, it was concluded that the hydroxyl groups are more isolated in the amorphous sample. The simulation of 2D-quadrupole separated local field spectra showed that this experiment is very sensitive to differences in the relative quadrupole and dipole tensor orientation.

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SOLID-STATE 93Nb NMR OF NIOBIUM B-SITE CHEMICAL ENVIRONMENTS AND ORDERING IN PMN AND PMN/PT FERROELECTRICS.

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Pb(Mg1/3Nb2/3)03 (PMN), and xPMN/(1-x)PbTiO3 (PMN/PT) solid-solutions are important ferroelectrics with a perovskite structure. Solid-state 93Nb NMR and 2D nutation studies of PMN, PMN/PT, and 93Nb NMR of Pb(Zn1/3Nb2/3)03 (PZN), are reported. 93Nb NMR spectra of alkali niobates, PMN, PZN, PMN/PT and PZN/PT indicate that 93Nb NMR is highly sensitive to the local atomic-level Nb(V) environments. 93Nb NMR spectra of single crystal and polycrystalline PMN and PMN/PT, and single crystal PZN and PZN/PT show at least three pseudo-octahedral Nb06 resonances with different frequency shifts and quadrupolar parameters. The 93Nb NMR and nutation spectra are interpreted

in terms of PMN containing different regions of local short range Mg/Nb order, that may correspond to various Nb(Onb)6-x(Omg)x next-nearest neighbor B-site configurations. This interpretation is consistent with PMN (and PZN) containing Nb(V) sites in Mg-rich (and Zn-rich) and Nb-rich regions. These studies show that solid-state 93Nb NMR and nutation techniques can provide new information about the local Nb(V) short-range order in PMN, PZN and PMN/PT systems, and that 93Nb NMR techniques may also be useful in correlating this atomic-level information with the temperature-dependent long-range order, A and B-site motion, and electrical properties of these relaxor ferroelectrics.

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IN SITU HETEROGENEOUS CATALYSIS STUDIES BY THE GRASSHOPPER METHOD.

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A new application of magic angle hopping (MAH), the GRASSHopper II (Gas Reactor And Solid Sample Hopper), allows for in situ NMR study of reactions under a variety of conditions. The basic NMR principals of this method and typical reaction apparatus will be presented. High-resolution solid state NMR spectra were obtained to follow the polymerization of ethylene on a Cp2ZrCl2/MAO/Si02 "supported" catalyst in a reaction cell under flow conditions. Preliminary results for the generation of the (C6H5)3C+ carbocation in a zeolite, along with its hydration and regeneration (via dehydration in the same cell) will be presented. Finally, approaches to studying heterogeneous catalysis in a variety of systems will be discussed along with future GRASSHopper improvements.

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THE NMR CHEMICAL SHIFT: INTRA- AND INTERMOLECULAR EFFECTS.

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Theoretical studies exploring trends between chemical shift tensors and peptide secondary structure will be presented. The principal axis system (PAS) of the carbonyl carbon chemical shift tensor is found to be intimately related to the amide plane. On the other hand, the PAS of the alpha carbon chemical shift behaves differently indicating, for example, large differences between the projection of the chemical shift tensor along the C-H vector of model helical and sheet fragments. Intermolecular effects on the chemical shift tensor as manifested in hydrogen-bonding in peptides will also be discussed. In addition, theoretical studies explaining the observed dependence of Rb chemical shifts on interionic distances in mixed halides will be shown. Chemical shift computations for the model peptides were performed using the density functional theory - individualized gauge for localized orbitals (DFT-IGLO) method while for rubidium shifts, the coupled Hartree Fock gauge-including atomic orbital (CHF-GIAO) method was employed.

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THE INTERPRETATION OF GAUGE-INCLUDING ATOMIC ORBITAL (GIAO) CALCULATIONS OF NMR SHIELDING TENSORS USING NATURAL CHEMICAL SHIELDING (NCS) ANALYSIS.

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Nuclear magnetic shielding tensors have been calculated using the GIAO (gauge including atomic orbital) method in the framework of HF-SCF (Hartree-Fock Self-Consistent-Field). By means of Natural Chemical Shielding (NCS) analysis (an extension of the Natural Bond Orbital - NBO method) the contributions to the shielding tensors are partitioned into magnetic contributions from chemical bonds and from lone pair electrons. NCS analysis complements the description provided by alternative localized orbital methods by directly calculating chemical shieldings due to delocalized features in the electronci structure, such as bond conjugation and hyperconjugation. Examples of NCS tensor decomposition are given for several small molecules including CH_4, CO and H_2CO.

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UNDERSTANDING INTERMOLECULAR 129Xe CHEMICAL SHIFTS. APPLICATIONS TO COMPETITIVE ADSORPTION IN ZEOLITES.

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The exquisite sensitivity of the Xe chemical shift to the environment in which the xenon atom finds itself has made Xe NMR spectroscopy a popular tool. In the past various empirical parameterized models have been used to interpret the chemical shifts of xenon in the gas phase, in liquid solvents, inside zeolites. These models continue to be used in current literature, although they have been found to be largely incorrect. Ab initio calculations of rare gas atom shielding in various systems will be presented as examples of parameter-free calculations of intermolecular chemical shifts, which demonstrate what is wrong with previous models. In particular, the ab initio anisotropic Xe shielding surface for the Xe-Xe, Xe-CO_2, Xe-CO and Xe-N_2 systemswill be discussed. The Xe chemical shifts of Xe in competitive adsorption with CH_4, CO_2, CO, and N_2 in zeolite NaA will demonstrate our ability to determine the answer to the question: "How many molecules of type 2 can be found in those cavities that have exactly n molecules of type 1?", based entirely on the chemical shifts observed.

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DEVELOPMENT OF AN ISOLATED FLOW VT MAS NMR PROBE.

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We are developing an isolated flow VT MAS NMR probe to enable simultaneous observation of events occurring on a surface with characterization of the effluent using an external analytical instrument. We utilize ceramic bearings and baffles to achieve isolation of gas streams and spin rates of 2kHz. We have observed methanol adsorption onto zeolite HZSM-5 via 13C flow MAS NMR and structural changes of a vapochromic sensor material when exposing it to volatile organic compounds. Currently we are incorporating variable temperature heating into the system for the observation of heterogeneous catalysis in-situ. Initial tests indicate we have achieved temperatures above 150oC and observed conversion of methanol (99.5% 13C) to dimethyl ether over zeolite catalyst HZSM-5. Future improvements will be centered around higher temperatures, heterogeneous catalytic applications, and improving isolation of gas streams.

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ERROR-TOLERANT RF LITZ COILS FOR MICROSCOPY.

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A new class of NMR rf volume coils has been developed that permits improved tuning range, tuning stability, B1 homogeneity, and sensitivity compared to birdcages under a wide range of practical conditions, especially for microscopy and wrap-around flexible applications. They are denoted litz coils, as their flux transparency and current distributions are obtained from woven foil patterns with insulated crossovers. Contrary to design criteria in phased arrays, the parallel routes in litz coils require high coupling coefficients to achieve an optimal current distribution that is independent to first order of tuning, balancing, and matching adjustments and is compatible with multiple capacitive segmentation. The motivation for exploring novel current topologies arose primarily from work in vertical bore magnets (7 T to 14 T) where tight space constraints make it extremely difficult to obtain high B1 homogeneity for asymmetric loads in birdcages, as the high-order rf homogeneity errors can only be addressed by a complex tuning procedure and the parasitics cannot be precisely controlled. Numerical modeling and experimental comparisons with balanced-high-pass birdcages are presented for a variety of birdcage and litz coils with frequency-diameter products from 5 to 30 MHz-m for frequencies at least to 600 MHz. Both linear and quadrature versions are discussed for both single and double-resonance.

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TOROID CAVITY NMR DETECTOR: APPLICATION TO ELECTROCHEMICAL SYSTEMS.

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The in situ investigation of electrochemical systems, including the transport properties of charge carriers in the bulk electrolyte, the spatial distribution and intercalation dynamics of the electroactive ions in novel anode and cathode materials, and the characterization of the near-electrode redox reactions is facilitated by the capabilities and geometry of the NMR toroid cavity imaging probe. Recent studies include (1) the radial concentration profile measurements of lithium cations and triflate anions acquired during cell operation, (2) imaging the penetration of the electrolyte into electrode surfaces composed of nanostructured carbon and synthetic vanadate materials designed for high capacity lithium ion intercalation, and (3) lithium concentration profiles in the metal's surface of a cylindrical aluminum/lithium alloy electrode. The toroid cavity imaging methodology, the unusual NMR properties of this detector geometry, and the fabrication of the toroid device will be presented in the context of several applications in electrochemical systems. This work is supported by the U. S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38.

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MATRIX ENDOR DETERMINATION OF THE MAGNETIC INTERACTION RANGE BETWEEN AN UNPAIRED ELECTRON SPIN AND NUCLEAR SPINS IN PMR-15 POLYIMIDE RESIN.

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In samples containing paramagnetic sites, detection of nuclear spins by a normal high resolution NMR technique is limited to the portion of spins that are not dipole coupled to an electron spin at the paramagnetic sites. This loss of detectable spins is the reason for the poor NMR signal-to-noise ratio of cured polyimide resins and coal samples. In this paper, we report an estimate of the range of the electron spin - nuclear spin magnetic dipole interactions obtained by an analysis of the matrix ENDOR spectrum of a PMR-15 sample.

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23NA MQMAS INVESTIGATIONS OF SODIUM ULTRAPHOSPHATE GLASSES.

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The application of solid-state multiple-quantum magic angle spinning (MQMAS) NMR experiments to quadrupolar nuclei provides a powerful method for separation of the quadrupolar interaction (SOQE) and the chemical shift not previously available. Here we report 23Na NMR investigations using triple quantum (3Q) z-filtered MQMAS techniques on a series of sodium ultraphosphates glasses. The z-filter allows the optimization and matching of the symmetric coherence pathways to produce phase pure spectra. From these MQMAS experiments the 23Na chemical shift and SOQE as a function of alkali modifier were obtained. Inversion of the 2D MQMAS spectra allowed the distribution in chemical shift and SOQE to be evaluated. The 23Na chemical shift was found to increase with increasing Na20 concentration, consistent with a decrease in the average number of oxygens coordinated to the Na. It is postulated that this decrease results from variations in the Na environment due to increasing number of non-bridging oxygens present within the Na coordination sphere. These results are discussed in terms of various proposed models of glass structure. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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QUANTITATIVE ANALYSIS OF 27Al MQMAS NMR SPECTRA OF MICROPOROUS MATERIALS.

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Quantitative analysis of 27A1 MAS spectra of zeolites is often a problem because of the distribution of chemical shifts and electric field gradients which strongly broaden the lines. Powder lineshapes can not be extracted properly from such spectra. MQMAS NMR technique partially solves the problem by increasing the resolution of the different species as a function of the coordination of each aluminium. However, their resonances are still broad and, moreover, their intensities are not directly comparable to the concentration of the various species. Fortunately, the analysis of such MQMAS spectra leads to a reliable information about the nature of the distribution, and quantitative information can be retrieved by using adequate simulation program for computation of the intensities. Details about the method used will be given and some applications to steam-dealuminated zeolite materials will be shown.

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POLARIZATION ENHANCEMENT IN ORGANIC MOLECULES VIA HYPERPOLARIZED SUPERCRITICAL XENON.

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We present a new method for obtaining high polarizations of hydrogen and carbon nuclei in organic compounds from hyperpolarized 129Xe. Many organics will dissolve in supercritical xenon fluid at room temperature and the relatively modest pressure of 50-100 atm. We take advantage of that phenomenon to create a solution of the organic in hyperpolarized Xe inside of a capillary tube. We are exploring a variety of polarization transfer techniques, including the Overhauser effect, low-field thermal mixing and Hartmann-Hahn.

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APPLICATION OF 'MAGIC ECHOES' TO OVERCOME THE DEAD-TIME IN LOW RESOLUTION NMR MEASUREMENTS.

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A major problem with quantitative NMR measurements such as solid fat content is receiver dead time. This obscures much of the solid signal and requires the use of a calibration factor. Measurement of SFC by NMR is routinely used and is precise (s = 0.54, n = 20) but inacurate (r = 0.9922). The inacuracy stems from the calibration factor. Bench top instrumentation is now available with pulse programming and data capture facilities capable of more sophisticated experiments. We have investigated the application of multiple pulse sequences on the MARAN bench top spectrometer (Resonance Instruments Ltd., UK) in an attempt to overcome the dead time. One such sequence is the magic echo, which recovers the solid signal very effectively on research grad instruments. We have sucessfully modified the magic echo for use on bench to instruments so that it is equally effective. This allows a direct calculation of the solid content- We demonstrate this method for SFC on a series of standards made from tristearin / triolein and show that it is both precise (s = 0.40, n = 20) and accurate (r = 0.9996).

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AN EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE OLEFINIC CARBON CHEMICAL SHIELDING TENSORS IN Pt(0) AND Pt(II) COMPLEXES.

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The olefinic carbon chemical shielding (CS) tensors of trans-stilbene, I, and (trans-stilbene)[bis(triphenylphosphine)]platinum(0), II, have been characterized by solid-state carbon-13 NMR spectroscopy. As well, a preliminary analysis of the carbon-13 NMR spectra of Zeise's salt, potassium trichloro(ethylene)platinate(II) hydrate, III, is presented. For all three compounds, the olefinic carbons are C-13 labelled. Analyses of the NMR spectra of stationary powder samples of these compounds, obtained at 4.7 and 9.4 T, yield the principal components of the CS tensors. The presence of a spin pair provides information about the orientation of these tensors in the dipolar frame of reference. The CS tensor principal components for I are 215, 120 and 49 ppm. The orientation of the tensor is the same as that of ethylene. The corresponding values for II, 92, 71 and 41 ppm, show that the increased shielding of the olefinic carbons of this molecule, compared to that of I, is a consequence of changes to the high frequency components of the CS tensor. Similarly, the CS tensor components of III, 148, 80 and 0 ppm, show that changes in shielding following coordination of ethene with Pt(II) is due primarily to changes in the high frequency components of the CS tensor. Experimental results are compared with those from ab initio shielding calculations. We show that the combined experimental-theoretical approach allows one to suggest probable orientations for carbon CS tensors measured experimentally. In addition, the shielding of the Pt-bound carbons of Pt(0)-buckminsterfullerenes is discussed.

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HIGH-RESOLUTION VARIABLE-TEMPERATURE 19F MAS NMR SPECTROSCOPY OF VINYLIDENE FLUORIDE BASED FLUOROPOLYMERS.

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Comercially available fluoroelastomers are often based on copolymers of vinylidene fluoride (VF2)/ hexafluoropropylene (HFP), VF2/ tetrafluoroethylene (TFE), or terpolymers containing all three monomer units. These

fluoroelastomers have remarkable resistance to flames, solvents, heat, and oxidation, but are often insoluble or intractable, making analysis of microstructure and determination of monomer composition difficult. We have used variable-temperature solid-state 19F NMR spectroscopy with high-speed magic angle spinning (25 kHz MAS) to study microstructure and monomer composition of copolymers containing VF2/ HFP, VF2/ TFE and terpolymers containing all three monomer units. We have also studied the curing process for a VF2/ HFP copolymer in-situ to obtain mechanistic information about that process.

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A *SOLUTE'S VIEW OF A LIQUID CRYSTAL.*

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NMR is a superior tool for investigation of anisotropic intermolecular forces in liquid crystals. The NMR spectra of "rigid" solute molecules yield very accurate values of solute orientational order parameters which are directly related to the anisotropic intermolecular interactions. The dominant anisotropic intermolecular interactions are short-range repulsive; however, longer-range electrostatic interactions are also important. Experiments designed to probe these interactions will be reviewed. Results for the proton, deuteron and tritium isotopomers of molecular hydrogen show that the dominant orientational mechanism for these solutes involves their electric quadrupole moment. Investigations involving several chloro- and methyl-substituted benzenes (which have similar size and shape) also point to the importance of the molecular quadrupole, and indicate that the presence of a molecular dipole has negligible influence on solute orientational order.

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SOLID-STATE NMR CHARACTERIZATION OF FEP FILMS FROM THE HUBBLE SPACE TELESCOPE.

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The Hubble Space Telescope (HST) is covered by aluminized Teflon (FEP) film that acts as an insulator. Recent service missions to the HST revealed tears and cracks in the FEP films in various locations on the telescope. Solid-state NMR has been used to aid in determining the mechanism/product(s) of degradation by probing changes in polymer morphology, this has been done by measuring the relaxation properties T1 and T1p of 13C and 19F. The polymer films have a mixed morphology consisting of both static (crystalline) and mobile (amorphous) regions. The TIS curve for 19F to 13C cross polarization for exposed samples indicates the presence of a new more mobile component in the exposed material that is not present in the pristine material. T1p © measurements at different CP times indicate an increase of tightly packed components in the exposed material that is consistent with the observed

increase in density. These results suggest the presence of chain scission with products having increased mobility and others having less mobility by aligning with crystalline or near crystalline regions.

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15N SOLID STATE NMR INVESTIGATION OF NORBORNENE-TERMINATED ADDITION POLYIMIDE CURE AND HYDROLYSIS REACTIONS.

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An entire family of high temperature processable polyimides have evolved based on the Polymerizable Monomer Reactants, or PMR, approach to polyimide chemistry. High molecular weight thermoplastic polyimides exhibit useful properties for high temperature, lightweight articles, but are very difficult to process - especially into fiber-reinforced composites. A multi-step scheme, known as "Polymerizable Monomer Reactants" (PMR) was developed by NASA Lewis Research Center (LeRC) to circumvent the processing issues. In PMR chemistry an oligomeric polyimide is formed with reactive terminations that allow post-processing into a high molecularweight, or cross-linked, polymer. cis-5-Norbornene-endo-2,3-dicarboxylic anhydride is commonly used as a functional termination in these addition polyimide formulations. These polyimides are known as "norborne-terminated" or "nadic-terminated" systems. Several commercially successful polyimides including PMR-15, developed by NASA LeRC, and AFR700B, developed by the U.S. Air Force Research Laboratory, utilize norbornene terminal groups. These systems undergo curing and post-curing reactions at temperatures up to *4000C* yielding a complex and poorly understood polymer network. In this study we have employed 15N isotope enriched model compounds of the backbone and terminal groups to investigate the curing and hydrolysis reactions of this family of high temperature polyimides. Since all primary reactions involve the imide ring nitrogen, 15N NMR spectroscopy is a natural tool to elucidate the chemistry of these polymers. We can observe and follow all reactions including the amic acid formation, condensation of amic acid to imide, retro Diels-Alder reaction, Michael addition reactions, and hydrolysis reactions.

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THE CONTRIBUTION OF BACKBONE DYNAMICS TO ENTROPY CHANGES OCCURRING ON OXIDATION OF CYTOCHROME B5: CAN REDOX LINKED CHANGES IN HYDROGEN BOND NETWORKS MODULATE REDUCTION POTENTIALS?

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Changes in backbone dynamics occurring upon oxidation of rat cytochrome b5 have been examined through model free analyses of 15N-relaxation rates of both oxidation states of the protein. Based on the observed changes, an upper bound for the contribution of backbone dynamics to the entropy change associated with oxidation has been calculated. The magnitude of this contribution, 70 J/KMole, is strikingly similar to the total entropy change associated with oxidation of the protein determined through an analysis of the temperature dependence of the reduction potential. Origins of the differences in dynamic behavior of the oxidized and reduced protein can be attributed to redox linked changes in hydrogen bond strengths based on largescale differences in amide proton exchange rates. Based on these observations the magnitude and the possible significance of entropic contributions to the electromotive force are discussed. Analysis of the 15N-relaxation rates included modeling of anisotropic diffusional behavior which was expected based on the distinct physical assymetry of the protein. An axially symmetric diffusion tensor model was found to fit the rotational reorientational properties of the protein in both oxidation states. The contribution of paramagnetic relaxation to the 15N-relaxation rates of the oxidized protein was calculated based on modified Solomon-Bloembergen equations. The determination of the electronic correlation time of the paramagnetic center was based on fits to the proton relaxation rate enhancements of protons in close proximity to the paramagnetic center. Analysis of the dynamic properties of the oxidized cytochrome b5 were based on multiple field measurements of 15N T1 and T2 relaxation times.

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HOST FRAMEWORK FLEXIBILITY AND FREEDOM OF MOTION OF GUEST MOLECULES IN SUPRAMOLECULAR HOST-GUEST COMPLEXES.

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Host molecules which bind guests through conformational changes of the host are called hemicarcerands. Guest molecules can escape at high temperatures, but remain incarcerated at ordinary temperatures through a process called constrictive binding. Cryptophane-E is a hemicarcerand and is a particularly good host molecule for small tetrahedral shaped guest molecules such as CHC13 and CH2C12. The role of framework flexibility in the complexation/decomplexation processes has been addressed in the literature with molecular modeling and with molecular dynamics simulations, but never with direct experimental studies. We have measured the carbon-13 NMR relaxation parameters for the framework carbons of the host cage as well as of the bound guest molecules. We have found that the bound CH2C12 guest molecule is virtually unhindered in its motion in spite of being incarcerated by the cryptophane host. Future work will involve studies of relaxation at elevated temperatures and efforts to model the motional behavior.

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COMPUTER ANALYSIS OF SINGLE CRYSTAL NMR DATA.

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A convenient method for retrieving parameters from "raw" single crystal data has been developed. This software application can analyze both quadrupolar (I>1/2) and non-quadrupolar nuclei (1=1/2), in single crystals. All types of NMR observable interactions (quadrupolar-coupling, chemical-shielding anisotropies, dipolar interaction and indirect spin-spin contributions) that give rise to orientation-dependent NMR frequencies are considered. Combined effects such as quadrupolar-coupling with chemical-shielding anisotropies are also taken into account. Symmetry properties of special and general sites in crystallographic space groups are also integrated into computations.

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INVESTIGATION OF PARTIAL OXIDATION CATALYSIS BY SOLID-STATE NMR.

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Partial oxidation catalysis is widely used industrially to convert alkenes or alkanes to more valuable chemicals with various functional groups. Despite extensive study, the mechanisms of most partial oxidation reactions are not unknown. We are applying solid-state NMR spectroscopy to investigate two commercially important partial oxidation reactions: the production of maleic anhydride from n-butane on vanadium phosphorus oxide (VPO) catalysts and the oxidation of propylene to acrolein over a bismuth molybdate catalyst. The reaction system was subjected to different heating methods: variable temperature NMR, extended oven heating and transient heating. 13C MAS NMR spectroscopy with labeled materials was used to study the reactant, products and intermediates during and after the reaction. 13C-label scrambling in the bismuth molybdate system indicates that an allylic intermediate is involved in the oxidation of propylene to acrolein. The relative merits of a batch reaction versus a flow reaction will be discussed.

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4-SPIN SPIN-DIFFUSION MECHANISM IN 19F 2-D NMR EXPERIMENTS OF OXYFLUORIDES.

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Negative cross-peaks have been observed in the 2D magnetization-exchange MAS NMR spectra of BaMo03F4 under fast-spinning conditions, which are explained by proposing a 4-spin spin-diffusion mechanism. There are four fluorine sites,

in the structure of BaMoO3F4, all separated by approximately 3.5 A. The 19F MAS NMR spectrum shows two groups of resonances (-24 and -28 ppm, and -100 and -108 ppm) with significant shift difference between the two groups (80 ppm); the chemical shift difference between two resonances within each group is, however, small and similar. 2D magnetization-exchange experiments were performed to measure spin diffusion rates. Negative cross-peaks were observed connecting the ;V24 and iV108 ppm, and -28 ppm and -100 ppm resonances. A 4-spin spin-diffusion mechanism, where two pairs of spins simultaneously undergo a flip-flop transition to compensate for the large energy mismatch, is proposed to explain these cross-peaks. Experiments with variable mixing times showed that the 4-spin spin-diffusion mechanism dominates at shorter mixing times, while the normal spin diffusion becomes more important at longer mixing time. A simple formalism is developed to explain these results.

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HETERONUCLEAR-CORRELATION EXPERIMENTS FOR CHEMICAL AND STRUCTURAL INVESTIGATIONS OF ALUMINOBOROSILICATE GLASS SYSTEMS.

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Intermediate-range order is probed in barium aluminoborosilicate glasses with a number of solid-state NMR heteronuclear-correlation techniques. One-dimensional cross-polarization magic-angle spinning (CPMAS), rotational-echo double-resonance (REDOR), and transfer of populations in double-resonance (TRAPDOR) experiments are used to provideinformation about network-former/network-former and network-former/network-modifier relationships. In particular, we perform 11B/29Si REDOR, 11B/27A1 TRAPDOR, and 1lB/137Ba TRAPDOR experiments on a range of glasses in the system r BaO : A1203 : 2 B203: 4 Si02. Indirect detection of barium cationic sites has been achieved by continuous irradiation of the 137Ba nucleus in TRAPDOR experiments, facilitating study of the role of barium within the glass microstructure. HX CPMAS (X = Al, B, Si) experiments have also been performed on acid-leached samples to identify the structural changes taking place within the glass network, and connectivities in leached samples will be compared to those observed in as-synthesized glasses.

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1 70 *MQ MAS NMR STUDIES OF ZEOLITES IN THE HIGH FIELD.*

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Oxygen-17 MQMAS NMR studies were performed in the high field of 17.6 Tesla. A good resolution between two oxygen signals due to SiOSi and SiOAl fragments in the 170 enriched zeolite Na-ZSM-5 could be obtained. From the residual linewidth of the isotropic SiOSi signal, it is concluded that a change of the bridging SiOSi angle by 13° gives rise to a change in the isotropic chemical shift of less than 6 ppm. For zeolite Na-A, the SiOAl angle varies by 14°, whereas the two resolved signals of the threee oxygen atoms sho a distance of 10 ppm. Four oxygen atoms exist in the zeolites of faujasite type. Three signals can be resolved, and the distance of 13 ppm is due to a variation of 14° in the SiOAl angles of the low silicate X zeolite (LSX).

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REDOR/REAPDOR EXPERIMENTS ON ZEOLITES USING HIGH SPEED CP-MAS PROBEHEAD.

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In zeolites both 1H and 29Si nuclei offer good detection sensitivity. Besides, being spin 1/2 nuclei, their spin manipulations by hard r.f pulses can be readily accomplished in heteronuclear dipolar recoupling experiments. From the experimental point of view also, a classical CP-MAS probehead would suffice for an easy implementation of the desired experiment and the high speed sample spinning (ca. 15 kHz) allows one to measure the REDOR/REAPDOR behavior at short dephasing times. This latter feature allows us to estimate shorter internuclear distances. We have carried out 29Si-1H REDOR and 1H-27A1 REAPDOR experiments in the zeolites H-Y, H-mordenite and H-ZSM-12. Highly resolved proton resonances due to the bridging hydroxyl groups of the zeolite framework (3.9 to 5.6 ppm), terminal SiOH groups at crystal surface and crystal defects (1.8 ppm) and residual NH4 ions (7.0.-7.5 ppm) allow us to measure the individual REDOR/REAPDOR behavior. In each case, the observed dephasing curves could be calculated by considering either an isolated pairwise interaction (Si(OH)Al) or a sum over N equivalent interactions (for the ammonium ions), using PULSAR.

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CHARACTERIZATION OF PHOSPHORUS CHEMICAL SHIELDING TENSORS IN A PHOSPHOLE TETRAMER - A COMBINED EXPERIMENTAL AND THEORETICAL STUDY.

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Phosphorus-31 1D NMR spectra of a stationary powder sample of a phosphole tetramer containing two phosphorus spin pairs have been obtained at 4.7 T and 9.4 T. As well, a 2D spin-echo spectrum at 9.4. T has been acquired. Previous P-31 CP/MAS NMR experiments indicate that, to a first approximation, the two spin pairs of the tetramer are equivalent and each may be treated as an isolated spin pair. Within a given spin pair the difference between the isotropic chemical shifts of the two phosphorus nuclei is 1.7 ppm. As well, they are coupled by both the indirect spin-spin and direct dipolar interactions, J = -362 Hz and R = 1.6 kHz, respectively. The relative orientation of the two phosphorus chemical shielding tensors with respect to the P,P dipolar vector can be determined using the dipolar-chemical shift technique; however, since the dipolar vector is axially symmetric, ambiguities in the chemical shielding tensor orientations result. Using the crystal structure, ab initio calculations and simulations of the 2D spin-echo spectra, many of these ambiguities can be removed.

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NMR STUDIES OF LITHIUM TRANSITION METAL OXIDE POSITIVE ELECTRODE MATERIALS.

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Lithium transition metal oxides are favored by many as cathode materials in lithium ion batteries due to their high energy densities and insertion potentials versus a lithium metal anode. Our solid state NMR studies of lithium manganese oxide spinels provides useful insights into the bonding properties of these materials. We have measured supertransferred hyperfine (STH) fields at the lithium-7 nuclei by variable temperature lithium-7 NMR of Li-Mn-Me-0 (Me = Ni, Co, or Li) spinels. We propose that the larger STH fields present in the substituted spinels arises from a greater covalent or metallic bonding in these materials relative to the parent Li-Mn-0 spinel. This finding may be related to the absence of the Jahn-Teller distortion and the consequent improvement in electrochemical cycling performances of particular substituted lithium manganese spinel oxides. We are also engaged in solid state NMR studies of other lithium transition metal oxides to investigate the relationship between their physical properties and electrochemical performances.

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Li-7 NUCLEAR MAGNETIC RELAXATION STUDIES OF METAL OXIDE ELECTRODES FOR Li-ION RECHARGEABLE BATTERIES.

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A wide variety of metal oxides are currently under investigation as possible electrode materials in Li-ion rechargeable batteries. Solid-state Li-7 NMR is an excellent tool with which to follow lithium behaviour as the cell is discharged. The most significant advantage of solid-state NMR is the ability to probe all types of lithium (crystalline, amorphous, metallic or ionic), simultaneously. Electrode materials share the ability to reversibly insert lithium, but aside from that, vary widely in composition and properties. Using Li-7 relaxation studies we have shown that the Li-ion environment can be examined, and the relaxation behaviour used to characterize the interaction between the lithium and the metal oxide electrode as the potential of the cell changes.

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SOLID STATE NMR AND AB INITIO INVESTIGATIONS OF THE RELATIONSHIPS BETWEEN 170

QUADRUPOLAR COUPLING PARAMETERS AND STRUCTURE IN ALKALINE EARTH SILICATES.

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In recent years we have seen an increase in the use of 170 solid state NMR as a probe of structure in a variety of oxygen containing materials. Despite this increase the assignment and interpretation of 170NMR spectra in solids has been complicated by an incomplete understanding of the relationships between 170 NMR parameters and structure. Through a combined use of ab initio calculations and 170 2D isotropic/anisotropic NMR measurements in crystalline materials of known structure we have begun investigation of the trends between 170 NMR parameters and structure in alkaline earth silicate systems. Using clusters of bridging and non-bridging oxygen environments coordinated out to a radius of -3.5A we have made a number of assignments for 170 resonances in Clinoenstatite(MgSi03),Wollastonite(CaSi03), and Diopside (CaMgSi206). On the basis of these trends we have established a number of trends in 170 quadrupolar coupling constants and asymmetry parameters with structure.

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APPLICATIONS OF NMR FOR NONDESTRUCTIVE EVALUATION OF NUCLEAR MATERIALS.

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The toroid cavity NMR technique will be presented and discussed in this study as a nondestructive evaluation (NDE) method for assessing water content in nuclear materials. The DOE-STD-3013-96 packaging standard mandates a maximum water content of <0.5% by weight in radioactive materials at the time of packaging and throughout storage life. Currently proposed NDEs for assessing water content rely on extensive and costly setups or on the reaction products of water radiolysis. In contrast, the toroid cavity NMR detector can assess water content directly. The detector geometry is suitable for radial concentration imaging and suggests a safe, inexpensive container design that is convenient for periodic integrity checks. Results from previous experiments have demonstrated the ability of the toroid cavity NMR detector to measure water content in silicon dioxide with a sensitivity of -0.5% by weight H20, comparable with other NDEs. The results of experiments using depleted uranium oxide (U02) samples prepared at different moisture levels will also be presented. U02 and bulk water calibration samples were interspersed at different radial locations within the detector. The analytical capabilities afforded by the toroid cavity radial imaging methodology will also be discussed for this application.

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1H-15N-13C TRIPLE RESONANCE SOLID-STATE NMR EXPERIMENTS FOR PEPTIDES AND PROTEINS.

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Structure determination of oriented samples by solid state NMR spectroscopy is being developed as a general method for membrane proteins. 1H-15N dipolar couplings, hydrogen chemical shift and nitrogen chemical shifts have been used to provide structural constraints. Several approaches are being used to sequentially assign the resonances in multidimensional solid state NMR spectra: 1) specific amino acid labeling; 2) amide nitrogen spin-exchange; 3) amide proton spin-exchange and 4) triple resonance 1H-13C-15N backbone total correlation. We have shown that a 1H-13C-15N triple resonance pulse sequence, combining 15N-13C cross polarization transfer and 1H-15N polarization inversion spin exchange at the magic angle (PISEMA), can be used to obtain high resolution 1H-15N dipolar coupling, 15N chemical shift, 13C chemical shift spectra. A series of 3D experiments with short (0.3 ms) and long (2 ms) 15N-13C cross polarization enables the sequential assignment of peptide backbone resonances in oriented samples.

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RECENT DEVELOPMENTS IN q-REDOR AND REAPDOR NMR.

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The measurement of heteronuclear dipolar couplings with rotational-echo, double-resonance NMR (REDOR) is straightforward for isolated S-I spin pairs. However, measuring the n dipolar couplings for an S spin coupled simultaneously to n I spins is not easy because of additional complications arising from the orientational dependencies between the n dipolar tensors. We present an important modification of REDOR, called q-REDOR, that is useful for systems with multiple dipolar couplings. This new experiment recovers the n dipolar couplings while eliminating the complicating orientational dependence between the dipolar tensors of the REDOR experiment. The measurement of heteronuclear dipolar couplings between spin-1/2 nuclei and quadrupolar nuclei can be made using rotational-echo, adiabatic-passage, double-resonance NMR (REAPDOR). Computer simulations and experimental data will be provided that show the usefulness of this experiment. Results will be presented for 2H, 170, 14N, and 63Cu containing spin systems.

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207PB AND 137 BA NMR OF SOLID SOLUTIONS.

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Lead strontium and barium nitrates, like the titanates of the same cations, form a continuous set of solid solutions. 207Pb NMR spectra of mixed crystals of lead/stronium nitrate and lead/barium nitrate each show up to 13 lines, arising from lead ions with from zero to twelve Pb2+ nearest-neighbor cations replaced by Sr2+ or Ba2+. In the case of (Pb,Sr)(N03)2 these shifted lines are further split by the multiplicity of inequivalent nearest-neighbor replacements. The average shift per Sr2+ ion is 21.8 ppm; that for Ba2+ is smaller. We tentatively attribute the effect to a difference in the quadrupolar polarizability of the ions. Using MonteCarlo/Metropolis calculations, the intensities of the resonances can be fit to statistical models of Pb2+ and Sr2+ ion distributions, and used to probe the microenergetics of solid solution formation. The data can be satisfactorialy fit by distributions in which the cations are slightly clustered, with like pairs of nearest neighbors being favored by 120 J/mol over unlike pairs. Interestingly, this finding is inconsistent with powder diffraction results for the mixed crystals, where the dependence of lattice parameter on composition shows a slight positive curvature, generally held to indicate a favorable interaction between unlike ions. We are currently trying to extend this technique to the corresponding titanates.

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SPECTRAL SIMULATION OF ROTATING SOLIDS BASED ON LANCZOS AND FLOQUET METHODS FOR COUPLED SPIN SYSTEMS UNDERGOING CHEMICAL EXCHANGE BETWEEN MULTIPLE SITES.

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Previous work in this lab has demonstrated that taking advantage of Liouville matrix sparsity using split operator and Chebyshev approximations significantly improves the performance of spectral simulation. Here, we consider the use of Lanczos tridiagonalization and direct spectrum computation via the solution of a pentadiagonal system of equations. The method is formulated for use in simulation of liquid and spinning solid systems. It avoids the prohibitive memory and cpu time requirements characteristic of a Floquet treatment using Householder methodology. Key features of the numerical method are as follows: (1) A quasiminimal residue strategy is employed, wherein errors associated with nonorthogonality of Lanczos vectors are eliminated by posing an underdetermined tridiagonal system of equations which is solved by the method of least squares (this gives rise to the pentadiagonal system). (2) A dual (asymmetric) Lanczos iteration is used to treat exchanging systems for which the Liouvillian is non-Hermitian.

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A MULTIFIELD 170 NMR DOR AND DAS STUDY OF SILICEOUS ZEOLITE FERRIERITE.

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As part of a program aimed at determining the utility of 170 NMR for investigating zeolites (L. M. Bull, A. K. Cheetham, T. Anupold, A. Reinhold, A. Samoson, J. Sauer, B. Bussemer, Y. Lee, S. Gann, J. Shore, A. Pines and R. Dupree, J. Am. Chem. Soc, 14, 3510-3511, (1998).) we have studied siliceous ferrierite using both Dynamic Angle Spinning and DOR. This material is an excellent candidate for examining the effects of local environment on the chemical shift and quadrupolar parameters as its structure has been determined to high precision by neutron diffraction and the NMR spectra are not complicated by aluminum or cation disorder. Ferrierite has ten crystallographically distinct oxygen sites in the symmetic unit and the Si-O-Si bond angles range between -173-138 degrees. Both DAS and multiple field DOR experiments clearly resolve at least 8 oxygen resonances. Attempts at determining the chemical shift and electric field gradient at each site are described.

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THE Si-29 AND B-11 NMR STUDY OF POLYMER PRECURSOR FOR HIGH TEMPERATURE CERAMICS.

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The development of the SiCBN ceramics materials has been of the great interest in recent years due to its unusual high temperature and oxidative stability. The ceramics prepared from polyborosilazane resin have been reported stable up to 2000 C. To tailor the ceramics for the desired properties, the understanding of resin structure, as well as the ceramic conversion and crystallization process is very important. In this presentation, the recent results of structural characterization of polyborosilazanes resin using solution (29-Si, 11-B) NMR techniques, and study of ceramic conversion and crystallization process by solid state NMR analysis will be addressed.

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SOLID-STATE 93Nb NMR STUDIES OF LEAD NIOBATE INTERMEDIATES AND LEAD MAGNESIUM NIOBATE (PMN).

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Solid-state 93Nb NMR is an important spectroscopic technique to investigate the solid-state synthesis and structural features of lead niobium oxide-based ferroelectrics of multiple B-site Pb(B'B")O3 perovskites. Solid-state 93Nb NMR studies have examined the local atomic-level chemical environments of B-site Nb(V) ions in (Pb(Mg1/3Nb2/3)03 (PMN), and in related lead niobate intermediates significant to the synthesis of PMN. Static and MAS 93Nb NMR spectra obtained at variable magnetic fields for PMN powders with different perovskite/pyrochlore phase contents (69-100%), and prepared by different solid-state reactions, have been examined. In addition, various lead niobates of varying Pb/Nb ratios in the binary PbO/Nb205 system, and a low-Mg content PMN with the pyrochlore structure, have also been studied. Results of these 93Nb NMR studies, including measured chemical shifts and quadrupolar parameters for PMN and lead niobates, are being used to develop structural models for the lead niobates (with different modes of interconnection of B06 and OA4 networks) and to understand the role of the various lead niobate intermediates in the solid-state transformations leading to the formation of

PMN.

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THE USE OF SOLID-STATE NMR TO STUDY PHOTOCATALYTIC REACTIONS ON TITANIUM DIOXIDE SUPPORTED BY POROUS VYCOR GLASS AND OPTICAL FIBERS.

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UV initiated photooxidation reactions of trichloroethylene and ethanol on titanium dioxide catalyst have been investigated using solid-state NMR techniques. In-situ irradiation of the catalyst allows the identification of long-lived reaction intermediates and final products using 13C MAS-NMR. Cross polarization experiments have detected the presence of surface bound intermediates (predominately acetates) which form through reaction with surface hydroxyl groups and are stable until irradiated further. Monolayer Ti02 coverage of porous vycor glass provides a UV transparent system capable of decomposing the majority of acetates while the use of Ti02 powder itself (Degussa P-25) scatters the light to create "dark" regions within the sample. In order to study photoreactions on Ti02 powders further, we have developed a method for transmitting the light to the interior of the sample by utilizing microscopic quartz fibers as a support for titanium dioxide particles. This creates a photocatalyst system similar to bulk Ti02 powder while the fibers allow the transmission of UV photons to the interior of the sample. The effectiveness of fiber supported Ti02 powders in photochemical reactions was evaluated by monitoring the degradation of trichloroethylene.

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RELAXATION MEASURMENTS WITH LOW-FIELD, ONE-SIDED NMR.

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There is interest in using NMR as a non-destructive method to determine properties of materials such as elastomers and composites. Experimental data exists which demonstrates that correlations can be drawn between variations in cross-link density, strain, and aging processes in elastomeric materials and NMR relaxation parameters, e.g., T,, T_{1p}, T_2. Until recently, most of the available data was from high field studies employing homogeneous magnetic fields (B_0 and B,). Some recent work by Benson and McDonald [JMR A 112, 17-23 (1995), JMR B 109, 314-317 (1995)] focused on understanding NMR relaxation in the case of stray-field imaging where B_0 is inhomogeneous but is homogeneous. The case where both fields are inhomogeneous is important for "one-sided" NMR where a fringe field and surface coil arrangement are used to obtain a localized relaxation measurement. Guthausen and co-workers [JMR **130**, 1-7 (1998)] explored the effects of pulse sequence parameters on apparent relaxation times for their MOUSE which utilizes a small magnet and surface coil to make near-surface NMR measurements. In this poster we expand on the existing bodies of work to consider in more depth how to best select pulse sequence parameters for an inspection (in terms of compromises between desired

volume, signal/noise, and most reliable relaxation measurement). Our application involves lower B_0 fields than the MOUSE and is appropriate for situations requiring deeper penetration through interfering conductive layers.

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NMR INVESTIGATIONS OF MESOSTRUCTURED ALUMINOPHOSPHATE.

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We present results of NMR investigations of mesostructured aluminophosphate synthesized by the liquid crystal templating (LCT) method. X-ray investigations revealed a basal spacing of 32A, that changes to 23A after heating the samples to 200°. It is assumed that this effect is caused by a different conformation of the template molecule after the thermal treatment. Also, it is not clear whether the layered structure of the aluminophosphate changes as well. Therefore, we carried out 1H, 13C, 27A1 and 31P MAS NMR including DQ NMR and REDOR. The results can be summarized as follows: i) There are obviously no significant changes of the conformation of the template molecule, ii) Using 1H-31P-REDOR we can assign the various 31P signals (up to 7)to P04 units at the inner surface and within the aluminophosphate layer structure, iii) Tetrahedrally co-ordinated aluminium and a small amount in octahedral coordination is found. 1H-27A1 REDOR allows a distinction of A104 units situated at the inner surface or within the layer structure, iv) Using 31P DQ NMR the connectivities of the tetrahedra are probed.
Obviously, the structure of the aluminophosphate layers seems to be tridymite-like which cannot by concluded from the X-ray investigations.

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HOMONUCLEAR CORRELATION SPECTROSCOPY INVOLVING QUADRUPOLAR NUCLEI.

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2D Exchange NMR can successfully be applied to verify connectivities of structural units both in crystalline and amorphous materials using the dipole coupling between spin-1/2 nuclei. In these 2D MAS NMR experiments the dipole coupling between the nuclei must be recoupled during the mixing time as MAS is applied. A variety of recoupling sequences are known, based on rotorsynchronized r.f. pulses, that provide efficient recoupling of the dipole interaction. However, for quadrupolar nuclei no such schemes have been developed so far. In this contribution we report on first results of homonuclear 2D Exchange NMR of quadrupolar nuclei (23Na, 11B) using the standard Exchange NMR schema with just three r.f. pulses. During the evolution and detection periods (t1 and t2) the sample rotates at the magic angle, whereas it spins off-angle during the mixing period, thereby recoupling the dipole interaction between the quadrupole nuclei efficiently. Applications to crystalline sodium aluminum diphosphate, sodium sulfite, and potassium borate glasses are shown.

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STRUCTURE INVESTGATIONS OF NaP03-Nb205 GLASSES BY NMR.

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The structural changes of the network of NaP03-xNb205 glasses (x=0.05, 0.1, 0.15, 0.4) are investigated by 31P and 23Na MAS NMR. Particularly, the Qn group distribution is of significant interest in order to understand how Nb is incorporated in the structure. To this end, the results of 31P MAS and Double Quantum (DQ) NMR are considered simultaneously. The 31P MAS lineshapes are shifter to lower field with increasing amount of Nb and get broader. DQ NMR provides independent information concerning the connectivities of the various phosphate building units. Furthermore, 31P-23Na TRAPDOR experiments have been used to probe the presence of Na ions around the various phosphate tetrahedra. Finally, the feasibility of 93Nb NMR in these glasses is considered.

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HIGH-PERFORMANCE 4 MM CP/MAS PROBES FOR VARIABLE TEMPERATURE STUDIES IN HIGH-FIELD LIQUID-STATE NMR SPECTROMETERS.

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Design of high-performance variable-temperature (VT) CP/MAS probes for high-field narrow-board magnet (i.e., liquid-state) NMR spectrometers will be presented. The probes are based on a new stator produced from different machinable high-tech ceramics and can accommodate 4, 5, or 7 mm o.d. rotors. The qualities of the probes are probably best illustrated by the performance of the 4 mm CP/MAS probes for which spinning speeds of 20-21 kHz are routinely obtained. At 9.4 Tesla (400 MHz spectrometer) an observe rf field strength (gammaB1) of 80 kHz at about 100 MHz is achieved with less than 300 W of power. Similarly, 1H decoupling at 400 MHz may be performed with gammaB2 = 95 kHz using less than 100 W of power. Sensitivity is excellent and illustrated by the 13C CP/MAS of HMB giving S/N = 145:1 (4 scans, 80 microlitre sample volume). On 500 and 750 MHz spectrometers the observed S/N ratios are about 200:1 and 300:1, respectively. For a 5 mm o.d. rotor we obtain a S/N = 400:1 at 750 MHz. Probably most importantly, during VT operation of our stator design it is shown, using Pb(NO3)2 as a thermometer, that the temperature gradient across the sample can be as low as 0.4 degree C, e.g. from 80 to 160 degrees C the gradient is between 0.4 and 1.0 degree C. To our knowledge a similar excellent VT performance has not been reported for other probes.

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CHARACTERIZATION OF POLYANILINE/DODECYLBENZENE SULFONIC ACID POLYMERIZED FROM AQUEOUS MEDIUM: A SOLIDS NMR STUDY.

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Our study focuses on aniline polymerized in aqueous medium in the presence of dodecylbenzene sulfonic acid (DBSA). The resulting polyaniline (PANI)/DBSA forms stable aqueous dispersions which offer attractive starting material for various applications. We report preliminary results on the characterization of PANI/DBSA - as synthesized doped, dedoped, and redoped forms. 13C CPMAS NMR shows that dedoping with NH4OH results in the non-conducting PANI base, from which only ca. 33% of the DBSA dopant is removed. Rotating frame relaxation measurements, T1rho(H), show that the remaining DBSA is mixed with the polymer on the molecular scale. The DBSA, possessing a bulky aliphatic chain, may be entrapped sterically within the polymer, or may be involved in specific interactions. To further delineate these possibilities we have synthesized 15N-labeled PANI, and dedoping was carried out with two dedopants - NH4OH and LiOH. For the latter, Li+ efficiently disrupts H-bonding, thus leading to the removal of 85% of the DBSA. In PANI samples dedoped with LiOH we identify by 15N CPMAS NMR the existence of two distinct environments, as reflected by two imine and two amine peaks. Since the the lithium cations counter balance the DBSA anions, we utilzed them to investigate their immediate local environment. 15N-7Li and 13C-7Li REDOR experiments clearly show that the Li+(-DBSA-) reside preferentially in the proximity of only one imine environment. Experiments are under way to refine the characterization of these two environments, and to relate them to the efficiency of the redoping process.

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SOLID-STATE NMR STUDIES OF THE VITAMIN B12 FAMILY.

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Vitamin B12 (cyanocobalamin) and its derivatives have been selectively labeled with H-2, C-13, or N-15 for a variety of solid-state NMR experiments including CPMAS, static, and relaxation studies. These relatively simply biologically-relevant complexes are being studied with a view to look at cobalamin-dependant enzymes in the solid state. The methyl rotation of methyl-d3-cobalamin has been determined to go through 3-fold jumps with a barrier to rotation of 8.3 +/-1.3 kJ/mol. The N-15 chemical shift tensor of cyano(N-15)cobalamin was determined to be axially symmetric with a span of 524.5 ppm which is significantly larger than other cyanide nitrogens (e.g. nitriles). Doubly labeled cyano(N-15,C-13)cobalamin allowed for the determination of the N-15,C-13 dipolar coupling constant of 1800 +/- 75 Hz. Our ongoing efforts in

C-13 and N-15 solid-state NMR of these and other cobalamins will also be presented.

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DETERMINATION OF THE FUNCTIONALITY AND FUNCTIONALITY DISTRIBUTION OF POLYETHER POLYOLS BY QUANTITATIVE 13C-NMR SPECTROSCOPY.

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The flexible polyurethane foams used in furniture and automotive seating are produced by the reaction of an isocyanate such as methylene diphenyl diisocyanate (MDI) and a polyfunctional hydroxy compound (polyol), together with a suitable package of catalyst(s), surfactant(s) and blowing agent(s). In these applications, the polyol is normally a polyether, formed by the base-catalysed addition polymerisation of ethylene oxide (EO) and propylene oxide (PO)onto. a low molecular weight, polyfunctional alcohol such as 1,2,3-propantriol (glycerol). Important parameters of the polyol include the relative amounts of PO and EO, the structure of the polymer chains (block or random), the ratio of the primary and secondary hydroxyl end groups and the relative amounts of species with different functionalities. The functionality of polyether polyols can vary from that of the pure initiator because of the presence of water in the raw materials, leading to the formation of diols, and also from a side reaction during propoxylation which produces an allyl alcohol ion as the initiator of mono-hydroxy molecules (mono-functional with respect to isocyanate). A method is described for the determination of the number average functionality and functionality distribution of polyether polyols based on the measured intensities of relevant end groups observed in 13C NMR spectra. Longitudinal (T1) relaxation time measurements on glycerol-, trimethylolpropane- and pentaerythritol-initiated copolymers of propylene oxide and ethylene oxide show that the slowest relaxing moiety which needs to be quantified is the vinyl CH2= group of the unsaturated side product of the propoxylation reaction. This more detailed characterisation has already proved to be of value in assessing the consistency of commercial polyols and in investigating production processes. The method will undoubtedly form a cornerstone of research and development of these types of polyether polyols in the future.

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ANISOTROPY IN THE P-31, CU-63/65 INDIRECT SPIN-SPIN COUPLING AND P-31 NUCLEAR SHIELDING TENSORS OF LINEAR COPPER(I) PHOSPHINES.

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Phosphorus-31 CP/MAS NMR spectra of two linear bis(tribenzylphosphine)cuprate(I) salts reveal significant anisotropy in the one-bond P-31,Cu-63/65 J-tensors. The well-characterized space group and

point symmetry of these compounds greatly simplifies the P-31 lineshape analysis, thus dispensing with the need to make assumptions about the interaction tensors involved. This offers an unique opportunity to study the anisotropy in J by calculating direct dipolar coupling constants from internuclear distances, and by using zero-field nuclearquadrupole resonance spectroscopy to obtain the magnitudes of the Cu-63/65 nuclear quadrupole coupling constants. The anisotropy of the J-tensor in these compounds is found to exceed +700 Hz. Spectral simulations which employ first-order perturbation theory to account for the Cu-63/65 quadrupolar effects fail - even at 9.4 T. Phosphorus-31 NMR spectra of non-spinning samples at three applied magnetic fields are also presented, along with lineshape calculations based on full-matrix Zeeman-quadrupolar Hamiltonian diagonalization. It is shown that exact P-31 lineshape calculations provide the relative signs of the quadrupole coupling constant, isotropic J-coupling and the effective dipolar coupling constant.

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SOLID-STATE NMR STUDY OF CESIUM EXCHANGED ZEOLITES.

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The ability to identify the cesium cation locations in zeolites is of growing interest in environmental and industrial applications. Environmentally, radioisotopes of cesium are products of nuclear fission and are a significant component of liquid radioactive waste from nuclear power plants and environmental pollution resulting from the Chernobyl accident. The encapsulation of radioactive cesium is desirable and zeolites show high selectivity for adsorbing cesium from aqueous solutions. Several zeolites of interest tend to include multi-structural intergrowths resulting from alternate structural stacking sequences, resulting in modified ion-exchange, sorption and catalytic properties. Solid-state NMR can be used to probe the different framework and cation environments yielding structural and chemical information related to the absorption and exchange process, potentially identifying intergrowth interfaces. Single-resonance magic-angle spinning (MAS) experiments provide information about the silicon, aluminum and cesium sites present. Double-resonance NMR experiments are important in determining the through-bond connectivities or through-space proximities of cations to the framework atoms. The cations exchanged into the zeolites create different environments which can be probed using techniques such as cross-polarization (CP), rotational-echo double-resonance (REDOR) and transferred-echo double-resonance (TEDOR). These experiments are used to provide information concerning the locations of the sorbed cations and their nanostructural relationships, so probing the coherency of the aluminosilicate framework.

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RIACT MULTIPLE QUANTUM (MQ) MAS NMR SIMULATIONS, MQMAS TRIPLE QUANTUM CP, AND CP MAS NMR EXPERIMENTS OF FLUORIDES.

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We have been using the Rotation-Induced Adiabatic Coherence Transfer (RIACT) MQ technique to study a variety of inorganic materials including zeolites. Numerical simulations of the anisotropic dimension of the RIACT MQ experiment have been performed as a function of the asymmetry parameter, h, for different spacings between the triple quantum (3Q) excitation and 3Q to single quantum (1Q) reconversion pulses. Large changes in the spectra were observed, in comparison to the spectra obtained with 1D MAS NMR methods. The method is very sensitive to the relative orientation of the quadrupolar tensor and rotor axis, and signal can only be obtained from a maximum of 60 % of powder. In addition, the intensity varies with the spacing between the two pulses. Good fits of the experimental data were obtained in the simulations, which allowed the quadrupole coupling constants and asymmetry parameters to be extracted. Single quantum cross polarization (SQCP) has been combined with the MQMAS NMR experiment to allow spectral editing of high resolution spectra of quadrupolar nuclei. We have been able to create triple quantum coherences of quadrupolar nuclei more effectively by triple quantum cross polarization (TQCP) from spin 1/2 nuclei. The efficiency of the 19F/23Na TQCP MQMAS experiment was compared with that of SQCP experiment combined with a three-pulse with z-filter, or a RIACT(II) sequence for an oxyfluoride compound. The effect of offset frequency, rf amplitude, and spinning speed, on the efficiency of the TQCP and TQCP dynamics, will be discussed. Cross-polarization experiments are applied to study HFC gases sorbed on zeolites.

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NMR OF SAMPLES CONTAINING METAL FOILS.

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By using striated spool configurations of a sample containing aluminum foil, in which the axis of the spool is colinear with the solenoid coil axis, one can obtain high-quality 13C NMR spectra of static samples of organic material attached to aluminum foil. By combining this striated spool configuration with the Magic Angle Hopping (MAH) technique, one can achieve a high degree of isotropic averaging of the 13C spectrum. This opens to NMR techniques the study of a variety of samples containing metal foils, e.g. thin films deposited on metal foils and electrochemical systems with species adsorbed on metal-foil electrodes.

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CROSS POLARIZATION AND DIRECT POLARIZATION TRANSFER TO SURFACE SPECIES USING LASER-POLARIZED XENON.

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We have extended the utility of optical pumping in surface NMR by implementing our optical pumping and magic angle spinning (OPMAS) methodology to transfer the high polarization of optically pumped 129Xe to surface carbon and silicon species under high resolution conditions. 29Si MAS spectra of fumed silica and 13C spectra of chemisorbed methanol on silica have been obtained using a steady flow of hyperpolarized xenon adsorbed onto the surface at 135K. Cross-polarization to 29Si from SPINOE enhanced hydroxyl protons and to 13C from enhanced methyl protons are observed with good efficiency. A direct SPINOE transfer from 129Xe to 13C is observed to give the highest enhancement under these conditions.

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A THEORETICAL DESCRIPTION OF THE 14N OVERTONE NMR EXPERIMENT IN STATIC AND SPINNING SOLIDS.

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Overtone NMR is an experiment introduced by LeGross, Bloom, Tycko and Opella (J. Phys., 64, 1522 (1986), J. Chem. Phys., 86, 1761 (1987)), capable of providing 14N powder spectra devoid of first-order quadrupole broadenings by irradiation and observation at twice the Larmor frequency. We present here a theoretical analysis of this technique based on the density matrix formalism, and geared at finding new ways to remove the second-order broadenings remaining in these line shapes. Using appropriate rotating-frame transformations and diagonalizations it can be shown that the spin-1 overtone irradiation and detection can be viewed as processes of a fictitious spin-1/2 experiment, albeit possessing an unusual angular dependence. This constitutes one of the a key differences between an overtone and a double-quantum excitation, and among other things it complicates the narrowing of overtone resonances by conventional sample spinning techniques. It is shown, however, that since this feature does not preclude the storage and recall of overtone coherences, the removal of all quadrupolar anisotropies by dynamic-angle spinning overtone methods is still feasible.

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129Xe NMR STUDIES OF PARTICULATE CARBON BLACKS USED IN POLYMER PROCESSING.

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A wide variety of carbon black particulate fillers are commonly available for processing with elastomers, and result in very substantial improvements in bulk physical properties (modulus, tensile strength, tear resistance, etc) compared with unfilled materials. The effectiveness of a given carbon black depends in large part on the surface area of filler in contact with the elastomer, the activity of the solid surface (based upon the chemical and physical nature of the filler in relation to that of the elastomer), the "structure" of the filler (determined by its void volume), and filler

porosity. Thus far, classification of carbon black fillers has relied primarily on classical methods such as optical microscopy, light reflectance and absorption, oil absorption, N2 adsorption, etc. The ability of 129Xe NMR methods to detect subtle variations in the microscopic environment of materials makes this a potentially powerful technique to augment existing methods of filler analysis. Here we investigate a wide variety of carbon blacks using 129Xe NMR analysis. In particular, variations in Xe chemical shift/ dispersion, Xe gas adsorption, and Xe gas exchange are considered in terms of the microscopic environment of filler particles.

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MODELING GLASS STRUCTURE BY COMBINING NMR, NEUTRON DIFFRACTION, AND X-RAY DIFFRACTION DATA.

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We have extended the Reverse Monte Carlo algorithm to include data obtained from NMR experiments consistently with diffraction data. This was accomplished by using the relationship between NMR distance measurements in the solid state, specifically second moments, and the pair distribution functions of the coupled nuclei. Combining a variety of complementary data sets is important for complex multicomponent glasses. We will present details of this modeling method, and application to sodium tellurite glasses. The experiments combined in the modeling algorithm for this application include NMR second moment measurements of the sodium distribution, neutron diffraction measurements emphasizing the tellurite network, and synchrotron x-ray diffraction, emphasizing the tellurium pair distribution.

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31P-19F REDOR: GENERATING DISTANCE CONSTRAINTS IN THE BACKBONE OF DNA AND RNA.

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Characterizing the structure of DNA's and RNA's by solution-state NMR yields many constraints regarding base stacking and sugar ring conformation. However, the backbone of nucleic acids is important for stabilization of protein-nucleic acid complexes as well as recognition in nucleic acid macro-structures. Liquid-state NMR cannot generate contraints to the backbone since the phosphates have no attached protons, precluding the use of the NOESY experiment. The insertion of 19F labels into either the bases or the sugar rings would allow the use of 19F-31P REDOR to generate long range constraints to the phosphate backbone. This will be demonstrated for a DNA 12mer.

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MULTINUCLEAR SOLID STATE NMR INVESTIGATIONS OF ALKALI METAL-LOADED ZEOLITES.

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The potential to fine-tune the electronic and/or magnetic properties of metal-loaded zeolites assures continuing interest in these unique materials. We have synthesized several series of alkali metal-loaded Zeolite A materials by full or partial ion-exchange of the charge-balancing extra-framework cations $[M^1]$ followed by chemical vapor deposition of various alkali metal atoms [M] within the dehydrated zeolite cavities. The resulting materials [M(x)/M']A, x = 1 to 5, are highly coloured, atmosphere-sensitive powders. The electronic structures of the encapsulated metal clusters are investigated using field- and temperature-dependent Na-23, Rb-87 and Cs-133 solid state NMR spectroscopy and effects on the framework tetrahedral atoms are examined with Al-27 and Si-29 MAS NMR. The extent of loading and ionization potentials of both the incoming 'guest' alkali metal and the charge-balancing extra-framework cations dictate the nature of the metal clusters formed within the aluminosilicate cages. In some stoichiometries, sharp features are observed in the Na-23 and Cs-133 spectra at unique and previously unreported chemical shifts, whilst in others the metal clusters strongly affect the observed Al-27 and Si-29 spectral shifts of the framework tetrahedral atoms.

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EXTRACTING DIPOLAR COUPLINGS IN SOLID STATE NMR BY TRANSFORM AND REGULARIZATION METHODS.

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Many NMR experiments have been designed to measure homonuclear or heteronuclear distances, and these experiments often generate time-domain dipolar signals that need to be analyzed to extract the relevant dipolar coupling constants. These constants yield internuclear distances directly, and therefore an accurate and easily understandable extraction of these couplings from potentially noisy data is a major concern. Several dipolar signals will be considered including those obtained from the REDOR, MELODRAMA, and SEDOR experiments, as well as a new series form for the C7 and related signals. A review and discussion of an existing transform-based method for dipolar signal analysis will be presented, along with two new generalized methods for the extraction of dipolar coupling constants. One of the new methods is based on asymptotic signal forms, while the other is a regularization method specifically formulated to account for experimental noise and shows significant performance gains when applied to noisy time-domain signals. In addition to its noise-handling ability, the regularization method also has wide application to many other types of dipolar signals currently available in NMR experiments, and is the only method of those discussed that can yield a "C7 transform."

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STRUCTURAL TRENDS IN TERNARY PHOSPHORUS-SULFIDE-SELENIDE AMORPHOUS MATERIALS.

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Structural trends in phosphorus chalcogenide glasses and melts have been investigated using a variety of solid and liquid state NMR techniques. Results have shown how the structural organization of glassy P-S and P-Se systems are strikingly different from each other. While samples throughout the P-S system are composed of molecular P4Sn units that organize above 25 at.% S to result in crystalline phases, the P-Se system is nearly devoid of analogous P4Sen units, but instead forms glasses over a wide region (0-52 at.% P) due to effective competition between three- and four- coordinate phosphorus bonding. The present study focuses on the largely unexplored ternary phosphorus-sulfide-selenide system. Systematic investigation by 31P MAS-NMR clearly shows a trend away from homogeneously bonded materials toward more heterogeneous samples in which P-S or P-S-Se molecular entities separate out from network bonded P-Se structures as the sulfur or phosphorus concentrations are increased. Variable-high-temperature 31P-NMR measurements allow investigation of the specific chemical equilibria existing in the melts of these samples which ultimately determine the makeup of the resulting glass after quenching. In samples with high phosphorus concentrations (40-50 at.% P) we have identified an equilibrium between molecular P-S and P-Se units and their respective network-bonded groups, described by: P4Se3 + [Se] --> P4Se3 + [S], where [Se] and [S] denote the concentrations of selenium and sulfur, respectively, that participate in network bonding in the glass structure.

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SOLID-LIQUID DYNAMIC NUCLEAR POLARIZATION TRANSFER IN AQUOUS CHAR SUSPENSIONS.

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A pulsed 1H Dynamic Nuclear Polarization (DNP) technique at low magnetic field has been used to study hyperfine interactions, molecular and spin dynamics in aquous suspensions of newly synthesized carbon chars. Proton DNP enhancement is reported in suspensions of several types of chars, where both positive and negative Overhauser effects were detected in different samples. Positive DNP enhancements were observed in water suspensions of several hardwood chars as a result of a intermolecular Fermi interaction which indicates solid-liquid electron density transfer. The increase of scalar polarization with temperature that was observed in char suspensions was in contrast to the temperature behavior of ordinary free radical solutions. Correlations of experimental and theoretical results has been achieved through consideration of the electron-proton spin dipole-dipole interaction and of chemical exchange of solvent molecules. The enthalpy of activation for surface exchange diffusion as well as the life time of water molecules on the surface and the hyperfine scalar constant are estimated. The results are characteristic of

weak short-lived chemisorption bonds at the solid/liquid interface. The heterogeneous 1H DNP effect is analyzed, the influence of "cage effects" on DNP enhancement in porous media is discussed. Partial support provided by NIH (GM 42208, GM 51630, RBC) and by Nycomed Innovation.

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PARTICLE SIZE EFFECT ON TRANSVERSE NMR RELAXATION IN AQUOUS CARBON-BASED CHAR SUSPENSIONS.

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Strong particle size influence on NMT transverse relaxation in aquous suspensions of several newly synthesized carbon based chars was observed. The results are quantitatively interpreted in terms of a two-stage molecular exchange, model. A porous "cage effect" leads to slow exchange between molecules inside and outside pores, in contrast to fast molecular exchange at the solid-liquid interface, where a familiar two-site formalism can be applied. The dependence of surface properties on the relaxation data was detected. The transverse NMR relaxation time value of water protons on the paramagnetic surface of chars was estimated to be 16 microsec, which is coparable with the EPR relaxation time of free radical centers in the char. Using effect of Dynamic Nuclear Polarization (DNP), the paramagnetic shift of water protons at the surface was estimated. The value obtained by DNP is much less than the transverse NMR relaxation rate of water protons on the paramagnetic surface. This inequality can account for the independence of the NMR transverse relaxation times on the interval observed in CPMG measurements. Partial support provided by NIH (GM 42208, GM 51630, RBC), by the US Department of Energy (DE FG22-96 PC 96205), and by Nycomed Innovation.

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MOLECULAR DIFFUSION AND DNP ENHANCEMENT IN AQUOUS CHAR SUSPENSIONS.

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Low magnetic field Dynamic Nuclear Polarization (DNP), Fourier Transform Pulsed-Field-Gradient spin-echo NMR spectroscopy, and Field-Cycling NMR relaxometry were applied to study heterogeneities in several newly synthesized carbon-based chars suspended in water. Several different self-diffusion coefficients have been observed in aquous char suspensions, corresponding to regions of differing water mobility in the porous structure. Proton spin-lattice relaxation data as well as field-cycling data generally confirm the results of molecular diffusion measurements. Utilizing the Torrey model, the influence of "cage effects" on DNP enhancement in porous media is discussed.

Results suggest that the main DNP processes in char suspensions occur in por spaces and the short-range nuclear-electron interactions have a dominant effect on the DNP enhancement. Long-range interactions associated with other (nuclear and electron-nuclear) relaxation processes at the remainder of the surface layer can have small or even negligible effects. Surface properties strongly effect DNP data in char suspensions. Hydrophylic character of chars is associated with positive DNP enhancement and Fermi contact hyperfine interactions at the solid-liquid interface. Partial support provided by NIH (GM 4220.8, GM 51 630, RBC) , by the US Department of Energy (DE FG22-96 PC 96205), and by Nycomed Innovation.

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SOLID-STATE 13C NMR AND FTIR STUDIES OF METAL OXALATE PRECURSORS TO ELECTRONIC MATERIALS.

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Metal oxalate complexes are precursors for electronic ceramics of the perovskite lattice, including barium titanate, lead titanate, and complex mixed B-site systems such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN). Solid-state ^{13}C MAS and CP/MAS NMR and FTIR have been used to investigate the complex structural issues for metal oxalates having the empirical formula $A_xMO(ox)_2.nH_2O$, where A = NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+} and Pb^{2+} ions, and M = Ti^{4+} ion. The ^{13}C MAS NMR spectra show multiple carboxyl ^{13}C resonances due to different crystallographic carbonyl carbons for the tetrameric $(NH_4)_2TiO(ox)_2.H_2O$ and proposed dimeric $BaTiO(ox)_2.4H_2O$ complexes. For example, eight ^{13}C resonances from 164-175 ppm are observed for the barium complex. ^1H ^{13}C CP/MAS NMR experiments have been used to aid assignments of the carbonyl resonances in the ammonium and barium complexes based on the ^1H-^{13}C dipolar interactions between the lattice water protons and the carbonyl carbons. In addition, ^{13}C NMR, FTIR and XRD measurements have also been used to study carbon-containing pyrolysis (300 - 1200°C) intermediates and ABO_3 products ($BaTiO_3$, $PbTiO_3$, $CaTiO_3$ (perovskite) and $MgTiO_3$ (ilmenite)) obtained from these mixed ligand precursors. These results suggest the utility of solid-state NMR to examine the structural features and pyrolysis reactions of more complex oxalato precursors.

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EXPERIMENTAL AND SIMULATED EFFECTS OF INSUFFICIENT DECOUPLING ON DRAWS DEPHASING CURVES.

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Experimental DRAWS dephasing curves were obtained for [^{13}C-4, ^{13}C-6] Thymidine as a function of proton decoupling field strength and it was found that the dephasing curves were highly perturbed at a ^1H/^{13}C field strength ratio below ~3. The corresponding simulations have the same trend. The numerical simulations included the two 13C labels and three nearby protons. This has implications for the demands made on the capabilities of commercial probes used to perform homonuclear recoupling experiments.

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DIRECT OBSERVATION OF DEFECT SITES IN POLY(LACTIDE) USING 13C SOLID-STATE NMR SPECTROSCOPY.

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Poly(lactide) is a partially crystalline biodegradable polymer. A number of physical and morphological properties of poly(lactide) are linked to its stereosequence distribution. The sequence of lactic acid units can be determined from the relationship between stereocenters and their influence on chemical shift in 1H and 13C solution NMR spectra. We have observed hexad stereosequence assignment resolution. Solid-state 13C NMR spectra provide information about polymer morphology and crystal structure. The carbonyl region of the spectrum exhibits the best resolution for poly(lactide) and suggests that there are five crystallographically inequivalent sites per unit cell. We have used two-dimensional exchange NMR to determine the connectivity of the monomer units which are in different environments. The degree of crystallinity of poly(lactide) is greatly influenced by its enantiomeric purity, where small amounts of the opposite enantiomer correspond to stereosequence defects. Stereo irregularities can be studied with solid-state NMR by introducing poly(lactide) that is 13C-enriched at the carbonyl position. We have found that stereosequence defects are located in both the crystalline and amorphous regions of the polymer and that it is possible to quantitate the amount of the opposite enantiomer that has been incorporated into each region.

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THE Li-6/Li-7 CHEMICAL SHIFT ANISOTROPIES AND QUADRUPOLAR COUPLING CONSTANTS IN ORGANOLITHIUM COMPOUNDS.

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The relatively small quadrupole moment of Li-6 makes it an excellent nucleus for the simultaneous obsrevation of the effects of both the CSA and the QCC on the powder lineshape. The measurement of the QCC (and in some cases the CSA) can be confirmed from the Li-7 lineshape. We will present the Li-6 and Li-7 powder spectra for several organolithium compounds, uncomplexed to solvent or lithium halide. We will also compare our values of the CSA and QCC to those calculated by ab initio molecular orbital theory. Cross polarization from proton to Li-6 will also be discussed.

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MEASURING INTERNAL ELECTRIC FIELDS IN PROTEINS WITH SOLID-STATE NMR.

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We have constructed a device that enables us to study the effects of externally applied electric fields of up to 4x106 V/cm on the NMR observable nuclear parameters, such as chemical shift or quadrupole coupling. This was done with the intention of calibrating the dependence of these parameters on the electric field and ultimately using this calibration to determine the internal naturally occurring electric fields in proteins. The device consists of a frequency source followed by two amplification stages and is capable of producing up to 12000V ac in the kHz range. A pulse sequence was utilized that provides synchronization of the NMR and the high voltage equipment and allows for the data acquisition in such a way that the resulting 2 dimensional spectrum has the CSA envelope in the direct dimension and the electric field induced chemical shift pattern in the indirect dimension. Two alternative designs for a high voltage sample cell have been implemented. The two channel NMR probe capable of delivering high voltage to the sample cell was constructed and the chemical shift/electric field experiments involving 19F and 205T1 have been conducted.

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PHOTOCHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION IN BACTERIAL REACTION CENTERS: MECHANISM AND SIMULATIONS OF THE SOLID-STATE NMR EXPERIMENTS.

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We propose a 3-spin coherent mixing mechanism to explain the nuclear polarization in the solid state. The nuclear coherences are generated on nano-second time scale due to the coherent mixing with the electrons zero-quantum states. The nuclear polarization which is 10^3-10^4 times bigger than the thermal, results from a combination of coherent spin dynamics and asymmetric chemical kinetics (faster decay of the excited triplet states). We simulate the experimental data within the three-spin mixing mechanism by solving the Stochastic Liouville equation in the presence of chemical kinetics and calculating the time-dependence of the density operator. Nuclear polarization is computed for a set of crystallites randomly oriented with respect to the magnetic field. Polarized powder patterns and MAS spectra are generated subsequently. The simulations are in good agreement with the experimental data and successfully account for the following: 1) magnitude and sign of polarization of the primary electron acceptor, BPheo; 2) time constants of the approach of the polarization to steady state; 3) MAS spectra of Bpheo. Several interesting features of the mechanism can be mentioned. First, unlike the Radical Pair Mechanism, the difference in spin-lattice relaxation rates between the excited (paramagnetic) states and the ground states is not the key point of the mechanism. Second, the largest effect is expected when delta g (the difference of the g-tensors of BChl and BPheo) is the smallest. This happens for certain crystallites; the resulting polarization is highly anisotropic. Third, the sign rules differ from Kaptein sign rules and are dictated by the relative signs of delta g and the A term of the dipolar hyperfine anisotropy tensor.

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MEASUREMENT OF HETERONUCLEAR DIPOLAR INTERACTIONS BETWEEN QUADRUPOLAR AND SPIN-1/2 NUCLEI IN SOLIDS BY MULTIPLE-QUANTUM REDOR NMR.

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New techniques are presented that add to the group of solid state NMR methods which utilize heteronuclear recoupling for measurements of the dipolar interactions in rotating solids. The experiments combine the capabilities of multiple-quantum magic angle spinning (MQMAS) with the rotational-echo double resonance (REDOR). We introduce two such methods. (1) MQ-t2-RED0R, which employs the dipolar recoupling between spin-1/2 (I) and quadrupolar (S) nuclei using a series of p pulses that are applied to I spins during single-quantum evolution t2. We demonstrate that MQ-t2-RED0R provides direct inference of the connectivities between spin-1*12* (e.g. 1H, 19F, 31P) and quadrupolar (e.g. 11B, 170, 23Na, 27A1) nuclei in solids under high resolution conditions and allows for a determination of internuclear distances. (2) In the alternative method, referred to as MQ-t1-REDOR, the p pulses are shifted into the MQ evolution time t1. This method allows for fast, but semi-quantitative determination of the internuclear distances in well crystallized compounds. Because the dipolar effect is enhanced by the MQ order, this technique exhibits improved sensitivity toward weak dipolar interactions.

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N-15 CHEMICAL SHIFT TENSORS IN NUCLEIC ACID BASES.

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This paper presents the first reported measurements of the principal values of the N-15 chemical shift tensors in adenine, cytosine, guanine, and thymine. The assignment of the solid state NMR resonances was done using the liquid values in the corresponding nucleosides and the results of quantum mechanical calculations of the N-15 tensors. The calculations were also used to assign the orientation of the principal axes of the tensors and to evaluate the effect of intermolecular interactions on the N-15 chemical shift tensors of the nucleic acid bases. The results indicate that calculations including intermolecular interactions produce results in better agreement with the experimental values than those in which these interactions are neglected.

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DYNAMIC NUCLEAR POLARIZATION AND N-15 NMR SPECTROSCOPY.

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As a result of collaboration between personnel at PNNL/EMSL and the University of Utah a totally different and new dynamic nuclear polarization (DNP) spectrometer combined with an electron spin resonance (ESR) capability is now operating at a magnetic field of 1.41 Tesla in the Utah laboratory. The corresponding Larmor frequencies for electron, H-1, C-13 , and N-15 are about 40 GHz, 60 MHz, 15 MHz, and 6 MHz, respectively. The spectrometer utilizes a small imaging magnet (31 cm clear bore) in order to accommodate the radio and microwave frequency components and is designed as a frequency sweep system in which the microwave frequency is generated by a frequency synthesized which is amplified by a 10W traveling wave tube amplifier. With this design a rapid in-situ ESR measurement is employed to set the optimum DNP condition. The spectrometer can be readily switched from the ESR to the DNP condition with a single switch. A large sample volume (10 mm o.d., 10 mm length) is also used to enhance the overall NMR sensitivity. To date we have employed static powder pattern experiments and have built a magic angle spinning (MAS) probe which is used for both high speed MAS applications as well as the slow spinning MAT experiments developed in the Utah laboratory. Preliminary results have been obtained on a number of model compouuds such as dibenzofuran, carbazole, purine, as well as some polymers and coal. A proton DNP enhancement of 38 has been achieved on a low volatile bituminous coal (Pocahontas #3). A H-1 DNP enhancement of 36 was obtained on carbazole doped with the BDPA free-radical while a H-1 DNP enhancement of 70 was obtained on purine doped with a mixture of BDPA and DPPH free radicals. With such large H-1 DNP enhancements it is possible to obtain the N-15 chemical shift anisotropy data from powder patterns at the natural abundance level in significantly less than one hour using the somewhat simpler proton cross polarization N-15 DNP experiment. We have succeeded in measuring the N-15 DNP enhancement in carbazole utilizing a single pulse SP-DNP experiment on a N-15 labeled sample. The results of this experiment on carbazole range between 900 and 1000. Data on other materials will be presented.

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13C SOLID STATE NMR OF GRAMICIDIN A IN A LIPID MEMBRANE.

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The natural abundance 13C NMR spectrum of gramicidin A in a lipid membrane was acquired under magic-angle spinning conditions. With fast sample spinning (15 kHz) at ca 65 C the peaks from several of the aliphatic, beta-, alpha-, aromatic, and carbonyl carbons in the peptide could be resolved. The resolution in the 13C spectrum was superior that observed with 1H NMR under similar conditions. The 13C linewidths was in the range 30 - 100 Hz, except for the alpha- and beta-carbons where the linewidth was about 350 Hz. The beta-sheet-like local structure of gramicidin A was observed as an upfield

shift of the alpha- and carbonyl resonances from gramicidin. Under slow sample spinning (500 Hz), the intensity of the spinning sidebands from 13C in the backbone carbonyls was used to determine the residual chemical shift tensor. As expected, the elements of the residual chemical shift tensor were consistent with the single-stranded, right-handed beta-6.3 helix structure proposed for gramicidin A in membranes.

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THE UNUSUAL PROPERTIES OF SODIUM-SILICON CLATHRATES: 23Na AND 29Si NMR,

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Sodium silicide, NaSi, heated under vacuum forms two host-guest materials, Na8Si46 and NaxSi136 where x is less than 24, consisting of frameworks built from tetrahedrally bonded Si atoms forming face-sharing cages, each of which can contain a Na atom. Interest stems from their unusual semi-metallic properties, reports of a metal-insulator transition at low Na loading and superconductivity in a Na/Ba/Si clathrate. The Na guest very strongly influences the properties of the Si host framework. We have been using solid state NMR to study problems associated with the synthesis and analysis of Na/Si clathrates and to gain an understanding of their interesting physical properties. The static, MAS and variable temperature NMR of both 23Na and 29Si can be interpreted in terms of transfer of electronic charge from the Na atoms to the Si framework. The temperature dependence of the very large 23Na shifts observed are atypical of classical Knight (no T) or paramagnetic (1/T) effects. Symmetry and some very small 23Na quadrupole coupling constants (QCC) enable assignmentof 23Na resonances to the different cages. Calculations give QCC's in close agreement with those observed. As the Na content is decreased the sharp 23Na resonances observed at high Na loadings are replaced by broader distributions and the 29Si spectra show dramatic changes.

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GAS PHASE MAGNETIC RESONANCE MICROIMAGING STUDIES OF POROUS MATERIALS WITH HYPERPOLARIZED XENON AND THERMALLY POLARIZED GASES.

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The characterization of the properties of porous materials is an important and challenging problem. Magnetic Resonance Imaging is expected to be a very useful tool in this area, particularly in studies concerning the homogeneity of the structure, connectivity of the pores, and the spatial distribution of the adsorbent in the solid matrix. The traditional method of obtaining MRI from a porous material consists of filling its pores with a suitable contrast agent. The use of gases as contrast agents has several advantages compared with liquids: generally gases are less invasive and more mobile, and thus are capable of sampling smaller pores. A significant drawback of imaging with gases is low sensitivity, because of their low density. This problem can be overcome through the use of hyperpolarized (HP) noble gases. MRI with hyperpolarized noble gases has been known for several years, however only very limited work has been done so far in the application of this technique to material science. The non-renewable character of polarization in HP xenon poses some serious experimental difficulties, restricting resolution and the choice of MRI experiments and requires some refitting of conventional MRI techniques when applied in such studies. We will demonstrate that for many experiments involving MRI of porous materials, imaging with normally polarized gases, particularly hydrocarbons, can offer superior resolution and sensitivity as compared to HP xenon. The application of HP xenon, however, can provide a great advantage, when time resolution is required. We will demonstrate this with an example of HP Xe in Porous Vycor, where diffusion of the gas can be monitored directly. Experimental details and a comparison of some techniques for imaging of gases in model porous systems will be given.

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TOWARDS DYNAMIC NUCLEAR POLARIZATION IN BIOLOGICAL SOLIDS: SIGNAL-ENHANCED SOLID-STATE NMR STUDIES.

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Detailed structural parameters can be extracted from biological systems using multi-dimensional solid-state NMR experiments. However, due to the low sensitivity of the technique most applications have been limited to small model compounds. Dynamic nuclear polarization (DNP) can be used to increase signal-to-noise ratios in solid-state NMR by factors of -200, allowing structural studies in systems that would otherwise be inaccessible. Signal enhancements of 50-100 have been observed in 1-dimensional spectra of the amino acid, arginine, and the 18.7 kD protein, T4 lysozyme, in a frozen TEMPO/water/glycerol solution (Hall, D.A., et.al., Science, 276, 930-932, 1997). As the next step in applying DNP to the study of biological systems, we are developing multi-dimensional static and MAS DNP correlation experiments. We present recent results and discuss experimental issues, including enhancement stability and spectral resolution.

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METHYLENE-ONLY 13C CP-MAS SPECTRA BY DOUBLE-QUANTUM FILTERED CP.

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Methodology for the assignment of 13C CPMAS spectra is still in its infancy; previous methods of CPMAS spectral editing have utilized differences in the strength of the 13C-1H dipolar interaction, or the rate and spin thermodynamics of cross-polarization from protons to carbon, to differentiate between quaternary, tertiary and methylene carbons. We introduce a different approach, which is based on the fact that double-quantum coherence develops between the protons of a methylene group considerably faster than between most other proton spin pairs in an organic solid. We generate this coherence,

filter it, convert it back to single quantum, and then cross-polarize selectively to carbon, followed by a short period of reversed cross polarization to null out unwanted coherence generated from longer distance spin pairs. While the signal to noise of this method is poorer than ordinary CP, it is comparable to previous methods for generating methylene-only spectra, and the technique is straightforward and easy to implement. Typical applications of the method will be demonstrated at the meeting.

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SOLID STATE NMR, X-RAY DIFFRACTION AND DSC INVESTIGATION OF THE STRUCTURE AND THE SOLID-SOLID PHASE TRANSITION IN 2(2,4-DINITROBENZYL)-3-METHYL PYRIDINE.

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The molecular crystals of 2-(2,4-dinitrobenzyl)-3-methyl pyridine (3MeDNBP) display a wealth of attractive characteristics. They posses two photoactive distinct crystallographic forms (A and B) - i.e. undergo photo-induced proton transfer and coloration, and a third, non-photoactive, metastable form C. The first two interchange reversibly, A<-->B, via a first order phase transition at a temperature of 318K. Phase C transforms irreversibly to phase B at 390K. We present here a detailed variable temperature (VT) structural study of 3MeDNBP. The crystal structure of the three phases was determined by X-ray diffraction. DSC, VT X-ray powder diffraction, and VT 13C and 15N CPMAS NMR were employed to monitor the phase transition. The first two methods identify a sharp first order phase transition. 15N CPMAS NMR measurements (on 3MeDNBP with doubly 15N-labeled nitro groups) show a finite temperature range over which the transition spreads. This NMR observation agrees with a prior observation of the decay rate of the photo-tautomer as function of temperature. The latter, being bi-exponential, corresponds to two distinct (slow and fast) decay processes of the photo-tautomer when embedded in either the A or B phases. These observations imply the coexistence of the two phases over a finite temperature range. Tailoring REDOR and selective TEDOR as unique spectral editing means, and carrying a MT-like temperature-jump experiment, we were able to obtain a total assignment of the 15N and 13C spectra, in both A and B phases. This work is the first demonstration of a TEDOR coherence transfer from enriched 15N nuclei to 13C nuclei at natural abundance, and as such, it manifests its usefulness in addressing a wide class of problems. Using the assignment to correlate the observed spectral changes (chemical shifts) with the crystallographic structures, enables us to point out how the variations in intermolecular packing affect the chemical environment.

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NEW EXAMPLES OF ALUMINUM CHEMICAL SHIELDING ANISOTROPY.

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Despite the large number of solution and solid-state Al-27 NMR studies reported in the literature, there have been very few reports of Al-27 chemical shielding anisotropy (CSA). From analyses of Al-27 spectra measured at 4.7 T, 9.4 T and 18.8 T, we report very small Al-27 CSA's in a series of octahedrally-substituted aluminum complexes, demonstrating that the effects of CSA are not negligible in the Al-27 NMR spectra of stationary samples. The relative orientation of the chemical shielding (CS) and electric field gradient (EFG) tensors is determined, and based on the geometry of the molecule and theoretically calculated chemical shielding parameters, probable orientations of the CS and EFG tensors in the molecular frame are proposed. In addition, large Al-27 CSA's in diatomic and linear triatomic molecules are calculated from spin-rotation constants obtained from previously published microwave spectroscopic data. All experimental data is compared to theoretically obtained CS and EFG parameters, calculated using both restricted Hartree-Fock methods and density functional theory.

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CHARACTERIZATION OF SELECTIVE SITE DISTRIBUTION IN MIXED-ALKALI CHABAZITE BY 23NA MQMAS AND 7LI MAS NMR.

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A low silica zeolite, chabazite, with varying ratios of Na and Li cations was studied using 23Na multiple-quantum magic angle spinning (MQMAS), taking advantage of the improved resolution and lineshape deconvolution, and 7Li MAS NMR spectroscopy. Non-statistical filling of the alkali cation sites was observed with lithium and sodium appearing to have different site preferences. 7Li MAS of the 100% Li form show the presence of two peaks which are attributed to cation positions in the six-ring window of the hexagonal prism and in the eight-ring window. The different sodium environments were differentiated by MQMAS on the basis of nuclear electric quadrupolar coupling constants. With increasing sodium content, the lithium cations demonstrate a preference for coordination at the six-ring window of the hexagonal prism whereas the sodium cations have a preference for coordination at the eight-ring windows.

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A HIGH EFFICIENCY HFXY 9.7 TESLA CPMAS PROBE.

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Recently our lab has developed a novel HFXY 9.4 Tesla CP-MAS probe capable of generating 125kHz decoupling fields on 1H and 19F with ~400watts of incident RF power. The XY channels of the probe are carried in a removable module allowing the rapid interconversion between resonant frequencies. In the case

of very low signal to noise samples the XY module can be truncated to a single channel further enhancing the efficiency. A novel result of the probe head tuning is a marked
insensitivity to high ionic concentration solutions. The performance of the probe will be presented along with DRAWS and REDOR data illustrating the capabilities of the probe.

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C-13 NMR INVESTIGATION OF PHOTO-ASSISTED DECOMPOSITION OF TRICHLOROETHYLENE AT THE AIR/SOIL INTERFACE.

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The photo-induced decomposition of trichloroethylene (TCE) adsorbed on whole soil and soil components (e.g., Ca-montmorillonite, kaolinite and humic acid) has been studied at the air/absorbent interface under long-wavelength UV irradiation. Solid-sample and liquid-solution C-13 NMR techniques were used to identify apparent products or intermediates of the photodecomposition. Dichloroacetic acid was identified as a major organic product/intermediate; substantial amounts of pentachloroethane and trichloroacetic acid were also identified. The production of suspected gases (C02, HC1 and phosgene) was detected in the TCE/Ca-montmorillonite case. The photodecomposition of trichloroethylene adsorbed on Zn-exchanged and Cu-exchanged montmorillonites, and other adsorbents (e.g., silica gel and TiO2), were also examined in less detail.

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SOLID STATE C-13 AND Si-29 NMR STUDIES OF METHYL-CAPPED SILICA GELS.

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The direct attachment of alkyl or aryl groups to the silica surface via Si-C bonds (not via Si-O-C linkages) generates a new class of highly stable, modified silicas. The work in this presentation has focused on methylation of the silica surface by formation of Si-C bonds via the reaction of methyllithium with a chlorinated silica. Solid-state C-13 and Si-29 NMR techniques were used to characterize these materials.

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DETERMINATION OF 13C INDIVIDUAL SPECTRAL DENSITY ANISOTROPIES.

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Anisotropic 13C spin-lattice relaxation times (T1Z) have been measured using variable angle correlation spectroscopy (VACSY) in order to investigate molecular motion at various carbon sites on a molecule. Calculations of T1Z

anisotropies for the various spinning angles used in the VACSY experiment sb' that the relevant spectral densities for a spinning sample are linear combinations of the static spectral densities, with coefficients determined the spinning angle. Thus, the individual static spectral densities can be calculated from measured relaxation times of a CSA lineshape for a variety oi spinning angles. Experimental measurements and analysis of T1Z anisotropies for ferrocene will be presented.

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CENTERBAND LINESHAPES OF PROTON MAS SPECTRA CALCULATED WITH AVERAGE HAMILTONIAN THEORY.

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The first-order term in the Magnus expansion of the homonuclear dipolar Hamiltonian is used to predict lineshapes of the centerband of fast magic-angle spinning proton spectra of solids. The building blocks of this average Hamiltonian are spin triads instead of the familiar spin pairs of the static Hamiltonian. The average Hamiltonian is expressed in terms of the geometry of the spin triangles. In the absence of chemical shifts the linewidths scale inversely with the rotation speed. The line broadening effect of dipolar interaction between nonidentical shifts is markedly reduced by the isotropic chemical shift differences. The effects of chemical shift anisotropies and methyl-group rotations are considered. Second moments of the lineshapes can be calculated, but they do not reflect the actual linewidths. Comparisons with some experimental examples will be presented.

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SOLID-STATE NMR STUDIES OF CONFORMATION AND DYNAMICS OF SURFACTANT MOLECULES IN MOLECULARLY ORGANIZED NANOSTRUCTURED MATERIALS.

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The conformation and dynamics of surfactant molecules in different environments (free surface of nanoparticles, within mesoporosities, and within the galleries of clay minerals) have been investigated using variable-temperature solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Two distinct conformations coexist for ODA in clay regardless of the D-spacing attained by the clay: all-trans and gauche while all-trans conformation has not been observed for surfactants on silica nanoparticles and in mesoporous silica. The temperature dependent NMR measurements suggest that ODA molecules are partially ordered in clay at 25 oC, and undergo melting at about 75 oC. Relaxation measurements including T1C, T1H, TCH, T1pH, and dipolar dephasing with variable-temperature NMR show that ODA in clay is more rigid than on mesoporous silica and on silica nanoparticles. The mobility of ODA in clay increases upon melting. The wetting property has been related to the conformation and dynamics of surfactants in the ceramic materials

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MAS-NMR STUDIES OF MODIFIED ZEOLITE CATALYSTS FOR USE IN ASYMMETRIC REACTIONS.

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The primary aim of any catalyst is to provide the required products with high selectivity, and this has been the main focus of catalytic research for many decades. More recently, with environmental pressures becoming more intense, industry has been focusing on the need for the adoption of cleaner technologies. One aspect of this is the requirement for synthetic routes to optically pure products, and the associated need for enantioselective heterogeneous catalysts. We have shown that zeolite HY when modified with small amounts, of chiral sulphoxide molecules such as 1,3-dithiane-1-oxide is an active enantioselective catalyst for the dehydration of butan-2-ol. MAS-NMR has been used to determine the interaction between sulphides, sulphoxides and the support zeolite under a range of conditions. Cross-polarisation and high power decoupling techniques have been used to probe the effect on the zeolite framework of modification, and to monitor the chemical integrity and mobility of the modifier molecules over a temperature regime equivalent to the reaction conditions of the catalytic study. NMR has shown that sulphoxides are protonated by the Brønsted acid hydroxy groups and these protonated sulphoxide species have been shown by ^{27}A1 NMR to coordinate with extraframework aluminium centres to produce high activity enantioselective sites. Further CP-MAS ^{27}A1 studies have shown that it is only a relatively small fraction of the extraframework aluminium that is capable of coordinating to the modifier molecule, possibly aluminium at a particular location. Further studies have been undertaken involving different chiral molecules including the amino acid cystine.

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FLOW AND RHEOLOGICAL STUDIES USING TOROID-CAVITY NMR.

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An effective new method for measuring coherent flow in a cylindrical toroid-cavity NMR detectors has been developed. Because of their unique geometric and electronic features, toroid cavities are routinely used in high-pressure high-temperature in situ NMR and in chemical-shift resolved rotating-frame NMR microscopy. In the microscopic applications, toroid detectors enable distance resolutions on the micrometer scale and facilitate measurements of both Fickian and non-Fickian diffusion to a high precision. From the two-dimensional, chemical-shift resolved spectra of diffusion measurements, coherent radial flow within the cylindrical cavity can also be determined. Recently, we have discovered that, in the same kind of detector, coherent tangential flow of matter (i.e., flow perpendicular to the direction of microscopic imaging) causes a phase or frequency shift of the detected NMR signals. In an appropriate setup, the frequency shift can be observed and quantified from the signal splittings that occur in regular one-dimensional NMR. Alternatively, the phase shift can be used for quantitative measurements of flow from two-dimensional NMR. If combined with the microscopic rotating-frame NMR technique, rheological studies of viscous solutions and polymers are feasible.

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SOLID STATE NMR STUDIES OF SELECTIVE CATALYTIC REDUCTION OF NO OVER ZEOLITE CATALYSTS.

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The zeolite catalysts, H-ZSM-5 and CuZSM-5, are active for emission abatement processes, such as selective catalytic reduction (SCR) of Nox with hydrocarbons in the presence of excess oxygen. One potential application for these catalysts is in the stationary sources, such as power plants. We have initiated solid state magic angle spinning (MAS) NMR studies to probe the role of the hydrocarbon reductants and the reaction mechanism for SCR of NOx over cation-exchanged ZSM-5. We have investigated potential reaction intermediates, such as acetone oxime and acetone, in the SCR of NOX over HZSM-5 and CuZSM-5. The carbon- and/or. nitrogen-containing surface species, as well as products formed during SCR of NO have been monitored with 13C and 15N MAS NMR experiemnts.

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A NEW MAGIC ANGLE HOPPING EXPERIMENT WITH BALANCED REFOCUSING FOR OBTAINING ONE-DIMENSIONAL HIGH RESOLUTION NMR SPECTRA OF SOLIDS.

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There are many applications in which the isotropic chemical shifts of solid samples are of main interest, but magic angle spinning (MAS) is difficult to apply. Renewed interest in using magic angle hopping (MAH) as an alternative to MAS has been stimulated by applications such as in-situ monitoring of heterogeneous chemical reaction under flowing conditions [D. Keeler, J. Xiong, H. Lock, S. Dec, T. Tao, and G. E. Maciel, Catalysis Today, submitted, 1998]. We have developed a new MAH pulse sequence for obtaining one dimensional high resolution NMR spectra of solids and demonstrated it using a newly built MAH probe with a 120 degree hopping time less than 30 ms. The new pulse sequence, MAPLE (magic angle hopping with balanced refocusing), employs two hops instead of the three hops used in the original pulse program [N.M. Szeverenyi, A. D. Bax, and G.E. Maciel, J. Magn. Reson., 61, 440, 1985]. Thus, the signal-to-noise ratio is increased by more than a factor of two. As the minimal number of steps for phase cycling is reduced form 8 to 4, as much as 50% of total experimental time can be saved, which is important, especially for chemical kinetics studies. To realize this two-hop approach, newly developed 8-pulse refocusing sequences are employed to obtain balanced refocusing on both x and y components of magnetization with

high efficiency. The methods for increasing S/N and reducing MAH experimental time will be discussed in detail.

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A STUDY OF RELATIONSHIP BETWEEN STRUCTURE AND O-17 ELECTRIC FIELD GRADIENT PARAMETERS IN SOME ALUMINOSILICATES.

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The relation between 0-17 quadrupolar parameters and the local structure in silicates is of considerable interest if these parameters are to be used as a local probe. Although there are a number of investigations and some theoretical work on Si-O-Si bonds, there seems to be very little experimental data on Si-O-Al. We have therefore investigated a number of sodalites, M8[AlSi04]Cl 2 where M is alkali cation, since these have only one oxygen site and a Si:Al ratio of one. By varying the alkali we were able to change the Si-O-Al bond angle in -5 degrees steps from -125 to -152 degrees. The value of electric- field gradient, Cq, followed a roughly similar angular dependence to that found for Si-O-Si bonds with a Cq(180)-4.2 MHz. The asymmetry parameter also behaved in a similar fashion to that found for Si-O-Si bonds although it increased more rapidly at small angles. Using cluster calculations we were able to model behaviour of the field gradient quite well, but the calculated asymmetry parameters were smaller than experimental values at low bond angles.

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PROCESSING INFLUENCES ON POLYANILINE BY SOLID-STATE NMR.

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Polyaniline has been shown to be a useful material for gas separation and can be synthesized in several forms including powder, hollow and solid fiber, and films. Gas diffusion through polymers is dependent on molecular motions including main-chain dynamics, phenyl group rotation, and the presence of additives. The frequency and amplitude of these motions can by characterized by measuring the relaxation parameters, T1 and T1p. In addition to the solvent,- n methyl pyrrolidinone (NMP), gel inhibitors such as pyrrolidine and 2-methylaziridine are introduced to aid in the processing of polyaniline films and fibers. The retention of these additives under various processing conditions is a concern for the determination of optimum synthetic avenues. 13C spin counts shows an average of 6 NMP molecules per ten polyaniline repeat units and a range of 2-5 pyrrolidine molecules per ten polyaniline repeat units, the amount increasing with more aggressive processing. In addition, the T1p(H) values of the solvent and gel inhibitor present indicate similar dynamic behavior as that of the polymer chain. This suggests the solvent and gel inhibitor is either physically trapped or chemically interacting with the polymer chain. These results will be correlated with gas permeability.

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MULTINUCLEAR NMR AS A PROBE IN NANOCOMPOSITES.

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Nanocomposites are dissimilar materials brought together in intimate (angstrom to nanometer) contact despite the absence of any chemical bonds. We have been exploring a variety of nanocomposites formed when polymers are coaxed into the gaps found between plates in common layered silicates. These composites exhibit some of the best bulk properties of both the organic and inorganic phases. We are exploring both microscopic structure and dynamics in these systems using a variety of techniques in solid state NMR. In this poster we review some of the results, with an emphasis on the novel differences found between bulk polymers and the intercalated polymers.

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INVESTIGATING POLYMORPHISM IN CRYSTALLINE ORGANIC COMPOUNDS USING SOLID-STATE NMR SPECTROSCOPY.

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13C CP/MAS NMR spectroscopy shows that aspartame (aspartyl-phenylalanine methyl ester) exists in three distinct forms at room temperature, depending on preparation conditions. We have been using two-dimensional exchange spectroscopy with high-speed MAS and TPPM decoupling to assign the solid-state NMR spectra of uniformly 13C labeled aspartame. Sufficient resolution has been obtained with these techniques to observe 13C-13C J-couplings in the 13C solid-state NMR spectrum. For one of the forms of aspartame that possesses multiple crystallographically inequivalent sites, we can readily identify connectivities between the nuclei of each conformation and/or arrangement of molecules. We have also been studying a closely related sweetener for the existence of polymorphs. A third compound we are investigating is nedocromil. For one of the carboxylate groups in nedocromil a significantly different chemical shift is observed when the carboxylate group lies in the plane of the tricyclic ring system than when it is out of plane. Linear correlations between chemical shift and conformation have been observed for several nedocromil salts. We are currently using solid-state NMR spectroscopy, X-ray diffraction, and computer simulation (molecular modeling and ab initio calculations) to investigate the conformation of related nedocromil salts for which the crystal structure has not been determined.

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ONE- AND TWO-DIMENSIONAL SOLID-STATE NIOBIUM-93 NMR SPECTROSCOPY.

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The variation and correlation with chemical structure of 93Nb chemical shift and quadrupolar parameters have been systematically investigated and used in the study of the piezoelectric Pb(Mg1/3Nb2/3)03 and related niobates. One- and two-dimensional 93Nb NMR spectra have been measured for a series of niobates, including: LiNb03, NaNb03, KNb03, Mg2Nb06, Zn2Nb06, Pb2Nb06, Pb2Nb07, Pb(Mg1/3Nb2/3)03 and xPb(Mg1/3Nb2/3)03/(1-x)PbTiO3. From these measurements 93Nb NMR spectroscopy is found to be sensitive to the local electronic environment of niobium and correlations between chemical shift and quadrupolar parameters with chemical environment have been explored. A comparison of two-dimensional NMR techniques such as, nutation spectroscopy and MQMAS for 93Nb has also been made. While 93Nb nutation spectroscopy has been used to resolve multiple sites and to determine quadrupolar coupling constants, 93Nb MQMAS spectroscopy yields dramatically higher resolution.

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FOURIER TRANSFORM RAMAN SPECTROSCOPY IN THE PHARMACEUTICAL INDUSTRY.

Bonnie L. Leimer and Roel Ferwerda, Nicolet Instalment Corporation, 355 River Oaks Parkway, San Jose, CA 95134

The use of Fourier Transform Raman Spectroscopy is becoming increasingly popular in the pharmaceutical industry. This is not only due to the wealth of information that can be obtained, but also because sampling preparation is negligible. The use of visible lasers for these applications is limited due to fluorescence, and therefore near-infrared lasers have to be used.

FT-Raman spectroscopy measures pharmaceutical samples in their natural form. This preserves physical characteristics such as crystallinity which are often lost while preparing materials for other analytical techniques. Furthermore, pharmaceutical products can be studied directly through the blister packaging for an easy Quality Assurance or Control method, resulting in a high turn-over of samples. The FT-Raman spectra of active ingredients are typically much stronger than those of excipients or coating materials. Therefore, active ingredients can be analyzed in formulations and mixtures at dosage form levels.

In this paper, a case study to the use of FT-Raman spectroscopy for industrially relevant pharmaceutical applications will be presented. It will be shown that polymorphic changes can be studied. Since the technique is very precise and reproducible, methods to quantify the different crystal structures give accurate results. Furthermore, examples of QA/QC methods will be shown and discussed.

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VALIDATING YOUR FT-IR: UNDERSTANDING THE VALIDATION PROCESS AND THE SYSTEM TESTS.

Bonnie L. Leimer, Nicolet Instrument Corporation, 355 River Oaks Parkway, San Jose, CA 95134

Many FT-IR users are currently being asked to establish procedures for verifying the performance of their instruments and the methods they use. For many users, establishing documented evidence that a system, process, or product does what it claims is a critical challenge. One of the most common types of certification for the pharmaceutical industry is the Food and Drug Administrations' Installation Qualification (IQ), Operational Qualification (OQ), Performance Qualification (PQ) or IQ, OQ, PQ. A number of tests can be performed to check the instrument precision, accuracy, reproducibility, stability, and alignment. The industry-wide recognized standard for these checks is found in ASTM E 1421. Nicolet has incorporated these tests into a software package called system validation that automatically tests the performance of your FT-IR and maintains a record of this performance over the lifetime of your infrared system. The requirements for DQ, IQ, OQ, PQ will be discussed along with a description of each of the tests performed in a system validation.

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ORALLY DELIVERED IMMUNOCONTRACEPTIVE VACCINE FOR RUMINANTS. Jerome C. Hurley, U.S.D.A., National Wildllife Research Center, 1716 Heath Parkway, Fort Collins, Colorado 80524

In the northeastern and to a lesser extent western states, the need for a benign population control mechanism for deer is approaching the panic situation. Both the expansion of humans into traditional deer environment and the adaptation of deer to humans have greatly increased the potential for conflict. Both political and practical concerns necessitate nonlethal control methods. Immunocontraceptive vaccines have been shown to be highly effective for population control in geographically contained deer populations (immunocontrol requires multiple injections over several weeks of time to achieve a booster effect). However, control of open populations with vaccines will require oral delivery be to cost effective. Additionally, immunocontraception response occurs principally in the lower intestinal area of an animal. For many animals a simple enteric coating will give adequate protection from stomach acids and ultimate delivery to the intestine. Ruminants complicate delivery because of multiple stomachs and varying pH regions. This presentation will discuss the approaches taken to surmount these problems and evaluation based on performance in stimulated test environments of the best current solution, a multiplely coated sugar beads. Animals tests will be initiated this fall.

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ADVANCES IN LC/MS TECHNIQUES IN CHEMICAL ANALYSIS. John MacKay, Andrew Braillesford, Beverly Kenney, Michael Swartz, Waters Corporation, Milford, MA.

Abstract Not Available.

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AUTOMATED PREPARATIVE CHROMATOGRAPHY WITH MASS SPECTROMETER AS THE TRAFFIC COP. John MacKay, Andrew Braillesford, Michael Swartz, Waters Corporation, Milford, MA.

Abstract Not Available.

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"MR SANDMAN, SEND ME A PEAK! MAKE IT NARROW AND WITHOUT MYSTIQUE!" AN OVERVIEW OF OPTIMIZING THE COLUMN (DIMENSION AND CHEMISTRY) AND SAMPLE CLEANUP STRATEGIES FOR YOUR LC/MS. John MacKay, Dorothy Phillips, Katie Sousa, Water Corporation, Milford, MA.

Abstract Not Available.

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IMPROVE PEAK SHAPE, RESOLUTION AND ANALYSIS TIME - LOOK BEYOND C8 AND C18. Marilyn A. Stadalius, Maureen J. Joseph, Julia F. Vasta Russel, Carl L. Zimmerman, MAC-MOD Analytical, Inc., 127 Commons Court, Chadds Ford, PA 19317

The most common HPLC column bonded-phase choice is C18, which is used in approximately 75% of separations. But this one type of bonded-phase will not work well for every separation. This talk compares C18 bonded-phases to a variety of other bonded-phases based on the same silica and bonding technology. A variety of different sample types are tested on a range of bonded-phases to put together a wide-ranging comparison. These additional bonded-phases include C8, Phenyl, CN and C3. These comparisons help us to put together a set of recommendations on choosing bonded-phases. These recommendations include selecting bonded-phases to minimize analysis time and improve resolution of difficult peak pairs.

This talk also tackles some specific problems with bonded-phases. For example, most C18 bonded-phases do not behave well in high aqueous mobile phases. Another problem is poor peak shape with base-deactivated columns. This talk provides examples and some theories of these situations and recommends appropriate bonded-phases for these difficult samples.

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RAPID RESOLUTION CHROMATOGRAPHY - PRACTICALITIES AND PITFALLS. Marilyn A. Stadalius, Maureen J. Joseph, Julia F. Vasta-Russel, Patrick J. Barthel, MAC-MOD Analytical, Inc., 127 Commons Court, Chadds Ford, PA 19317

The phrase Rapid Resolution Chromatography (RRC) refers to the technique of reducing column dimensions possibly combined with increased flowrate and reduced particle size, to provide sufficient resolution of components in the shortest possible time. The intent here is not obtaining more resolution, but achieving adequate resolution faster. The development of new techniques such as LC-MS, new high throughput applications such as combinatorial chemistry, and the overall need of the industry for increased productivity, has driven the development of RRC. The theory of Rapid Resolution Chromatography will be discussed, relating resolution (R) and efficiency (N) to particle size, column length and flow rate. Gradient theory will be used to optimize gradient parameters for shorter columns and increased flow rates. Rapid Resolution Chromatography is not for everyone or every application. Limitations of the technique, such as dwell volume, extra column volume, gradient mixing, and sample size will be discussed along with ways of overcoming these limitations.

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VALIDATED HPLC METHODS - TO TWEAK OR NOT TO TWEAK. Marilyn A. Stadalius, Maureen J. Joseph, Julia F. Vasta-Russel, Carl L. Zimmerman, MAC-MOD Analytical, Inc., 127 Commons Court, Chadds Ford, PA 19317

Regulatory HPLC methods do not always work as expected and there is a strong assumption that no changes can be made to the method without revalidating it. But the USP states that "adjustments to chromatographic conditions may be necessary to meet system suitability". This leaves chromatographers confused about the line between simply adjusting a method and modifying and revalidating a method. The result is many chromatographers use methods with obvious limitations which diminish their chance of success. This talk will consider some proposed limits for adjusting HPLC methods. We will also examine a method with reported problems and identify potential solutions. We will evaluate the ease of implementing these solutions and determine whether adjustments or modifications must be made. Then we will discuss and show the process by which the method is revalidated. This will include the specific experiments for determining method robustness and the system suitability recommendations. Key robustness experiments will be done over ranges exceeding the proposed limits for adjusting HPLC methods to better understand how these limits affect actual methods.

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HIGH THROUGHPUT PROTEIN CHARACTERISATION: PROTEOMICS FROM 2D GELS TO PROTEIN STRUCTURE. PE/PerSeptive Biosystems.

Abstract Not Available.

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PROTEIN CHARACTERISATION AND DETERMINATION OF POST TRANSLATIONAL MODIFICATIONS. PE/Sciex.

Abstract Not Available.

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MASS SPECTROMETRIC ANALYSIS OF FREE RADICAL DERIVED EICOSANOIDS FROM PLASMA MEMBRANE PHOSPHOLIPIDS. Tatsuji Nakamura, Robert C. Murphy, National Jewish Medical and Research Center, Denver, CO

Abstract Not Available.

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COMPLIMENTARY STRENGTHS OF MALDI-TOF AND ESI-TRIPLE QUADRUPOLE MASS SPECTROMETERS IN PROTEIN ANALYSIS AND IN PROTEOME STUDIES. Katheryn Resing, Dept. Chem. & Biochem., University of Colorado Boulder, Boulder, CO.

Abstract Not Available.

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SAMPLE PREPARATION USING EXTRACTION CHROMATOGRAPHY, Lawrence Jassin, Eichrom Industries

Environmental, bioassay, process and waste samples may require preconcentration and the elimination of interfering elements prior to analysis of radioactive isotopes. Many of these analyses are associated with characterizing former defense establishments as well as personnel contamination monitoring and isotope geology. Extraction chromatography is recognized as an efficient technique to both preconcentrate the sample and remove radioactive and non-radioactive interferences from a sample matrix. The isolated analyte of interest is then measured by an appropriate counting technique such as alpha spectrometry, liquid scintillation counting, gas proportional counting or ICP-MS. Typical analytes determined with extraction chramtography include isotopes of Sr, Pb, Ni, Fe, Tc, rare earth and actinide elements.

Extraction chromatography utilizes very selective solvent extraction chemistry on a chromatographic support. These particles are packed into small (typically 2 mL) columns for sample preparation. Numerous uptake curves for many analytes from nitric and hydrochloric acids have been published. This data has been used to develop analytical methods resulting in less waste and analyst hands-on-time than traditional solvent extraction, ion exchange and precipitation methods.

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EXPERIENCE WITH EXTRACTION CHROMATOGRAPHIC RESINS AT THE QUANTERRA RICHLAND LABORATORY. Matt Lardy, Jackie Waddell and Roxie Ross, Quanterra, 2800 George Washington Way, Richland, WA 99352

Quanterra continues to evaluate how it can decrease response times for analyzing and reporting analytical results, while at the same time maintaining or improving quality and reducing cost. There is also an awareness of the need to reduce waste generation, use of hazardous materials, and subsequent waste handling and disposition. One of the enhancements of productivity improvement in the laboratory has come from the use of new analytical products in Radioanalytical separations. One example of these products is the variety of extraction chromatographic resins, which Quanterra Richland Laboratory is using in some of its analytical procedures. These resins can increase the speed of analysis, improve selectivity for analytes over other techniques, and reduce waste generation. Extraction chromatographic resins are currently being used at Quanterra for the analysis of nickel, lead, uranium, plutonium, and americium. A summary of the use of these resins will be presented with a discussion of quality control and productivity enhancements.

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RADIUM IN GROUNDWATER ASSOCIATED WITH A COAL STORAGE PILE, SAVANNAH RIVER SITE, SOUTH CAROLINA, M.E. Denham* D.M. Beals, and W.G. Winn, Westinghouse Savannah River Company, Savannah River Site, Aiken, SC 29808

Radium isotopes were measured by high resolution gamma spectroscopy to investigate the source and transport behavior of elevated radium concentrations in groundwater contaminated by leachate from a coal storage pile at the Savannah River Site, South Carolina. Groundwater samples were obtained from monitoring wells downgradient from an unlined basin that collects surface runoff from the coal pile. The groundwater samples had a pH range from 2 to 4 and contained high concentrations of sulfate, iron, and aluminum. In addition, samples of the basin water, coal, and aquifer sediments were analyzed. Understanding the transport of radium at this site is complicated by the relatively high natural concentration of radium in aquifer sediments that is subject to leaching by the acidic groundwater.

Preliminary data suggest that interaction with aquifer sediments alters the isotopic composition of the dissolved radium in groundwater originating from the basin. Coal samples and the basin water had Ra-226/Ra-228 ratios that ranged from 1.1 to 1.4, whereas the ratio in 7 of 8 sediment samples was near or below 0.8. The groundwater samples had Ra-226/Ra-228 ratios that were similar to or below the sediment ratio. Disequilibrium between Ra-228 and Ra-224 was observed in the groundwater samples with Ra-224/Ra-228 ratios negatively correlated with pH and positively correlated with sulfate concentration. Processes that may explain these effects include alpha recoil and differential solubility of radium and thorium in the acidic groundwaters. Such effects have important implications for the transport of radium in acidic groundwater.

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COMPARISON OF RESULTS OF TWO GAMMA-SPECTROSCOPIC APPROACHES FOR DETERMINING RADIUM-224 CONCENTRATIONS IN GROUND WATER. Zoltan Szabo and Vincent dePaul, U.S. Geological Survey, 810 Bear Tavern Rd., W. Trenton, NJ 08628; T.F. Kraemer, U.S. Geological Survey, 12201 Sunrise Valley, Dr., Reston, VA, 20192; and Bahman Parsa, N. J. Dept. Health and Senior Services, Box 361, Trenton, NJ 08625.

Radium-224 (^{224}Ra) (^{232}Th decay series; half life, 3.64 days) contributes to gross alpha-particle activity in ground water in the Coastal Plain of New Jersey. Two approaches to ganima-spectroscopic determination of ^{224}Ra were evaluated by comparing results of analyses of 20 randomly selected sequential duplicate ground-water sample pairs. The 238.6 keV gamma-ray energy en-dtted by the ^{212}Pb (half life, 10.64 hours) ingrown into the barium- or lead-sulfate precipitate that bears the radium was counted for 1,000 minutes in both approaches. The "quick" technique (N. J. Dept. Health and Senior Services, Trenton, N.J.) requires initiation of counting 37 hours after collection, the time of maximum activity of ingrown ^{212}Pb; thus, this technique is more suitable for use with a coaxial detector with low (about 10, percent) efficiency. The "slow" technique (U.S. Geological Survey, Reston, Va.) requires initiation of counting 53 hours after precipitation, when activity of unsupported ^{212}Pb has declined to about 5 percent of that at the time of collection. Results of the quick technique may be biased high ff the sample contains unsupported ^{212}Pb; this bias can be corrected by counting the 212Pb activity in the sample more than once. Concentrations in the samples analyzed ranged from less than 0.5 (the reporting limit) to 12.6 pCi/L (picocuries per liter) with a median of 2.7 pCi/L. Results of the two-tailed paired t-test indicate that the differences between concentrations in sample pairs were not different from zero at the 95-percent confidence level. The maximum difference between analytical results for any sample pair was 0.8 pCi/L and all but three pairs overlapped within the bounds of the counting error. Both approaches are suitable for analysis of ground water in which the concentration of ^{224}Ra is high and that of unsupported ^{212}Pb is low. Detector efficiency, acceptable level of positive bias, and requested turnaround time are factors to be considered when determining the more suitable approach.

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NOVEL LIQUID SCINTILLATION COUNTER FOR MEASURING** a, B **AND** y **EMITTERS IN THE FIELD. M.P. Neary, J. Fields and J.E. Noakes, University of Georgia, Center for Applied Isotope Studies 120 Riverbend Road, Athens, GA 30605

The Finnish company Hidex designed and is manufacturing and selling a new liquid scintillation (LS) counter that has a built in Nal(TI) detector and is capable of measuring environmental levels of most alphas, betas and gamma emitters. The instnunent design employs a single photomultiplier tube, modem fast pulse shape discrimination electronics, both linear and log amplification and a 1024 channel MCA and very little shielding. By pulse shape discrimination, background is reduced to 40 cpm in a wide open window even with a single tube. The instrument is well suited for field work weighing only 11 kg, is the size of a shoe box, and can be powered by a 12 VDC battery equipped with an inverter. Counting efficiencies for ^{14}C are > 60% with a background of < 20 cpm, for ^{3}H > 40% with a background of < 20 cpm. Alpha counting efficiencies are > 90% with a background of 8 to 10 cpm. Center for Applied Isotope Studies at UGA has conducted research to develop the means to use the Nal(TI) detector as a guard detector when counting alphas and betas or beta gamma coincidence to drastically reduce the environmental background. The instrument has been successfully used in the field to measure radon in water at wellhead of a dozen wells in a single day.

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MARLAP(MULTI-AGENCY RADIATION LABORATORY POTOCOLS MANUAL) John Griggs, U.S. Environmental Protection Agency, NAREL, 540 South Morris Ave., Montgomery, AL 36115-2601.

No Abstract Available.

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AN EVALUATION OF GROSS ALPHA - AND GROSS BETA-PARTICLE RADIOACTIVITY IN WATER FROM THE SNAKE RIVER PLAIN AQUIFER AT THE IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY, IDAHO. LeRoy L. Knobel, Roy C. BaTtholomay, and Linda M. Williams, U.S. Geological Survey, WRD, INEEL, MS II60, Idaho Falls, Idaho 83403.

The U.S. Geological Survey, in cooperation with the U.S. Department of Energy, routinely samples 60 sites on or near the Idaho National Engineering and Environmental Laboratory (INEEL) for dissolved concentrations of gross alpha- and gross beta-particle radioactivity to determine what, if any, effects radioactive-waste disposal at the INEEL has on the water quality of the Snake River Plain aquifer. In addition, 61 sites were sampled for a special study. Concentrations of gross alpha- and gross beta-particle radioactivity in water from on or near the INEEL generally were at the background concentrations of 0-3 micrograms per liter as uranium for gross-alpha particle radioactivity and 0-8 picocuries per liter as cesium-1 37 for gross-beta particle radioactivity. This suggests that radioactive particles in INEEL ground water result from the natural breakdown of radioisotopes in aquifer rocks. A few samples contained concentrations larger than background values and these samples either can be associated with waste disposal at the RNEEL, the natural breakdown of radioisotopes in recharge-area rocks containing more radioisotopes than Snake River Plain aquifer rocks, or possibly, by the breakdown of radioisotopes contained in agricultural products used in areas upgradient from the TNEEL.

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DERIVATION AND APPLICATION OF RISK-BASED SURFACE CONTAMINATION RELEASE CRITERIA FOR A RADIOLOGICALLY CONTAMINATED BUILDING. R.V. Graham,[1] J.W. Lively[2], D.M. Smith[3], 'U.S. Environmental Protection Agency, 999 Je Street, Suite 5 00, Denver, CO 80202-2405, [2]MACTEC-ERS, 2597 B3/4 Road, Grand Junction, CO 81503,[3]TMSS, Inc., 73 Spyglass Drive, Littleton, CO 80123

A privately-owned industrial facility on the Monticello CERCLA site, currently used as a machine shop, was discovered to be contaminated with uranium "yellow cake" from past DOE (AEC) uranium production operations. The disposition of the structure became the subject of costly options involving decontamination or demolition and replacement. To determine whether decontamination or demolition was warranted, from a risk perspective, collaboration between the EPA, DOE, and the State of Utah was formed. A systematic approach to derive and demonstrate compliance with site-specific, risk-based clean up levels (DCLS) was implemented. This paper illustrates the use of DOE's RESRAD family of exposure and does assessment models to derive acceptable risk-based surface contamination limits, and the development of a DQO driven sampling and analysis plan (SAP) to measure the contaminant concentrations relative to the allowable concentration. Statistical tools were used to design a SAP with sufficient power to readily discern whether the contamination in the building might exceed the allowable concentration while minimizing sampling costs. Field implementation of the SAP produced appropriate data to support verification without disturbing machine shop operations. Close coordination and cooperation between technical and managerial personnel, and collaboration between the DOE, the regulators, and the building owner were critical to the project's success. Data analysis indicates that the contaminant concentrations are well below the risk-based derived criteria; therefore, based on human health risk, decontamination or demolition and replacement are not warranted. Cost avoidance is estimated to save the federal government 2.3 million dollars.

*(Work supported by U.S. Department of Energy, Albuquerque Operations Office, Grand Junction Office under Contract DE-AC 13 -96GJ873 3 5.)

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USE OF HIGH PRECISION GAMMA -RAY SPECTROMETRY TO ESTIMATE THE AGE OF RADIOBARITE CONTAMINATION AT OILFIELD SITES. Robert A. Zielinski, James R. Budahn, and James K. Otton, U.S. Geological Survey, Denver Federal Center, Denver, CO 80225

Naturally occurring radioactive materials (NORM) at sites of oilfield production are largely composed of radium-bearing scale and sludge that have precipitated from oilfield brines. Oilfield equipment or soil contaminated with radioactive scale and sludge are sources of potential liability under newly enacted or pending State NORM regulations. High precision gamma-r spectrometry of packaged and sealed samples provides accurate determinations of $^{22<s}$Ra (t,$_{c}$=1600 y) and ^{228}Ra (t$_{U2}$=5.76 y) in support of site assessment, and also indicates the degree of radioactive equilibrium with daughter products such as ^{210}Pb (t$_{1/2}$=22.6 y) and ^{22a}Th (t$_{1/2}$=l-90 y). These data can be used to estimate the average age of radium-bearing precipitates, provided that highly insoluble radiobarite is confirmed to be the principle carrier of radium. The ^{228}Ra/^{226}Ra activity ratio in radiobarite precipitates decreases from an original value that typically falls within a range of 0.5 to 2.0, depending on the Th/U ratio of the oil- and brine-produciniz formation. The rate of decrease is controlled by the 5.76 year half-life of ^{228}Ra. Direct measurement of the original ^{228}Ra/^{226}Ra ratio in fresh radiobarite precipitates or in modern brines at a site improves the accuracy of apparent age calculations. Additional estimates of age that are based on ingrowth of ^{210}Pb or ^{228}Th daughters are maximum ages unless the original activities of these isotopes in fresh radiobarite can be determined and corrected for. In soils containing minor radiobarite contamination additional corrections should be made for radium and daughter isotopes that are supported by natural concentrations of U and Th. This application is potentially useful for determining the history of radium contamination during the last 50 years at oilfield sites that are scheduled for cleanup and/or acquisition.

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EFFECTS OF RADIOACTIVE-WASTE DISPOSAL AT THE IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY ON CONCENTRATIONS OF SELECTED RADIOCHEMICAL CONSTITUENTS IN WATER FROM THE SNAKE RIVER PLAIN AQUIFER IN THE MAGIC VALLEY STUDY AREA, IDAHO. Roy C. Bartholomay and LeRoy L. Knobel, U.S. Geological Survey, WRD, INEEL, MS 1160, Idaho Falls, Idaho 83403.

The U.S. Geological Survey and the Idaho Department of Water Resources, in cooperation with the U.S. Department of Energy, routinely sample 55 sites downgradient from the Idaho National Engineering and Environmental Laboratory (INEEL) in the Magic Valley study area (MVSA) for selected radiochemical constituents to determine what, if any, effects radioactive-waste disposal at the INEEL has on the water quality of the Snake River Plain aquifer downgradient from the INEEL. Samples from these sites and selected sites at the INEEL are analyzed for tritium, strontium-90, and gross alpha- and gross beta-particle radioactivity. In October 1995, tritium and strontium-90 concentrations in water from many wells at the INEEL were greater than the reporting level and were as large as 25,1 00 +/-1,000 picocuries per liter (pCi/L) and 76 +/- 3 pCi/L; respectively. In contrast, tritium concentrations in water from sites in the MVSA during 1989-96 were from 1.00 +/- 0.29 to 134.4 +/-12.8 pCi/L, and strontium-90 concentrations in water from all sites were less than the reporting level. Concentrations of gross alpha- and gross beta-particle radioactivity in water from the INEEL were variable and may result from the natural breakdown of radioisotopesinaquiferirocksor,insomeareas,thedisposalofradioactivewaste. Concentrations of gross alpha-and gross beta-particle radioactivity in water from sites in the MVSA also were variable and probably are the result of the natural breakdown of radioisotopes in aquifer rocks. Data indicate that concentrations of radiochemical constituents in water from the Magic Valley study area can be attributed to local or regional sources and are not measurably affected by radioactive-waste disposal at the INEEL.

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STRONTIUM-90 DISTRIBUTION COEFFICIENTS OF BASALTS AND SEDIMENTS AT THE IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY. Molly Pace[1,2], Roy C. Bartholomay[2], and Jeffery J. Rosentreter[1], [1]Idaho State University Department of Chemistry, Pocatello, Idaho 83209; and [2]U.S. Geological Survey, WRD, FNEEL, MS 1160, Idaho Falls, Idaho 83403.

Idaho State University and the U.S. Geological Survey, in cooperation with the U.S. Department of Energy, are determining strontium distribution coefficients (K_d's) of subsurface materials at the Idaho National Engineering and Environmental Laboratory (INEEL) to aid in assessing the variability of strontium K_d's and their effects on chemical transport of strontium-90 in the Snake River Plain aquifer system. Strontium K_d's were deten-nined for six basalt samples and five sediment-infill samples from basalt vesicles and fractures, from a selected core at the FNEEL. Batch experiments with water: rock ratio of 20 ml: 0.25 g and synthesized solutions representative of wastewater in disposal ponds at the INEEL were used to determine the Kd's. Strontium K_d's of the basalt samples varied from 1.3 to 9.3 ml/g (milliliters per gram). Strontium K_d's determined previously for other basalt samples from the INEEL were from 3.6 to 29.4 ml/g. Strontium K_d's of the vesicle- and fracture-infill samples ranged from 201 to 356 ml/g. These values are similar to previously determined strontium K_d's of surficial and interbedded sediments (26±1 to 326±41 ml/g) at the INEEL. The experiments show that the main sorption processes are physisorption for the basaits and ion exchange for the sediments. The significantly larger K_d's Of the sediments compared to those of the basalt samples indicate that sediment may have a greater effect than basalt on the chemical transport of strontium-90.

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A CASE STUDY LOOKING AT ISSUES ENCOUNTERED AND RESOLVED AT RAMP, IND., R.V. Graham, *C. Mattson, M.W. Lammering, R. Quillin*, United States Environmental Protection Agency, Region VIII, 999 le Street Suite 600, Denver, CO 80202-2466

The objective of this presentation is to document the issues involved in the cleanup of radiologically contaminated EPA emergency response site, Industries (RAW).was a privately owned radiological waste broker, accepting radiologicalwaste shipments from multiple generators throughout the U.S. from 1984 until it was abandoned on August 31,1994. The site contained over 4,000 35-and 55-gallon drumscontaining hazardous chemicals, mixed wastes containing liquid scintillationfluids, sealed brachytherapy and industrial radiography sources, dry activated wastes, and biohazardous materials all located less than 100 feet from a mixed industrial/residential neighborhood. Site activities included drum washing, scintillation vial crushing operations, opening and repackaging wastes, decontaminating material and equipment, storing various radioactive containers in the yard and warehouse, and receiving and shipping radioactive wastes for disposal. USEPA initiated an emergency removal action at the request.of the State of Colorado to address the wastes left in these containers. Since the NRC has financial emergency response limitations, the next source for responding to emergency actions is US EPA under the National Priorities List (CERCLA actions). However, in this case the site contained an Agreement State license. Since US EPA, a non-licensed federal agency, assumed responsibility for the site, the question of NRC/Agreement State requirements was the first hurdle faced in response to this emergency. Similarly, EPA is currently acting as both Radiation Safety/Protection Official for the site but also has regulatory and compliance oversight of the site. Other issues that have come up include: 1) site oversight and cleanup activities of both State and other Federal regulatory agencies; 2) mixed wastes and improperly documented waste manifests; 3) field and laboratory detection and quantitation limitation while characterizing mixed wastes and debris which has lead to the identification of LLWR non-licensed materials; 4) sealed sources have been placed in previously constructed 2R containers but EPA can not guarantee to the disposal facility that the containers were properly constructed; 5) drums containing mixed wastes exceed volatile levels that constitutes "Listed or Characteristic" wastes; 6) orphan wastes or out of compact waste disposal. As remediation continues, cleanup levels for the soil, building, and radiological risk assessment options must be clarified. Both NRC D&D guidance, RESRAD risk, fate and transport models, and EPA RAGS risk guidance and associated cleanup levels are currently being utilized. Cleanup continues today with over 3,545 cubic yards radioactive material shipped off site for disposal and a projected 180 cubic yards awaiting treatment.

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INTRODUCTION OF EICHROM TEVA DISC: TC-99 ANALYSIS, Anil Thakkar, Lawrence Jassin. Michael Fern, Eichrom Industries and John Sisler

Eichrom has developed a new **47** mm disc containing TEVA Resin. A Tc-**99** procedure is now available using this disc which relies on the proven chemistry of TEVA Resin. The advantage of the new format is speed in handling one liter and larger water samples with out the typical evaporation steps used to reduce volume. Data from two laboratories will be presented showing the outstanding performance of this new product.

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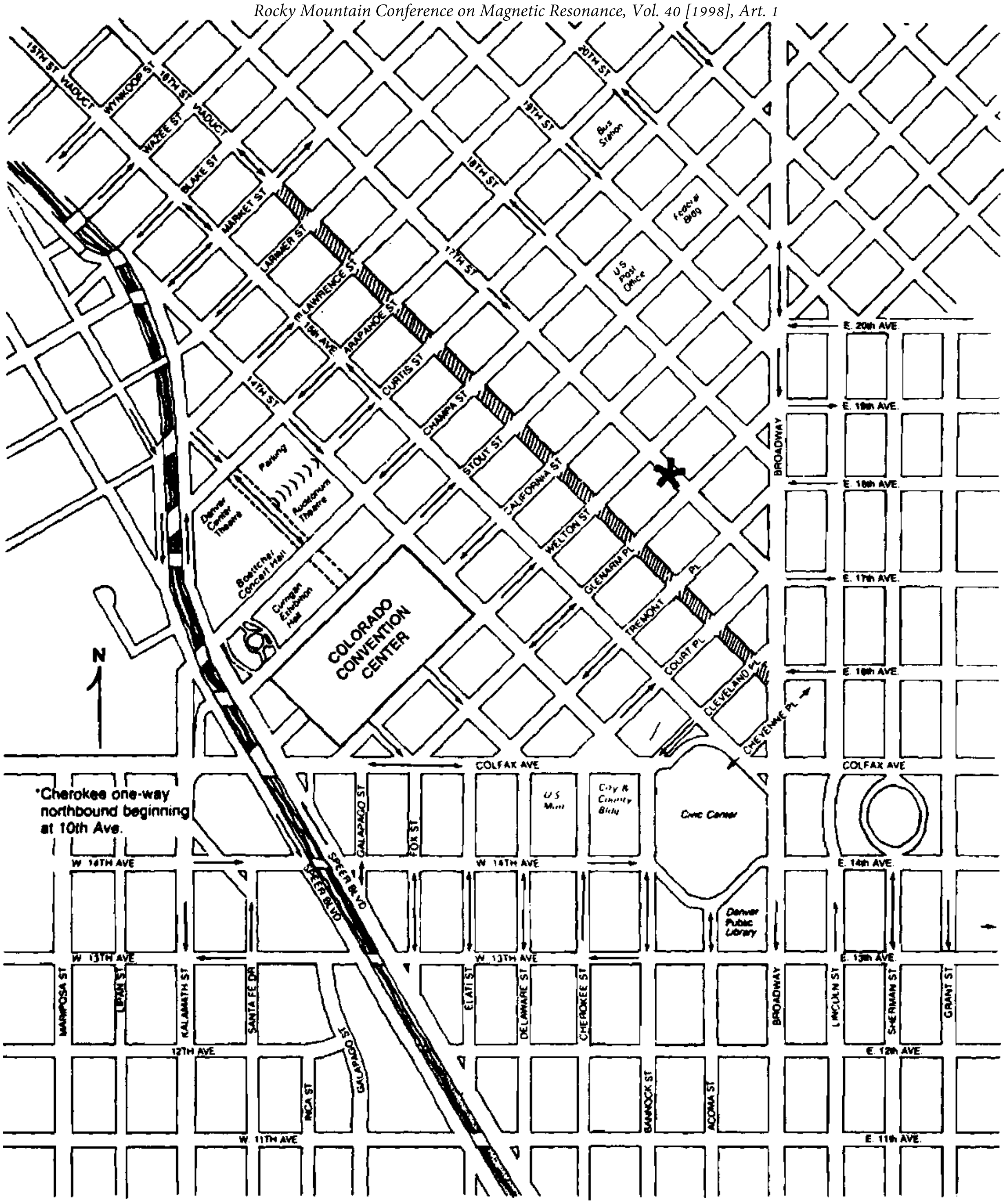

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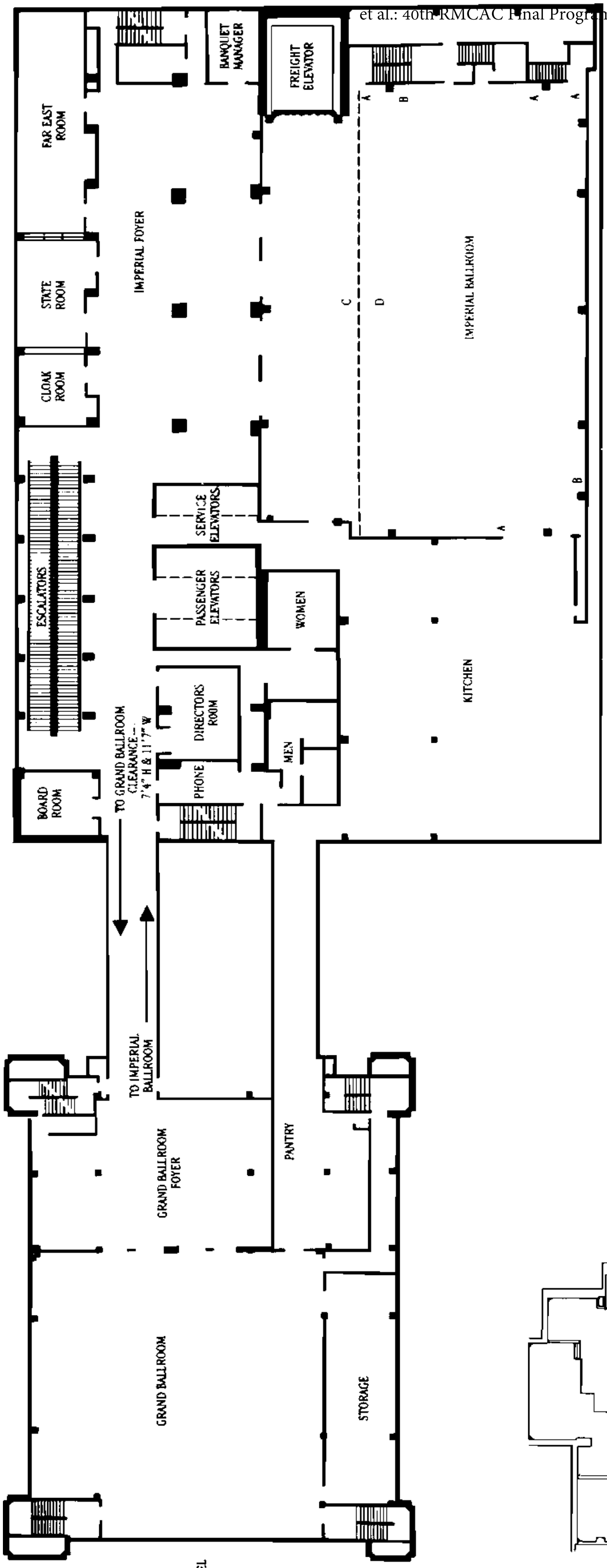

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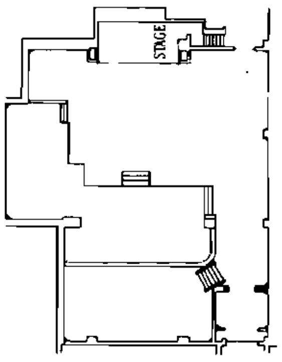

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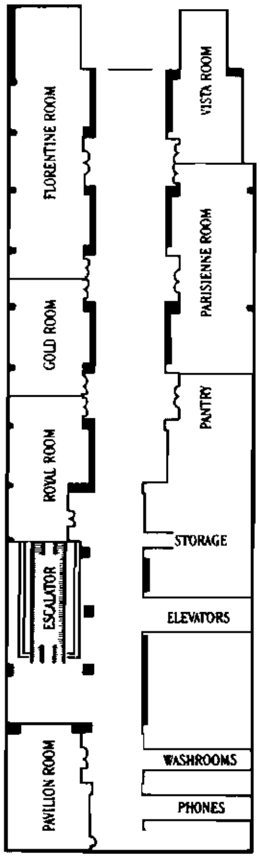

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