45TH Rocky Mountain Conference on Analytical Chemistry
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INFORMATION

Registration

Admission to all technical sessions and the exhibition is by name badge only. Registration materials may be picked up at the RMCAC registration area located at the Hyatt Regency Denver between 8:00 a.m. and 5:00 p.m. anytime Sunday, July 27 through Thursday, July 31.

Schedule of Social Events

Monday, July 28

Exhibition	10:00 a.m. – 7:00 p.m.
Conference Reception	5:00 p.m. – 7:00 p.m.

Tuesday, July 29

Exhibition	9:00 a.m. – 5:00 p.m.

Wednesday, July 30

Exhibition	9:00 a.m. – 2:00 p.m.

Conference Reception

Monday evening from 5:00 p.m. – 7:00 p.m., all attendees are cordially invited to join in on cocktails and hors d'oeuvres. Unwind from the day's events and continue the "Rocky Mountain Conference" experience. Check out all of the latest products and services as the reception is held right in the exhibit hall.

EPR Symposium Banquet

The banquet will take place at the Old Spaghetti Factory (1250 18th Street) at 6:15 p.m. on Tuesday, July 29. Contact Sandra Eaton to make a reservation. Cost: $12.

Shuttle Service To And From DIA

SuperShuttle offers service between DIA and the Hyatt.
The SuperShuttle counter is located on the Baggage Claim level of the airport terminal.
For schedules or reservations call 303-370-1300.

Messages

Messages will be accepted and posted on the message board located next to the Rocky Mountain Conference registration desk. Call 800-996-3233 to leave messages.

Hotel Accommodations

Room rates for participants of the 45th Rocky Mountain Conference on Analytical Chemistry are $165.00 single/double occupancy plus taxes. Call 800-223-1234 or 303-295-1234 and mention "Rocky Mountain Conference on Analytical Chemistry" to receive your special rate. Reservations must be made by July 2, 2003 to receive your special rate. After July 2, 2003, reservations and rate are subject to availability.

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CONFERENCE-AT-A-GLANCE

SYMPOSIA	ROOMS	Monday July, 28		Tuesday July, 29		Wednesday July, 30		Thursday July, 31	
		A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
Advances in Separations Science	Parisienne								
Analytical Methods Applied to Homeland Security	Florentine								
Environmental Chemistry	Florentine								
EPR Lectures	Grand Ballroom								
EPR Posters	Grand Ballroom Foyer								
Exhibition	Imperial Ballroom								
Luminescence	Far East								
MS, GC/MS, LC/MS	Far East								
Nanotechnology	Parisienne								
NMR Lectures	Moulin Rouge								
NMR Posters	Imperial Ballroom								
Pharmaceutical Analysis	Far East								
Speaker Prep	Board								

Advances in Separations Science

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Tuesday, July 29, 2003

9:00	**Opening Remarks**
9:05	**1.** *Mechanism and Use of High Efficiency Microbial Separations.* Daniel W. Armstrong, Iowa State University
9:45	**2.** *Design and Evaluation of an Autonomous Micro GC for Environmental Applications.* Richard D.Sacks, University of Michigan
10:25	**Break** (refreshments in exhibit hall)
10:55	**3.** *Flow Field-Flow Fractionation for Particle Size Analysis of Emulsions.* M. Cecilia Lazo, Mohammed K. Khalid and S. Kim R. Williams, Colorado School of Mines
11:15	**4.** *Studying Sample-Membrane Interactions Using Flow Field-Flow Fractionation.* M. Cecilia Lazo, R. L. Hartmann and S. K. R. Williams, Colorado School of Mines
11:35	**5.** *Applications of Room-temperature Ionic Liquids in Analytical Chemistry. Formation of Micelles in Ionic Liquids.* Veronica Pino, Jared Anderson and Daniel W. Armstrong, Iowa State University
12:10	**Lunch**
1:30	**6.** *The Enantioseparation of Substituted Furocoumarins, Substituted Furoflavones, and Other Biologically Important Molecules by High Performance Liquid Chromatography.* Douglas D. Schumacher, Clifford R. Mitchell and Daniel W. Armstrong, Iowa State University
1:55	**7.** *Selection of Mobile Phases for Normal-Phase Chromatography on Silica of Substituted Tetrahydroisoquonolinones with Complex Structure Using the LSChrom Software.* Christo E. Palamarev, Malinka P. Stoyanova and Mariana D. Palamareva, University of Sofia
2:20	**8.** *Improved Analysis of Sulfur Compounds by Sulfur Chemiluminescence Detection and Gas Chromatography.* R. L. Shearer, Ionics Instruments
2:40	**Break** (refreshments in exhibit hall)
3:10	**9.** *The Identification of Nitropolycyclic Aromatic Hydrocarbons in Mainstream Tobacco Smoke Using Electron Monochromator Mass Spectrometry.* A. John Dane, Crystal D. Havey and Kent J. Voorhees, Colorado School of Mines; Robert B. Cody, JEOL USA
3:35	**10.** *The Polycyclic Aromatic Hydrocarbon Content of Combustion Soots by SFE Extraction and GC/MS Analysis.* Cullen C. Jones, Abdul R. Chughtai, Balasingam Murugaverl and Dwight M. Smith, University of Denver
4:10	**Closing Remarks**

Analytical Methods Applied to Homeland Security

Symposium Chair:
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Monday, July 28, 2003

	Kent J. Voorhees, Presiding
8:25	**Opening Remarks**
8:30	**11.** *Edgewood Chemical Biological Center: Equipment Evaluation for Chemical and Biological Applications in Homeland Defense.* Emory W. Sarver, Edgewood Chemical Biological Center
9:00	**12.** *Technologies in Biological Detection.* Patrick L. Berry and Kate K. Ong, Biological Detection Systems
9:30	**13.** *Real World Uses of Portable GC/MS.* Stephan DeLuca, Charles Sadowski and Robert Miller, INFICON, Inc.
10:00	**Break** (refreshments in exhibit hall)
10:30	**14.** *A Mobile Mass Spectrometer-Based System for Chemical and Biological Agent Detection — The Block III CBMS.* Jochen Franzen, Roland Schnurpfeil, Joachim Stach, John Wronka and Frank Thibodeau, Bruker Daltonics Inc.
11:00	**15.** *Detection of Bio-Aerosol With Mass Spectrometry.* Michael P. McLoughlin, Johns Hopkins Applied Physics Laboratory
	Lunch
1:30	**16.** *Small, Unobtrusive Ion Mobility Spectrometers for Analytical Measurements in Field Tests Involving Outdoor Releases of Chemical Warfare Agent Simulants — Airborne and Ground Operations.* Robert J. Schafer, Vincent M. McHugh, Charles S. Harden, Donald B. Shoff, Brian S. Ince, Stephen E. Harper and Gretchen E. Blethen, US Army Edgewood Chemical Biological Center; Paul Arnold, Simon Pavitt, Martin Thomas, Tony Connor and Eddie Terzic, Graseby Dynamics, Ltd.
2:00	**17.** *Field Examples of Ion Mobility Spectroscopy Used for Explosives Detection.* Philip Rodacy, Pamela Walker and Stephen Reber, Sandia National Laboratories
2:30	**Break** (refreshments in exhibit hall)
3:00	**18.** *Chemical/Biological Aerosol Warning System (C/BAWS).* David Sickenberger, Richard Smardzewski, Felix Reyes and James Cress, U.S. Army SBCCOM; Col. James Swaby USAF Force Protection Battlelab
3:30	**19.** *Honey Bees: Flying Chemical Detectors.* Garon C. Smith, Jerry J. Bromenshenk and Colin B. Henderson, The University of Montana
4:00	**Closing Remarks**

Environmental Chemistry

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Tuesday, July 29, 2003

	Maria W. Tikkanen, Presiding
8:30	**Opening Remarks**
8:35	*INVITED SPEAKER IN ENVIRONMENTAL CHEMISTRY* **20.** *Environmental Applications of Field-Flow Fractionation — Inductively Coupled Plasma Mass Spectrometry.* Ramon M. Barnes, University Research Institute for Analytical Chemistry; Dula Amarasiriwardena, Hampshire College; Atitaya Siripinyanond, Mahidol University
9:30	**21.** *Extraction of Semivolatile Organic Compounds Using Modified and Micro Liquid-Liquid Extraction.* Vicente C. Marti, Renee Bellew and Jesse Kiernan, US EPA Region VIII Laboratory
10:00	**22.** *Monitoring for Intentional Contamination of a Drinking Water System: Contaminants of Concern, Early Warning Monitoring.* Maria W. Tikkanen, Kennedy/Jenks Consultants
10:30	**Break** (refreshments in exhibit hall)
11:00	**23.** *Quantifying Vapor-Soil Interactions Using Surrogate Soil Stationary Phases in Gas Chromatography.* Thomas J. Bruno and Keith E. Miller, Chemical Science and Technology Laboratory, National Institute of Standards and Technology
11:30	**24.** *Clay Adsorbent Evaluation by Liquid Chromatography.* Keith E. Miller and Thomas J. Bruno, Chemical Science and Technology Laboratory, National Institute of Standards and Technology
12:00	**Lunch**
	Maria W. Tikkanen, Presiding
1:30	**25.** *Environmental Chemistry — Challenges of the 21st Century.* Theodore C. Rains, High-Purity Standards
2:00	**26.** *A Batch Enzymatic Reduction Method for Automated and Manual Colorimetric Determination of Nitrate in Water.* Jennifer R. Kryskalla and Charles J. Patton, U.S. Geological Survey, National Water Quality Laboratory
2:30	**27.** *Portable Sensor for the Detection of Nitrates and Nitrites in Groundwater.* Veronica M. Cepak, Michael T. Carter, Erica R. McDaniel and Gregory R. Bourgon, Eltron Research, Inc.
3:00	**Break** (refreshments in exhibit hall)
3:30	**28.** *Mercury and Selenium in Water, Sediments, and Plants from the Las Vegas Wash, USA.* J. V. Cizdziel and J. E. Pollard, Harry Reid Center for Environmental Studies, University of Nevada; Xiaoping Zhou, Southern Nevada Water Authority
4:00	**29.** *Propagation of Error in the Determination of Silicon Concentrations in Tungsten Hexafluoride Residue Samples by Graphite Furnace Atomic Absorption Spectrometry.* Greg W. Johnson; Virginia H. Houlding, Matheson Tri-Gas
	Closing Remarks

EPR

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Sunday, July 27, 2003

	Workshop: Measuring Electron-Electron Distances by EPR
1:15	**Bus departs from Hyatt Regency Denver for University of Denver, Olin Hall**
2:00	**Workshop**
5:15	**Break**
	Bruker Presentation and University of Denver EPR Labs Open House
4:45	**Bus departs from Hyatt Regency Denver for University of Denver, Olin Hall**
5:30	**Bruker Presentation of New Developments**
6:30	**Food, Beverages and Ice Cream**
7:15	**Open house in University of Denver EPR Laboratories**
9:00	**Bus departs from University of Denver for Hyatt Regency Denver**

Monday, July 28, 2003

	Session I, Dedicated to Larry Kevan. D. Goldfarb and S. Schlick, chairing
8:30	**Welcoming Remarks, Sandra S. Eaton**
8:35	**Introductory Comments, L. Kispert, M. K. Bowman, S. Schlick and D. Goldfarb**
8:55	**30.** *New Insights into the Photosystem II Oxygen Evolving Complex via Pulsed EPR.* R. David Britt, University of California, Davis
9:25	**31.** *Structure and Dynamics of Synthetic and Biological Macromolecules by Using a Multitude of EPR Methods on Spin Probes and Labels.* Gunnar Jeschke and D. Hinderberger, Max Planck Institute for Polymer Research
9:55	**32.** *Structure of Co^{II}-Radical Pair Intermediate States in B_{12} Enzyme Catalysis Revealed by Orientation-Selection and Powder ^2H ESEEM Spectroscopy.* Kurt Warncke and Jeffrey M. Canfield, Emory University
10:25	**Break** (refreshments in exhibit hall)
11:00	**33.** *The ESEEM and Pulsed ENDOR of High Spin/Weak Crystal Field Ions.* Arnold Raitsimring, Andrei V. Astashkin, University of Arizona; Peter Caravan, EPIX Medical, Inc.
11:30	**34.** *Characterization of Active Sites in Zeolites by Means of EPR Spectroscopy.* Andreas Pöppl, Marlen Gutjahr, Thomas Rudolf and V. Umamaheswari, University of Leipzig; Martin Hartmann, Kaiserslautern University of Technology
12:00	**Lunch**
	Session II, Dedicated to Larry Kevan. M. K. Bowman and L. Kispert, chairing
1:30	**35.** *Applications of Pulsed EPR to Transition Metal-Exchanged Zeolites and Mesoporous Materials.* Sarah C. Larsen, University of Iowa
2:00	**36.** *Application of Pulsed EPR Spectroscopy to the Study of Radiation Lithography.* Tsuneki Ichikawa, Hokkaido University
2:30	**37.** *ESR Investigations of Niobium-containing Aluminophosphates.* Martin Hartmann, Kaiserslautern University of Technology; V. Umamaheswari, Andreas Pöppl and Winfried Böhlmann, University of Leipzig
2:50	**Break** (refreshments in exhibit hall)
3:20	**38.** *ESR and ESEM Study of Incorporation of Zirconium into Silicoaluminophosphate SAPO-5 Microporous Material.* Pesak Rungrojchaipon, Jianming Lu, Larry Kevan, University of Houston
3:40	**39.** *Electron Spin Resonance Investigations of Zirconium in Mesoporous Aluminophosphate and Silicoaluminophosphate.* Jian-Ming Lü, Koodali T. Ranjit, Pesak Rungrojchaipan and Larry Kevan, University of Houston
4:00	**40.** *A Discrete Water Exit Pathway in the Membrane Protein Cytochrome c Oxidase.* Bryan Schmidt, Shelagh Ferguson-Miller and John McCracken, Michigan State University
4:20	**41.** *Characterizing the Invisible: ENDOR Characterization of Intermediates in the Activation of Dioxygen by Fe Enzymes.* Brian M. Hoffman, Northwestern University
4:50	**Break** (visit the exhibits)
5:00	**Conference Mixer in Exhibit Hall**

Tuesday, July 29, 2003

	Session III, Dave Britt, chairing
8:30	**42.** *Spectroscopic Evidence for Fe(I)-Fe(II) in Fe-only Hydrogenase Models.* Shirley A. Fairhurst, Christopher J. Pickett, Mathieu Razavet, Xiaming Liu, Simon J. George, David J. Evans, J. Elaine Barclay, David L. Hughes and Sian C. Davies, John Innes Centre; Stacey J. Borg and Stephen P. Best, University of Melbourne
8:55	**43.** *Probing Protein Folding with High Field EPR but without Spin-Labeling.* Tatyana I. Smirnova, North Carolina State University
9:20	**44.** *Conformational Changes and Bound State Conformation of Maltose Binding Protein (MBP) Upon Interaction with the Chaperone SecB: ESR and Fluorescence Studies.* M.V.L.N. Raju and Wolfgang E. Trommer, University of Kaiserslautern; Raghavan Varadarajan, Indian Institute of Science
9:45	**45.** *ESR Spin Label Study of Local Segmental Dynamics of Polymers in Dilute Solutions.* J. Pilar and A. Marek, Academy of Sciences of the Czech Republic
10:10	**Break** (refreshments in exhibit hall)
10:45	**46.** *EPR Study of Isomerization Efficiency and Electron Transfer of Carotenoids in Metal Substituted MCM-41 Molecular Sieves.* Yunlong Gao, Lowell Kispert, Tatyana Konovalova and Jesse Lawrence, The University of Alabama
11:10	**47.** *Study of the Formation of the Mesoporous Material SBA-15 by EPR Spectroscopy.* Sharon Ruthstein, Veronica Frydman, Shifra Kababya and Daniella Goldfarb, Weizmann Institute of Science; Miron Landau, Ben-Gurion University of the Negev
11:35	**48.** *EPR, NMR and ENDOR Study of Extrinsic and Intrinsic Defects in Congruent and Stoichiometric Lithium Niobate.* Galina Malovichko, Montana State University; Valentin Grachev, Osnabrück University
12:00	**Lunch**
	Session IV, Lawrence H. Piette Memorial Lecture
1:30	**Introduction by Monte Lai, Medinox**
1:35	**48b.** *Role of Iron, Hydrogen Peroxide, and Hydroxyl Radicals in Biological Toxicity — Revisited after 30 Years.* Balaraman Kalyanaraman, Medical College of Wisconsin
2:25	**Break** (refreshments in exhibit hall)
	Session V, Posters, Sandra Eaton, chairing
3:00	**Authors Present for Posters Labeled A** *(see below)*
4:00	**Authors Present for Posters Labeled B** *(see below)*
5:00	**International EPR/ESR Society General Business Meeting**
6:00	**EPR Symposium Banquet — The Old Spaghetti Factory, 1250 18th Street. Reservations are required, see S. Eaton.**

EPR POSTER SESSIONS A & B

3:00 – 4:00	**Authors present for posters labeled A**
4:00 – 5:00	**Authors present for posters labeled B**
	(Posters are listed alphabetically by presenting author, A–I) * Identifies recipients of Jules Stein Student Travel Awards † Identifies posters in the session dedicated to Larry Kevan
A	**49.** *Stability of the Missing Angle Algorithm For 4D Spectral-Spatial EPR Imaging.* * Kang-Hyun Ahn, Benjamin Williams, Howard Halpern, Xiaochuan Pan, University of Chicago
B	**50.** *Substrate-Supported Lipid Nanotubes with Bilayer-like Properties.* Ali M. Alaouie, Yevgeniy Degtyarev, and Alex I. Smirnov, North Carolina State University
A	**51.** *One-half Wavelength Spaced Tuning Elements for Iris Coupling Structures for Higher Frequency EPR Cavities.* James R. Anderson, Richard R. Mett and James S. Hyde, Medical College of Wisconsin
B	**52.** *ENDOR Enhancement.* Andrei V. Astashkin and Arnold M. Raitsimring, University of Arizona

A	**53.** *Divalent Metal Cation Templating in Thermally-Driven Amino Acid Copolymerization.* Chris Bender, Fordham University
B	**54.** *Experimental Methods of Double-Quantum Coherence ESR.* Peter P. Borbat, Boris N. Naumov and Jack H. Freed, Cornell University
A	**55.** *Study of Membrane Proteins by Double-Quantum Coherence ESR: Gramicidin A.* Peter P. Borbat, Boris Dzikovsky and Jack H. Freed, Cornell University
B	**56.** *Conformational Changes in the Rieske Subunit of Cyt bc_1 Complex.* Michael K. Bowman, Battelle Northwest Labs; Arthur Roberts and David M. Kramer, Washington State University
A	**57.** *Metal Binding to Apurinic Endonuclease (APE-1).* † Michael K. Bowman, Pacific Northwest National Labs; Jonathan Cape and David M. Kramer, Washington State University
B	**58.** *HYSCORE Lineshapes for I=1 Nuclei with Isotropic Hyperfine and Arbitrary Quadrupolar and Zeeman Interactions.* † Alexander G. Maryasov, Institute of Chemical Kinetics and Combustion, Russia; Michael K. Bowman, Battelle Northwest Labs
A	**59.** *EPR Studies on Nitric Oxide and Ceruloplasmin in Patients with Rheumatoidal Diseases.* Anna Bratasz, Mariola Koziel and Stanislaw Lukiewicz, Jagiellonian University; Jolanta Bucka, Cracow Hospital of Rheumatological Diseases; Antoni Skura, Hospital of Joseph Dietel in Cracow
B	**60.** *EPR Monitoring of Chemotherapy in Leukemic Patients.* Kinga Marciniak, Anna Bratasz and Stanislaw Lukiewicz, Jagiellonian University; Dorota Krochmalczyk and Aleksander Skotnicki, Hematological Clinic, Kraków, Poland
A	**61.** *Measurement of Thiol Levels in Human Ovarian Cancer Cells Treated with Cisplatin.* Anna Bratasz, Valery V. Khramtsov and Periannan Kuppusamy, The Ohio State University
B	**62.** *Novel EPR Investigations of Molecular Nanomagnets.* Brant Cage, Stephen Russek, National Institute of Standards and Technology; J. Micah North and Naresh Dalal, Florida State University
A	**63.** *Orientation-Selection ESEEM Spectroscopic Characterization of the Structure of the Co^{II}- Product Radical Pair State of Coenzyme B_{12}-Dependent Ethanolamine Deaminase.* Jeffrey M. Canfield and Kurt Warncke, Emory University
B	**64.** *X-band EPR Studies of Membrane Proteins Incorporated into Bicelles.* * Thomas B. Cardon, Tia Dorozonski, Nisreen Nussair and Gary A. Lorigan, Miami University
A	**65.** *Modes of Cu(II) Binding in the Prion Protein.* * Madhuri Chattopadhyay, Colin S. Burns, Glenn L. Millhauser, Christine C. Dunham and William Scott, University of California, Santa Cruz; Eliah Aronoff-Spencer, Jack Peisach and Gary J. Gerfen, Albert Einstein College of Medicine; Guiseppe Legname, Stanley B. Prusiner, Universitty of California, San Francisco; William Antholine, Medical College of Wisconsin; Marilyn M. Olmstead, University of California, Davis
B	**66.** *Comparative ESR and Catalytic Studies of Ethylene Dimerization on Ni(II)-exchanged Clinoptilolite and Pd(II)-exchanged Clinoptilolite, Mordenite, Ferrierite and SUZ-4.* † Hosun Choo, Western Kentucky University; Suk B. Hong, Taejon National University of Technology; Larry Kevan, University of Houston
A	**67.** *Spectroscopic Studies on Pounamu or New Zealand Greenstone.* Cuthbert Wilkins, Bryce Williamson, Craig Tennant, Rod Claridge, University of Canterbury
B	**68.** *Speciation of Mn^{2+} in Aqueous Bicarbonate Solutions: Electrochemistry and EPR Study.* * J. Dasgupta, A.M. Tyryshkin and G.C. Dismukes, Princeton University; Yu.N. Kozlov, A.A. Kazakova, S.V. Baranov and V.V. Klimov, Russian Academy of Sciences
A	**69.** *Improving Signal-to-Noise in Pulsed ENDOR and Resolution in Continuous-Wave ENDOR Experiments.* Peter E. Doan and Brian M. Hoffman, Northwestern University
B	**71.** *Multifrequency Tests of Nitroxyl Relaxation Mechanisms.* Rikard Owenius, Garth E. Terry, Sandra S. Eaton and Gareth R. Eaton, University of Denver
A	**72.** *Large Pulsed Electron-Electron Double Resonance on Multi-Nuclear Metal Clusters: Assignment of Spin Projection Factors Based on the Dipolar Interaction.* * Celine Elsaesser, Marc Brecht and Robert Bittl, Freie Universität Berlin
B	**73.** *Impact of Geometry on Spin Lattice Relaxation for CuN_4 Complexes.* Alistair Fielding, Gareth R. Eaton,and Sandra S. Eaton, University of Denver

A	**74.** *Rectangular Loop-Gap Resonator with the Light Access to the Sample.* Malgorzata Dutka, Tadeusz Oles and Wojciech Froncisz, Jagiellonian University
B	**75.** *Determination of Electron-Electron Interspin Distance Between the Spin Label and Fe-NO Radical in Cytochrome c.* Wojciech Blicharski, Janusz Pyka, Artur Osyczka, Malgorzata Dutka, Sebastian Szytula, Ryszard J. Gurbiel, Bohdan Turyna and Wojciech Froncisz, Jagiellonian University
A	**76.** *Digital Receiver for EPR Spectroscopy.* Jerzy Koziol, Malgorzata Dutka, Ryszard J. Gurbiel and Wojciech Froncisz, Jagiellonian University
B	**77.** *EPR Studies of Interactions of Cytochromes c with their Physiological Partners.* Janusz Pyka, Artur Osyczka, Sebastian Szytula, Bohdan Turyna and Wojciech Froncisz, Jagiellonian University
A	**78.** *Transport and Metabolism of Glycosilated Spin Probes in Escherichia Coli.* Kôichi Fukui, Regional Joint Research Project of Yamagata Pref.; Shingo Sato and Jun-ichi Onodera, Yamagata University; Masaaki Aoyama and Hiroaki Ohya, Institute for Life Support Technology
B	**79.** *Distribution of the Microwave Magnetic Field in the Ferroelectric Resonators for EPR Experiments.* I.N.Geifman, EMS Inc.; Iryna Golovina, Ukrainian Academy of Sciences
A	**80.** *Intramolecular or Intermolecular Reactions Between a Phosphinine and Its Radical Anion: DFT Calculations and EPR Spectra.* M. Geoffroy, L. Cataldo, S. Choua and C. Dutan, University of Geneva; P. Le Floch, N. Mézailles and Audrey Moores, Ecole Polytechnique
B	**81.** *The Structure of the iSH2 Domain of Class Ia PI-3 Kinase Determined by Site Directed Spin Labeling EPR and Homology Modeling.* Eliah Aronoff-Spencer, Zheng Fu, Jonathan M. Backer and Gary J. Gerfen, Albert Einstein College of Medicine of Yeshiva University
A	**82.** *Overmoded Cavity Resonators for Use in High Frequency EPR Spectroscopy.* Vladimir Krymov, Ukrainian National Academy of Sciences and Gary J. Gerfen, Albert Einstein College of Medicine of Yeshiva University
B	**83.** *Analysis of the Tuning and Operation of Reflection Resonator EPR Spectrometers.* Vladimir Krymov, Ukrainian National Academy of Science; Gary J. Gerfen, Albert Einstein College of Medicine of Yeshiva University
A	**84.** *EPR and ENDOR of Chromium in Li-deficient and Li-rich Lithium Niobate Crystals.* Valentin Grachev and Galina Malovichko, Montana State University; Ortwin Schirmer, Osnabrück University; Edward Kokanyan, Institute for Physical Researches
B	**85.** *Acqiris Averager: Application to FT-EPR.* I. Gromov, A. Schweiger, ETH-Hönggerberg; B.Epel , Max Planck Institute of Radiation Chemistry; Phil Gregor, Acqiris USA
A	**86.** *Folding of Spin-labeled T4 Lysozyme in the Time Regime from 50 Microseconds to 10 Seconds as Elucidated by Dielectric Resonator-Based Flow and Stopped-Flow EPR.* Hassane S. Mchaourab, Vanderbilt University School of Medicine; Vladimir M. Grigoryants and Charles P. Scholes, University at Albany
B	**87.** *Scaling of EPR Spectra-spatial Images With Size of Sample: Images of Samples Greater Than 5 cm in Linear Dimension.* Chad R. Haney, Kazuhiro Ichikawa, V.S. Subramanian, Colin Mailer, Eugene D. Barth, Benjamin F. Williams and Howard J. Halpern, University of Chicago
A	**88.** *Reduction of Image Artifacts by Bladder Flushing with a Novel Double Lumen Urethral Catheter.* Chad R. Haney, Kazuhiro Ichikawa, Adrian Parasca, Benjamin B. Williams, Eugene D. Barth, Martyna Elas and Howard J. Halpern, University of Chicago
B	**89.** *Structural Characterization of the Mo(V) High-g Unsplit Species from Rhodobacter Capsulatus Dimethylsulfoxide Reductase and its Role in Catalysis.* Graeme R. Hanson, Ian Lane, Christopher J. Noble and Alastair G. McEwan, The University of Queensland; Neil Benson, The University of East Anglia
A	**90.** *CW and Pulsed EPR Spectroscopy Reveal a New Structural Motif for the Active Site Mo Centre and an Unusual [4Fe-4S]$^{+}$ Cluster in Dimethylsulfide Dehydrogenase.* Graeme R. Hanson, Christopher J. Noble, Christopher McDevitt and Alastair G. McEwan, The University of Queensland, Australia
B	**91.** *A Quasioptical, High Power Pulsed ESR Spectrometer at 95 GHz.* Wulf Hofbauer, Curt R. Dunnam, Keith A. Earle and Jack H. Freed, Cornell University
A	**92.** *Photoinduced Higher Oxidation States in Manganese Dimers Aimed at Modelling the Water Oxidizing Complex in Photosystem II.* * Joakim Högblom, Ping Huang, Ann Magnuson and Stenbjörn Styring, Lund University; Magnus F. Anderlund and Licheng Sun, Stockholm University

B	**93.** *Discrete Approach of High Spatial Resolution Multi-Site EPR Oximetry.* Ferenc Horváth, University of Debrecen; O.Y. Grinberg and H.M. Swartz, Dartmouth Medical School
A	**94.** *Anisotropy of Rotation of 2,2,6,6-tetramethyl piperidine 1-oxide in the Vicinity of the Nematic-to-Isotropic Phase Transition of 4-n-pentyl-4'-cyanobiphenyl.* Jimmy S. Hwang and Ghassan A. Oweimreen, King Fahd University of Petroleum & Minerals
B	**95.** *Modeling Spin Trapped Superoxide Adducts of 5-substituted-5-methyl-1-pyrroline N-oxide; Evidence Against Hydrogen Splitting.* Kazuhiro Ichikawa, Chad R. Haney, Eugene D. Barth, Adrian Parasca, Colin Mailer and Howard J. Halpern, University of Chicago; Bruce H. Robinson, University of Washington; Gerald M. Rosen, University of Maryland

Wednesday, July 30, 2003

	Session VI, Protein Structure, Periannan Kuppusamy, chairing
8:30	**96.** *Membrane + Protein + Site-directed Spin Labeling EPR: A Winning Combination.* Yeon-Kyun Shin, Iowa State University
9:00	**97.** *Internitroxide Proximities in Protein Structure Determination.* Hassane S. Mchaourab, Vanderbilt University
9:30	**98.** *Double-Quantum Coherence ESR: Distance Measurements in Large Biomolecules.* Peter P. Borbat and Jack H. Freed, Cornell University
10:00	**Break** (refreshments in exhibit hall)
10:30	**99.** *The Prion Protein Within Us: EPR Distances and Structural Insights into PrP Function.* Glenn L. Millhauser and Colin S. Burns, University of California, Santa Cruz; Eliah Aronoff-Spencer, Gary J. Gerfen and Jack Peisach, Albert Einstein College of Medicine; William E. Antholine, Medical College of Wisconsin; Giuseppe Legname and Stanley B. Prusiner, University of California, San Francisco
11:00	**100.** *A pH-sensitive Nitroxide for Site-Directed Spin-Labeling.* Igor A. Grigor'ev, Vladimir A. Reznikov and Maxim A. Voinov, Novosibirsk Institute of Organic Chemistry, Russia; Andres Ruuge and Alex I. Smirnov, North Carolina State University
11:30	**101.** *Molecular modeling techniques in EPR spectroscopy.* Peter Fajer, Ken Sale, Khaled Khairy, National High Magnetic Field Laboratory and Florida State University; David Budil, Northeastern University
12:00	**Lunch**
	Session VII, Gary Gerfen, chairing
1:30	**102.** *Lewisite (L), an Arsenic-derived Vesicant Chemical Warfare Agent (CWA), Inhibits the Inflammatory Cytokine, Tumor Necrosis Factor-alpha (TNF-a), via a Mechanism Involving Reactive Oxygen Species (ROS): Implication for Mechanism of Genotoxicity.* C. M. Arroyo, D. W. Kahler, M. R. Nelson, C. M. Corun, J. J. Guzman, M. A. Smith, S. D. Soni and C. A. Broomfield, U.S. Army Medical Research Institute of Chemical Defense; D. L. Burman and B. E. Hackley, Oak Ridge Institute for Science and Education
1:55	**103.** *Aqueous Sample in EPR Cavity: Field Distribution and Signal Intensity.* Yu. E. Nesmelov and D. D. Thomas, University of Minnesota (also presented as poster)
2:20	**104.** *Aqueous Flat Cells Perpendicular to the Electric Field for Use in Electron Paramagnetic Resonance Spectroscopy.* Richard R. Mett and James S. Hyde, Medical College of Wisconsin *(also presented as poster)*
2:45	**Break**
	Session VIII, Posters, Sandra Eaton, chairing

EPR POSTER SESSIONS C & D

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, J–Z) * Identifies recipients of Jules Stein Student Travel Awards † Identifies posters in the session dedicated to Larry Kevan
C	**105.** *Electron Spin Resonance Studies on Anthracite Coals and Soots.* Yi Jin Jiang, Mark S. Solum, Ronald J. Pugmire and David M Grant, University of Utah
D	**106.** *ESR Study of y-Irradiation on the Photosynthetic Biomembrane System.* Y.S. Kang and D.K. Lee, Pukyong National University
C	**107.** *EPR and ENDOR Studies on the Effect of Bicarbonate on Copper Site and Free Radical Formation in WT and W32F Human and Bovine Copper, Zinc Superoxide Dismutase.* Chandran Karunakaran, Hao Zhang, William Antholine and Balaraman Kalyanaraman, Medical College of Wisconsin; John Crow, University of Alabama-Birmingham; Joseph Beckman, Oregon State University
D	**108.** *The Distances Between Electron Transfer Components in Photosystem II Studied by Spin Polarized ESEEM.* Asako Kawamori, Kwansei Gakuin University; Hideyuki Hara, Bruker Biospin; K.K. Tsukuba; Robert Bittl, Free University, Berlin; Sergei A. Dzuba, Russian Academy of Sciences
C	**109.** *Distance Measurement in RNA Molecules using EPR Spectroscopy.* Nak-Kyoon Kim, Ayaluru Murali and Victoria J. DeRose, Texas A&M University; Michael K. Bowman, Pacific Northwest National Laboratory
D	**110.** *Characterization of External Surface Area of MFI Zeolites Using EPR.* * Zhiqiang Liu, Xuegong Lei and Nicholas J. Turro, Columbia University; Lloyd Abrams, E. I. duPont de Nemours and Co.; M. Francesca Ottaviani, University of Urbino
C	**111.** *Notre Dame Radiation Chemistry Data Center, 2003 Status Report.* Keith P. Madden, University of Notre Dame
D	**112.** *The Bonding in MCH_3 (M= Cd, Mg, Hg, Zn) Radicals Revealed by Neon Matrix Isolation EPR.* A. J. McKinley, J. Davis and E. Karakyriakos, University of Western Australia
C	**113.** *Spin Dependent Recombination of Deep Level Defects at Silicon Carbide — Silicon Dioxide Heterointerfaces.* * David Meyer, Aaron Leese, Morgen Dautrich, N.A. Bohna and P.M. Lenahan, Pennsylvania State University; Aivars Lelis, Army Research Laboratory; Robert Okojie, NASA-Glenn Research Laboratory
D	**114.** *ESR and ESEEM Study of Silver Clusters in ZK-4 Zeolites.* † J. Michalik, J. Sadlo, M. Danilczuk, Institute of Nuclear Chemistry and Technology; L. Kevan, University of Houston; Jong-Sung Yu, Hannam University
C	**115.** *Electron Spin Resonance Studies of Manganese Ions in the Hammerhead Ribozyme.* Matthew Vogt, Ayaluru Murali and Victoria J. DeRose, Texas A&M University
D	**116.** *Relationships Among the Different Components of a CW EPR Spectrum.* * Robert D. Nielsen and Bruce H. Robinson, University of Washington; Albert H. Beth and Eric J. Hustedt, Vanderbilt Medical Center
C	**117.** *Orientation of Stearic Acid in Magnetically Aligned Phosphatidylcholine Bilayers by X-band EPR Spectroscopy: Cholesterol, Chain Length and Temperature Effects.* * Nisreen A. Nusair and Gary A. Lorigan, Miami University
D	**118.** *EPR Study on Free Radicals Produced by Hydrogen Addition to Alknylsilanes at 77K.* † Nobuaki Ohta, Hiroshima University
C	**119.** *The Antisymmetric Part of the g-Matrix: Can It Be Observed?* Alexander Maryasov, Institute of Chemical Kinetics and Combustion; Andrew Primak and Michael K. Bowman, Battelle Northwest Labs
D	**120.** *High Power Pulse Amplifiers for 250 MHz EPR.* Richard W. Quine and Gareth R. Eaton, University of Denver
C	**121.** *Pulsed Proton ENDOR Spectroscopy of Gadolinium Complexes.* Arnold M. Raitsimring and Andrei V. Astashkin, University of Arizona; Peter Caravan, EPIX Medical, Inc.
D	**122.** *Photoinduced Charge Separation of Organic Molecules in Chromium Containing Silicoaluminophosphate (SAPO-5) Microporous Materials at Room Temperature.* † Koodali T. Ranjit and Larry Kevan, University of Houston

C	**123.** *Design, Construction and Performance of a Large EPR Imaging Magnet for use at 250 MHz.* George A. Rinard, Richard W. Quine and Gareth R. Eaton, University of Denver; Charles A. Pelizzari and Howard J. Halpern, University of Chicago
D	**124.** *On Redfield Theory: A Novel Relaxation Equation of Motion.* Robert D. Nielsen and Bruce H. Robinson, University of Washington
C	**125.** *Aqueous Sample Heating at X- and W-band: Towards a Microwave T-jump EPR Experiment.* Andres Ruuge, Ali M. Alaouie, Yevgeniy Degtyarev and Alex I. Smirnov, North Carolina State University
D	**126.** *Metal Binding to Anthracis Repressor (AntR).* * Kadir Ilker Sen, Timothy M. Logan, Piotr G. Fajer, Florida State University, National High Magnetic Field Laboratory; John Love and John R. Murphy, Boston University School of Medicine
C	**127.** *Experimental Limitations of High Spatial Resolution Multi-Site EPR Oximetry.* V.O. Grinberg, eCentricus Internet Consulting; A. I. Smirnov, North Carolina State University; O. Y. Grinberg, J. A. O'Hara and H. M. Swartz, Dartmouth Medical School
D	**128.** *Deuterated OX-031: A Non-toxic Trityl Spin Probe With Significantly Narrower Spectral Lines for In-vivo Oximetry.* Jeon-Hyun Sohn, T Jagadeeswar Reddy, Tetsuo Iwama, Colin Mailer, Howard J. Halpern and Viresh Rawal, University of Chicago; Sandra S. Eaton and Gareth R. Eaton, University of Denver
C	**129.** *Distance Measurement by T1 Enhancement.* * Likai Song, Louise Brown and Piotr Fajer, Florida State University
D	**130.** *Rapid-Scan EPR.* James W. Stoner, Richard W. Quine, George A. Rinard, Sandra S. Eaton and Gareth R. Eaton, University of Denver
C	**131.** *Saturation-Recovery at Q-Band.* W.K. Subczynski, T.G. Camenisch, C.S. Klug and J.S. Hyde, Medical College of Wisconsin
D	**132.** *Lipid Raft Domains: EPR Discrimination by Oxygen Transport.* W.K. Subczynski and J.S. Hyde, Medical College of Wisconsin; A. Kusumi, Nagoya University
C	**133.** *Spin Probe Monitoring of Starch Gelatinisation in Bread Dough Modelled Using Wheat and Pea Starch.* Duncan G. Gillies, University of Surrey; E. N. Clare Mills, James A. Robertson and Les. H. Sutcliffe, Institute of Food Research
D	**134.** *EPR Measurements of Interspin Distances in Spin Labeled Myoglobin.* Dmitriy Ulyanov, Bruce Bowler, Sandra S. Eaton and Gareth R. Eaton, University of Denver
C	**135.** *Substrate and Cofactor Interactions With Lysine 2,3-aminomutase Studied by 35 GHz ENDOR.* Charles J. Walsby and Brian M. Hoffman, Northwestern University; Dawei Chen and Perry A. Frey, University of Wisconsin-Madison
D	**136.** *A Liquid-Solution EPR and ENDOR Study of Two 2,2-Diphenyl-1-monosulfo, Dinitrophenyl Hydrazyl Salts.* David F. Howarth, Monika D. Lafond and John A. Weil, University of Saskatchewan; Ralph T. Weber, Bruker Biospin Corp.
C	**137.** *Pulsed EPR Studies of Vanadium-Exchanged Zeolites.* * James F. Woodworth and Sarah C. Larsen, University of Iowa; Michael K. Bowman, Pacific Northwest Laboratory
D	**138.** *PELDOR Studies on the Spatial Properties of Trapped Radicals in Irradiated DNA.* Michael K. Bowman, Pacific Northwest National Laboratory; David Becker and Michael D. Sevilla, Oakland University; John D. Zimbrick, Colorado State University

Thursday, July 31, 2003

	Session IX, New Developments, Shirley Fairhurst, chairing
8:30	**Presentation of International EPR Society Young Investigator Award to Stephen Zech by Shirley Fairhurst, IES**
8:35	**139.** *Insight into Structure and Function of Photosynthetic Reaction Centers from Time-resolved EPR Spectroscopy.* Stephan G. Zech, Columbia University
9:05	**140.** *95-287 GHz EPR Study of Radical Intermediates Formed in the Reaction of Myoglobin with H_2O_2.* Tatyana Konovalova and Lowell Kispert, University of Alabama; Johan van Tol and Louis-Claude Brunel, National High Magnetic Field Laboratory
9:35	**141.** *Rapid Freeze Quench EPR with Dead Times Below 100 Microseconds: Applications in High Frequency EPR.* Vladimir Krymov, Yu Lin, Denis Rousseau, Syun-Ru Yeh and Gary J. Gerfen, Albert Einstein College of Medicine of Yeshiva University and Donetsk Physical-Technical Institute, Ukraine
10:05	**Break**
10:20	**142.** *High Resolution ESR Microscopy.* Aharon Blank, Curt Dunnam, Peter Borbat, and Jack H. Freed, Cornell University
10:50	**143.** *Nanoparticulate Spin Probes for EPR Cell-Tracking and Oximetry.* Periannan Kuppusamy, Ramasamy P. Pandian, Narasimham L. Parinandi, Anna Bratasz, Govindasamy Ilangovan and Jay L. Zweier, The Ohio State University
11:20	**144.** *Biological Correlates of EPR Oxygen Images: Preliminary Images of Response to Radiation Plus Adenovirus Delivered EGR-TNF Anti-cancer Therapy.* Charles A. Pelizzari, Chad R. Haney, Adrian Parasca, Kazuhiro Ichikawa, Eugene D. Barth, Benjamin B. Williams, Martyna Elas, V.S. Subramanian, Marta A. Zamora, Jonathan N. River, Gregory S. Karczmar, Helena J. Mauceri, Ralph R. Weichselbaum, Howard J. Halpern, University of Chicago and Jagiellonian University
12:00	**Closing Remarks, Gareth R. Eaton**

Luminescence

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Monday, July 28, 2003

	James R. Gord, Presiding
8:55	**Opening Remarks**
9:00	**145.** *Two-Beam Fluorescence Cross-Correlation Spectroscopy for Discriminating Positive and Negative Ions in Continuous Flow Capillary Electrophoresis.* Keir Fogarty and Alan Van Orden, Colorado State University
9:20	**146.** *Lateral Diffusion Measurement on Cell Surfaces by Total Internal Reflection Fringe (TIRIF) Photobleaching Recovery.* Guy M. Hagen, B. George Barisas and Deborah A. Roess, Colorado State University
9:40	**147.** *Time-Resolved Fluorescence Studies of Sol-Gel Derived Nanocomposite Materials Suitable for Biosensor Applications.* Gillian L. Goring and John D. Brennan, McMaster University
10:00	**148.** *Design and Applications of Highly Luminescent Metal Complexes.* J. N. Demas, Wenying Xu, Z. F. Fuller, W. D. Bare and A. Periasamy, University of Virginia; B. A. DeGraff, James Madison University; Kristi Kneas and R. D. Bowman, Maryville College
10:20	**Break** (refreshments in exhibit hall)
10:50	**149.** *Single Pyrene Labeled Dendrimers: pH-Dependent Fluorescence Behavior.* Rebecca A. Redden and Siddharth Pandey, New Mexico Institute of Mining and Technology; Darryl Y. Sasaki, Sandia National Laboratories
11:10	**150.** *On the Formation of Self-Assembled Aggregates within the Room-Temperature Ionic Liquid 1-ethyl-3-butylmethlylimidazolium bis (trifluoromethylsulfonyl)imide.* Kristin A. Fletcher and Siddarth Pandey, New Mexico Institute of Mining and Technology
11:30	**151.** *Solid-Matrix Luminescence Properties of Benzo[e]pyrene and Dibenzo[a,l]pyrene Diolepoxide-DNA Adducts.* Allison L. Thompson and Robert J. Hurtubise, University of Wyoming
11:50	**Lunch**
	Robert J. Hurtubise, Presiding
1:30	**Opening Remarks**
1:35	**152.** *Optical Sensor Platforms for Quantifying Pollutant Emissions in Combustion Exhausts.* James R. Gord, Air Force Research Laboratory, Propulsion Directorate; Rodolfo Barron-Jimenez and Thomas N. Anderson, Texas A&M University; Robert P. Lucht, Purdue University; Sukesh Roy and Michael S. Brown, Innovative Scientific Solutions, Inc.; Scott Stouffer, University of Dayton Research Institute
1:55	**153.** *Effects of Dynamic Strain on OH* and CH* Luminescence in Counterflow Diffusion Flames.* Joseph D. Miller, Terrence R. Meyer and Michael S. Brown, Innovative Scientific Solutions, Inc.; James R. Gord, Air Force Research Laboratory, Propulsion Directorate

2:15	**154.** *Dual-Pump, Dual-Broadband Coherent Anti-Stokes Raman Scattering for Characterization of Liquid-Fueled Combustors.* Sukesh Roy and Terrence R. Meyer, Innovative Scientific Solutions, Inc.; Robert P. Lucht, Purdue University; Vincent M. Belovich, Edwin Corporan and James R. Gord, Air Force Research Laboratory, Propulsion Directorate
2:35	**Break** (refreshments in exhibit hall)
2:55	**155.** *Energy Deposition in "Nonresonant" Transient Grating Thermometry.* Michael S. Brown and Terrence R. Meyer, Innovative Scientific Solutions, Inc.; Dale T. Shouse and James R. Gord, Air Force Research Laboratory, Propulsion Directorate
3:15	**156.** *Quenching Studies of Highly Luminescent CdS Nanoparticles in the Presence of Sulfur Containing Compounds.* Justyna Widera, James R. Gord and Christopher E. Bunker, Air Force Research Laboratory, Propulsion Directorate
3:35	**157.** *Solvatochromic Shifts of Pyrene in Supercritical Fuels.* Donald K. Phelps, Christopher E. Bunker and James R. Gord, Air Force Research Laboratory, Propulsion Directorate
3:55	**Closing Remarks**

MS, GC/MS, LC/MS

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Tuesday, July 29, 2003

	Opening Remarks
8:45	**158.** *HPLC/MS/MS Quantitative Bioanalysis of Drugs Used to Protect Against Chemical Warfare Agents.* Shane Needham and Binying Ye, Alturas Analytics, Inc.; J. Richard Smith and Benedict R. Capacio, US Army Medical Research Institute of Chemical Defense
9:15	**159.** *Fourier Transform-Infrared Imaging of Aortic Tissue: A Novel Approach for the Study of Atherosclerosis.* Manoj Mehta, Elaine Holmes and George E. Tranter, Imperial College London; Elaine McKilligin, GlaxoSmithKline
10:00	**Break** (refreshments in exhibit hall)
10:30	**160.** *Accurate Mass Measurement in Drug Stability Studies on an Enhanced Mass Resolution Triple Quadrupole Mass Spectrometer.* Gary Paul, Thermo Electron Corporation
11:30	**Lunch**
1:30	**161.** *Composition of Pharmaceutical Production Equipment Materials.* Don H. Miller, Ph.D.
2:30	**Break** (refreshments in exhibit hall)
3:00	**162.** *Structural Characterization of Organometallic Macrocomplexes Utilizing Electrospray Mass Spectrometry and Matrix-Assisted Laser Desorption Ionization Mass Spectrometry.* Christina Sorensen and B.P.Sullivan, University of Wyoming
3:20	**163.** *Fatty Acid Ethyl Ester Quantitation with a Novel Gas Chromatography Column and Automatic Injection System, and Correlation with Blood Ethanol Levels.* Clark C. Kulig, Thomas P. Beresford and Gregory T. Everson, University of Colorado Health Sciences Center
3:40	**163b.** *The Role of the AccuTOF Mass Spectrometer in Biochemical Analyisis.* Adrian W. Pike, Zhanpin Wu and Chip Cody, JEOL USA Inc.
	Closing Remarks

Nanotechnology

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Monday, July 28, 2003

9:30	**Opening Remarks**
9:30	**164.** *De Novo Design, Synthesis and Self-Assembly of Nanometer Scale Membrane Proteins.* Krishna Kumar, Tufts University
10:10	**165.** *Lipid Nanotube Arrays for Biochip Applications.* Alex I. Smirnov and Ali M. Alaouie, North Carolina State University; Oleg G. Poluektov, Argonne National Laboratory
10:50	**166.** *Multi-functionalized Mesoporous Silica Nanosphere-Based Fluorescence Sensor and Controlled Release Delivery System.* Victor S.-Y. Lin, Cheng-Yu Lai, Daniela R. Radu and Brian G. Trewyn, Iowa State University
11:30	**Lunch**
1:30	**167.** *Proton-Carrier Sol Gel Composites for High-Temperature PEM Applications.* F. John Pern and J. A. Turner, National Renewable Energy Laboratory; A.M. Herring, Colorado School of Mines
2:10	**168.** *Physical Characterization of Nanotechnology Materials.* M.C. Pohl and R.B. Heninger, Horiba Instruments, Inc.
2:50	**Break** (refreshments in exhibit hall)
3:30	**169.** *Probing the Electronic Structure of Cubane [Fe_4S_4]: Nature's Favorite Cluster for Electron Transfer and Storage.* Xue-Bin Wang, Xin Yang, You-Jun Fu and Lai-Sheng Wang, Pacific Northwest National Laboratory and Washington State University; Shuqiang Niu, Toshiko Ichiye, Washington State University; Christopher J. Pickett, John Innes Centre
4:10	**170.** *Morphological Analysis of Sol-Gel Derived Nanocomposite Materials Suitable for Biosensor Applications.* Gillian L. G. Goring and John D. Brennan, McMaster University
4:40	**Closing Remarks**

NMR

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Monday, July 28, 2003

7:55	**Opening Remarks, Terry Gullion**
	Imaging, Philip Grandinetti presiding
8:00	**171.** *Extensions of Solid-State NMR Methodology to Dipolar Field Effects in Solution.* W. S. Warren, Motohiro Mizuno and Xiaoping Tang, Princeton University
8:30	**172.** *MRI Strategies for the Study of Permeable Media.* Rudi Michalak and A. Ted Watson, Colorado State University
9:00	**173.** *Recent Developments in GARField Magnets for Broad-line Imaging.* Peter J. McDonald, University of Surrey
9:30	**Break** (refreshments in exhibit hall)
10:15	**174.** *High-temperature Rheological NMR of Polymer Melts.* Antje Gottwald and Ulrich Scheler, Institute for Polymer Research Dresden
10:45	**175.** *Imaging What We Eat to Maintain Quality and Ensure Safety.* Michael J. McCarthy, Kathryn L. McCarthy and Jeffrey H. Walton, University of California, Davis
11:15	**176.** *Dynamics of Methane Combustion by In Situ NMR Spectroscopy Using High Density Xenon-129 Optical Pumping.* Satyanarayana Anala, Galina E. Pavlovskaya, Prakash Pichumani, Todd J. Dieken, Michael D. Olsen and Thomas Meersmann,Colorado State University
11:45	**Lunch**
	New Methods, Dominique Massiot presiding
1:15	**177.** *Satellite-Transition MAS NMR of Quadrupolar Nuclei in Solids: New Techniques, Applications and Observations.* Stephen Wimperis, University of Exeter
1:45	**178.** *NMR Development of Functionalized ^{129}Xe as a Biosensor.* E. Janette Ruiz, Sandra Garcia, Tom Lowery, Seth M. Rubin, David E. Wemmer and Alexander Pines, University of California at Berkeley; Nicolas Winssinger and Peter G. Schultz, The Scripps Research Institute; Thierry Brotin and Jean-Pierre Dutasta, Stéréochimie et Interactions Moléculaires, École Normale Supérieure de Lyon
2:15	**179.** *Double-Quantum-Filtered STMAS and Magic-Angle Effect from Homonuclear Dipolar Coupling in Solid State NMR of Quadrupolar Nuclei.* HyungTae Kwak, Parthasarathy Srinivasan, John Quine and Zhehong Gan, National High Magnetic Field Laboratory
2:45	**Break** (refreshments in exhibit hall)
3:30	**180.** *High Field Solids NMR of Proteins and Nucleic Acids.* Kurt W. Zilm, Eric K. Paulson, Rachel W. Martin, John D. Gehman and Corey R. Morcombe, Yale University
4:00	**181.** *High Resolution Proton Solid-State NMR with Fast Magic-Angle Spinning: Exploring the Effects of Spin Dilution and Multiple Pulse Decoupling for Multidimensional Correlation Spectroscopy.* Chad M. Rienstra, Donghua Zhou and W. Trent Franks, University of Illinois at Urbana-Champaign
4:30	**Poster Session A**
5:00	**Conference Mixer in Exhibit Hall**

Tuesday, July 29, 2003

	Nanostructures and Confined Environments, Sarah Larsen presiding
8:00	**182.** *Real Examples of Catalysts Functionalized on the Nanometer Scale.* James F. Haw, University of Southern California
8:30	**183.** *Magnetic Resonance Studies of Hierarchically Ordered Replicas of Wood Cellular Structures Prepared by Surfactant-Mediated Mineralization.* Li-Qiong Wang, Yongsoon Shin, W.D. Samuels and Gregory J. Exarhos, Pacific Northwest National Laboratory; I.L. Moudrakovski, V.V. Terskikh and J.A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council
9:00	**184.** *2D NMR and MRI Applications in Formation Evaluation.* Boqin Sun and Keh-Jim Dunn, ChevronTexaco
9:30	**Break** (refreshments in exhibit hall)
10:15	**185.** *Xe NMR Studies in Cavities and Channels.* Cynthia J. Jameson, University of Illinois at Chicago
10:45	**186.** *Nitrogen-14 and Xenon-129 NMR Study of Trapped Gases in Microstructured Amorphous Carbohydrate Matrices.* Eric Hughes, Mike MacInnes, Gilles Vuataz, Catherine Gretsch, Johan B. Ubbink, Annemarie Schoonman, Heribert J. Watzke, Nestlé Research Centre, Vers-chez-les-Blanc, CH-1000 Lausanne 26, Switzerland
11:15	**187.** *^{129}Xe and ^{131}Xe Nuclear Magnetic Resonance Studies of Carbon Nanotubes*. Catherine F. M. Clewett, Tanja Pietraß and Kai Shen, New Mexico Tech
11:45	**Lunch**
	Dynamics, Karl Mueller presiding
1:15	**188.** *Dynamical NMR: Filling in the Blanks?* David B. Zax and Doo-Kyung Yang, Cornell University; Evangelos Manias, The Pennsylvania State University
1:45	**189.** *Probing the Structural and Dynamic Properties of the Integral Membrane Protein Phospholamban Using Solid-State NMR Spectroscopy.* Elvis K. Tiburu, Paresh C. Dave, Krishnan Damodaran and Gary A. Lorigan, Miami University
2:15	**190.** *Solid-State NMR Evidence For Entropy-Driven Miscibility in Macromolecules.* Jeffery L. White, J. E. Wolak, X. Jia, E. O. Stejskal and H. Gracz, North Carolina State University
2:45	**Break** (refreshments in exhibit hall)
3:30	**191.** *Sweeping and Burning in Fringe-field NMR Diffusometry: New Micro-slice Manipulations.* Eric E. Sigmund and William P. Halperin, Northwestern University; Philip L. Kuhns and Arneil P. Reyes, National High Magnetic Field Laboratory
4:00	**192.** *A Novel Method for Detecting Diffusion: Stimulated Echo/CPMG.* Xiaoping Tang and Warren S. Warren, Princeton University
4:30	**Poster Session B**
6:30	**Vendor Carnival**

Wednesday, July 30, 2003

	Vaughan Lecture, Terry Gullion presiding
8:00	**193.** *Zeolite Host / Guest Structure Determinations by High Resolution Solid-State NMR Spectroscopy.* Colin A. Fyfe, Darren H. Brouwer, Andrew R. Lewis, J-S. Joseph Lee, Anix C. Diaz, Yi Feng and Hiltrud Grondey, University of British Columbia
9:00	**194.** *A Concept for Structure Determination of Small Membrane Proteins by 3D Magic Angle Spinning NMR and its Application to the α-spectrin SH3 Domain.* Federica Castellani, Bart van Rossum, Anne Diehl, Kristina Rehbein, Ludwig Krabben, Jutta Pauli and Hartmut Oschkinat, Forschungsinstitut für Molekulare Pharmakologie; Chris Weise and Ferdinand Hucho, Freie Universität Berlin; Alexander Arseniev, Shemyakin & Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences; Marc Baldus, Adriaan van Gammeren, Jan Hollander and Huub de Groot, Solid State NMR Secretariat, Gorlaeus Laboratoria
9:30	**Break** (refreshments in exhibit hall)
10:15	**195.** *Local Order in Polycarbonate Glasses by REDOR.* Robert D. O'Connor, Thomas K. Weldeghiorghis, Karen L. Wooley, and Jacob Schaefer, Washington University; Barbara Poliks, Binghamton University
10:45	**196.** *Investigating Structural Changes in the Membrane Protein Bacteriorhodopsin by Solid State NMR.* James A. Mason, Miya Kamihira, Stephan L. Grage, Anthony Watts, and Suzana K. Straus, University of Oxford; Thomas Vosegaard and Niels Chr. Nielsen, University of Aarhus; Clemens Glaubitz, Centre for Biomolecular Magnetic Resonance, Institut für Biophysikalische Chemie
11:15	**197.** *Characterization and Quantification of Acid Sites in Solid Acid Catalysts.* Shang-Bin Liu, Qi Zhao, Wen-Hua Chen and Shing-Jong Huang, Academia Sinica, Institute of Atomic and Molecular Sciences
11:45	**Lunch**
	Biological Structures, Bill Power presiding
1:15	**198.** *Solid State ^{19}F-NMR of Polypeptides in Oriented Membranes.* Sergii Afonin and Parvesh Wadhwani, Forschungszentrum Karlsruhe, IFIA; Ralf Glaser and Carsten Sachse, Friedrich-Schiller-University of Jena; Ulrich Dürr, Marina Berditchevskaia and Anne S. Ulrich, University of Karlsruhe
1:45	**199.** *Solid State ^{17}O NMR of Amino Acids, High Precision Experiments and Calculation of Parameters.* Ray Dupree, Andy P. Howes, Kevin J. Pike, Mark E. Smith and Andreas Kukol, University of Warwick; Vincent Lemaitre and Tony Watts, University of Oxford; Ago Samoson, National Institute for Chemical Physics and Biophysics, Estonian Academy of Sciences; Christel Gervais, Christian Bonhomme, Francisco Mauri and Mickael Profeta, Université Pierre et Marie Curie; Chris J. Pickard and Jonathan Yates, Cavendish Laboratory
2:15	**200.** *Solid State NMR Studies of Membrane-Associated HIV-1 and Influenza Viral Fusion Peptides.* Jun Yang, Rong Yang, Paul D. Parkanzky, Christopher M. Wasniewski, Michele L. Bodner and David P. Weliky, Michigan State University
2:45	**Break**
3:30	**201.** *Structure of Silk Fibroins Studied with Solid-State NMR.* Tetsuo Asakura,Yasumoto Nakazawa and Jun Ashida,Tokyo University of Agriculture and Technology
4:00	**202.** *Cell-Wall Complexes of Vancomycins in Whole Cells of S. Aureus.* L. Cegelski, S. J. Kim, A. K. Mehta, R. D. O'Connor, D. R. Studelska, and J. Schaefer, Washington University; J. Jusuf and P. A. Axelsen, University of Pennsylvania School of Medicine
4:30	**203.** *Towards a Complete Structural Model of Alzheimer's ß-Amyloid Fibrils by Solid State NMR.* Aneta T. Petkova, Richard D. Leapman, Wai-Ming Yau, and Robert Tycko, National Institutes of Health

Thursday, July 31, 2003

	Quantum Information Processing, Joel Miller presiding
8:00	**204.** *NMR and Quantum Information Processing.* R. Laflamme, University of Waterloo and Perimeter Institute for Theoretical Physics
8:30	**205.** *NMR Quantum Information Processing with a Single-Crystal Solid.* Garett Leskowitz and Leonard J. Mueller, University of California, Riverside
9:00	**206.** *Quantum Information Processing With Solid State NMR.* Chandrasekhar Ramanathan, Massachusetts Institute of Technology
9:30	**Break**
10:15	**207.** *Spin Processor.* Anatoly Khitrin, Kent State University
10:45	**208.** *The Rational Reduction Algorithm for Off-Period Observations of Periodic Hamiltonians.* John W. Logan, Wyndham B. Blanton and Alexander Pines, Lawrence Berkeley National Laboratory and University of California, Berkeley
11:15	**209.** *SPINEVOLUTION: A Powerful Tool for the Simulation of Solid and Liquid State NMR Experiments.* Mikhail Veshtort and Robert G. Griffin, Massachusetts Institute of Technology
11:45	**Closing Remarks**

NMR Poster Sessions

4:30 – 6:00	**Monday, July 28, 2003 — Authors present for posters labeled A**
4:30 – 6:00	**Tuesday, July 29, 2003 — Authors present for posters labeled B**
A	**210.** *Solid-State ^{13}C-^{75}As TRAPDOR NMR Spectroscopy Studies of Organo-Arsenic Compounds.* Todd M. Alam, Sandia National Laboratories
B	**211.** *Vanadium-51 Solid State NMR Spectroscopy: Homonuclear Dipolar Couplings in Inorganic Solids.* Becky Gee, Long Island University
A	**212.** *Simultaneous Frequency-selective Solid-state NMR Analysis of Internuclear Distances and Through-bond Connectivities in the Presence of Quadrupolar Nuclei.* J. Trebosc, JP. Amoureux and L. Delevoye, LCPS, CNRS; J. Wiench and M. Pruski, Ames Laboratory; D. Massiot, CRMHT-CNRS
B	**213.** *^{17}O NMR of Phosphate and Borophosphate Glasses.* C. Jaeger and M. Zeyer, Friedrich Schiller University; L. Montagne, Ecole Nationale Superieure de Chimie de Lille
A	**214.** *A High-Field ^{27}Al and ^{29}Si MAS NMR Investigation of Portland Cement Hydration in the Presence of Sodium Aluminate.* Morten Daugaard Andersen, Hans J. Jakobsen, and Jørgen Skibsted, University of Aarhus
B	**215.** *NMR Structural and Ion Binding Studies of the Domain V from Group II Self-splicing Intron RNA.* Hua Li, Case Western Reserve University and Lerner Research Institute, Cleveland Clinic Foundation; Richard A. Padgett and Kwaku T. Dayie, Lerner Research Institute, Cleveland Clinic Foundation
A	**216.** *1D and 2D ^{13}C CPMAS NMR Study of PMAA/PVAc Miscible Blends.* A. Asano, M. Shimizu and T. Kurotsu, National Defense Academy, Department of Applied Chemistry
B	**217.** *Domain Selective Solid-State Flourine NMR Spectroscopy of Fluoropolymers — The Direct DIVAM Experiment.* Paul Hazendonk, Nicole Andres and Guangxin Lin, The University of Lethbridge
A	**218.** *Natural Abundance ^{17}O NMR.* S. E. Ashbrook and I. Farnan, University of Cambridge
B	**219.** *The Effects of Cholesterol on Acyl Chain Dynamics of Magnetically Aligned Phospholipid Bilayers.* Junxia Lu, Marc A. Caporini and Gary A. Lorigan, Miami University
A	**220.** *Using ^{129}Xe NMR to Probe the Void Structure of a Series of Periodic Mesoporous Organosilicas.* A. J. Baer, K. Landskron, H. Grondey and G. A. Ozin, University of Toronto
B	**221.** *Quadrupolar Coupling Constants and Chemical Shifts in Zeolites A Investigated by ^{27}Al MQMAS and ^{29}Si MAS-NMR.* W. Masierak and A. Gutsze, Medical Academy of Bydgoszcz; T. Emmler and G. Buntkowsky, Freie Universität Berlin

A	**222.** *Simple Signal Enhancement Schemes for ½-Integer Quadrupolar Nuclei.* Larry W. Beck, Kathryn J. Hughes and Mark V. Wilson, University of Michigan
B	**223.** *Through-Bond and Through Space characterisation of AP_2O_7 Phosphates.* F. Fayon and D. Massiot, CRMHT-CNRS;I. King and R.K. Harris, University of Durham
A	**224.** *Investigation of Cinnamic Acid as a Powder and Single-Crystal: ^{1}H and ^{13}C Spectra and Simulations.* Marko Bertmer, Ryan C. Nieuwendaal, Alexander B. Barnes and Sophia E. Hayes, Washington University
B	**225.** *Solid-state NMR Characterization of Oxygen Sites in Organically Modified Aluminosilicate Xerogels.* Dominique Massiot and Franck Fayon, CRMHT-CNRS; Aurélie Lafuma and Clément Sanchez, LCMC, Univ. Paris VI
A	**226.** *Temperature Dependence, Structural Plasticity, and Resonance Assignment of Selectively and Uniformly Labeled HIV-1 Fusion Peptides Associated with Membranes.* Michele L. Bodner, Charles M. Gabrys, Paul D. Parkanzky, Jun Yang, Craig A. Duskin and David P. Weliky, Michigan State University
B	**227.** *Structural Study of Yttrium Silicate Compounds by ^{89}Y and ^{29}Si MAS-NMR Spectroscopy.* M.D. Alba, A.I. Becerro, A. Escudero and J.M. Trillo, Universidad de Sevilla-CSIC; P. Florian and D. Massiot, CRMHT-CNRS
A	**228.** *Quantitative GIAO Prediction of Nuclear Shielding Anisotropies and Tensor Components via Extrapolation to the Complete Basis-Set Limit.* Teobald Kupka, Branko Ruscic and Robert E. Botto, Argonne National Laboratory
B	**229.** *Circularly Polarized NQR With a Surface Coil Array.* J. B. Miller and A. N. Garroway, Naval Research Laboratory
A	**230.** *Fate of Nerve Agent Simulants on Concrete Substrates.* C. A. S. Brevett and J. L. Edwards, GEO-CENTERS, Inc.; G. W. Wagner, U. S. Army Edgewood Research, Development and Engineering Center (ERDEC)
B	**231.** *Applications of Solid NMR Techniques for Liquid Samples.* Motohiro Mizuno and Warren S. Warren, Princeton University
A	**232.** *40 Tesla ^{27}Al MAS NMR and ^{1}H and ^{17}O NMR of Methylaluminoxane (MAO).* Jan L. Eilertsen, Petia Bobadova-Parvanova, Lacramioara Negureanu, Randall W. Hall and Leslie G. Butler, Department of Chemistry, Louisiana State University; Larry S. Simeral, Albemarle Corporation; Zhehong Gan, National High Magnetic Field Laboratory
B	**233.** *^{1}H-^{15}N Correlation Spectroscopy of Nanocrystalline Protein.* Corey R. Morcombe, Eric K. Paulson and Kurt W. Zilm, Yale University; Vadim Gaponenko, Barbara Dancheck and R. Andrew Byrd, Structural Biophysics Laboratory, National Cancer Institute
A	**234.** *Material Characterization with High Speed Solid-State ^{1}H MAS and Double Quantum NMR.* Brian R. Cherry, Todd M. Alam, Cy H. Fujimoto and Christopher J. Cornelius, Sandia National Laboratories
B	**235.** *Environmental Weathering of Aluminosilicate Clay Minerals: Solid-State NMR Studies of Transformations Leading to Radionuclide Sequestration.* Garry S. Crosson and Karl T. Mueller, The Pennsylvania State University; Sunkyung Choi, Mary K. Amistadi and Jon Chorover, University of Arizona
A	**236.** *Quantification of Difficult Pharmaceutical Ingredients by NMR Spectroscopy.* George Crull, Robert Francis, Leticia Quiones, John Grosso and Stephen Gozo, Bristol-Myers Squibb
B	**237.** *Uniform-sign Cross-peak Double-Quantum-Filtered Correlation Spectroscopy in Solids.* Leonard J. Mueller and Douglas W. Elliott, University of California, Riverside; Jochem Struppe, Bruker BioSpin Corporation
A	**238.** *^{31}P and ^{2}H Solid-State NMR Spectroscopic Studies of the Transmembrane Domain of the Membrane-Bound Protein Phospholamban.* Paresh C. Dave, Elvis K. Tiburu, Krishnan Damodaran and Gary A. Lorigan, Miami University
B	**239.** *A ^{13}C CP/MAS and ^{31}P NMR Study of the Interactions of Dipalmitoylphosphatidylcholine with Respirable Silica and Kaolin.* David K. Murray, Yau-Hsin Wang, Joel C. Harrison and William E. Wallace, National Institute for Occupational Safety and Health
A	**240.** *Solid-State NMR of Membrane Proteins in Phospholipid Bicelles.* A. A. De Angelis, A. A. Nevzorov , S. H. Park and S. J. Opella, University of California, San Diego
B	**241.** *^{1}H Detected ^{1}H-^{15}N Correlation Spectroscopy in Deuterated Nanocrystalline Ubiquitin.* Eric K. Paulson, Corey R. Morcombe and Kurt W. Zilm, Yale University; Vadim Gaponenko, Barbara Dancheck and R. Andrew Byrd, Structural Biophysics Laboratory, National Cancer Institute

A	**242.** *Carbon-Protonation of 2,4,6-Triaminopyrimidines: NMR and Quantum Chemical Study.* Ádám Demeter, and Csaba Wéber, Gedeon Richter Ltd.; Tamás Veszprémi and Németh Balázs, Technical University of Budapest
B	**243.** *Colors in Silver Exchanged Zeolites: ^{109}Ag Solid State NMR Study.* Galina E Pavlovskaya, Charlene F. Horton and Thomas Meersmann, Colorado State University; Cecil Dybowski, University of Delaware; David R. Corbin, DuPont Company
A	**244.** *Fitting of Wide-line Deuterium Spectra Using Simulated Annealing and Spectral Libraries.* M. A. Eastman, Oklahoma State University
B	**245.** *Improvement of 3QMAS Using Shaped Pulses For I=5/2 Nuclei.* Jun Gu and William P. Power, University of Waterloo
A	**246.** *Fast ^{1}H-MAS NMR studies of Water on coated Silica-Nanoparticles.* Thomas Emmler, Guanytao Li, Sheshanath Bhosale, Jürgen Fuhrhop and Gerd Buntkowsky, Freie Universität Berlin
B	**247.** *Detection of the Degradation of Perfluoropolyethers Adsorbed on Solid Surfaces.* Kerri A. Pratt, Ruth A. Rivers, A. Daniel Jones and Karl T. Mueller, The Pennsylvania State University
A	**248.** *A Structural Study of the V_2O_5-WO_3 System by MAS and Static Vanadium-51 NMR.* Becky Gee, Long Island University
B	**249.** *Influence of Hydration the Slow and Fast Dynamics of Collagen: A Solid-state NMR Study.* D. Reichert, University of Halle; Tito J. Bonagamba, Universidade São Paulo; D. Huster, University of Leipzig
A	**250.** *A Ferroelectric Resonator Insert Used for Increasing the Sensitivity of NMR Method.* I.N.Geifman, EMS Inc.; I.S.Golovina, Institute of Semiconductor Physics of National Academy of Sciences of Ukraine
B	**251.** *Phase Separation and Hydrogen Bonding in Polymer Blends and Complexes.* Toshikazu Miyoshi, National Institute of Advanced Industrial Science and Technology; Ulrich Scheler, Institute for Polymer Research Dresden
A	**252.** *NMR Studies of Confined Molecules in Porous Al_2O_3 Films.* R.E. Gerald II, D.N. Sears, K.J. Ruscic, R.J. Klingler and J.W. Rathke, Argonne National Laboratory
B	**253.** *DANTE-based, Frequency-Selective REDOR: Methodology and Applications.* Oshrat Cabri, Osnat S. Lipson, Lilia Kaustov and Asher Schmidt, Technion 32000
A	**254.** *Measuring Distance, Angle Distributions and Correlations in Oxide Glasses with RAPT-Enhanced O-17 DAS.* Philip J. Grandinetti and Ted M. Clark, Ohio State University; Pierre A. Florian, CNRS; Jonathan F. Stebbins, Stanford University; Jeffrey L. Yarger, University of Wyoming
B	**255.** *Structure and Dynamics of Peptides Controlling Cell Signaling Using Solid State NMR.* Wendy J. Shaw and Allison A. Campbell, Battelle; Michele Gilbert, University of California Berkeley; Allison Golden and Pat S. Stayton, University of Washington
A	**256.** *Resource for Solid-state NMR of Proteins.* Christopher. V. Grant, Chin. H. Wu and Stanley. J. Opella, University of California, San Diego
B	**257.** *A Metabonomic Study of Interspecies Variation Following Acute Exposure to Mercury.* Jasmin Sidhu and Jeremy Nicholson, Imperial College London; Julian Griffin, University of Cambridge; Richard Shore and Lee Walker, Centre for Ecology and Hydrology, Monks Wood
A	**258.** *^{13}C-^{2}H REDOR: A Universal Dipolar Dephasing Curve and Applications.* Terry Gullion, West Virginia University
B	**259.** *Application of Carr-Purcell-Meiboom-Gill (CPMG) Experiments to Characterize NMR Powder Patterns in Solids.* Renée Siegel, Roderick E. Wasylishen and Thomas T. Nakashima, University of Alberta
A	**260.** *Structures of Vanadium Ions in Monolithic Vanadia-Silica Composite Gels.* Oc Hee Han, Sunha Kim and Sang Guel Lee, Korea Basic Science Institute; Young-Uk Kwon, Sungkyunkwan University
B	**261.** *Effects of T_2-Relaxation in MAS NMR Spectra of the Satellite Transitions for Quadrupolar Nuclei: A ^{27}Al MAS NMR Study of $KAl(SO_4)_2{\cdot}12H_2O$ (Alum).* Morten Daugaard Andersen, Hans J. Jakobsen, and Jørgen Skibsted, University of Aarhus
A	**262.** *WISE NMR Characterization of Nanoscale Heterogeneity and Mobility in Supercontracted Nephila Clavipes Spider Dragline Silk.* Gregory P. Holland, Randolph V. Lewis and Jeff L. Yarger, University of Wyoming
B	**263.** *Measurement of Diffusion Coefficients by ^{1}H NMR Spectroscopy for the Investigation of Protein-ligand Binding.* Eleni Skordi, John C. Lindon and Jeremy K. Nicholson, Imperial College London

A	**264.** *Restricted Water Diffusion Through Silica Sol-Gel Made Particles Measured by Pulsed-Field Gradient NMR.* Susanne Veith, Sotiris E. Pratsinis, Particle Technology Laboratory; Eric Hughes and Gilles Vuataz, Nestlé Research Centre; Matthias Perren, Nestlé Product Technology Centre
B	**265.** *Probing the Dynamics and Side Chain Motion of Leucine Residues in Phospholamban Using ^{2}H Solid-State NMR Spectroscopic Techniques.* Elvis K. Tiburu, Paresh C. Dave, Krishnan Damodaran and Gary A. Lorigan, Miami University
A	**266.** *Quantitative Measurements of Quadrupolar Nuclei.* Kathryn J. Hughes and Larry W. Beck, The University of Michigan
B	**267.** *Solid and Solution-State Investigation of The Dynamics and Structure of Aluminum Tris (Quinoline-8-olate).* Marcel Utz, Changqing Chen, Martha Morton, Magesh Nandagopal, Mathew Mathai and Fotios Papdimitrakopoulos, University of Connecticut
A	**268.** *Complete Ring Assignment of the ^{13}C Signals of Bacterial Cellulose.* C. Jaeger and J. Pauli, Federal Institute for Material Research and Testing; H.-P.Schmauder, Research Center of Medical Technology and Biotechnology
B	**269.** *Universal Curves for Internuclear-distance Determination from REAPDOR Dephasing Curves for Quadrupolar Nuclei With Spin 1, 3/2, or 5/2.* Amir Goldbourt and Shimon Vega, Weizmann Institute of Science; Eric Hughes and Terry Gullion, West Virginia University; Alexander J. Vega, DuPont Central Research and Development
A	**270.** *Solid State NMR Studies of Zeolite Catalysts.* Conrad Jones, Donald Stec and Sarah Larsen, University of Iowa
B	**271.** *$^{47,49}Ti$ Wideline and ^{31}P and ^{13}C MAS NMR Study of GD Reactions With TiO_2 and Titanium.* G. W. Wagner, L. R. Procell, U.S. Army Edgewood Chemical Biological Center; S. Munavalli, Geo-Centers, Inc.
A	**272.** *^{17}O MQMAS and CP/MAS Studies on Non-Crystalline Aluminophosphate and Calcium Aluminosilicate Glass.* K. Kanehashi and K. Saito, Nippon Steel Corporation
B	**273.** *High Temperature and Ambient Temperature NMR Investigation of Metal Selenophosphate Syntheses.* Christian G. Canlas, Mercouri G. Kanatzidis and David P. Weliky, Michigan State University
A	**274.** *Caesium Motion in Potential Ceramic Radioactive Waste Host Phases From ^{133}Cs NMR Experiments at High Temperature.* L. Le Pollès, K. R. Whittle and I. Farnan, University of Cambridge
B	**275.** *Obtaining Structural Clues in Non-Ideal Solids via Dipolar Coupling NMR Spectroscopy.* Erin Wilson and Larry W. Beck, University of Michigan
A	**276.** *Multi-scale NMR Characterization of Mesostructured Materials Using ^{1}H-^{13}C Through Bond Polarisation Transfer, Fast MAS, and 1H Spin Diffusion.* B.Alonso and D. Massiot, CRMHT - CNRS
B	**277.** *Simple Central Transition Enhancement and Quadrupolar Coupling Constant Estimation of Spin — 3/2 and 5/2 Quadrupolar Nuclei via MAS NMR.* Mark V. Wilson and Larry W. Beck, University of Michigan
A	**278.** *Heteronuclear Correlations Involving Quadrupolar Nuclei, a Through Bond Approach Using J-couplings.* D. Massiot, F.Fayon and B.Alonso, CRMHT - CNRS; V.Montouillout and C.Fernandez, ISMRA; C.Morais and J.Rocha, University de Aveiro
B	**279.** *NMR Detection of Dynamics in Metallic Supercooled Liquids and Glasses.* Lilong Li and Yue Wu, University of North Carolina
A	**280.** *Characterization of Guest-Ions in Cement Minerals and in the Calcium-Silicate-Hydrate Phase by High-Field Solid-State NMR Spectroscopy.* Jørgen Skibsted, Morten Daugaard Andersen, Michael Ryan Hansen and Hans J. Jakobsen, University of Aarhus
B	**281.** *Insight into Structure and Function of Proteins and Protein-ligand Complexes from Solid-State-NMR Spectroscopy.* Stephan G. Zech and Ann E. McDermott, Columbia University

Pharmaceutical Analysis

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Tuesday, July 29, 2003

	Opening Remarks
8:45	**158.** *HPLC/MS/MS Quantitative Bioanalysis of Drugs Used to Protect Against Chemical Warfare Agents.* Shane Needham and Binying Ye, Alturas Analytics, Inc.; J. Richard Smith and Benedict R. Capacio, US Army Medical Research Institute of Chemical Defense
9:15	**159.** *Fourier Transform-Infrared Imaging of Aortic Tissue: A Novel Approach for the Study of Atherosclerosis.* Manoj Mehta, Elaine Holmes and George E. Tranter, Imperial College London; Elaine McKilligin, GlaxoSmithKline
10:00	**Break** (refreshments in exhibit hall)
10:30	**160.** *Accurate Mass Measurement in Drug Stability Studies on an Enhanced Mass Resolution Triple Quadrupole Mass Spectrometer.* Gary Paul, Thermo Electron Corporation
11:30	**Lunch**
1:30	**161.** *Composition of Pharmaceutical Production Equipment Materials.* Don H. Miller, Ph.D.
2:30	**Break** (refreshments in exhibit hall)
3:00	**162.** *Structural Characterization of Organometallic Macrocomplexes Utilizing Electrospray Mass Spectrometry and Matrix-Assisted Laser Desorption Ionization Mass Spectrometry.* Christina Sorensen and B.P.Sullivan, University of Wyoming
3:20	**163.** *Fatty Acid Ethyl Ester Quantitation with a Novel Gas Chromatography Column and Automatic Injection System, and Correlation with Blood Ethanol Levels.* Clark C. Kulig, Thomas P. Beresford and Gregory T. Everson, University of Colorado Health Sciences Center
3:40	**163b.** *The Role of the AccuTOF Mass Spectrometer in Biochemical Analyisis.* Adrian W. Pike, Zhanpin Wu and Chip Cody, JEOL USA Inc.
	Closing Remarks

Advances in Separations Science • Tuesday Oral Sessions

1. *Mechanism and Use of High Efficiency Microbial Separations.*
Daniel W. Armstrong, Iowa State University

It has been recognized for decades that charged colloids and particulate matter will transport in direct current electric fields. However, routine, high efficiency separation and analysis of colloidal or larger particles by electrophoresis has not been as successful as it has for small molecules and macromolecules. Selective, high efficiency separations of intact microbes (e.g., bacteria, viruses, etc.) may, in some cases, allow them to be identified and quantified in much the same way that molecules are done today. Two different capillary electrokinetic approaches can be utilized. The first approach used a dissolved polymer based CE separation that may be affected by the size and shape considerations. Another approach uses capillary isoelectric focusing (CIEF). Remarkably high peak efficiencies (10^6 - 10^9 theoretical plates per meter) in capillary electrophoresis (CE) can be achieved in the separation of microorganisms. No deliberate stacking is used in these applications. Seemingly, the investigated living organisms behave differently than molecules under an applied electric field. For molecules, these extremely high efficiencies are very unusual, and have not been reported thus far. Using a 488nm argon-ion laser coupled to a charge-coupled device camera (CCD), it was possible to monitor the migration behavior of stained microorganisms of a length of a 10cm capillary. In some cases, 60 - 70% of the monitored detection window could be filled with analyte without significant loss in peak efficiency. The effect of pH, polymer concentration, buffer concentration, etc. on the ultra-high efficiency and reproducibility of the separation was investigated.

Advances in Separation Science Oral Session
Daniel W. Armstrong, Iowa State University, Chemistry Department, Gilman Hall, Ames, Iowa 50011-3111
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2. *Design and Evaluation of an Autonomous Micro GC for Environmental Applications.*
Richard D.Sacks, University of Michigan

A completely autonomous micro gas chromatograph (μGC) is under development at the University of Michigan. This large collaborative effort, which involves scientists and engineers from several departments and from several Michigan universities, is part of an Engineering Research Center for the development of wireless integrated micro-system. The instrument will occupy a volume of a few cubic centimeters and will require less than 10 mW average power. Completely autonomous operation is achieved by the use of two-way wireless communication for instrument control and data transmission, vacuum-outlet GC with ambient air as carrier gas and remote (radio frequency transmission) battery charging. The goal of the μGC project is the development of a generic vapor analysis instrument with high selectivity and sub-ppb detection limits. The instrument will target 30-50 volatile organic compounds in air samples. A micro-fabricated vacuum pump, consisting of an array of valves and actuators, will be used to pull ambient air and injected samples through a series-coupled ensemble of two micro-fabricated columns and an array of micro-fabricated chemiresistor sensors. Preconcentration of organic compounds from large-volume air samples is accomplished with a multi-bed carbon-based sorption trap. Thermal desorption is used to inject the preconcentrated samples into the carrier gas (ambient air) stream. The burden of selectivity is shared between a series-coupled dual-column ensemble with programmable selectivity and the sensor array. Programmable selectivity is achieved by pulsed carrier-gas flow modulation at the junction point between the columns. The column ensemble uses a non-polar dimethyl polysiloxane coated channel dry etched in silicon and a similar channel coated with trifluoropropylmethyl polysiloxane. Basic design features of the instrument will be discussed. Preliminary characterization of micro-fabricated components including the preconcentrator, the three-meter-long etched columns and the four-sensor array will be presented.

Advances in Separation Science Oral Session
Richard D.Sacks, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, rdsacks@umich.edu

3. *Flow Field-Flow Fractionation for Particle Size Analysis of Emulsions.*
M. Cecilia Lazo, Mohammed K. Khalid and S. Kim R. Williams, Colorado School of Mines

Octenyl succinylated starch is a modified starch used as a stabilizer, thickener, binder, and emulsifier in the food industry [1]. Its effectiveness is dependent on physico-chemical characteristics such as size and size distribution. Flow field-flow fractionation (FFF) is a separation technique capable of characterizing particles with diameters ranging from 0.01 μm to ~50 μm. The separations are achieved on the basis of differences in diffusion coefficients and hence, the size information yielded by flow FFF corresponds to hydrodynamic diameters. The octenyl succinylated starch in oil (50% medium chain triglyceride and 50% abietic acid) emulsions studied in this work were determined to have size distributions of ~0.2 to ~0.8 μm with mean diameters of ~0.4 μm.

Various particle sizing techniques are based on different principles and can yield different types of diameters, e.g., number-average, volume average, etc. Comparison of results obtained using different techniques may yield additional information about shape and structure. Flow FFF diameters have been compared to those obtained by Low Angle Laser Light Scattering. The good agreement between the two sets of results are reflective of the shell structure of these emulsions.

In this presentation, we report and discuss the potential for separation and particle sizing using flow FFF. Possibilities of coupling FFF with other techniques to yield additional information will also be discussed.

[1] Class Names and the International Numbering System for Food Additives, 18th session of the Codex Alimentarius Commision, July 1989.

Advances in Separation Science Oral Session

Mohammed K. Khalid, Department of Chemistry & Geochemistry, Colorado School of Mines, Golden CO 80401

4. *Studying Sample-Membrane Interactions Using Flow Field-Flow Fractionation.*

M. Cecilia Lazo, R. L. Hartmann and S. K. R. Williams, Colorado School of Mines

Field-flow fractionation (FFF) is traditionally known as a family of techniques for separating and characterizing macromolecules, colloids, and particles. In this work, we are presenting flow FFF as a novel method to rapidly quantify initial fouling and to assess the performance of filtration membranes.

Flow FFF is ideally suited for studying sample-membrane interactions because the separation process occurs in the proximity of the membrane surface. Undesirable interactions between the sample and the membrane will cause a shift in the measured retention times, peak shape, or peak area. By monitoring these parameters, we are able to obtain information about sample recovery and operating conditions that enhance or minimize membrane fouling.

The specific systems that have been investigated are polyamide nanofiltration and reverse osmosis membranes used in water treatment processes. The sample is humic substances (a large group of organic compounds that are the natural decomposition products of plant and animal debris). As a result of being present in aquatic and terrestrial systems, humic materials pose a wide variety of problems, especially for municipal and commercial water treatment plants and systems. Substantial membrane fouling occurs due to the wide molecular weight distribution and high surface activity of humic substances.

Results will be presented to demonstrate the use of flow FFF to quantitate fouling, to determine that fouling by humic substances is mainly due to irreversible adsorption, and to investigate the effects of flowrate and solution composition effects. Flow FFF has also been coupled to a multi-angle laser light scattering detector to assess whether certain molecular weight and size fractions of humics are primarily responsible for membrane fouling.

Advances in Separation Science Oral Session

M. Cecilia Lazo, Colorado School of Mines, Department of Chemistry and Geochemistry, Golden, CO 80401

5. *Applications of Room-temperature Ionic Liquids in Analytical Chemistry. Formation of Micelles in Ionic Liquids.*

Veronica Pino, Jared Anderson and Daniel W. Armstrong, Iowa State University

Room-temperature ionic liquids (RTILs) are a new class of "green" solvents commonly used in organic chemistry. They have the ability to dissolve an enormous range of inorganic and organic substances at very high concentrations. Their properties include good thermal stability (over 300 ºC) and negligible vapor pressure. These properties allow them to be quite useful in analytical chemistry, especially in liquid-liquid extraction[1], as MALDI matrixes[2] and in gas-liquid chromatography (GLC)[3]. In addition, we have recently demonstrated the formation of micelles in RTILs. These micelles have been studied using small-angle neutron scattering (SANS) and light scattering. Moreover, micelle/RTIL solutions have also been coated as GLC stationary phases and unique selectivity observed. These stationary phases can easily be characterized by a linear free energy approach to deconvolute which interactions originate from the surfactant/micelle present in the RTIL stationary phase.

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Advances in Separation Science Oral Session

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6. *The Enantioseparation of Substituted Furocoumarins, Substituted Furoflavones, and Other Biologically Important Molecules by High Performance Liquid Chromatography.*

Douglas D. Schumacher, Clifford R. Mitchell and Daniel W. Armstrong, Iowa State University

The enantioselectivity of native and derivatized cyclodextrin stationary phases for substituted chiral furocoumarins and substituted chiral furoflavones were evaluated using high performance liquid chromatography (HPLC). Many enantiomers could be baseline resolved using derivatized cyclodextrin stationary phases in the reverse phase mode. The most important factor influencing enantioselectivity is steric effects, and the ability of the solvent to hydrogen bond. The dimethyl-β-cyclodextrin exhibited the broadest enantioselectivity for the substituted furoflavones while the hydroxypropyl-β-cyclodextrin exhibits the broadest enantioselectivity for the substituted furocoumarins. Native cyclodextrins were unsuccessful in separating these classes of compounds.

Advances in Separation Science Oral Session

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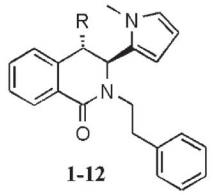
7. *Selection of Mobile Phases for Normal-Phase Chromatography on Silica of Substituted Tetrahydroisoquonolinones with Complex Structure Using the LSChrom Software.*

Christo E. Palamarev, University of Sofia, Department of Chemistry, 1 James Bouchier Avenue, Sofia 1164, Bulgaria; Malinka P. Stoyanova, University of Sofia, Department of Chemistry, 1 James Bouchier Avenue, Sofia 1164, Bulgaria; Mariana D. Palamareva, University of Sofia, Department of Chemistry, 1 James Bouchier Avenue, Sofia 1164, Bulgaria

Based on the Snyder theory (Snyder, L.R.; Glajch, J.L.; Kirkland, J.J., Practical HPLC Method Development, John Wiley, New York, 1988), the LSChrom software (Palamarev, Ch.E., Meyer, V.R., Palamareva, M.D., J. Chromatogr. A, 1999, 848, 1; Palamarev, Ch.E., Palamareva, M.D. LSChrom, Ver. 2.1, http://www.members.tripod.com/LSChrom) calculates energy of adsorption of mobile phases and organic compounds and predicts their retention. The latest version of the software allows the user to select mobile phases for normal-phase chromatography with an appropriate strength ε and different solvent composition. A recent application (Palamareva, M.D., Stoyanova, M.P. Kozekov, I.D., J. Liq. Chrom. & Rel. Technol., 2003, 26, 1249, and the references cited therein.) of the software permitted an automatic selection of mobile phases for thin-layer chromatography on silica of trans-2-phenethyl-3-(1-methyl-1H-pyrrol-2-yl)-4-substituted-1,2,3,4-tetrahydroisoquinolin-1-ones (see the picture below). The selection of the mobile phases is based on literature data for the adsorption properties of the solvents and the composing structural elements of the compounds in the study.



1-12

R = CO_2CH_3, CH_2OH or heterocyclic group

Advances in Separation Science Oral Session

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8. *Improved Analysis of Sulfur Compounds by Sulfur Chemiluminescence Detection and Gas Chromatography.*

R. L. Shearer, Ionics Instruments

Gas chromatography (GC) with sulfur chemiluminescence detection (SCD) possesses a number of advantages over other technologies for volatile sulfur speciation. These advantages include the realization of a selective, linear, stable and equimolar response to sulfur. The accurate analysis of trace sulfur compounds in hydrocarbons is crucial in the petrochemical industry and is becoming even more so, as environmental regulations require lower sulfur levels in fuels while sulfur levels in feed-stocks are generally rising. With these facts in mind, improvements have been made in GC/SCD sulfur measurement techniques to deliver better selectivity, sensitivity and method robustness. This technique is based on a new burner for the sulfur chemiluminescence detector using dual plasma combustion. In comparison to a currently practiced technique, the new analytical approach is approximately 4 times more sensitive and 10 times more selective. This approach, application examples and performance will be described.

Advances in Separation Science Oral Session

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9. *The Identification of Nitropolycyclic Aromatic Hydrocarbons in Mainstream Tobacco Smoke Using Electron Monochromator Mass Spectrometry.*
A. John Dane, Crystal D. Havey and Kent J. Voorhees, Colorado School of Mines; Robert B. Cody, JEOL USA

Numerous studies on tobacco smoke are being conducted in order to identify potentially toxic compounds contained within the smoke. One particularly important class of compounds that are formed as products of combustion processes are nitro polycyclic aromatic hydrocarbons (NPAHs). These compounds are known to be potent mutagens and carcinogens that have been shown to cause lung cancer and remote metastases in laboratory animals. Previous research has shown the presence of nitro aromatic hydrocarbons in tobacco smoke[1]. However, the identification of these compounds required the sampling of a large number of cigarettes as well as significant clean up of the combustion particulate matter. The goal of this research is to show the presence of NPAHs using solid phase extraction in conjunction with the new, highly specific and sensitive technique of GC electron monochromator mass spectrometry (GC/EM-MS). The EM, which has the capability to select an ionization energy between 0-25eV with a resolution of +/-0.3eV, utilizes electron capture resonances to control the fragmentation of the NPAH molecules. All of the NPAH compounds studied produce a peak at m/z 46 (NO_2^-) using an electron capture resonance in the 3-4eV range.[2] This m/z 46 fragment was then used to distinguish the NPAHs from interferences. Additionally, these compounds produce molecular radical anions at near zero eV electron energies. The correspondence between the m/z 46 anion peaks at electron energies between 3-4eV and the molecular anion peaks at near zero eV provided resolved peaks that were used to identify the NPAHs found within the mainstream tobacco smoke samples. Using this technique, a number of NPAHs have been isolated from the background with selective ion monitoring of the m/z 46 anion.

[1] Hoffmann and Rathkamp, Analytical Chemistry, 1970, 42, 1643.

[2] Voorhees et al., Proceedings from 49th ASMS Conference, 2001.

Advances in Separation Science Oral Session
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10. *The Polycyclic Aromatic Hydrocarbon Content of Combustion Soots by SFE Extraction and GC/MS Analysis.*
Cullen C. Jones, Abdul R. Chughtai, Balasingam Murugaverl and Dwight M. Smith, University of Denver

We have examined patterns of polycyclic aromatic hydrocarbon (PAH) content in the extracts of combustion soots, generated at various air/fuel combustion ratios (A/F) from diesel and JP8 aircraft fuels as well as from the reference hydrocarbon n-hexane. The analysis demonstrates that, with increasing A/F, there is a significant loss of higher molecular weight PAHs and an increasing abundance of oxidized lower molecular weight compounds. An increase in the PAH mass distribution with hydrocarbon molecular weight also is observed. A comparison of soxhlet with supercritical fluid extraction (SFE) is reported, with SFE extraction demonstrated as more effective and reproducible than the traditional soxhlet method. EPR evidence of extraction of moieties containing unpaired electrons is presented. The trends observed in the PAH content of these hydrocarbon combustion soots are related to the effects of A/F on such particle properties as surface oxidation, unpaired electron spin density, surface area, hydration, and ozone oxidation, studied earlier in these laboratories *(J. Atmos. Chem. 43: 21-43, 2002)*.

Advances in Separation Science Oral Session
Cullen C. Jones, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208

Analytical Methods Applied to Homeland Security • Monday Oral Sessions

11. *Edgewood Chemical Biological Center: Equipment Evaluation for Chemical and Biological Applications in Homeland Defense.*
Emory W. Sarver, Edgewood Chemical Biological Center

The Edgewood Chemical Biological Center (ECBC) has a long history of evaluating detection and personal protective equipment against chemical and biological warfare agents. Equipment testing began as a military program. At that time, the focus was to find or develop suitable equipment for battlefield conditions and to adequately protect the soldier. In 1996, Congress passed Public Law 104-201 (Defense Against Weapons of Mass Destruction Act of 1996), directing the Department of Defense (DoD) to assist other federal, state, and local agencies in enhancing preparedness for terrorist attacks using weapons of mass destruction. The DoD responded by forming the Domestic Preparedness Program that same year. One of the objectives of the Domestic Preparedness Program is to enhance federal, state and local emergency and hazardous material (HAZMAT) response to nuclear, biological and chemical (NBC) terrorism incidents. The Domestic Preparedness (DP) Program expanded ECBC's testing and evaluation mission to include commercially available products. As a result, ECBC initiated an impartial testing project. During this time, ECBC bought off-the-shelf equipment, tested them, and provided an objective analysis of each item tested. These evaluation reports can be found on ECBC's Homeland Defense website, http://hld.sbccom.army.mil. This was provided as a public service to the first responder community so they would have unbiased data upon which to base their decisions to purchase equipment. As the DoD phases out the DP testing program, ECBC maintains the capability to provide testing of commercial equipment with both live and simulated chemical and biological warfare agents. The chemical and biological threat, the current capabilities at ECBC, and the testing methodologies and protocols are discussed.

Homeland Security Oral Session

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12. *Technologies in Biological Detection.*

Patrick L. Berry and Kate K. Ong, Biological Detection Systems

The need for biological detection and identification capability has grown exponentially. In the early 1990s, commercially available biological instruments were integrated onto platforms and introduced to the warfighters to satisfy urgent requirements. A system architecture was established and an evolutionary acquisition strategy was implemented. As new technologies arose, they were evaluated and inserted as appropriate. The overall focus was on the development of faster, lighter, more automated systems that would meet more of the user's needs. This paper will provide a brief overview of how biological detection and identification have evolved from Operation Desert Storm to Operation Iraqi Freedom.

Homeland Security Oral Session

Kate K. Ong, Biological Detection Systems, 5183 Blackhawk Road, Aberdeen Proving Ground, Maryland 21010.

13. *Real World Uses of Portable GC/MS.*

Stephan DeLuca, Charles Sadowski and Robert Miller, INFICON, Inc.

A recent article in the analytical industry press discussed the "future" of bringing analytical techniques such as GC and GC/MS out of the laboratory and into the field. In fact, commercially available portable GC/MS products that give definitive quantitative results in the field have been available for years. The technology of portable GC/MS is not the limiting factor of doing analysis on site, rather it is the extensive laboratory infrastructure that inhibits growth of field analysis. Results from several on-site studies are presented, showing the success of portable GC/MS in obtaining "laboratory quality" results.

Heightened concern over responding to potential chemical exposures due to accident or terrorist acts has driven the demand for portable analytical devices into emergency response applications. Several evaluation and real world case studies are presented showing the capability of portable GC/MS to detect TICs and CWAs in the field and how information provided by portable GC/MS guided responders in handling potential chemical exposure incidents.

Homeland Security Oral Session

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14. *A Mobile Mass Spectrometer-Based System for Chemical and Biological Agent Detection — The Block III CBMS.*

Jochen Franzen, Roland Schnurpfeil, Joachim Stach, John Wronka and Frank Thibodeau, Bruker Daltonics Inc.

Rapid detection and identification of chemical and biological agents remains an important and challenging area as there continues to be both a domestic and international threat of the use of these agents by terrorist organizations and selected nations. The Block III Chemical and Biological Mass Spectrometer (CBMS) is an integrated detector for the battlefield near-real time detection and identification of both chemical (CW) and biological (BW) warfare agents. It was designed to be a rugged, fieldable tandem mass spectrometer capable of operation at a fixed position (point detection) as well as while on the move in rough terrain, but with improved interference rejection over field mobile GC/MS systems. Design goals include operation in a wide range of environmental, radiation and vibration/shock conditions with minimal operator intervention. As such, the Block III CBMS has features important to emergency response and anti-terrorism missions.

The Bock III CBMS is an ion trap mass spectrometer electron impact (EI) mode based on adding a multi-port sample transport valve to rapidly switch sampling between a combination BW-air/CW-air interface and a CW-ground interface to the Block I CBMS. Bio-detection for bacterial, viral and toxin targets is accomplished by concentrating particles in the 2-10 micron range from air into a quartz pyrolysis tube where the sample is pyrolyzed and the liberated chemical biomarkers are mass analyzed during a 3 minute detection cycle. CWA detection is either performed concurrently through the air intake path of the pyrolysis tube or from the CWA ground sampling probe.

For the U.S. Army mission profiles, the CBMS has been tested against 22 CWAs and simulants and a series of BWAs and simulants. An overview of the mission profiles and system operation will be presented including results of field operation trials. Possible uses of the CBMS in homeland security will be discussed.

Homeland Security Oral Session

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15. *Detection of Bio-Aerosol With Mass Spectrometry.*
Michael P. McLoughlin, Johns Hopkins Applied Physics Laboratory

The Johns Hopkins University Applied Physics Laboratory, with sponsorship from the Defense Advanced Research Projects Agency, has developed a fully automated mass spectrometer to detect bio-aerosols. We are especially concerned with bio-aerosols that represent a health hazard to humans, whether manmade or naturally generated. A brassboard design of this system has been completed and is currently undergoing extensive performance testing. Features of this system include, fully automated aerosol collection and concentration, automated sample preparation, robotic sample transport, automated data acquisition and detection processing. The potential advantages to the field operator are: rapid detection, high sensitivity, ability to detect a wide range of biological materials, low consumables and ease of operation. In this paper we will describe the operation and key developmental challenges in developing the brassboard system. We will also show variation on this baseline embodiment to tailor this technology for use by a variety of users.

Homeland Security Oral Session
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16. *Small, Unobtrusive Ion Mobility Spectrometers for Analytical Measurements in Field Tests Involving Outdoor Releases of Chemical Warfare Agent Simulants — Airborne and Ground Operations.*
Robert J. Schafer[1], Vincent M. McHugh[1], Charles S. Harden[1], Donald B. Shoff[1], Brian S. Ince[1], Stephen E. Harper[1], Gretchen E. Blethen[1], Paul Arnold[2], Simon Pavitt[2], Martin Thomas[2], Tony Connor[2], Eddie Terzic[2] [1]US Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD 21010, USA [2]Graseby Dynamics, Ltd., Park Avenue, Bushey, Watford, Herts, WD2 2BW, UK

The United States Army (Edgewood Chemical Biological Center, APG, MD) has integrated a modified, hand-held Ion Mobility Spectrometers (IMS) into a mini-Unmanned Aerial Vehicle (mini-UAV) for real-time detection and identification of chemical clouds. The IMS technology is based on a small, unobtrusive, hand-held instrument that has been developed for use by the military for protection against toxic chemical substances. The smallness of the device provides for an ideal approach to rapid, real-time chemical vapor detection, identification and quantification in fast moving vehicles. In the airborne device, a capability for redundant vapor sample retention has been incorporated into the detection payload for subsequent retrieval and forensic analysis.

As an integral part of the field tests of the airborne detector, equivalent devices to those in the UAV-mounted system were employed on the ground during the field trials. The field trials consisted of explosive releases of hundreds of pounds of surrogated chemicals for chemical warfare agents. Single chemical and double chemical releases were accomplished. In the ground applications an array of small IMS detectors were set out downwind of the chemical release points. Real time detector response information was relayed back to a central location by radio frequency modems. The plan for this exercise was to gather real time chemical concentration information from within the chemical clouds above the surface and at ground locations downwind from a simulated chemical warfare agent attack. In addition, the concentration information should be useful to verify models of chemical cloud travel from such a release. Details and results of the ground based field experiments will be presented. Comparisons of actual concentration measurements and concentration predictions using cloud travel models will be discussed.

Homeland Security Oral Session
Robert J. Schafer, U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD 21010, USA.

17. *Field Examples of Ion Mobility Spectroscopy Used for Explosives Detection.*
Philip Rodacy, Pamela Walker and Stephen Reber, Sandia National Laboratories

The ability to reliably detect trace amounts of explosives for both military and civilian applications is one of the most serious challenges facing our society today. Many of the current techniques, such as canines, x-ray, current ion mobility spectrometry and thermal neutron activation, suffer from some of the following: poor specificity, lack of sensitivity, high false alarm rates, lack of portability, and high cost of deployment and maintenance. Recent advances in the field of Ion Mobility Spectrometry (IMS) promise to address and overcome many of these shortcomings. These improved IMS-based systems can be used to prevent illegal possession and use of explosives through screening of personnel and vehicles, to assist first responders in evaluating the hazards during an emergency response, and to aid investigators in post-event inquiries. This talk will focus on the use of IMS-based systems that have been developed for use on land and in the marine environment. Field applications of several land-based systems, ranging from small, portable, hand-held systems to large personnel and vehicle-screening portals will be discussed. The utility of the marine system will be illustrated using examples from several field tests that have been performed in the United States and Canada.

Homeland Security Oral Session
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18. *Chemical/Biological Aerosol Warning System (C/BAWS).*

David Sickenberger, Richard Smardzewski, Felix Reyes, U.S. ARMY SBCCOM, E-3549 APG-EA MD 21010-5425; James Cress U.S. Army SBCCOM, Maneuver Support Battlelab, FT Leonard Wood MO 65373; COL James Swaby USAF Force Protection Battlelab Lackland AFB TX 78236-5558

The U.S. Army Soldier and Chemical Biological Command (SBCCOM) initiated a program to demonstrate a lightweight, easily deployed biological warfare detection and warning capability based on networked sensors now identified as the Chemical/Biological Aerosol Warning System (C/BAWS). The C/BAWS consists of an array of point detectors networked to a central command and control node. The deployment concept is to place the detectors around valued assets to detect C/B clouds as they approach. C/B clouds are detected by these detectors and reported to the command and control node where appropriate warnings are issued. The actual agent determination is made based on the synergistic responses of multiple detectors as processed at the central command and control node. In addition to making the attack warning determination, the command and control node can direct the collection of samples at the detectors for subsequent confirmation and presumptive identification purposes.

The sensor array's remote communication is achieved using lightweight, remote hubs, known as the Tier-I sensors. These sensors contain the radios, GPS position location devices, and meteorological sensors. They also include particle counters to provide some degree of information of the presence of potential biological agent clouds. The Tier-I's also include interfaces to other sensors to include the more powerful Tier-III biological agent detector and chemical agent detectors.

The Tier-I sensors report the alert status of attached sensors in addition to the hub's location and basic meteorological data. The Tier-I's also contain an internal processing capability that can be used to influence the sensor determination if a sensor alarm is real. Unusual biological activity, for example, can be cross-checked against an unusual meteorological condition.

The central command and control node or base station receives data from the Tier-1 sensors and generates a graphical display showing the location of the different sensors, meteorological conditions and sensor status. An alarm is produced when the number, spatial orientation, and type of detectors in an alert status exceeds preset thresholds. From the base station, the operator can easily determine if the upwind chemicals agent detectors are in alarm and its likely path from the displayed wind direction vectors. Similarly, the operator can detect a biological cloud on the upwind perimeter sensors and track it as it transverses the area monitored by the sensors.

Homeland Security Oral Session

David Sickenberger, U.S. ARMY SBCCOM, E-3549, APG-EA, MD 21010-5425, David.Sickenberger@us.army.mil.

19. *Honey Bees: Flying Chemical Detectors.*

Garon C. Smith[1], Jerry J. Bromenshenk[2], and Colin B. Henderson[2], [1]Chemistry Department and [2]Division of Biological Sciences, The University of Montana, Missoula, MT 59812-1006

Domestic honeybees (Apis mellifera) offer the potential of using free-flying organisms to search wide areas for the presence of explosives, unexploded ordnance (UXO) and landmines. As bees perform normal foraging, they may bring back residues of toxic contaminants in a "passive search mode". We briefly describe our use of honeybees to find hazardous air pollutants (HAPs), toxic heavy metals and radionuclides through passive searching at Aberdeen Proving Ground, MD. A more powerful use of the honeybees is gained by conditioning them with scented sugar-syrups to conduct an "active search" for compounds of interest to the military. We present results of conditioning trials that demonstrate how honeybees serve as real-time detectors for the TNT-family explosives at low ppt to ppq levels. This use is analogous to search dogs, except that a colony of bees can be trained in about one hour, does not require a leash and will not set off any mines. During DOD-supervised field trials at the Southwest Research Institute in San Antonio, TX, honeybees yielded a 98.7% detection rate of plumes in the 0.7 – 13.0 ppb range with less than 1% false positive and false negative responses. Subsequent tests have pushed thresholds an order of magnitude lower. An informal comparison between honeybees and a Nomadics Fido sensor showed that, under identical field conditions, the bees were capable of detecting the same level of 2,4-DNT vapors as the Fido instrument. The bees correctly located and identified the DNT targets in an area 200m across in less than one hour with no need for a person to enter the test area. For Fido, the operator had to be led to the target so that is could be "sniffed". Searching the 200m diameter test area without this guidance would have required hours or days.

Homeland Security Oral Session

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20. *Environmental Applications of Field-Flow Fractionation — Inductively Coupled Plasma Mass Spectrometry.*
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Field-flow fractionation (FFF) is a unique size separation technique applicable to both macromolecules and particles found in biological, botanical, environmental, and industrial samples. Coupling FFF with ICP-MS offers the possibility of size-based elemental analysis. Information obtained from this combined technique includes size and molecular weight distributions, diffusion coefficient, polydispersity, and molecular conformation. Since FFF-ICP-MS was first introduced in 1991[1], most FFF-ICP-MS publications have considered environmental samples[2–4], but applications to biological[5] and industrial[6] samples show great promise. We have exploited FFF-ICP-MS to characterize elemental size distributions of macromolecules and particles in river sediments and natural suspended particulate matter[3, 4], biomolecules[5], and soil-derived humic and fulvic acids[7]. The technique has been used to detect oligomer formation and aggregation of naturally existing macromolecules. Types of molecular interactions also are characterized, and on-line preconcentration techniques permit examination of natural and industrial waters. In this presentation FFF-ICP-MS theory, approaches, and applications for environmental applications[8] will be described and reviewed.

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Environmental Chemistry Oral Session
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21. *Extraction of Semivolatile Organic Compounds Using Modified and Micro Liquid-Liquid Extraction.*
Vicente C. Marti, Renee Bellew and Jesse Kiernan, US EPA Region VIII Laboratory

This procedure utilizes two different designs of liquid-liquid extractors (LLEs) to separate semivolatile organics from waters and wastewaters. Most published semivolatile analysis methods require a one-liter sample and up to 500 ml of extracting solvent. The EPA Region VIII Laboratory has minimized the amount of sample and solvent required for its semivolatile organics analysis using new LLE designs. The need for improved LLE design arose from problems encountered using solid phase extraction. Solid phase disks did not provide the required recoveries and sensitivity for the analysis of phenols (acid fraction) of method 8270. Our first design, the modified LLE, is a one-liter extractor modified to allow extraction and concentration to occur in the same vessel. A three-ball Snyder column was added to the extractor, and the bottom of the vessel was modified to allow for the removal of methylene chloride. Concentrating of analytes is occurring in the extraction vessel, so there is no need for separate Kuderna-Danish concentrator and nitrogen blow-down steps. With this modification, the volume of methylene chloride was reduced from 500 ml to 130 ml. Recoveries of phenols were improved to better than 85% for all phenols listed. Base-neutrals recoveries were also improved. Further modification of the extractor, to the micro LLE, allowed additional reduction of sample size and solvent volumes used in extraction. The laboratory is able to reduce the total volume of methylene chloride used in extraction to 20 ml. This volume is comparable to that of solid phase extraction. The sample size was reduced to 50 ml. Data obtained proves that the modified and micro extractor provide higher recoveries with considerable savings in solvent and total cost of sampling and disposal.

Environmental Chemistry Oral Session
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22. *Monitoring for Intentional Contamination of a Drinking Water System: Contaminants of Concern, Early Warning Monitoring.*
Maria W. Tikkanen, Kennedy/Jenks Consultants

Since 9/11, securing the safety of drinking water systems in the United States has become a high priority. This paper will present the findings of an evaluation of potential agents that might be used to intentionally contaminate a water system. Particular attention will be paid to the biological, chemical (CDC) and radiological agents of warfare. Considering these potential agents, desirable properties of the ideal agent were determined to include, but not be limited to, human toxicity, solubility, and stability in water, attainability, portability, and historic precedence. A short list of potential agents that might be used against a drinking water system was developed. This will be discussed. As well, monitoring for these potential contaminants within a drinking water system by continuous, on-line monitoring (pH, chlorine residual, total organic carbon, UV absorbance, conductivity, turbidity and particle counting) was investigated and will be detailed.

Environmental Chemistry Oral Session

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23. *Quantifying Vapor-Soil Interactions Using Surrogate Soil Stationary Phases in Gas Chromatography.*
Thomas J. Bruno and Keith E. Miller, Chemical Science and Technology Laboratory, National Institute of Standards and Technology

Quantifying the interaction of pollutants on soil surfaces is critical to understanding the migration potential of contaminant releases. The enthalpy of adsorption is one of the fundamental parameters that must be known to effectively predict migration potentials on various soil substrates. A NIST-developed metrology for determining heats of adsorption and interaction for organic vapors on clay and organo-clay substrates will be presented. The measurements are made using wall coated open tubular (WCOT) column gas chromatography with stationary phases formed with the synthetic clay Laponite-RD. The clay stationary phases are subsequently modified to create organo-clay stationary phases. Two examples of environmental significance are presented. First, the soil interaction of pollutants associated with fuel spills is presented. Adsorption data of alkyl and aromatic hydrocarbons, as well as fuel additives, are presented for two surrogate soil surfaces. A comparison of the data to those made by packed column approaches will be made. Second, the interaction of sulfur compounds with surrogate soils will be presented. Sulfur compounds are added to fuel gases [natural gas and liquefied petroleum gas (LPG)] to make the gases detectable in the event of fuel leaks. When leaks occur in transfer and service lines, sorption processes between the odorants and the soil result in diminished odorant concentration and soil contamination. Our experimental results show that, as a class, the sulfide odorants have larger adsorption enthalpies on clay and organo-clay surfaces than the thiol odorants. Therefore, thiols are less likely to be sequestered on soil surfaces. Proposed retention mechanisms will be presented, representing a significant step in quantifying and understanding contributions of sorption interactions between odorants and natural soils.

Environmental Chemistry Oral Session

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24. *Clay Adsorbent Evaluation by Liquid Chromatography.*
Keith E. Miller and Thomas J. Bruno, Chemical Science and Technology Laboratory, National Institute of Standards and Technology

Composite materials derived from clay minerals are used or are being proposed for use as selective adsorbents for various industrial and analytical applications. These applications range from controlled-pesticide release applications in agriculture to solid-phase concentration media for aqueous environmental samples containing nitro-aromatic compounds. We present an evaluation of the adsorption characteristics of clay-based adsorbents. First, development of clay agglomerates using the synthetic-clay Laponite-RD will be discussed. Sintered-clay agglomerates are prepared by a spray-drying technique followed by a period of heat treatment. Particles obtained from this process are 0.5 to 25 μm in diameter. These particles are subsequently packed in liquid chromatographic (LC) columns for evaluation. Second, adsorption characteristics between aqueous phase aromatic hydrocarbons and sintered-clay substrates will be discussed using retention data obtained using these columns. These preliminary data indicate that retention of aromatic hydrocarbons on sintered clay agglomerates is significantly higher when compared to the pure clay material. By examining a series of substituted aromatic compounds, correlations between the collective structural and functional group properties of compound classes with retention characteristics are made. Third, thermodynamic data obtained using the prepared LC columns are presented from specific environmental and pharmaceutical applications. These data indicate that sintered-clay particles are highly-selective adsorbents with promising applications in water-treatment processes, solid-phase pre-concentration media, and industrial separation processes.

Environmental Chemistry Oral Session

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25. *Environmental Chemistry — Challenges of the 21st Century.*
Theodore C. Rains, High-Purity Standards

Problems encountered by the environmental chemist are numerous. They may include sampling, preservation of sample for testing, method of analysis, instrument calibration, and evaluation of data. The environmental sample may be in the form of a liquid, solid or gas. Each of these forms may become a challenge for the analyst. The concentrations may vary from percent levels to subpart per billion. This presentation will address many of these problems as seen from the eyes of a chemist with fifty plus years of experience.

Environmental Chemistry Oral Session
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26. *A Batch Enzymatic Reduction Method for Automated and Manual Colorimetric Determination of Nitrate in Water.*
Jennifer R. Kryskalla and Charles J. Patton, U.S. Geological Survey, National Water Quality Laboratory

Nitrate and nitrite are two of the most universally determined anions in water because at elevated concentrations they promote eutrophication and are toxic to unborn and young humans and livestock[1]. For natural water analysis, nitrate usually is determined by reduction to nitrite and colorimetric reaction with Griess reagents[2]. Cadmium has been the reagent of choice for these applications because it reduces nitrate to nitrite quantitatively with negligible reduction of nitrite to lower oxidation states[3]. The toxicity and waste-disposal concerns associated with cadmium use, however, have led to the exploration of nontoxic alternatives[4]. Nitrate reductase (YNaR1; EC 1.7.1.2, formerly EC 1.6.6.2), produced using recombinant expression in the yeast Pichia pastoris, is a more environmentally benign reduction reagent than cadmium. Here we describe a batch YNaR reduction method that in comparison to on-line reduction methods allows much simpler instrumentation to be used for automated or manual nitrate determinations. In this approach, a digital pipettor/dilutor is used to dispense sample aliquots and YNaR reagent into autoanalyzer cups or disposable spectrophotometer cuvettes. Nitrite resulting from the batch YNaR reduction then can be determined automatically by air-segmented (CFA) or flow-injection (FIA) analysis or manually. Throughout this study, two CFA analyzers, one configured for cadmium reduction analysis and the other configured for YNaR analysis, were used to characterize the analytical performance of the enzymatic reduction method. Method detection limits were 0.004 mg NO3- + NO2--N/L for the cadmium method and 0.006 mg NO3- + NO2--N/L for the enzymatic reduction. The batch enzyme method results compare favorably with cadmium results over a wide concentration range (0.05 – 5.00 mg NO3- + NO2- -N/L). Results obtained with FIA and manual spectrophotometry also are presented and discussed. *The authors gratefully acknowledge partial support for this work by the Nitrate Elimination Company in Lake Linden, Michigan, through U.S. Department Agriculture SBIR Phase II grant number 2002-33610-12300.*

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27. *Portable Sensor for the Detection of Nitrates and Nitrites in Groundwater.*
Veronica M. Cepak, Michael T. Carter, Erica R. McDaniel and Gregory R. Bourgon, Eltron Research, Inc.

Nitrates are one of the most problematic and widespread of the vast number of potential groundwater contaminants. Most nitrogenous materials in natural water tend to be converted to nitrate, so all sources of combined nitrogen including ammonia and organic nitrogen should be considered as potential nitrate sources. Since nitrates/nitrites are very soluble and do not bind to soils, these ions have a high potential to migrate to groundwater. In addition, nitrates can persist in groundwater for decades and accumulate to high levels; they remain in water until consumed by plants and other organisms. Hence, there is a large need to monitor groundwater and agricultural runoff for nitrate and nitrite. Recent work at Eltron Research is examining the feasibility of constructing a field portable amperometric sensor for the detection of both nitrate and nitrite in agricultural waters and groundwater. We will successfully demonstrate that screen-printable conductive electrodes with an incorporated electrocatalyst can be used for the detection of nitrate, nitrite, and mixtures thereof in water samples. A prototype sensor employing amperometric detection and a flow injection analysis system is in development. Key aspects of the sensor will be discussed along with its operation in a variety of environmental conditions. Amperometric sensors can offer a viable, low cost solution to field monitoring in environmental analysis. The goal of our sensor development is affordable, real-time, on-site monitoring of environmental pollutants in water.

Environmental Chemistry Oral Session
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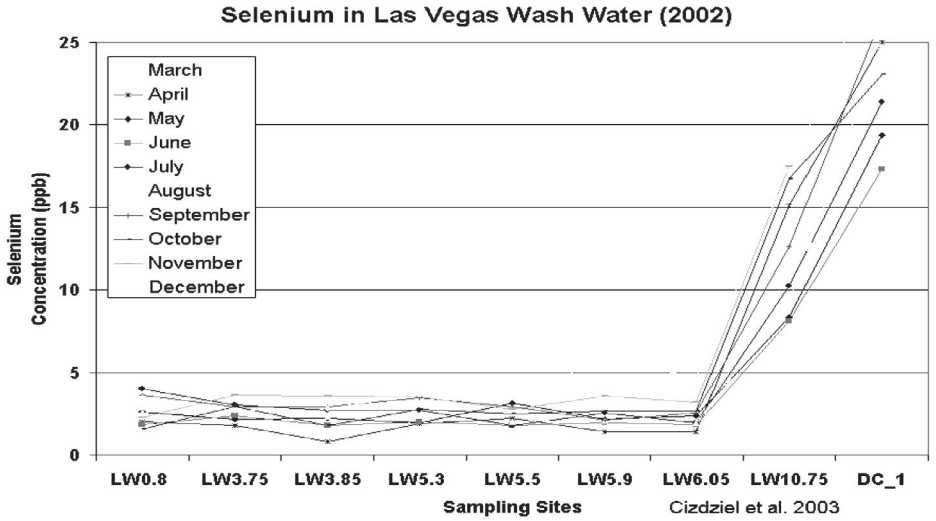
28. *Mercury and Selenium in Water, Sediments, and Plants from the Las Vegas Wash, USA.*

J. V. Cizdziel and J. E. Pollard, Harry Reid Center for Environmental Studies, University of Nevada; Xiaoping Zhou, Southern Nevada Water Authority, 1900 E. Flamingo, Suite 255, Las Vegas, NV 89119

The Las Vegas (LV) Wash is a stream containing urban runoff, flows from natural artesian springs, precipitation events, and treated wastewater effluent. It originates from the LV valley, populated by well over a million people, and flows into LV Bay in Lake Mead. Over the past two decades, wetland areas associated with the Wash have decreased significantly due to erosion from increased water flows related to the growth in population and water usage. Currently restoration efforts are underway to re-establish wetlands. Due to concerns about mercury and selenium in the system, this study was initiated to characterize and monitor mercury and selenium levels in the Wash water, sediments, and biota (plants) as the system evolves. High-Resolution ICP-MS was used to determine selenium, while CV-AFS and combustion-AAS was used for mercury. Levels of selenium are relatively low in the main-stem of the Wash (<5 ug/L) but are higher in certain tributaries (~15-25 ug/L). Mercury levels are low in the water (<10 ng/L) but higher in the sediments (5-15 ng/g, ww). Selenium varies widely in the plants by species and plant structure. Leaves and flowers have higher concentrations than roots and are generally an order of magnitude higher than water levels. Except for rare precipitation events, there was little temporal trend in the data collected over a year period, along with implications for proper management of the LV Wash and Wetlands.



Environmental Chemistry Oral Session

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29. *Propagation of Error in the Determination of Silicon Concentrations in Tungsten Hexafluoride Residue Samples by Graphite Furnace Atomic Absorption Spectrometry.*

Greg W. Johnson; Virginia H. Houlding, Matheson Tri-Gas

A method to determine Si concentrations in Tungsten Hexafluoride Residue Samples was previously developed and reported by Johnson at the 36th Rocky Mountain Conference on Analytical Chemistry (1994). Interferences were identified that were associated with atomic Si population losses due to SiF4 formation and atomic Si population losses due to SiC formation. The errors were reduced to tolerable levels by use of a matrix modifier and a pyrolytic graphite tube preconditioning procedure. The matrix modifier was 0.02 M 2-amino 2-hydroxymethyl 1,3-propanediol (TRIS) plus 0.02 M citric acid. The preconditioning procedure involved formation of tungsten carbide using an aliquot of 100 µg W/mL solution followed by graphite tube heating, repeated ten times. For the current work, errors of -100.0% and -83.3% were noted for Si concentration estimates due to SiF4 and SiC formation without the use of a matrix modifier or tube preconditioning, respectively. In addition, errors of - 20% or more were noted to result from systematic errors in micro liter pipette delivery volumes. Finally, errors as great as ±10 µg Si/L were noted to be due to □50 µg Si present as a contamination per gram TRIS(s). Use of 20 µL 0.02 M TRIS (from re-crystallized TRIS(s)) plus 0.02 M citric acid matrix modifier, pyrolytic tube preconditioning, calibration of micro liter pipette delivery volumes with dial settings using first order linear regression statistics, and re-crystallization of TRIS(s) to remove Si contamination resulted in detection limits in the 0.62 µg Si per gram WF6 range with an accuracy of better that 2.0%.

Environmental Chemistry Oral Session

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30. *New Insights into the Photosystem II Oxygen Evolving Complex via Pulsed EPR.*
R. David Britt, University of California, Davis

The Photosystem II (PS II) component of the photosynthetic apparatus of chloroplasts and cyanobacteria utilizes light energy to drive electron transfer reactions that result in the oxidation of water and the reduction of membrane diffusable plastoquinone. The water oxidation chemistry occurs in the Oxygen Evolving Complex (OEC), which involves a tetranuclear manganese complex, a proximal redox-active tyrosine (Yz), and associated chloride and calcium cofactors. Pulsed electron paramagnetic resonance (EPR) methods serve as powerful tools for studying the structure and local environment of the paramagnetic Mn cluster and the oxidized tyrosyl radical. I will discuss recent data concerning the binding of substrate waters, water analogs, inhibitors, and cofactors in the vicinity of the Mn cluster, and discuss how the data relate to recent models of the water-splitting cycle.

EPR Oral Session
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31. *Structure and Dynamics of Synthetic and Biological Macromolecules by Using a Multitude of EPR Methods on Spin Probes and Labels.*
Gunnar Jeschke and D. Hinderberger, Max Planck Institute for Polymer Research

Spin probes or labels are well suited for studying complex materials, as they can provide detailed information on selected sites of interest. Such studies profit tremendously from the broad range of techniques developed to date in EPR spectroscopy. Information on dynamics, distribution of paramagnetic centers, and intermolecular contacts can thus be obtained separately and can then be combined into a comprehensive model of the selected site. To further such a strategy we have increased precision and sensitivity of distance measurements between two electron spins, developed the mathematics to directly transform EPR data to spin-spin pair correlation functions[1], and studied ways to precisely measure small hyperfine couplings. The current sensitivity limit of double electron-electron resonance (DEER) distance measurements is assessed for the example of the most abundant membrane protein complex, plant light harvesting complex II. The measurement and analysis of very narrow and very broad distance distributions is demonstrated in the determination of the persistence length of shape-persistent polymers and the co-conformation of [2] catenanes, respectively. A multi-method approach, including the use of electron spin echo envelope modulation (ESEEM) depths pioneered by Larry Kevan, is illustrated in the quantification of polyelectrolyte-counterion interactions.

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32. *Structure of Co^{II}-Radical Pair Intermediate States in B_{12} Enzyme Catalysis Revealed by Orientation-Selection and Powder ^2H ESEEM Spectroscopy.*
Kurt Warncke and Jeffrey M. Canfield, Emory University

Orientation-selection and powder X-band ESEEM and EPR spectroscopies performed in the disordered solid state have been used to determine the active site geometry of the reactant centers that participate in radical migration, hydrogen atom transfer and radical rearrangement reactions catalyzed by the coenzyme B_{12}-dependent enzyme, ethanolamine deaminase, from Salmonella typhimurium. The low spin (S=1/2) Co^{II}-substrate radical pair and Co^{II}-product radical pair intermediates were prepared by cryotrapping holoenzyme during steady-state turnover on aminopropanol or aminoethanol as substrate, respectively. Hydrogen positions in the 5'-deoxyadenosine C5' methyl group in both intermediates, and in the product radical itself, were ^2H-labeled. The Co^{II}-C1 radical center (substrate radical state) and Co^{II}-C2 radical center (product radical state) distances were determined (10-12 Å) from EPR spectral simulations, and the orientation of the ^2H in the C5' methyl group of 5'-deoxyadenosine relative to these centers was determined by orientation-selection two-pulse ^2H ESEEM. The orientation selection is created in the EPR spectrum of the radical pair by the axial electron-electron dipolar interaction[1]. Global simulations of ESEEM collected at different magnetic field values were weighted by the orientation-dependence of the EPR lineshape. The results show that C5' is located near to both C1 and C2 (r≈3.3 Å), and close to the Co^{II}-C1 and Co^{II}-C2 axes. Simulation of three-pulse ^2H ESEEM collected from the Co^{II}-product radical pair state provides additional insight into the conformation and dynamics of the product radical. Comparison of the reactant center geometries in the Co^{II}-substrate and Co^{II}-product radical pair states reveals principal nuclear coordinates that contribute to radical-mediated catalysis in ethanolamine deaminase. *Supported by NIH DK54514.*

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33. *The ESEEM and Pulsed ENDOR of High Spin/Weak Crystal Field Ions.*

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The weak *cfi* of high-spin ions results in a noticeable departure of the electron spin quantization axes from the direction of the external magnetic field, and the resulting quantization axes are different for different electron spin manifolds. This results in the implicit contribution of *cfi* to the transition frequencies of ligand nuclei, and leads to various unusual features and complications when analyzing the ESEEM and ENDOR spectra of such systems. For nuclei of spin ½, these features include unusual shifts, or even the disappearance of the sum combination line (*scl*) in 2- and 4-pulse ESEEM, asymmetric distortions as well as a broadening of the ENDOR spectra. In practical applications, this means that the *scl* position and intensity cannot be used to determine ion-nuclei distances. The theory that we developed[1] shows that although the *cfi* causes severe distortions in the shapes of ENDOR spectra, there is only a slight affects on the positions of singularities, which can be used for the determination of anisotropic hyperfine interactions as well as ion-nuclei distances. Applying our theory, using simulations and employing 2D pulsed (Mims) ENDOR to disentangle the ENDOR spectra of different electronic states, we determined the inner shell proton - Gd^{+3} distances of numerous MRI agents, with an accuracy approaching single crystal measurements. This approach finally allows the factorization of the relaxivity of MRI agents, and provides a comprehensive understanding of relaxivity variation for different MRI agents. *Supported by NSF grant DBI-0139459*

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34. *Characterization of Active Sites in Zeolites by Means of EPR Spectroscopy.*

Andreas Pöppl, Marlen Gutjahr, Thomas Rudolf, V. Umamaheswari , University of Leipzig, Faculty of Physics and Earth Science, Linnéstr. 5, D-04103 Leipzig, GERMANY; Martin Hartmann, Kaiserslautern University of Technology, Department of Chemistry, D-67661 Kaiserslautern, Germany

One major challenge in the research of microporous materials is the spectroscopic characterization of surface adsorption complexes. If the adsorbed molecules are paramagnetic the structure of the formed complexes, the dynamics of the adsorbed molecules, and the specific adsorption sites at the metal oxide surface can be accessed by EPR spectroscopy. Such studies may provide a unique understanding of the various physical processes giving rise to the observed adsorption phenomena but also allow a detailed characterization of the nature of the respective adsorption sites and their chemical properties. In that way, adsorption of nitric oxide and di-tert-butyl nitroxide in ZSM-5 and Y zeolites is employed to study the electron pair acceptor properties of Lewis acid sites such as alkali metal cations and aluminum defect centers in these molecular sieve systems. Two strategies are presented to deduce the electron pair acceptor strength of the surface sites from the spin density distribution in the formed adsorption complexes and the desorption behaviour of the probe molecules on basis of cw EPR experiments. However an unambiguous evidence of the direct coordination of the probe molecules to the specific surface sites is a necessary requirement of the proposed methods. Therefore, particular emphasis is given to the determination of the structure of the adsorption complexes by pulsed ENDOR and HYSCORE spectroscopy.

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35. *Applications of Pulsed EPR to Transition Metal-Exchanged Zeolites and Mesoporous Materials.*

Sarah C. Larsen, University of Iowa

Transition metal-exchanged molecular sieves have many potential applications in heterogeneous catalysis. CW and pulsed electron paramagnetic resonance (EPR) were used to investigate the local environment of vanadium in vanadium exchanged zeolites and mesoporous materials. EPR spectra were obtained for hydrated and dehydrated samples and for samples with adsorbed ammonia. Proton ligand hyperfine coupling constants for water were determined and were interpreted using model complexes and density functional theory (DFT) calculations. Nitrogen hyperfine and quadrupole coupling constants for adsorbed ammonia were measured and were compared with the results from DFT calculations for related complexes. The agreement between the calculated and experimental nitrogen hyperfine coupling constants for equatorial nitrogen ligands was very good. Vanadium nuclear quadrupole coupling constants were also calculated with good accuracy.

EPR Oral Session

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36. *Application of Pulsed EPR Spectroscopy to the Study of Radiation Lithography.*
Tsuneki Ichikawa, Hokkaido University

The migration distances of electrons generated in γ-irradiated organic matrices have been determined by electron spin-echo method for estimating the final spatial resolution of radiation lithography. The average migration distance depends not on the concentration of electron scavengers but on the polarity of matrix molecules, which indicates that ejected electrons react with scavengers after loosing their excess kinetic energies. The final spatial resolution determined by the migration distances of electrons is estimated to be ca. 7 nm.

EPR Oral Session

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37. *ESR Investigations of Niobium-containing Aluminophosphates.*
Martin Hartmann, Kaiserslautern University of Technology, Department of Chemistry, D-67661 Kaiserslautern, Germany; V. Umamaheswari, Andreas Pöppl, Winfried Böhlmann, University of Leipzig, Department of Physics and Geosciences, D-04103 Leipzig, Germany

The synthesis of transition metal-containing molecular sieves (microporous as well as mesoporous) is one of the fastest developing areas in molecular sieve science. In this work, we report the hydrothermal synthesis and characterization of crystalline niobium-containing aluminophosphates with AFI, AEL, AFO and ATO structure. Results from powder X-ray diffraction, UV-Vis, ^{27}Al and ^{31}P-NMR and X-band ESR spectroscopy are discussed to investigate the incorporation of niobium into the aluminophosphate framework. The ESR spectra were recorded after X-ray radiation at 77 K. In all niobium-containing samples a signal with g_{av} = 2.022 and a 10-line hyperfine structure with a splitting of ca. 23 x 10^{-4} cm^{-1} due to the interaction with the ^{93}Nb nucleus (I = 9/2) were observed. The g-value of this signal is larger than the free-electron g-value of 2.0023, which indicates that this signals are for hole centers and not electron centers. The signal is ascribed to radiation-induced hole centers trapped in the lone pair p-orbitals of the associated oxygen atoms. Therefore, the signal with the 10-line hyperfine structure can clearly be assigned to hole centers located on P-O-Nb or Al-O-Nb units located in the framework of NbAPO-5.

EPR Oral Session

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38. *ESR and ESEM Study of Incorporation of Zirconium into Silicoaluminophosphate SAPO-5 Microporous Material.*
Pesak Rungrojchaipon, Jianming Lu, Larry Kevan, University of Houston

Zirconium containing silicoaluminophosphate molecular sieve, ZrAPSO-5, was synthesized and compared with liquid ion-exchange sample (ZrH-SAPO-5). Electron spin echo modulation (ESEM) and electron spin resonance (ESR) were successfully used to distinguish the environment of zirconium between the framework and extraframework position. The zirconium containing microporous materials were also characterized by XRD and N_2 adsorption isotherms. At ratios of Zr/Al ≥ 0.026, zirconium is probably present in both framework and extraframework positions. ^{31}P ESEM was used to identify the location of Zr(III) species in ZrAPSO-5 generated by γ-irradiation in ZrAPSO-5 at low Zr/Al ratios. Simulation of the ^{31}P modulation suggests that zirconium substitutes into a phosphorus site rather than aluminum site.

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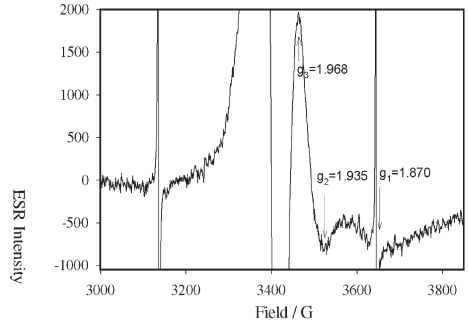
39. *Electron Spin Resonance Investigations of Zirconium in Mesoporous Aluminophosphate and Silicoaluminophosphate.*
Jian-Ming Lü, Koodali T. Ranjit, Pesak Rungrojchaipan and Larry Kevan, University of Houston

Zirconium containing mesoporous aluminophosphate and silicoaluminophosphate materials were synthesized by using Pluronic 123 triblock co-polymer as the template. The mesoporous materials were characterized by X-ray diffraction (XRD), N_2 adsorption/desorption measurements, Transmission electron microscopy (TEM), Electron microprobe analysis (EMPA) and electron spin resonance (ESR) spectroscopy. The XRD pattern indicated d_{100} spacing between 35 to 60 Å with different Zr content. The N_2 adsorption/desorption isotherms shows an average pore size around 40Å and surface area of about 400 – 600 m^2/g. Reduction of the zirconium from +4 to +3 state was achieved by γ-ray irradiation at 77 K. In samples with Zr/Al ratio ranging from 0.016 to 0.12, ESR studies established that Zr is located mostly in the pore walls in the substitutional location with rhombic symmetry (g_1=1.870, g_2=1.935, and g_3=1.968).



ESR spectrum of mesoporous ZrSAPO (Zr/Al=0.08) after γ-irradiation at 77 K

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40. *A Discrete Water Exit Pathway in the Membrane Protein Cytochrome c Oxidase.*

Bryan Schmidt, Shelagh Ferguson-Miller and John McCracken, Michigan State University

Using the non-redox active Mg^{2+}/Mn^{2+} site of cytochrome c oxidase as a probe, water access from the outside of the enzyme and from the active site were studied. Water movement was time-resolved by the magnetic interaction of $H_2{}^{17}O$ with the Mn^{2+} by using a rapid freeze-quench – electron spin echo envelope modulation (ESEEM) technique. Rapid (ms) access of water from the bulk phase to the Mn^{2+} was demonstrated by mixing CcO with $H_2{}^{17}O$. To detect water exit from the active site, samples incubated in $^{17}O_2$ were allowed to turnover before freezing. The product $H_2{}^{17}O$ was detected at the Mn^{2+}. The significant broadening of the Mn^{2+} signal after a limited number of turnovers strongly suggests the water exits the protein via one discrete pathway, not by random diffusion. *Supported by NIH GM 26196 (S.F.M.) and P01-GM 57323 (S.F.M and J.M.)*

EPR Oral Session

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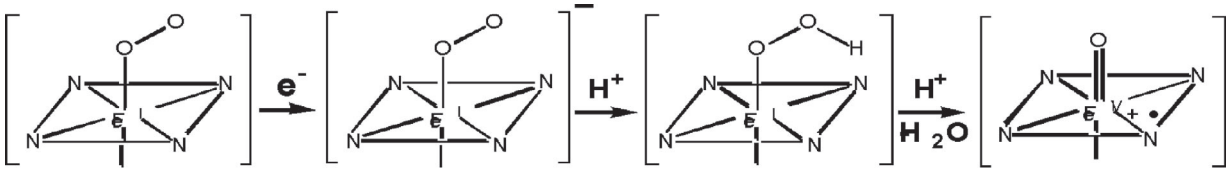
41. *Characterizing the Invisible: ENDOR Characterization of Intermediates in the Activation of Dioxygen by Fe Enzymes.*

Brian M. Hoffman, Northwestern University

Dioxygen activation by heme enzymes is perhaps the most widely studied enzymatic reaction: during the 1990's, on average roughly one paper was published on cytochromes P450 alone, every five hours of every day (Prof. Martin Newcomb, private communication). It has long been thought that heme hydroxylations involved the intermediates in **Scheme 1**, with the rate-limiting reduction of the dioxygen-bound ferriheme generating the peroxo-ferriheme, which then accepts one proton to generate the hydroperoxoferri-heme, followed by delivery of the second proton and heterolytic O-O cleavage to produce Compound I, *the* reactive, hydroxylating intermediate. However, all three intermediates are potentially capable of reacting with a substrate, and there are substantial reports that different combinations of enzyme/substrate involve reaction by a different intermediate.

We therefore initiated a program designed to characterize the intermediates in heme hydroxylations. It employs cryogenic γ-irradiation of an oxy-ferrous enzyme to inject the electron that initiates the catalytic process. Subsequent stepwise annealing stages permit an enzyme to traverse its catalytic cycle, through to product formation, with a combination of epr and endor measurements providing an optimal means of characterizing catalytic intermediates. We have applied this approach to studies of heme oxygenase in collaboration with Prof. Masao Ikeda-Saito and coworkers, studies of P450cam in collaboration with Prof. Steve Sligar and coworkers, and of nitric oxide synthase in collaboration with Profs. Bettie Sue Siler Masters, John Dawson, and coworkers. The status of this work will be presented.

Dioxygen activation by mononuclear nonheme-Fe enzymes likewise plays an important role, and is involved in many processes of environmental, pharmaceutical, and medical significance. Studies of nonheme Fe enzymes such as napthalene dioxygenase and superoxide reductase may be presented as well.



EPR Oral Session

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42. *Spectroscopic Evidence for Fe(I)-Fe(II) in Fe-only Hydrogenase Models.*

Shirley A. Fairhurst, Christopher J. Pickett, Mathieu Razavet, Xiaming Liu, Simon J. George, David J. Evans, J. Elaine Barclay, David L. Hughes, Sian C. Davies, Biological Chemistry Department, John Innes Centre, Norwich NR4 7UH, UK; Stacey J. Borg, Stephen P. Best, School of Chemistry, University of Melbourne, 3010 Victoria, Australia.

The di-iron sub-site of the H-cluster of all-iron hydrogenase catalyses the reduction of protons to dihydrogen at very high rates. The sub-site is extraordinary in that: (i) carbon monoxide and cyanide ligands are essential structural elements; (ii) biologically unprecedented Fe(I) oxidation states are probably involved in turnover; and (iii) interconversion of bridging and terminal CO ligands may play a key part in the catalysis at the binuclear centre. We describe the first synthetic [2Fe3S]-carbonyl and carbonyl cyanide compounds, the X-ray crystallographic structural data for three of the di-iron molecules, including that for the first [2Fe3S]-carbonyl cyanide, EPR, NMR and FTIR spectroscopic properties of the assemblies, including ^{57}Fe Mössbauer spectra pertinent to differential coordination at the di-iron centers and detection of a mixed valence Fe(I)-Fe(II) bridging carbonyl intermediate. *Supported by BBSRC, JIF (JIC) and ARC(Melbourne).*

EPR Oral Session

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43. *Probing Protein Folding with High Field EPR but without Spin-Labeling.*

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Understanding protein folding is central to many areas of biophysical chemistry, biotechnology, and medicine. This fundamental problem is approached from different directions. Electron Paramagnetic Resonance Spectroscopy in combination with site-directed spin-labeling allows one to probe dynamics of site-specific changes in protein structure and to track protein folding events with a millisecond or better time resolution. Recently, the local folding/unfolding kinetics of spin-labeled protein was studied with X-band stop-flow EPR[1-2] The disadvantage of the spin-labeling EPR approach is that it requires chemical modification of the site of interest.

Here we demonstrate HF EPR experiments to study folding process using ingenuous metal paramagnetic centers in protein, specifically, Mn(II) center in Concanavalin-A (ConA). Typically, for many paramagnetic metal ions at ambient temperatures and conventional EPR frequencies the electronic relaxation time is too short even for continuous wave (CW) experiments. However, with an increase in magnetic field the solution EPR line width of Mn(II) becomes sufficiently narrow, allowing to resolve signals from folded and unfolded forms of the protein. We will show that this excellent spectral resolution allowed us to monitor both the equilibrium chemical denaturing of Con-A and to study kinetics of protein unfolding. Effect of binding sugar molecules on stability of the protein is discussed. *This work is supported by grants from the NSF MCB-0196326 and NCSU (T.I.S.).*

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[2] V. M. Grigoryants, A. V. Veselov, and C. P. Scholes, 2000, Biophys. J., 78: 2702.

EPR Oral Session

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44. *Conformational Changes and Bound State Conformation of Maltose Binding Protein (MBP) Upon Interaction with the Chaperone SecB: ESR and Fluorescence Studies.*

M.V.L.N. Raju, Wolfgang E. Trommer, Department of Chemistry, University of Kaiserslautern, D-67653 Kaiserslautern, Germany; Raghavan Varadarajan, Molecular Biophysics Unit, Indian Institute of Science, Bangalore 560012, India

SecB is a homotetrameric chaperone that forms part of the protein translocation machinery in *E. coli*. We have previously investigated the bound state conformation of the model substrate bovine pancreatic trypsin inhibitor (BPTI) as well as the conformation of SecB itself by using proximity relationships based on site-directed spin labeling and pyrene fluorescence methods. The data suggested that SecB binds a collapsed coil of reduced unfolded BPTI, which then undergoes a structural rearrangement to a more extended state upon binding to SecB. In addition ESR showed that also SecB undergoes a conformational change during this process. We have now studied the interaction of MBP with SecB by the same techniques.

EPR Oral Session

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45. *ESR Spin Label Study of Local Segmental Dynamics of Polymers in Dilute Solutions.*
J. Pilar and A. Marek, Academy of Sciences of the Czech Republic

Copolymers of 2-hydroxyethyl methacrylate (HEMA) and styrene (ST) with spin-labeled methacrylic acid units (less than 5 mol %) distributed randomly along the main chain were synthesized. ESR spectra of both copolymers were measured at X-band (9 GHz) in solution over a broad temperature range. The temperature dependence of parameters characterizing local segmental dynamics of polymer chains was determined by fitting experimental to theoretical ESR spectra calculated using the Nonlinear-Least-Squares analysis[1] and MOMD model[2]. The spin-labeled HEMA copolymer was studied in methanolic solution only due to its limited solubility in other solvents. Dependence of the parameters on temperature and on polymer concentration in solution up to entangled solutions revealed details of local HEMA dynamics in dilute and non-dilute solutions. Spin-labeled PS was studied in dilute solutions (ca. 1%) in solvents differing in thermodynamic quality, viscosity, and activation energy of viscous flow. Unlike so far published conclusions,[3,4] the data show that dilute solutions of the PS copolymer in the solvents used - Θ solvent dioctyl phthalate (DOP), marginal solvent dibutyl phthalate (DBP) and good solvents toluene (TOL) and dimethylformamide (DMF) - exhibit the non-Kramers behavior characterized by parameter $\alpha = 0.73 \pm 0.02$ and by the height of the potential barrier for local conformational transitions $E_a = 10.5 \pm 0.6$ kJ/mol. *Supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Project A4050306).*

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[4] Glowinkowski et al., Macromolecules, 1990, 23, 3520.

EPR Oral Session

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46. *EPR Study of Isomerization Efficiency and Electron Transfer of Carotenoids in Metal Substituted MCM-41 Molecular Sieves.*
Yunlong Gao, Lowell Kispert, Tatyana Konovalova and Jesse Lawrence, The University of Alabama

Mesoporous MCM-41 molecular sieves have been studied extensively by Kevan and coworkers as heterogeneous hosts for catalytic reactions of bulky organic molecules. Extending their studies, we have used multifrequency EPR techniques to examined the photoxidation of carotenoids (antenna and photoprotect components in photosynthesis), in MCM-41 as well as in transition metal (Ni, Al, Ti, Fe and Cu) substituted MCM-41. Electron transfer (ET) characteristics and isomerization properties of the carotenoids imbedded in the molecular sieves were measured. In MCM-41, the highest ET efficiency occurred for the carotenoid with the lowest oxidation potential. The presence of transition metal ions in the framework of MCM-41 increased the ET efficiency for all carotenoids, but the enhancement did not depend on oxidation potential but rather on whether complexes were formed between carotenoid and the metal ion. A very high *trans* to *cis* isomerization of the carotenoids was observed in the solid hosts that depended on the particular host and the type of carotenoid included. *This work was supported by DOE Grant DE-FG02-86ER13465.*

EPR Oral Session

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47. *Study of the Formation of the Mesoporous Material SBA-15 by EPR Spectroscopy.*
Sharon Ruthstein[1], Veronica Frydman[1], Shifra Kababya[1], Miron Landau[2] and Daniella Goldfarb[1] [1]Department of Chemical Physics, Weizmann Institute of Science, Rehovot, 76100, Israel; [2]Blechner Center for Applied Catalysis and Process Development, Chemical Engineering Department, Ben-Gurion University of the Negev, Beer-Sheva, 84105, Israel

SBA-15 is an hexagonal mesoporous material, which is synthesized with nonionic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers (Pluronics, $EO_xPO_yEO_x$) templates. It possesses large, uniform and ordered channels (2-30 nm) , along with complementary net of micropores, which provide connectivities between the ordered channels through the silica. This study focuses on the investigation of the formation mechanism of SBA-15 with emphasis on the PEO interactions with the silica and the initiation of the micropores. This was achieved using in-situ X-band EPR spectroscopy in combination with electron spin echo envelope modulation (ESEEM) experiments using spin-labeled Pluronic L62 ($EO_6PO_{30}EO_6$), where nitroxides replace the OH groups at the end of the polyethylene oxide (PEO) blocks (L62-NO). The locations of the nitroxides of L62-NO within the micelles of the Pluronics P123 (x=20, y=70) and L64 (x=13, y=30) were determined by three-pulse ESEEM experiments on D_2O solutions through comparison with a series of small spin-probes. The NO group of L62-NO was found to be close to the core-corona interface of the micelles in both types of Pluronics. The temporal evolution of the EPR spectrum during the reaction showed that for SBA-15 made with P123 the most significant changes in the L62-NO spectrum occur within the first 100 min, this was also confirmed by ESEEM measurements. A partitioning of L62-NO between the precursors of the mesoporous and micropores of the SBA-15 structure takes place at the very early stages of the reaction and a continuous depletion of water within the corona-core interface of the micelle was observed. The EPR spectrum of final product show that the majority of NO groups are located in the

micropores and are immobile. In contrast, in the material prepared with L64, practically all the NO groups of L62-NO are located within the silica network and experience a single environment.

EPR Oral Session

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48. *EPR, NMR and ENDOR Study of Extrinsic and Intrinsic Defects in Congruent and Stoichiometric Lithium Niobate.*

Galina Malovichko, Montana State University, EPS 264, Physics Department, Bozeman, Montana 59717, USA; Valentin Grachev, Osnabrück University, Department of Physics, Osnabrück, Germany

Due to specific character of the phase diagram the crystals of Lithium Niobate ($LiNbO_3$, LN) grown by conventional Czochralski way are always Li-deficient, even if the melts have essential Li excess. Different dopants were used for desirable modification of crystal properties; however some observed discrepancies and partial irreproducibility of characteristics were not properly clarified. Essential progress in understanding of LN features was achieved after development of several ways enabling to obtain materials with [Li]/[Nb]≈1 (VTE treatment, double crucible growth, growth with K_2O). Strong mutual dependence of subsystems of extrinsic (impurity) and intrinsic (nonstoichiometric) defects forms the talk topic. Spectra of EPR, NMR, ENDOR, HREM, optical and X-ray data have been analysed for crystals with different compositions, diverse modifiers and various probe impurities. Most of the results show clearly: 1) presence of correlated complexes of intrinsic defects in undoped samples; 2) correlated entering of impurities and charge compensating defects in doped crystals; 3) qualitative difference between structures of the impurity centers substituting for Li or Nb ions in conventional and stoichiometric materials. Crystals with the extremely low concentration of defects offer extraordinary informative opportunities (due to tremendous resolution enhancement), whereas materials of nonstoichiometric composition are especially suitable for tailoring material properties.

EPR Oral Session

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48b. *Role of Iron, Hydrogen Peroxide, and Hydroxyl Radicals in Biological Toxicity — Revisited after 30 Years.*

Balaraman Kalyanaraman, Medical College of Wisconsin

Some 30 years ago, Professor Piette's group proposed that hydroxyl radicals could play a critical role in biological toxicity, triggering lipid peroxidation, protein oxidation, and DNA damage. In one of the first examples of biological spin-trapping, Lai and Piette demonstrated that hydroxyl radicals generated from rat liver microsomes in a reaction involving iron and hydrogen peroxide were actually responsible for lipid peroxidation. Looking back, I perceive this work as a significant advancement in biological ESR. The seminal papers originated from Piette's laboratory have since generated a great deal of excitement in free radical biology. As with all original discoveries, this was challenged, debated and discussed in various national and international meetings in free radical biology. As I fondly recall, the discussions pertaining to this work were often animated, and sometimes argumentative—clearly hallmarks of an exciting and emerging area of science. Some 30 years later, I find myself wondering and confused, perhaps at a slightly higher level, about the same things—iron and hydrogen peroxide and their role in apoptotic cell signaling. In this lecture, following a brief summary of Professor Piette's contributions in this area, I will present a few relevant examples in cellular biology where iron and hydrogen peroxide presumably play a key role in apoptosis (or programmed cell death).

EPR Oral Session

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EPR TUESDAY POSTER SESSIONS A & B **(Posters are listed alphabetically by presenting author, A–I)**

* Identifies recipients of Jules Stein Student Travel Awards † Identifies posters in the session dedicated to Larry Kevan

49. *Stability of the Missing Angle Algorithm For 4D Spectral-Spatial EPR Imaging.*

***** Kang-Hyun Ahn, Benjamin Williams, Howard Halpern, Xiaochuan Pan, University of Chicago, Department of Radiation Oncology and Radiology, Chicago, IL 60637 and the Center for EPR Imaging in Vivo Physiology

For spectral-spatial EPR imaging, the number of data sets needs to be increased to compensate for a decreased SNR as the gradient is increased in amplitude. Missing angle algorithms can significantly reduce the imaging time by iteratively replacing the highest gradient part with

the projection obtained from the data sets of lower gradient.[1] An implementation of the missing angle algorithm for 4D spectral-spatial EPR imaging will be presented. Generally, an iterative method to evaluate the missing projections may be inefficient and highly susceptible to noise if the algebraic system turns out to be ill-conditioned.[2] The use of successive over-relaxation (SOR) and other preconditioning approaches will be explored as remedies for this problem[3]. *Supported by NIH P41RR12257.*

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[3] R. Barrett et al., Templates for the Solution of Linear Systems: Building Blocks for Iterative Methods, SIAM, Philadelphia, 1994 (http://www.netlib.org/templates/Templates.html)

EPR Poster Session

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50. *Substrate-Supported Lipid Nanotubes with Bilayer-like Properties.*

Ali M. Alaouie, Yevgeniy Degtyarev, and Alex I. Smirnov, Department of Chemistry, North Carolina State University

Recently, we have reported formation of nanotubular lipid structures inside aligned through-film rigid nanopores of anodic aluminum oxide (AAO) substrates [1]. Initial high field (HF) EPR experiments with spin-labeled phospholipids indicated that the static order parameter for the phospholipids labeled at the lipid chain position 5 is exceptionally high S≈0.9. Here we describe systematic studies of the lipid nanotube properties carried out with spin-labeling EPR at 9.0 (X-band) and 95 GHz (W-band) as well as microcalorimetry. We have varied the size of nanopores in AAO substrates from ca. 20 nm to over 100 nm by changing etching conditions of fabrication of AAO substrates in our lab. The results of variable-temperature spin-labeling experiments and microcalorimetry measurements demonstrated that the lipid nanotubes composed from either phospholipid DMPC (1,2-dimyristoyl-*sn*-glycero-3-phosphocholine) and DPPC (1,2-dipalmitoyl-*sn*-glycero-3-phosphatidylcholine) have the main phase transition temperature essentially the same as unsupported bilayer. Spin-labeling oxygen accessibility experiments and dynamic order parameter measurements confirmed formations of bilayered structures inside the nanopores. Lipid nanotube arrays prepared in our lab are remarkably stable: without being covalently attached to the surface the nanotubular phospholipid assemblies remained confined to AAO substrates for more than one month period. All this increased our enthusiasm for using our design to build robust lipid nanotube arrays for biochip applications. *The work at NCSU is supported by the DOE Contract DE-FG02-02ER15354 and NATO (both to AIS).*

[1] Smirnov, A. I., Lewis, M. S., and Poluektov, O. G., 44-rd Rocky Mountain Abstract book, Conference on Analytical Chemistry, Denver, CO, July 28- August 1, 2002.

EPR Poster Session

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51. *One-half Wavelength Spaced Tuning Elements for Iris Coupling Structures for Higher Frequency EPR Cavities.*

James R. Anderson, Richard R. Mett and James S. Hyde, Medical College of Wisconsin

Normal Varian-style variable iris coupling structures[1] consist of a coupling hole or slot and an adjustable slug directly in front of the opening. At frequencies above 30 GHz, the structure becomes very compact. The supporting screw mechanisms are small, subject to very small tolerances and have limited adjustment accessibility. In principle, placement of the slug ½ wavelength from the opening would be equivalent, and would solve this problem. Detailed numerical (using Ansoft HFSS) and experimental studies of the coupling structure at 35 GHz with the spacing of the tuning slug approximately ½ wavelength away from the iris slot were carried out. It was found that the correct placement is about ⅝ of a wavelength. The increase from ½ wavelength is attributed to the finite dimensions of the tuning slug as well as the thickness of the coupling hole. This separation provides room for normal sized support and adjustment structures. The tuning slug is re-entrant at this location. This coupling structure has been constructed and evaluated. Design criteria and performance data will be presented showing tuning range, sensitivity of adjustment and stability. Suitable materials for fabrication will be discussed. The structure works well, in our judgment, and we are contemplating its use at higher frequencies.

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EPR Poster Session

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52. *ENDOR Enhancement.*
Andrei V. Astashkin and Arnold M. Raitsimring, University of Arizona

The ENDOR intensity is proportional to the rf pulse spectral width, while the resolution is inversely proportional to it. The optimal observation conditions correspond to the rf pulse spectral width being about equal to the required resolution. In proton ENDOR experiments with orientationally disordered solid samples, for example, even the narrowest features are usually several tenths of a megahertz wide, while for strongly coupled protons the linewidths may be up to several MHz. The optimal duration of the rf pulse then would be no more than 5 μs. At the same time, a typical rf pulse duration used in pulsed ^{1}H ENDOR experiments is on the order of 10 μs, which is determined, for a given resonator design, by the power of the rf amplifier (usually, several hundred Watt). To obtain shorter rf pulses, a more powerful rf amplifier may be used. To decrease the rf pulse length two or three times, the power should be increased four to nine times and reach several kilowatt. Such amplifiers are extremely expensive, and not every magnetic resonance lab can afford them. In this work we suggest a simple solution to increase the rf excitation width based on a more efficient use of the rf power amplifier. This approach employs several rf pulses with different carrier frequencies that can be obtained using two or more rf synthesizers. Since the synthesizers are typically much less expensive than the powerful rf amplifiers, this solution may be attractive to many groups routinely employing pulsed ENDOR in their research, especially if they already have an equipment for TRIPLE experiments. *Supported by NSF DBI-0139459.*

EPR Poster Session
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53. *Divalent Metal Cation Templating in Thermally-Driven Amino Acid Copolymerization.*
Chris Bender, Fordham University

Thermally-driven copolymerization of amino acids is one plausible route that has been proposed for the chemical evolution of protein. Significantly, the amino acid composition of the resultant polymers was non-statistical, which suggests that thermodynamic or kinetic factors might be responsible for the first appearance of what we now call polypeptide motifs, both structural and catalytic. Rationalizing a geochemical influence, thermal copolymerizations of amino acids have been performed in melts of carboxylic acid salts (e.g. ammonium formate), the first consequence of which being the ability to drive the polymerization at significantly lower temperature. The addition of divalent cations such as copper accelerates the polymerization, leading to peptides whose spectroscopic properties are reminiscent of classic proteins.

EPR Poster Session
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54. *Experimental Methods of Double-Quantum Coherence ESR.*
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A new Fourier-Transform ESR spectrometer, tailored for Double-Quantum Coherence (DQC) ESR and 2D-ELDOR, is described. It has an 8-18 GHz tuning range and is used with 10 and 17 GHz high-power TWTAs, where it features multi-kilowatt pulses. It provides π-pulses with a duration of only a few nanoseconds using low-Q dielectric resonators, and with time resolution measured in picoseconds. In addition it provides flexible phase cycling, and a 1 Gsps data capture rate with a signal averaging speed of several tens of kilohertz. The real-time timing system is provided by a dedicated microprocessor and the use of modern components which reduce the system size to less than 1 dm^3. Its extension to a higher working frequency of 35 GHz is also described. The performance is illustrated with applications ranging from short-distance organic biradicals and large biomolecules, such as T4-lysozyme and RNA, using DQC-ESR, to small aligned lipid samples using 2D-ELDOR. *Supported by grants from NIH/NCRR, NIH/GM and NSF.*

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55. *Study of Membrane Proteins by Double-Quantum Coherence ESR: Gramicidin A.*
Peter P. Borbat, Boris Dzikovsky and Jack H. Freed, Cornell University

Double-quantum coherence (DQC) ESR is a method that can be routinely used to report on distances in membrane proteins, which are notoriously difficult to study by other physical methods. A clear-cut example is the study of Gramicidin A dimer formation. Gramicidin A was nitroxide-labeled at its C-terminus and has been studied in multi-bilayer phospholipid dispersions and macroscopically-aligned samples of DPPC and DMPC. Here, DQC was clearly able to establish that in DMPC, Gramicidin A exists mostly in the form of a dimer with a well-defined distance of 30.9 Å between the nitroxides, at the C-termini. This distance may be related to the head-to-head dimerization, as confirmed by molecular modeling. In contrast, this DQC signal, that can be attributed to the dimer, was not observed in DPPC, which has longer acyl chains, providing strong evidence that hydrophobic mismatch strongly suppresses their formation. However, in this latter case, aggregation of Gramicidin A was apparent from the DQC, supporting the data from Atomic Force Microscopy which points to the lateral aggregation of Gramicidin A in several lipid systems. The DMPC/Spin-Labeled-Gramicidin A system was macroscopically-aligned by using the Isopotential Spin Dry Ultracentrifugation (ISDU) technique, and the DQC signal pattern was recorded at several orientations, leading to results that support the conclusions obtained with dispersions. The application of ISDU to DQC distance measurements is also described. *Supported by grants from NIH/NCRR, NIH/GM, and NSF.*

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56. *Conformational Changes in the Rieske Subunit of Cyt bc_1 Complex.*
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The cytochrome bc_1 complex is an important component of mitochondria and many organisms. It couples the flow of electrons in the respiratory chain to the translocation of protons across a membrane. This proton pumping action drives the synthesis of ATP and makes an important contribution to the energetics of the organism. As part of the catalytic cycle, the Rieske iron-sulfur subunit undergoes a large-scale conformational change that moves the 2Fe2S cluster about 1.6 nm to gate the flow of electrons from a two-electron carrier, quinol, to a one electron carrier, cyt *c*. This change can be measured through the orientation of the g-tensor in partially-oriented samples and related to the physical motion through the measured orientation of the g-tensor in the molecular frame. Changes in the g-tensor and the nitrogen hyperfine interaction are produced by interactions with substrate analogs and inhibitors in the catalytic site. The effect of most acceptors are consistent with changes in the ligand-field model for the g-factors. *Supported by NIH GM61904.*

EPR Poster Session
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57. *Metal Binding to Apurinic Endonuclease (APE-1).*
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The apurinic/abasic endonuclease (APE-1) is a magnesium-dependent DNA repair enzyme that cuts the DNA at a site with a missing base as an initial step in the repair of that site. It has also recently been identified as a proofreader for the mistake prone DNA Polymerase-β or Pol-β. We are studying the Mg(II) sites in APE-1 using oxovanadium, VO(II), as an EPR-active probe and correlating that with isothermal titration calorimetry (ITC) measurements. VO(II) titrations show cooperative binding of two oxovanadium ions to apo-APE-1 at two distinct sites in very close proximity. ITC shows sequential binding of two Mg(II) under similar conditions. Mixed metal derivatives of APE-1 have been prepared with VO(II) exclusively in one site and Mg, Ca, Pb or Zn in the other site. HYSCORE on these mixed metal species show that the oxovanadium has at least two nitrogen ligands, including a histidine, that is compatible with the assumed active site. *Supported by OBER, DOE.*

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58. *HYSCORE Lineshapes for I=1 Nuclei with Isotropic Hyperfine and Arbitrary Quadrupolar and Zeeman Interactions.*

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HYSCORE spectra of paramagnetic centers having nuclei of spin I=1 with isotropic hfi and arbitrary NQI consist of ridges having zero width. A parametric representation of these ridges is found. A new approach for the calculation of HYSCORE spectra is presented that does not require calculation of eigenvectors or the Mims matrix, **M**, but is based on spectral decomposition of the Hamiltonian using projection operators. Examples of nitrogen ligands to metals in proteins and small complexes illustrate the ease with which the full nitrogen quadrupole tensor can be determined. *Supported by NIH GM61904.*

EPR Poster Session

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59. *EPR Studies on Nitric Oxide and Ceruloplasmin in Patients with Rheumatoidal Diseases.*

Anna Bratasz, Mariola Koziel, Stanislaw Lukiewicz, Jagiellonian University, Faculty of Biotechnology, Laboratory of Radiospectroscopy of Cancer, 30-387 Krakow; Jolanta Bucka, Cracow Hospital of Rheumatological Diseases; Antoni Skura, Hospital of Joseph Dietel in Cracow

The level of nitric oxide and ceruloplasmin (CP) has been studied in various body fluids and tissues in a variety of pathological states in this laboratory. They included brain, hematological, neoplastic and infectious diseases. This sort of EPR investigations were extended for the first time in 2001 to the field of autoimmune diseases, as presented by Aneta Zajac in her master of science thesis[1]. A continuation of this line of studies may be found in an unpublished master of science thesis, defended at the Jagiellonian University by Mariola Koziel[2] in 2002. The current status of knowledge in this new field appears to deserve a brief recapitulation during this conference. The conclusions are based on the examination of 62 patients. Only 40% of them revealed a detectable amount of NO. In contrast, the EPR signals of ceruloplasmin could be seen in all patients. The intensity of generation of NO was found to depend: 1) on the type of rheumatoidal disease, 2) on the sex of patient – being twice as high in women, 3) on the age of patient – concentration of NO decreasing in parallel with immunity in females, whereas in men it is increasing with age. The intensity of generation of CP was associated: 4) with the type of rheumatoidal disease, 5) with the sex of patient to a small degree, but 6) not with the age of patients, 7) concentration of CP in the synovial fluid was 3 times higher than the amount of NO. The EPR measurements were done at 77 K using Brucker X-band spectrometer. EPR determination of NO and CP content in the synovial fluid seems to be a useful source of information of prognostic value.

[1] Zajac, MSc Thesis, Jagiellonian University, Krakow 2001

[2] Koziel, MSc Thesis, Jagiellonian University, Krakow 2002.

EPR Poster Session

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60. *EPR Monitoring of Chemotherapy in Leukemic Patients.*

Kinga Marciniak, Anna Bratasz, Stanislaw Lukiewicz, Jagiellonian University, Faculty of Biotechnology, Laboratory of Radiospectroscopy of Cancer, 30-387 Kraków; Dorota Krochmalczyk, Aleksander Skotnicki, Hematological Clinic, Kraków, Poland

Previous studies have shown[1] that the level of ceruloplasmin in human body fluids may vary in many pathological states, including hematological diseases. In leukemic patients the amplitude of EPR signals was found to be at least 6 times larger. The absorption lines were about 50% wider, revealing also some difference in the value of the spectroscopic splitting factor. This suggested that the structure of ceruloplasmin in the patients with blood diseases might differ as compared with normal controls. Using EPR spectroscopy, the question has been examined whether the amplitude of ceruloplasmin signals can change as a result of chemotherapy, so that conclusions of a prognostic value could be drawn[2]. The data appear to indicate that the level of ceruloplasmin in leukemic patients is regularly changing in the course of chemotherapy and reaches its maximum in the middle of treatment. Substantial rise in the CP level as a response to chemotherapy is a good prognostic, whereas a poor increase in the amount of CP may mean that the effectiveness of treatment is not satisfactory. Such a view is based on the observation of 30 leukemic patients 15 of which died. Within this latter group 10 patients revealed very high values of CP level. Such extremely elevated levels of CP might probably be considered a warning signal, since many of the patients revealing a very high concentration of CP did not survive. The EPR measurements were done at 77 K using Brucker X-band spectrometer. Further investigations are in progress. They are intended to establish whether EPR parameters describing variations in the level of CP may be used to monitor the progress of chemotherapy.

[1] Bratasz et al., 42nd Rocky Mountain Conf. on Analytical Chem., Broomfield 2000.

[2] Bratasz et al., 5th Symposium Free Radicals in Biology and Medicine, Lodz 2000.

EPR Poster Session

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61. *Measurement of Thiol Levels in Human Ovarian Cancer Cells Treated with Cisplatin.*
Anna Bratasz, Valery V. Khramtsov and Periannan Kuppusamy, The Ohio State University

Ovarian cancer is the second most commonly diagnosed gynecological malignancy and the fourth leading cause of death from cancer among women. The high mortality rate is attributed to the lack of early diagnosis of the malignancy and difficulties encountered during treatment. Cytoreductive surgery is followed by cisplatin+taxol as a chemotherapeutic drug in the standard treatment. However, administration of cisplatin causes development of drug resistance and limits the efficacy of the treatment. Increased concentrations of cellular thiols are implicated in the acquired resistance to cisplatin. This study was conducted to establish the utilization of EPR spectroscopy to determine the cellular thiol levels and to study the involvement of cellular thiols in cisplatin-sensitive (CS) and cisplatin-resistant (CR) human ovarian cancer cells (HOCC). The cells were exposed to cisplatin ± taxol for different times of incubation time and at various doses. An imidazolidine nitroxyl biradical, a thiol-specific EPR probe, was used to determine the cellular thiol concentration. Cisplatin treatment markedly elevated cellular thiol levels in both CS and CR cells. The CR cells showed higher thiol levels than the CS cells upon cisplatin treatment. Treatment of cells with BSO (to deplete cellular GSH) caused a significant reduction in the thiol levels and subsequent cisplatin treatment caused attenuation of the effect of BSO. This study supports the utilization of EPR spectroscopy to measure cellular thiol levels in HOCC and suggests that cisplatin treatment elevates cellular thiol levels, which apparently play a role in the cytotoxic efficacy of the drug.

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62. *Novel EPR Investigations of Molecular Nanomagnets.*
Brant Cage, Stephen Russek, National Institute of Standards and Technology, Boulder CO, 80305; J. Micah North, Naresh Dalal, Dept. of Chemistry, Florida State University, Tallahassee FL, 32306.

Currently, many investigations in magnetic recording and sensing technologies have focused on reducing magnetic structures to smaller dimensions. This is a large part of the impetus behind the synthesis and characterization of magnetic molecules that behave as single-molecule magnetic domains with dimensions of <10 nm. Interesting examples are $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$, or Mn_{12}, and $[Fe_8O_2(OH)_{12}(triazacyclononane)_6]Br_8\cdot 9H_2O$, or Fe_8, both of which behave as large electronic spin, S=10, materials. We will present multi-frequency EPR measurements of molecular nanomagnets, up to ~140 GHz, and describe an EPR experimental setup that utilizes a high power (500 mW) 95 GHz klystron. Novel approaches to W-band cavities and a cost benefit analysis of home built W-band EPR systems will also be described. The goal is to develop high sensitivity measurements of the magnetic properties of molecular nanomagnets capable of detecting single molecular monolayers and measuring the shifts in the anisotropies and g factors due to molecular bonding to substrates.

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63. *Orientation-Selection ESEEM Spectroscopic Characterization of the Structure of the Co^{II}- Product Radical Pair State of Coenzyme B_{12}-Dependent Ethanolamine Deaminase.*
Jeffrey M. Canfield and Kurt Warncke, Emory University

X-band continuous-wave electron paramagnetic resonance (EPR) and 2-pulse electron spin echo envelope modulation (ESEEM) spectroscopies in the disordered solid state at T=6 K are being used to characterize the distances and orientations among the C5' methyl group of 5'-deoxyadenosine, the radical-bearing C2 carbon atom and β-hydrogen atom of the product radical, and the low spin (S=1/2) Co^{II} in cob(II)alamin in the active site of coenzyme B_{12}-dependent ethanolamine deaminase from *Salmonella typhimurium.* Samples are prepared by cryotrapping the Co^{II}-product radical pair intermediate during steady-state enzyme turnover on $^2H_4$-aminoethanol. Under these conditions, the C5' methyl and product radical C-H hydrogen sites are ^2H-labeled. Our approach, which we have used previously to determine the geometry of reactant centers in the Co^{II}-substrate radical pair intermediate[1], exploits the orientation selection created in the EPR spectrum of the biradical by the axial electron-electron dipolar interaction and axial Co^{II} g- and hyperfine tensors. Simulation of the radical (g≈2.0) EPR lineshape yields electron-electron exchange and dipole interaction terms, which are used to calculate the Co^{II}-C2 distance and the dependence of the EPR lineshape on the angle between the electron-electron (Co^{II}-C2) axis and steady magnetic field. The ^2H ESEEM obtained at five magnetic field values across the EPR spectrum displays significant orientation selection in the line shapes of both the C5'-^2H and β-^2H hyperfine couplings. Global ESEEM simulations, weighted by the orientation-dependence of the EPR lineshape, are being performed for the five magnetic fields to specify the C2-to-^2H distances and relative orientations with respect to the Co^{II}-C2 axis. The derived geometry of the reactant centers provides insight into the coordinates for radical migration and hydrogen atom transfer. *Supported by NIH DK54514.*

[1] Canfield and Warncke, J. Phys. Chem. B, 2002, 106, 8831

EPR Poster Session
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64. *X-band EPR Studies of Membrane Proteins Incorporated into Bicelles.*

* Thomas B. Cardon, Tia Dorozonski, Nisreen Nussair and Gary A. Lorigan, Miami University

Our lab is developing new methods for X-band EPR spectroscopy to study the structure, dynamics, and orientation of uniaxially aligned spin-labeled membrane proteins that have been incorporated into model phospholipid bilayered membranes. We have developed a method to magnetically align a highly hydrated (75 mol%) model membrane system that is described as discoidal bilayered micelles or bicelles. Bicelles are composed of a binary mixture of a long-chain phospholipid (which form a disk-shaped bilayer) and a short-chain phospholipid (which packs around and stabilizing the edge of the bilayered disks). These bicelles can be induced to magnetically align with the bicelle normal being parallel or perpendicular to the direction of the magnetic field in the EPR spectrometer by adding strong paramagnetic (Tm^{3+}) or diamagnetic (Dy^{3+}) lanthanide ions, respectively, and raising the temperature from 307 K to 318 K in the presence of a magnetic field strength of 0.64 T. The model pore-forming α-helical membrane peptide, nicotinic acetylcholine receptor (AchR), and a site-directed spin-labeled AchR (SL-AchR) were synthesized and have been incorporated into bicelle samples. To assess whether SL-AchR was successfully incorporated into the bicelle disks, power saturation studies and the accessibility of the spin label to reduction to its EPR-silent hydroxylamine form by ascorbic acid were performed to determine the depth immersion of the spin label within the bilayered membrane. Various bicelle sample compositions and peptide-to-lipid ratios were prepared and studied using various phospholipid membrane spin probes (i.e., cholestane, n-doxyl stearic acids, and SL-AchR). The factors governing the magnetic alignment of bicelle disks with incorporated AchR or SL-AchR will be discussed.

EPR Poster Session

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65. *Modes of Cu(II) Binding in the Prion Protein.*

* Madhuri Chattopadhyay, Colin S. Burns, Glenn L. Millhauser, Christine C. Dunham, William Scott, Dept. of Chemistry and Biochemistry, UC Santa Cruz, CA 95064; Eliah Aronoff-Spencer, Jack Peisach, Gary J. Gerfen, Department of Physiology and Biophysics, Albert Einstein College of Medicine, 1300 Morris Park Avenue, Bronx, New York 10461; Guiseppe Legname, Stanley B. Prusiner, Institute for Neurodegenerative Diseases, UC San Francisco, CA 94143; William Antholine, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee Wisconsin 53226, Marilyn M. Olmstead, Department of Chemistry, University of California, Davis, California 95616.

The prion protein (PrP) has been shown to be the causative agent in a number of diseases in mammals such as scrapie in sheep, BSE in cows and CJD in humans. Very little is understood the physiological function of this protein. Because of its ability to bind Cu(II), PrP has been speculated to act as an extracellular copper sensor, a superoxide-dismutase or a copper transporter *in vivo*. The octarepeat region of this protein consists of four repeats of the sequence PHGGGWGQ, each binding one Cu(II). CW X-band EPR of full-length Syrian Hamster PrP (sHaPrP) and model peptides of the octarepeat region show two prominent modes of Cu(II) binding, each characterized by distinct g_{II} and A_{II} values. One of these, labeled Component 1, consists of Cu(II) bound to the N-1 of the imidazole ring of H, the deprotonated amide nitrogen atoms of the following two glycines and the carbonyl oxygen of the second glycine in the sequence HGGGW of the octarepeat, as demonstrated by ESEEM, S-band EPR, HYSCORE and X-ray crystallography. Very little information could be gleaned about the other mode of Cu(II) binding, labeled Component 2, from peptide studies as the smaller peptides bound to Cu(II) almost exclusively in the Component 1 form. However, blocking the ability of these peptides to adopt a conformation suitable for Component 1 binding of Cu(II) allowed binding exclusively in the Component 2 form. This was achieved by methylating amide nitrogens of the first and second glycines in the peptide HGGGW. We report CW and pulsed EPR studies of the Cu(II) complexes of these methylated peptides which provide the first experimental insight into the ligand environment around Cu(II) in Component 2. We also report the results of our preliminary efforts towards site-specific ^{15}N incorporation in the prion protein by subtiligase-catalyzed ligation of the ^{15}N-labeled N-terminal peptide to recombinant sHaPrP C-terminus. By incorporating ^{15}N glycines site-specifically, we will be able to extend the results of our Cu(II)-binding studies on model peptides to the full-length PrP.

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EPR Poster Session

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66. *Comparative ESR and Catalytic Studies of Ethylene Dimerization on Ni(II)-exchanged Clinoptilolite and Pd(II)-exchanged Clinoptilolite, Mordenite, Ferrierite and SUZ-4.*

† Hosun Choo, Materials Characterization Center, Western Kentucky University, Bowling Green, KY 42101; Suk B. Hong, Department of Chemical Technology, Taejon National University of Technology, Taejon 305-719, Korea; Larry Kevan, Department of Chemistry, University of Houston, Houston, TX 77204.

The formation of monovalent nickel and palladium and their interaction with various adsorbates are studied in channel-type zeolite, clinoptilolite, mordenite, ferrierite and SUZ-4, where Ni(II) and Pd(II) are incorporated into the extraframework sites of these zeolites by liquid-state ion exchange at room temperature. Electron Spin Resorance (ESR) and Electron Spin Echo Modulation (ESEM) spectroscopic methods have been used to deduced the locations and environments of Ni(I) and Pd(I) in these zeolites. The catalytic activity and selectivity for ethylene

dimerization have been investigated using a static reactor and gas chromatography. The catalytic results supported by ESR and ESEM results show that Ni(I) and Pd(I) are active for ethylene dimerization in these channel-type zeolites. The catalytic activity for the formation of n-butenes is dependent on the location and accessibility of active Pd(I) and Ni(I), the structure of the supporting zeolites and the reaction temperature. The mechanism of the formation of n-butenes in NiNaK-Clinoptilolite is different from other materials. Ethylene dimerization occurs in clinoptilolite via direct reduction of Ni(II) by ethylene at high temperature. This catalytic performance of clinoptilolite is also affected by the type of cocations and the amount of nickle ions incorporated into extraframework site of clinoptilolite.

EPR Poster Session

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67. *Spectroscopic Studies on Pounamu or New Zealand Greenstone.*

Cuthbert Wilkins, Bryce Williamson, Craig Tennant, Rod Claridge, University of Canterbury

New Zealand jade has long been prized by the Maori, for whom the name Pounamu carries a deep cultural and spiritual significance. The European term is usually the non-specific "greenstone." Early structural studies identified greenstone as a nephrite mineral. Nephrite occurrences are widespread throughout the world: usually in small and localized lenses associated with ultramafic exposures close to tectonic boundaries. In New Zealand greenstone is principally found in Westland close to the Alpine Fault. Although there has been much work on the formation and properties of nephrite sourced in various parts of the world none had been done on the New Zealand mineral, despite its rich colouring ranging from shades of green and even to black or white, and attractive flecking. This poster gives an overview of a spectroscopic study, utilizing epr, Mössbauer and optical methods, to compare the New Zealand material with occurrences in other parts of the world.

EPR Poster Session

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68. *Speciation of Mn^{2+} in Aqueous Bicarbonate Solutions: Electrochemistry and EPR Study.*

* J. Dasgupta[1], A.M. Tyryshkin[1], Yu.N. Kozlov[2], A.A. Kazakova[2], S.V. Baranov[2], V.V. Klimov[2] & G.C. Dismukes[1*], [1]Princeton University, Department of Chemistry, [2]Institute of Basic Biological Problems, Russian Academy of Sciences.

The complex formation between Mn^{2+} and bicarbonate is crucial to its transport properties and ability to participate in assembly of the Mn_4 core of the Water Oxidizing Complex (WOC) in PSII. We used electrochemistry (EC) and EPR methods to study the speciation of Mn^{2+} in aqueous bicarbonate solution. EC shows that two Mn^{2+}-bicarbonate complexes are formed in solution and have their oxidation potentials E_0= 0.67V and 0.52V. Titration of the Mn^{2+} EPR signal with respect to bicarbonate and Mn^{2+} concentrations reveals that both complexes are mono-Mn^{2+}. Pulsed EPR (^{1}H ENDOR, ^{13}C ESEEM and HYSCORE) were used to characterize the ligand coordination structure of the complexes. The complete (rhombic) ^{13}C hyperfine tensor of $H^{13}CO_3^-$ was determined, establishing that bicarbonate is a mono-dentate ligand to Mn^{2+}. ^{1}H ENDOR shows that 1-2 water ligands are lost upon HCO_3^- binding. The dominant species responsible for the EC oxidation at E_0= 0.52V is formulated to be $Mn^{2+}(HCO_3^-)_2(OH_2)_4$.

EPR Poster Session

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69. *Improving Signal-to-Noise in Pulsed ENDOR and Resolution in Continuous-Wave ENDOR Experiments.*

Peter E. Doan and Brian M. Hoffman, Northwestern University

The strengths and weaknesses of pulsed and continuous-wave ENDOR methods are complimentary: pulsed ENDOR can provide exceptional resolution but suffers from lower S/N than its CW counterpart; CW ENDOR excels in S/N but often suffers from poor resolution. These observations have led us to investigate techniques that can trade off between S/N and resolution, permitting higher S/N in pulsed experiments and higher resolution in CW experiments. The technique we use to increase S/N levels in pulsed ENDOR is extremely robust and exceedingly simple to implement. Increasing the resolution of CW ENDOR spectroscopy has been successful in many samples but the techniques are neither robust nor simple.

EPR Poster Session

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71. *Multifrequency Tests of Nitroxyl Relaxation Mechanisms.*
Rikard Owenius, Garth E. Terry, Sandra S. Eaton and Gareth R. Eaton, University of Denver

The temperature and microwave frequency dependence of T_{1e} for 2,2,6,6-tetramethylpiperidinyl-1-oxy (tempol) doped into a solid host indicated a contribution from a thermally-activated process with an activation energy that is consistent with rotation of the ring methyl groups. We seek to determine the role of methyl rotation in spin lattice relaxation for nitroxyl radicals in fluid solution. Spin lattice relaxation times for natural abundance tempol, tempol-d_{17}, and tempol-^{15}N-d_{17} were measured at 1.9, 3.2, and 9.2 GHz. Mixtures of water and glycerol or water and sorbitol were used to vary solution viscosity. Nitroxyl tumbling correlation times were calculated from peak height ratios and by lineshape simulation using the NLSL software (D. E. Budil, S. Lee, S. Saxena, and J. H. Freed, J. Magn. Reson. A120, 155-189 (1996)) kindly provided by Prof. Budil. Tumbling correlation times were between about 0.1 and 10 ns. The dependence of T_{1e} on tumbling correlation time and on microwave frequency was modeled to determine the relative contributions from ring methyl rotation, from modulation of g and hyperfine anisotropy by molecular tumbling, and from spin rotation. Spin rotation makes a relatively small contribution to T_{1e} at the tumbling correlation times examined in these studies. The contribution to relaxation due to rotation of the ring methyl groups at a rate comparable to the microwave frequency dominates at tumbling correlation times longer than about 2 ns. Deuteration of the nitroxyl and replacement of ^{14}N by ^{15}N decreases the relaxation rates as predicted for samples in which modulation of hyperfine anisotropy contributes to relaxation. At the microwave frequencies studied, modulation of hyperfine anisotropy makes a substantially larger contribution than modulation of g anisotropy. Deuteration of the solvent does not affect T_{1e}, which indicates that electron-nuclear interaction with solvent nuclei does not make a significant contribution to T_{1e} of nitroxyl radicals in this motional regime.

EPR Poster Session
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72. *Large Pulsed Electron-Electron Double Resonance on Multi-Nuclear Metal Clusters: Assignment of Spin Projection Factors Based on the Dipolar Interaction.*
* Celine Elsaesser, Marc Brecht and Robert Bittl, Freie Universität Berlin

The interaction between two paramagnetic metal centers, a $[3Fe\text{-}4S]^+$ cluster and a [NiFe] center, is investigated in the hydrogenase from *Desulfovibrio vulgaris* Miyazaki~F by pulsed ELDOR (electron-electron double resonance). The distance between the metal centers is known from X-ray crystallography.

The experimental dipolar spin-spin coupling deviates from the value expected for two point-dipoles located at the centers of the metal clusters. An extended spin-coupling model accounting for the spin distribution in the $[3Fe\text{-}4S]^+$ cluster yields the observed coupling under the assumption of a particular magnetic coupling scheme for the three Fe ions. These results demonstrate that pulsed ELDOR can be used to gain insight into the inner structure of a multi-nuclear metal cluster.

EPR Poster Session
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73. *Impact of Geometry on Spin Lattice Relaxation for CuN_4 Complexes.*
Alistair Fielding, Gareth R. Eaton,and Sandra S. Eaton, University of Denver

The g values and copper hyperfine splittings in the CW EPR spectra for a series of Cu(II) complexes of pyrrolate-imine complexes with R = H, methyl, n-butyl, tert-butyl, benzyl, diphenylmethyl, 1-adamantyl, and 2-adamantyl and X-ray crystal structures for four of the complexes indicate that the dihedral angle between the ligand planes varies from 0º to 67º (C. M. Wansapura, C. Juyong, J. L. Simpson, D. Szymanski, G. R. Eaton, and S. S. Eaton, J. Coord. Chem, in press). This series of CuN_4 complexes provides the opportunity to examine the effect of changing geometry on spin lattice relaxation. Long-pulse saturation recovery measurements were performed on the complexes in 2:1 toluene:chloroform solution at temperatures between the 10 K and about 140 K. The analysis of the data in terms of contributions from the direct process, the Raman process, and local modes and the geometry-dependence of the coefficients of these processes will be discussed.

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74. *Rectangular Loop-Gap Resonator with the Light Access to the Sample.*
Malgorzata Dutka, Tadeusz Oles and Wojciech Froncisz, Jagiellonian University

A new rectangular geometry of the loop-gap resonator for EPR studies of aqueous samples was presented in our previous publication (Piasecki et al.). In the present work that geometry is slightly modified in order to make the structure more practical and to make provision for the light access to the sample. These modifications as well as the redesigned coupling structure lead to the better thermal and mechanical stability of the resonator. The sensitivity of the resonator for aqueous samples as well as an experimentally tested microwave magnetic field homogeneity will be presented. *Supported by the grant 3 P04A 043 23 from the State Committee for Scientific Research (Poland).*

[1] W. Piasecki, W. Froncisz and W. L. Hubbell, "A Rectangular Loop-gap Resonator for EPR Studies of Aqueous Samples", J. Magn. Reson. 36-43, 134 (1998).

EPR Poster Session

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75. *Determination of Electron-Electron Interspin Distance Between the Spin Label and Fe-NO Radical in Cytochrome c.*
Wojciech Blicharski, Janusz Pyka, Artur Osyczka*, Małgorzata Dutka, Sebastian Szytula, Ryszard J. Gurbiel, Bohdan Turyna, Wojciech Froncisz, Jagiellonian University, Faculty of Biotechnology, Department of Biophysics, 30-387 Kraków, Poland; **Present address*: 1005 Stellar-Chance Laboratories, 422 Curie Boulevard, Department of Biochemistry and Biophysics, School of Medicine, University of Pennsylvania, Philadelphia, PA 19104/6059, USA.

In order to observe possible structural changes of the cytochrome *c* molecule in which one of its native heme iron coordination ligand is replaced by nitric oxide (NO), the electron-electron interspin distance between Fe-NO radical and covalently attached spin label has been estimated using the EPR pulse techniques. Three modified forms of yeast cytochrome *c* were used for these studies: the wild-type protein labeled at naturally occurring C102, and two mutated proteins, S47C and L85C, labeled at positions 47 and 85, respectively (Pyka et al.). Both S47C and L85C were derived from the protein in which C102 had been replaced by threonin. The temperature dependence of the spin relaxation times for the Fe-NO radical center and its influence on the relaxation times of the spin label have been measured. Those results were used to estimate the distance between the Fe-NO center and spin label for all three mutated proteins. The estimated distances were compared with the results of molecular dynamics simulations. It was observed that the experimentally determined distances are slightly bigger than those obtained from molecular dynamics simulations. The observed differences very likely arise from the structural changes in cytochrome *c* induced upon binding of the NO molecule. *Supported by the grant 3 P04A 043 23 from the State Committee for Scientific Research (Poland).*

[1] Pyka et al., Acta Biochim. Pol., 1999, 46, 889.

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76. *Digital Receiver for EPR Spectroscopy.*
Jerzy Koziol, Malgorzata Dutka, Ryszard J. Gurbiel and Wojciech Froncisz, Jagiellonian University

Digitalization of the analog EPR signal as close as possible to its source is very advantageous. The most attractive benefit of this approach is a minimization of the signal distortion. This feature is especially important for the multi-quantum EPR spectroscopy in which the useful signal is generated by the nonlinearity of the spin system. Therefore, any distortions of the receiving tract of the spectrometer cause severe instability of the baseline. In the present work we describe a prototype of the digital receiver that can sample an EPR signal at the rate up to 800 MHz. Its input analog bandwidth approaches 2,2 GHz. The digitized EPR signal is averaged in real time by the field programmable gate array and then sent to the DSP processor. Finally it arrives at the PC memory for storing, visualization and farther processing if necessary. The digital receiver is intended to be used for the CW EPR spectroscopy with the magnetic field modulation, MQ EPR spectroscopy or for pulse EPR spectroscopy. *Supported by a grant TECHNE Nr 8/2002 from The Foundation for Polish Science.*

EPR Poster Session

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77. *EPR Studies of Interactions of Cytochromes c with their Physiological Partners.*

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Cytochromes *c* are electron transfer proteins localized in the intermembrane space of mitochondria. They function as the mobile electron carriers between the cytochrome bc_1 complex and cytochrome *c* oxidase. Although it is known that cytochrome *c* docks to either physiological partner via electrostatic interactions, the whole mechanism of this process is not fully understood. In the present study, the complex formation between spin-labeled cytochromes *c* and their either partner is monitored using an EPR spectroscopy. Cytochromes from different sources are employed: horse heart cytochrome *c* modified with the lysine-specific spin label (succinimidyl-2,2,5,5-tetra-methyl-3-pyrroline-1-oxyl-carboxylate) (Turyna et al.), and site-directed mutants of iso-1-cytochrome *c* from *Saccharomyces cerevisiae* (2) and bacterial cytochrome c_2 from *Rhodobacter capsulatus* modified with cysteine specific spin label ((1-oxyl-2,2,5,5-tetramethyl-Δ^3-pyrroline-3-methyl)-methanethiosulfonate). The EPR spectra of unbound spin-labeled cytochromes *c* are compared to those of spin-labeled cytochromes *c* bound to either cytochrome bc_1 complex or cytochrome *c* oxidase. Also, the ionic strength dependence and the reversibility of complex formation are analyzed. *Supported by the grant 3 P04A 043 23 from the State Committee for Scientific Research (Poland).*

[1] Turyna et al., Biochem. Biophys. Acta, 1998, 1386, 50.

[2] Pyka et al., Acta Biochim. Pol., 1999, 46, 889.

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78. *Transport and Metabolism of Glycosilated Spin Probes in Escherichia Coli.*

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Sugars are absolute sources of energy for organisms, and all viable cells possess transport and metabolism systems for various sugars. It is therefore natural to expect that glycosidation can confer new functions on spin probes by modulating their cell transport and metabolism properties. Indeed, in a pioneering work by Struve and McConnel (*Biochem. Biophys. Res. Commun*. **1972**, 49, 1631–1637), it was reported that 4-galactosyloxy-TEMPO (Gal-TEMPO) is transported into *Escherichia coli* cells via a distinct transporter, galactoside permease (LacY). However, no further studies seem to be carried out after that. Furthermore, transport and metabolism of commonly used non-glycosidated spin probes are still not completely understood. In this study, we investigated transport and metabolism of spin probes in *E. coli* cells with the aim to elucidate fundamental properties of them and to examine whether there are differences between glycosidated and non-glycosidated probes. Two glycosidated spin probes, 4-glucosyloxy-TEMPO (Glc-TEMPO), Gal-TEMPO, and four non-glycosidated spin probes, TEMPO, 4-oxo-TEMPO (TEMPONE), 4-hydroxy-TEMPO (TEMPOL), and carbamoyl-PROXYL, were examined. *E. coli* cells incubated for 1 h in a 1 mM spin probe solution were centrifuged and washed thoroughly with PBS. EPR measurements of the *E. coli* cells (with $K_3Fe(CN)_6$ added) showed a remarkable difference in the EPR signal intensity between the glycosidated probes (15–20 μM/cell) and the non-glycosidated probes (< 3 μM/cell). This suggests an advantage of glycosidated probes in transport into cells. Effects of the glycosidation on the cellular reduction of spin probes were also investigated, and the results will be also presented.

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79. *Distribution of the Microwave Magnetic Field in the Ferroelectric Resonators for EPR Experiments.*

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Earlier it was shown a significant improvement (in 5-50 times) of EPR sensitivity by using ferroelectric resonator (FR) inserts of different types.[1,2] For introducing the samples, the hole was drilled through the resonator with an axis aligned with the axis of the FR. Microwave coupling is achieved by placing the FR into the center of a standard cylindrical TE_{011} cavity. Here we present an optimized geometry of the FR. To develop optimization criteria we obtained the distribution of the microwave magnetic field in the FR. The field computations were made for two types of cylindrical FR from single-crystal potassium tantalate - with hollow sample hole and with 'dead-end' sample hole. In the calculations we assume that a ferroelectric resonator has the "magnetic" walls along any axis. We also consider a FR as an *open* resonant structure. The computation starts with the Helmholtz equation (quasi-stationary oscillations) and is based on the single-wave approximation of the fields in the partial regions formed by the coordinate surfaces of the FR. Since the EPR signal intensity in this case is proportional to the microwave magnetic field on the sample, the main attention was paid to the H-field distributions. The results indicate that sample hole affects

enough on the H-field component: 1) the smaller sample hole diameter, the higher H-field value; 2) the depth of the sample hole ('dead-end' type) plays an important role in the efficiency of the FR and its optimized value equals the half of the length of the FR. The theoretical and experimental results are in good agreement.

[1] Geifman, I.N. et al. *Ferroelectrics* **234**, 81-88 (1999).

[2] Geifman, I.N. et al. *Technical Physics* **45**, 263-266 (2000).

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80. *Intramolecular or Intermolecular Reactions Between a Phosphinine and Its Radical Anion: DFT Calculations and EPR Spectra.*

M. Geoffroy, L. Cataldo, S. Choua , C. Dutan, University of Geneva, Department of Physical Chemistry, Geneva , Switzerland; P. Le Floch, N. Mézailles, Audrey Moores, Ecole Polytechnique, Palaiseau, France.

Phosphinine — a benzene ring in which a C-H group has been substituted by a phosphorus atom — posses a low energy π^* orbital which facilitates the formation of the corresponding radical anion. Monophosphinine **1**, which contains two silyl groups in *ortho* positions and a phenyl ring in *meta* position, has been reduced by reaction with Na naphthalenide or with a potassium mirror. The resulting EPR spectra are very sensitive to temperature. Above 200 K, they exhibit ^{31}P and ^{1}H isotropic couplings which agree with DFT calculations on $\mathbf{1}^{\bullet-}$. The calculated tensors, however, clearly indicate that some of the lines recorded on the frozen solution spectrum result from the reaction between $\mathbf{1}^{\bullet-}$ and **1**. In this species the unpaired electron is located in a bonding orbital formed by the overlap of two phosphorus p-orbitals. The temperature effects are reversible. Molecule (**2**) contains two monophosphinines **1** linked by a $SiMe_2$ group. Its reduction on a K mirror at 240K reveals the presence of both a radical anion localized on only one phosphinine ring and a radical resulting from the intramolecular formation of a one-electron P-P bond. With Na naphthalenide, only this last species is formed. In both cases, only the species resulting from the reaction of the phosphinine radical anion with a neutral phosphinine is observed on the frozen solution spectrum. These interpretations are confirmed by DFT calculated ^{31}P tensors. They show that interaction between phosphinines and their radical anions lead to a form of auto-organization when the temperature decreases.

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81. *The Structure of the iSH2 Domain of Class Ia PI-3 Kinase Determined by Site Directed Spin Labeling EPR and Homology Modeling.*

Eliah Aronoff-Spencer,[1] Zheng Fu,[2] Jonathan M. Backer[2] and Gary J. Gerfen[1] [1]Department of Physiology and Biophysics, [2]Department of Molecular Pharmacology, Albert Einstein College of Medicine of Yeshiva University, 1300 Morris Park Avenue, Bronx, NY 10461.

Phosphoinositide-3 (PI-3) kinases catalyze the phosphorylation of the D3 position of the inositol ring of PI and its phosphorylated derivatives and play important roles in many intracellular signal transducing pathways. Class Ia PI 3-kinases contain distinct regulatory (p85) and catalytic (p110) subunits. p110 is stabilized and inhibited by constitutive association with p85, and is disinhibited when the SH2 domains of p85 bind to tyrosyl-phosphorylated proteins. Since the two subunits do not dissociate, disinhibition of p110 presumably occurs by an allosteric mechanism. To explore the means by which p85 regulates the activity of p110, structures of the inter-SH2 (iSH2) domain of p85 were determined with and without phosphopeptide using a combination of site directed spin labeling electron paramagnetic resonance (SDSL-EPR) and homology modeling and molecular dynamics. The iSH2 domain is assigned as a rigid anti-parallel coiled-coil whose primary function is to bind p110, facilitating inhibition of p110 by the amino-terminal-SH2 (nSH2) domain of p85.

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82. *Overmoded Cavity Resonators for Use in High Frequency EPR Spectroscopy.*

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Overmoded cavity resonators were designed and constructed for use in Continuous Wave High Frequency (CW HF) EPR spectroscopy using a reflection spectrometer. Under certain experimental conditions, overmoded cavity resonators offer three potential advantages over fundamental mode cavities and/or Fabry-Perot resonators: 1) low B_1 density over the sample, allowing larger incident microwave powers to be used before the onset of saturation effects (relative to fundamental mode cavities); 2) high value of the maximum filling factor (relative to fundamental mode cavities); 3) large sample volumes with geometries that facilitate the preparation and handling of samples, particularly using Rapid Freeze Quench techniques (relative to fundamental mode and Fabry-Perot resonators). The overmoded cavities described here are of

cylindrical shape and designed primarily to resonate in the TE_{11N} mode. The external B_0 field is parallel to the resonator cylindrical axis and therefore the cross B_1 field is active for EPR. The internal resonator diameter and length are 5.0 mm and 17 – 25 mm, respectively, and the EPR sample maximum diameter and length are 4.5 mm and 10 mm, respectively. The optimal size of a frozen aqueous solution EPR sample (at a temperature of 10K) is 4.0 mm diameter and 4.2 mm length. Distorting saturation effects (also at 10K) occur at powers ~15 dB higher than for fundamental TE_{011} cylindrical resonators. The maximum concentration sensitivity of the overmoded resonator with a frozen aqueous solution sample at 10K is approximately 30 times that of the TE_{011} cylindrical resonator. The design and construction of the overmoded resonator together with its application in CW HF EPR experiments will be presented.

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83. *Analysis of the Tuning and Operation of Reflection Resonator EPR Spectrometers.*

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This paper investigates basic characteristics of the electron paramagnetic resonance (EPR) signal obtained from spectrometers employing reflection resonators. General equations are presented which reveal the phase and amplitude dependence on instrumental parameters of both components of the continuous wave (CW) EPR signal (absorption and dispersion). New phase vector diagrams derived from these general equations are presented for the analysis of the EPR response. The dependence of the phase and absolute value of the CW EPR signal on the local oscillator (LO) phase and on resonator offset and coupling is presented and analyzed. The EPR spectrometer tuning procedures for both balanced and unbalanced heterodyne receivers are analyzed in detail using the new phase diagrams. Extraneous signals at the RF input of the microwave receiver (resulting from circulator leakage and reflections in the resonator transmission line) have been taken into account and analyzed. It is shown that a final tuning condition that corresponds to an extremum of the receiver output as a function of the resonator frequency is necessary and sufficient for the acquisition of pure absorption signal. This condition is universal: it applies to all spectrometer configurations in all frequency ranges. High Frequency EPR spectrometer (130 GHz) data are used to generate experimental phase diagrams that illustrate the theoretical concepts presented in the paper. Conditions are presented under which the absorption signal can be measured with complete suppression of the dispersion, independent of the mutual frequency offset between the microwave source and the EPR sample resonator. Equations describing the approximate relationship between changes of the resonator properties (Q-factor and frequency) and paramagnetic susceptibility are derived and analyzed.

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84. *EPR and ENDOR of Chromium in Li-deficient and Li-rich Lithium Niobate Crystals.*

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Observed difference of coloration and optical spectra of Li-deficient and Li-rich lithium niobate crystals doped with chromium was clarified with the help of the EPR and ENDOR. Li-deficient crystals (including conventional congruent ones) contain always great number of intrinsic defects (Li and Nb vacancies, antisite ions). This facilitates entering crystals for trivalent impurities like chromium, since proper charge compensator can be easily found among intrinsic defects. Our EPR and ENDOR study has shown that chromium in Li-deficient crystals substitutes for Li and creates a family of similar centers with the crystal field splitting about 0.7-0.8 cm^{-1}. Dominating axial center has no intrinsic defects in the nearest neighborhood (distant charge compensation of the positive charge excess), whereas other satellite centers have low C_1 symmetry due to the presence of cation vacancies. In the crystals of stoichiometric or very close to stoichiometric Li-rich composition the new axial chromium centers with the crystal field splitting 0.043 cm^{-1} were found. These centers are randomly distributed over the crystal and are not associated in the complexes with the old centres. The ENDOR spectra have shown that they have completely different structure in comparison with the centres in the crystals of non-stoichiometric composition. In Li-rich crystals trivalent chromium ions substitute for Nb and the positive charge deficit is compensated by incorporated hydrogen ions (protons which are located in one of 6 possible O – O bonds) or by additional Li ions. They also create a family due to different possible location of the charge compensator. A comparison of the EPR/ENDOR and optical spectra for Li-deficient and Li-rich crystals helped us to make reliable identification of optical absorption bands.

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85. *Acqiris Averager: Application to FT-EPR.*

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The Acqiris AP200 board has been incorporated into a pulse EPR-oriented acquisition system developed at ETH-Hönggerberg in the Physical Chemistry Laboratory. The system is controlled via the SpecMan program (see www.esr.ethz.ch) which was developed in collaboration with Weizmann Institute of Science. The capabilities of the system will be illustrated with FT-EPR of the phenalenyl radical in solution at X-band.

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86. *Folding of Spin-labeled T4 Lysozyme in the Time Regime from 50 Microseconds to 10 Seconds as Elucidated by Dielectric Resonator-Based Flow and Stopped-Flow EPR.*

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We are probing the folding of T4 lysozyme from the initial compacting of the chain, to establishment of tertiary interactions, and to the final folded conformation. Our initial work has focused on a bi-labeled cysteine-directed mutant of T4 lysozyme where the labeling sites E22C and Q141C are distant in sequence and belong to different folding subdomains but are close to each other in the final folded protein. Continuous wave electron paramagnetic resonance spectroscopy has shown that the nitroxides of the labeled side chains are less than 10 Å distant (Mchaourab et al., 1997 *Biochemistry* **36**, 3017-3016). To determine the kinetics of protein folding above ten milliseconds at a single field, we have used a dielectric-resonator grid mixer probe similar in design to that reported by Sienkiewicz et al. (1994 *Rev. Sci. Inst.* **65**, 68-74). For more rapid submillisecond observation, a ball mixer dielectric-resonator flow system (Grigoryants et al., 2000 *Biophys. J*. **78**, 2702-2708) was used both at a single field and with rapid magnetic field scan to obtain entire time-evolved spectra. Details of the ball mixer, the resonant structure, and the field sweep/data gathering will be presented. Evidence for prefolding and compacting shown by a diminished EPR derivative intensity was found on the 50 microsecond time scale. Folding to the final conformation occurred within several hundred milliseconds after the start of folding. We are currently investigating the time scale for the onset of the dipolar interaction between the E22C and Q141C side chains, where dipolar broadening will show establishment of tertiary interactions across the active site.

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87. *Scaling of EPR Spectra-spatial Images With Size of Sample: Images of Samples Greater Than 5 cm in Linear Dimension.*

Chad R. Haney, Kazuhiro Ichikawa, V.S. Subramanian, Colin Mailer, Eugene D. Barth, Benjamin F. Williams and Howard J. Halpern, University of Chicago

We have recently fully implemented a new much larger EPR imaging spectrometer than that from which most of the work from our laboratory has come. The main magnetic field of this imager has a sphere of 30 ppm uniformity of approximately 15 cm. Low inductance allows rapid scanning. This imager allows us to begin to answer questions that are crucial for the application of EPR imaging to in vivo systems larger than small rodents: how does spatial and linewidth resolution scale for larger specimens? Preliminary images of a homogeneous phantom 4.5 cm in diameter and 6 cm in length demonstrate that images obtained with B_1 equivalent to that used in the smaller imager gives linewidth resolution similar to that of the smaller system. A forty minute image in both systems gives voxel linewidth population distributions of width ~ 0.2 microtesla (2 mG). Spatial resolution appears to have modest degradation. We will display images obtained from both homogeneous and heterogeneous phantoms to demonstrate the effect of the object enlargement on spatial and spectral resolution. We will show the results of the scan of parameter space optimization on the larger image. We will demonstrate the use of the homogeneous phantom to map the magnetic field of the magnet. *Support in part by DAMD17-02-1-0034 and NIH P41 RR12257 is gratefully acknowledged.*

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88. *Reduction of Image Artifacts by Bladder Flushing with a Novel Double Lumen Urethral Catheter.* Chad R. Haney, Kazuhiro Ichikawa, Adrian Parasca, Benjamin B. Williams, Eugene D. Barth, Martyna Elas and Howard J. Halpern, University of Chicago

The triarylmethyl spin probe (OX063) developed by Nycomed Inovations (Malmo, Sweden) is useful as a narrow spin probe for *in vivo* imaging. However, the accumulation of spin probe in the bladder creates a tremendous source of signal, often greater than that of the tumor due to self broadening, not the broadening by oxygen (the desired measurement). Due to the paucity of methods available for a non-invasive, MRI/EPRI friendly procedure for flushing a mouse bladder, a novel double lumen urethral catheter was developed. Using a standard 20 gauge IV catheter (1.1 mm ID, Introcan Safety IV Catheter, B. Braun Medical Inc., Bethlehem, PA) with a rubber tube extension, PE10 tubing (0.28 mm ID, 0.61 mm OD, Clay Adams INTRAMEDIC Polyethylene, BD Franklin Lakes, NJ) was threaded into the IV catheter and the PE10 was stretched such that it is able to curl within the bladder. Using a Harvard 22 syringe pump, (Harvard Apparatus, Inc., Holliston, MA), water at 15 mL/hr was infused into the bladder via the PE10 tubing. The effluent from the bladder exits the 20 gauge catheter. Further refinement maybe necessary, e.g. the placement of the catheter such that it does not get impinged against the wall of the bladder is critical. However, the double lumen urethral catheter provides a substantial reduction in artifacts when compared to images taken without bladder flushing. The artifacts generated by the large bladder signal are demonstrated using phantoms. The reduction of bladder signal artifacts are shown *in vivo* using mice with PC3 tumors. *This work was supported by grants P41RR12257 (NIH) and DAMD17-02-1-0034 (DOD).*

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89. *Structural Characterization of the Mo(V) High-g Unsplit Species from Rhodobacter Capsulatus Dimethylsulfoxide Reductase and its Role in Catalysis.* Graeme R. Hanson[1,2], Ian lane[1,2,3], Christopher J. Noble[1,2], Alastair G. McEwan[1,3] and Neil Benson[4] [1]Centre for Metals in Biology, [2]Centre for Magnetic Resonance, [3]School of Molecular and Microbial Sciences, The University of Queensland, St. Lucia, 4072 Queensland, Australia, [4]School of Biological Sciences, The University of East Anglia.

Dimethyl sulfoxide reductase of *Rhodobacter capsulatus* contains a *bis*(molybdopterin guanine dinucleotide) molybdenum cofactor (*bis*-MGD-Mo) and can reduce dimethylsulfoxide to dimethylsulfide and trimethylamine-N-oxide to trimethylamine. Tryptophan-116 forms a hydrogen bond with the single oxo ligand coordinated to the molybdenum ion. Optical and EPR redox potentiometric titrations identified a single Mo(V) species, the high-g unsplit species with Mo(VI/V) and Mo(V/IV) redox potentials of +155, +60 mV at pH 8.0 with respect to the standard hydrogen elecrode. Multifrequency EPR studies of the ^{95}Mo enriched enzyme allowed the accurate determination of the ^{95}Mo hyperfine matrix which in conjunction with the g matrix from computer simulation of the native enzyme, shows that the unpaired electron is in a predominantly $|z^2>$ based molecular orbital. Orientation selective HYSCORE measurements reveal the presence of proton and nitrogen hyperfine coupling arising from coupling of the unpaired electron with the proton and nitrogen on tryptophan-116.

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90. *CW and Pulsed EPR Spectroscopy Reveal a New Structural Motif for the Active Site Mo Centre and an Unusual [4Fe-4S]$^{+}$ Cluster in Dimethylsulfide Dehydrogenase.*
Graeme R. Hanson[1,2], Christopher J. Noble[1,2], Christopher McDevitt[1,3], Alastair G. McEwan[1,3] [1]*Centre for Metals in Biology,* [2]*Centre for Magnetic Resonance and* [3]*School of Molecular and Microbial Sciences, The University of Queensland, St. Lucia, 4072 Queensland, Australia*

Variable temperature CW EPR spectroscopy has identified multiple redox centres (Mo(V), [3Fe-4S]$^{+}$, [4Fe-4S]$^{+}$) in 'as isolated' dimethylsulfide dehydrogenase (DMSDH)[1]. A pH dependent EPR study of the Mo(V) centre in $^{1}H_2O$ and $^{2}H_2O$ reveals the presence of three Mo(V) species in equilibrium, Mo(V)-OH_2 (predominates between pH 6 and 8.2), Mo(V)-X (X, probably Cl^-) and Mo(V)-OH. Comparison of the rhombicity and anisotropy parameters for these species with Mo(V) centres in other molybdoenzymes showed that they were most similar to the low pH nitrite species from *E. coli* nitrate reductase (NarGHI). Phylogenetic studies have shown that DMSDH, selenate reductase and NarGHI form a distinct class (Clade 2) of oxomolybdenum enzymes within the dimethylsulfoxide reductase family.[2] Whilst CW EPR studies have shown that the Mo ion is coordinated by 4-thiolate sulfur atoms from two pterins, and an aqua ligand, sequence homology suggests the protein side chain is either Ser195, Thr214, or His220. Orientation selective pulsed HYSCORE spectra show unambiguously that His220 is ligated to the Mo ion. This represents the first example of an oxomolybdenum enzyme with Histidine (nitrogen) coordination.

A [4Fe-4S]$^{+}$ cluster with an unusual g matrix (2.0158, 1.8870, 1.8620) which was very similar to that found for the minor conformation of Centre 1 in NarH has also been identified.[3] The two conformers in NarH may arise from an equilibrium involving the coordination/dissociation of a fifth ligating atom (N or O) to an Fe atom in the cluster. The minor conformer corresponds to the cluster in which the fifth ligand is coordinated.

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91. *A Quasioptical, High Power Pulsed ESR Spectrometer at 95 GHz.*

Wulf Hofbauer, Curt R. Dunnam, Keith A. Earle and Jack H. Freed, Cornell University

Most pulsed HF/HF spectrometers suffer from low output power and significant power losses in conventional waveguides at mm-wave frequencies, resulting in severely limited bandwidth. High bandwidth is, however, essential for correlation experiments that yield dynamic information about the sample such as COSY and 2D-ELDOR[1]. We present a high power pulsed ESR, polarization coded induction mode spectrometer at 95 GHz. A commercial 95 GHz superheterodyne transceiver (ELVA-1, Russia) is used to generate phase agile, short, 90 mW pulses. An extended interaction klystron (CPI, Canada) amplifies the mm-wave power to 1 kW, and quasioptical techniques are used to minimize path losses on the way to/from the Fabry-Pérot type resonator. A new technique for creating mm-wave mirrors with variable reflectivities has been developed to implement a diffraction-controlled, compact coupling mechanism. With this setup, we achieve $\pi/2$ pulse durations of less than 5 ns. Using real-time averaging digitizers (Acqiris, Switzerland), fully phase-cycled 2D experiments on spin labels at physiological temperatures can be performed in less than a minute. We thank Peter Borbat for help with the timing system and the ELVA-1 specifications. Funding by NIH/NRCC is gratefully acknowledged.

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92. *Photoinduced Higher Oxidation States in Manganese Dimers Aimed at Modelling the Water Oxidizing Complex in Photosystem II.*

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We have synthesised a manganese dimer, in which each Mn atom has a N_2O_4 ligand sphere. This complex serves as a model for the oxygen evolving Mn-complex in Photosystem II (PSII), and has been studied by EPR spectroscopy. We found that the Mn dimer together with RuII$(bpy)_3$ as a photo-sensitizer, and Cobalt(III)-chloropentaamin-chlorid (Co(III))as an electron acceptor in solution, are capable of undergoing light-induced electron transfer (ET) from the Mn dimer to Co(III) via $Ru^{III}(bpy)_3$, in a 50:50 water:acetonitrile solution. We then observe an EPR signal from the $Mn_2^{III/IV}$ state with typical hyperfine structure. When the mixture is exposed to even more light, the $Mn_2^{III/IV}$ decreases, due to oxidation of $Mn_2I^{II/IV}$ to $Mn_2^{IV/IV}$, which is EPR silent. To probe the $Mn_2^{IV/IV}$ we have used ascorbate as a reductant, which reduces the $Mn_2^{IV/IV}$ back to $Mn_2^{III/IV}$. Reduction of $Mn_2^{III/IV}$ with ascorbate results in a decrease of the EPR signal without any appearance of new signals. If the manganese dimer gets oxidised too far, beyond $Mn_2^{IV/IV}$, the complex is destroyed and is not possible to reduce with ascorbate. Oxidizing the Mn-dimer to higher oxidation states with light has high relevance for our work towards biomimicking models of the Mn cluster in the Oxygen Evolving Complex in PS II.

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93. *Discrete Approach of High Spatial Resolution Multi-Site EPR Oximetry.*

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A method for data analysis that enhances the spatial resolution of multi-site EPR oximetry[1] was reported previously[2]. It is based on the use of magnetic field gradients with the same direction but different magnitudes, uses a convolution-based fitting algorithm to derive the line width of each individual peak of the EPR spectrum, and corrects distortions of lineshape by the gradient. However, this method is applicable only for particulate materials whose EPR spectra can be approximated by a Lorentzian or a superposition of Lorentzian functions. Unfortunately, some

useful oxygen sensitive materials, such as wood chars, have more complex spectra. To enhance the utilization of this method we have developed a discrete approach and software that makes it feasible to apply HSR MS EPR oximetry to any oxygen sensitive material. The material is calibrated by obtaining spectra of the material immersed in water at different oxygen tensions (pO_2) in the expected range with steps of the desired accuracy in the pO_2 measurements, e.g. ten spectra $S(B)_J$ at pO_2=16, 17,…, 25 mmHg could provide 3% accuracy for pO_2=20mmHg in rat muscle. Two EPR spectra in vivo of the implant $^1S(B)$ and $^2S(B)$ are taken at two gradients with the same direction but different magnitudes, $(\text{grad } B)_2 > (\text{grad } B)_1$. In order to keep the same projection function the re-scaled spectrum $^2S(B')$ is derived by multiplying $(B-B_0)*(\text{grad } B)_1/(\text{grad } B)_2$ of the spectrum $^2S(B)$. The best spectrum from the set of calibrations is chosen using a fitting procedure in discrete Fourier space by minimizing the operator: $\chi = \Sigma \left| \{^1S\} \bullet \{S'_J\} - \{^2S'\} \bullet \{S_J\} \right|$ where parentheses denote discrete Fourier transforms, superscripts 1 & 2 and apostrophe denote the spectra at two field gradients applied and re-scaled spectra respectively, subscript J denotes calibration spectra, and the dots symbolizes simple multiplication of arrays. The algorithm and software were successfully tested using EMS charcoal implanted in rat muscle.

[1] A.I. Smirnov, et al., Magn. Reson. Med., 1993, 30:213-220.

[2] O.Y. Grinberg et al., J. Magn. Reson., 2001, 152:247-258.

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94. *Anisotropy of Rotation of 2,2,6,6-tetramethyl piperidine 1-oxide in the Vicinity of the Nematic-to-Isotropic Phase Transition of 4-n-pentyl-4'-cyanobiphenyl.*

Jimmy S. Hwang and Ghassan A. Oweimreen, King Fahd University of Petroleum & Minerals

An EPR line shape simulation for nitroxide spin probes in the motional narrowing region was carried out assuming axially symmetric ***g*** and ***A*** tensors and using different anisotropies of rotation N ($= R_{||}/R_{\perp}$) where $R_{||}$ and $R_{\perp}$ are, respectively, elements of the diffusion tensor along and perpendicular to its principal axis z'. Each of three cases $z' = x$, $z' = y$ and $z' = z$, which result from cyclic permutations of the molecular axes x, y and z with the z', y' and x' axes of the diffusion tensor, yields its typical EPR spectrum that is characterized by the relative intensities of the low-, center- and high-field lines. A parameter δ defined by and calculable from the intensities of the three lines was found to vary linearly with N for the $z' = x$ and $z' = y$ cases and, as anticipated, to be practically constant at a value of 1 for the $z' = z$ case. This suggested a method for estimating N for a probe from its EPR spectrum. Experimental spectra over a narrow temperature range (1 °C) in the vicinity of the nematic-to-isotropic transition (≈ 34.6 °C) of *N*-(4-*n* butylbenzilidene) 4-amino 2,2,6,6-tetramethyl piperidine 1-oxide (BBTMPO) at a mole fraction of 9.89×10^{-4} in 4-*n*-pentyl-4'-cyanobiphenyl (5CB) showed a pattern of peak heights characteristic of the $z' = x$ case with δ values that gave rise to higher and lower N values in the nematic and isotropic regions respectively. Analysis of other similar systems in the literature gave similar results. *Supported by King Fahd University of Petroleum & Minerals, Department of Chemistry, Dhahran 31261, Saudi Arabia.*

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95. *Modeling Spin Trapped Superoxide Adducts of 5-substituted-5-methyl-1-pyrroline N-oxide; Evidence Against Hydrogen Splitting.*

Kazuhiro Ichikawa[1,2], Chad R. Haney[1,2], Eugene D. Barth[1,2], Adrian Parasca[1,2], Colin Mailer[1,2], Bruce H. Robinson[3], Howard J. Halpern[1,2], and Gerald M. Rosen[1,4] [1]Department of Radiation and Cellular Oncology, The University of Chicago, IL 60637 [2]Center for Low Frequency EPR Imaging for *In Vivo* Physiology, The University of Chicago, IL 60637 and University of Maryland, Baltimore, Baltimore, MD 21201 [3]Department of Chemistry, University of Washington, Seattle, Washington, 98195 [4]Department of Pharmaceutical Sciences, University of Maryland School of Pharmacy, Baltimore, MD 21201, and Medical Biotechnology Center, University of Maryland Biotechnology Institute, Baltimore, MD 21201

Nitroxides, derived from the reaction of superoxide with 5-substituted-5-methyl-1-pyrroline N-oxide analogues where substituted=methyl, tert-butyl ester, and methyl ester, show 12-line EPR spectra at X-band. The standard interpretation of these spectra attributes the lines to nuclear hyperfine splittings from a spin 1 nitogen, a triplet with a_N~14.5 G, a β-hydrogen with $a_{H\beta}$~11.5 G and an γ-hydrogen giving a final small splitting of~1.2 G. The origin of the single γ-H splitting is uncertain, since there are two Hs at the 3-position and also two equivalent Hs at position 4. A mathematical fitting program developed recently [1], makes it possible to fit composite spectra of multiple radical species with their hyperfine splitting models. In the present study, these nitroxides were generated using xanthine/xanthine oxidase as a source of superoxide. Spectra were fit with this new program. In addition to the γ-H origin of the approximate 1.2 G splitting the following hypotheses for these nitroxides were tested: two isomeric species having the same or different a) g-values, b) line width, c) H- and N- hyperfine splittings or d) populations. The fitting was much better assuming different populations of two species and adequate assuming the same population with different g-values and line widths. If equal populations and line widths were assumed for two species, similar to γ-H splitting model, fitting was much worse, which supports the model by which spectra consists of two isomeric species. From these data it is implied that the EPR from these nitroxides derive from two species with different hyperfine splitting constants and with unequal populations. *Supported by NIH P41RR12257.*

[1] B.H Robinson, et al., poster session, 45th Rocky Mountain Conference

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EPR • Wednesday Oral Sessions

96. *Membrane + Protein + Site-directed Spin Labeling EPR: A Winning Combination.*
Yeon-Kyun Shin, Iowa State University

Amphipathic membrane proteins, consisting of functional soluble domains and a functional membrane domain, are not currently amendable to x-ray crystallography and NMR. SDSL EPR offers a unique opportunity to investigate this class of proteins in the native like phospholipid bilayer. In my laboratory, SDSL EPR is used to investigate the structure and function of neuronal SNARE proteins. SNARE proteins are amphipathic membrane proteins that play essential roles in driving membrane fusion at synapses, a required step for neurotransmitter release. The EPR distance measurement method and the EPR saturation method are used to determine structures and membrane topologies of individual SNAREs, their assembly of intermediates, and the final complex. EPR results suggest the detailed mechanism by which SNARE assembly is regulated.

EPR Oral Session
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97. *Internitroxide Proximities in Protein Structure Determination.*
Hassane S. Mchaourab, Vanderbilt University

The geometric information encoded in the dipolar coupling between two nitroxides, site-specifically introduced into a protein sequence, can provide critical spatial constraints in the process of structure determination. The distance component can be readily determined to within about 3Å from the continuous-wave electron paramagnetic resonance spectrum of the doubly labeled protein using deconvolution methods introduced by Shin and coworkers. However, there is no general approach to translate these distances into restraints between the corresponding α-carbons. This is primarily due to the flexible arm linking each nitroxide to the protein. In addition, the experimental throughput is limited by the need of constructing a double cysteine mutant for each pair. To address these two problems, our laboratory has developed a fold recognition approach that is based on the restriction of the conformational space available to a polypeptide chain as a result of the topological rules of secondary structure packing. Sets of nitroxide pairs are designed to test for the presence of a pattern of proximity unique to a structural motif. The pairs are selected such that the expected differences in the proximity patterns are larger than the uncertainties associated with the nitroxide linking arm. Examples of the application of this approach include the proteins T4 Lysozyme and αA-crystallin. Patterns of internitroxide proximities can also be used as a fingerprint of the quaternary structure of a protein. When introduced at a subunit interface near a symmetry axis, nitroxides are brought into close proximity resulting in dipolar interactions. We used this type of spatial constraint to understand the evolution of the oligomeric structure in small heat-shock proteins and to determine the structure of the substrate binding pocket in the multidrug transporter EmrE.

EPR Oral Session
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98. *Double-Quantum Coherence ESR: Distance Measurements in Large Biomolecules.*
Peter P. Borbat and Jack H. Freed, Cornell University

The principles of Double-Quantum Coherence ESR (DQC-ESR) are outlined and the biological applications are illustrated with measurements of a wide range of distances. They include routine measurements by 17 GHz DQC-ESR of distances in the 20Å-55Å range in water soluble proteins, such as T4-lysozyme, and in RNA. Distances as large as 70Å can be assessed by DQC-ESR, as shown for RNA with 26 base pairs. DQC is sensitive to dipole-dipole interactions over a broad range and abates the problems arising from presence of singly-labeled species. In particular, at higher working frequency, ESEEM is rarely a problem and deuterated solvents are used to extend the upper range of distances by slowing down phase relaxation, particularly that caused by proton spin-diffusion. DQC is especially suitable in work with low spin concentrations of 10-100μM, typical for nitroxide-labeled biomolecules such as large proteins, their complexes, and RNAs. This advantage is due to the broad spectral excitation, and the fact that only the signal originating just from the dipolar coupling is sensed. It also means that only nano-and picomolar quantities of protein are needed, thus DQC-ESR can be used for proteins that are difficult to express. A sensitive ESR method to study the structure and function of membrane proteins is an important goal, as the other physical methods are difficult to apply.

DQC-ESR of membrane proteins is illustrated with a study of the potassium ion-channel, KcsA. This also addresses the case of more than two coupled spins. *Supported by grants from NIH/NCRR, NIH/GM and NSF.*

EPR Oral Session

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99. *The Prion Protein Within Us: EPR Distances and Structural Insights into PrP Function.*

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The prion protein (PrP) is responsible for a class of infectious, fatal dementing diseases called the transmissible spongiform enephalopathies (TSEs), which include mad cow disease and the human affliction Creutzfeldt-Jakob disease. PrP is a globular, membrane-bound, glycoprotein found in all mammals and avian species. Despite nearly twenty years of research on this remarkable protein, its physiological function has been unclear. Recent work, however, demonstrates that the flexible N-terminal domain of PrP binds copper ions cooperatively and with high affinity. Physiological studies now suggest that PrP plays a crucial role in copper homeostasis within the central nervous system. Using X-band and S-band CW EPR, ESEEM and HYSCORE along with recombinant PrP a library of isotopically labeled PrP peptides, we have constructed the first 3D model of the protein's Cu binding domain[1-3]. In turn, this model allows us to hypothesize about PrP's normal function and how loss of function may participate in the TSEs. *NIH GM65790*

[1] Aronoff-Spencer et al. *Biochemistry*, 39 13760-13771, 2000.

[2] Burns et al. *Biochemistry*, 41 3991-4001, 2002.

[3] Burns et al. *Biochemistry*, in press.

EPR Oral Session

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100. *A pH-sensitive Nitroxide for Site-Directed Spin-Labeling.*

Igor A. Grigor'ev, Vladimir A. Reznikov and Maxim A. Voinov, Novosibirsk Institute of Organic Chemistry, Russia; Andres Ruuge and Alex I. Smirnov, North Carolina State University

Site-directed spin labeling (SDSL), which is based on covalent attachment of a nitroxide to specific protein site(s), is rapidly developing into a valuable tool to study local structure and dynamics of complex macromolecules. This method, pioneered by Hubbell and coworkers (UCLA), involves cysteine-substitution protein mutagenesis which is followed by a covalent attachment of a nitroxide using methanethiosulfonate (MTS) or maleimide attachment groups. Labels with the MTS attachment group have an advantage over the maleimides because of the high specificity for the sulfhydryl moiety of proteins. Although, in principle, many nitroxide labels can be attached to the protein sulfhydryl groups using MTS chemistry, almost all SDSL EPR studies up to this date were carried out with methanethiosulfonate spin-label (MTSSL, (1-oxyl-2,2,5,5-tetramethyl-3-pyrroline)methanethiosulfonate). While MTSL has been proven to be a very useful probe in many structural EPR protein studies, clearly, some new probes are needed to study complex local electrostatics and surface potentials that govern protein folding and function. Here we describe our initial studies of using a newly-synthesized MTS-derivative of an imidazoline nitroxide (IMTSSL; methanethiosulfonic acid S-(1-oxyl-2,2,3,5,5- penta-methylimidazolidin-4-ylmethyl) ester) for mapping local pH of proteins. Magnetic parameters of this new pH-sensitive spin label for both protonated and nonprotonated forms were characterized by high field (HF) EPR at W-band (95 GHz, 3.4 T). We show that although EPR spectra of IMTSSL are affected by both the protonation stage and the local electric field, the use of high resolution HF EPR allowed us to differentiate these effects clearly. We have characterized the label alone and when attached to model proteins yeast iso-cytochrome *c* and human serum albumin in a variety of polar and non-polar solvents and at different pH. *This work is supported by the NATO Collaborative Linkage Grant LST.CLG.977528. The work of the Novosibirsk lab is also supported by the Russian Foundation for Basic Research (RFBR), grant 01-03-32452a.*

EPR Oral Session

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101. *Molecular modeling techniques in EPR spectroscopy.*

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The value of molecular modeling in structural biology is clear and widely accepted. While recent efforts (*Persson et al., Biophys. J. 80, '01; Columbus et al., Biochem. 40 '01*) have made progress, the applications in EPR spectroscopy are somewhat lagging due to the lack of methods for predicting spin label behavior with respect to the protein. Our efforts have concentrated on the development of energy minimization and molecular dynamics methods to predict spin label (a) orientations, (b) mobility and (c) inter-spin distances*. We have developed a Monte Carlo minimization method that predicts whether or not an arbitrary spin label is immobilized on the surface of the protein (*Sale et al. JMR 156 '02*). This method removes the trial and error aspect in choosing a spin label/label-site pair, which has traditionally been a serious bottleneck in EPR studies using extrinsic probes. In cases of complete probe immobilization we accurately predicted the orientation of the probe with respect to the protein on numerous cases where the orientation of the label was experimentally determined. The ability to accurately predict spin label orientation with respect to the protein affords interpretation of the orientational changes of the label in terms of the molecular domain rearrangements that are of biological importance. We have also developed a method to account for librational motion of the label in cases where the nitroxide is neither fully immobilized nor completely floppy. Combining molecular dynamics trajectories with the stochastic Liouville approach we have predicted the motion of the label with respect to protein and deconvoluted this motion from the protein domain/backbone motion of biological interest (*Sale et al. Biophys. J. 82 '02*). An important component of our methods is the use of optimization algorithms in EPR spectra fitting routines. To this end we have evaluated various optimization strategies, including Simplex, Levenberg-Marquardt, NLS2NO and Monte-Carlo and have determined that combination of Simplex/Monte Carlo methods is the most efficient way of analyzing EPR spectra (*Khairy et al. Biophys. J. 82 '02*).

* forcefields and topology files developed for number of popular nitroxide labels can be obtained at http://fajerpc.magnet.fsu.edu

EPR Oral Session

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102. *Lewisite (L), an Arsenic-derived Vesicant Chemical Warfare Agent (CWA), Inhibits the Inflammatory Cytokine, Tumor Necrosis Factor-alpha (TNF-a), via a Mechanism Involving Reactive Oxygen Species (ROS): Implication for Mechanism of Genotoxicity.*

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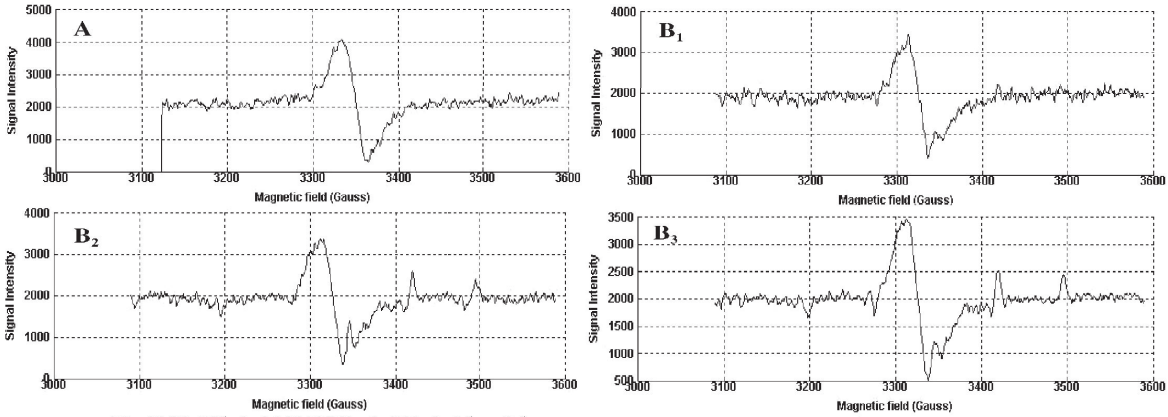
Lewisite (L) is an arsenical vesicant. We have postulated that arsenic-induced mutagenesis in mammalian cells by the following sequence of events: arsenic, reactive oxygen species such as hydroxyl radicals (·OH) → inhibition of tumor necrosis factor-alpha (TNF-α) → genotoxicity. Electron Paramagnetic Resonance (EPR) spectroscopy with 3, 3, 5, 5-tetramethylpyrroline N-oxide (M_4PO) as a spin trap probe indicates that this arsenical vesicant increases the levels of hydroxyl radicals in normal human epidermal keratinocyte (NHEK) cells. Concurrent treatment of NHEK with L reduced the release of the inflammatory cytokine, TNF-α, to control levels as measured by enzyme-linked immunosorbent assay (ELISA). Furthermore, the inhibition of TNF-α in L-treated NHEK cells was also verified by a multi-analyte bioassay, *Luminex* 100, flow cytometry detection system. The data are consistent with previous reported results applying the radical scavenger dimethyl sulfoxide (DMSO), which reduced the mutagenicity of arsenic in human cells, and provide convincing evidence that hydroxyl radicals play an important role in the genotoxicity of arsenical vesicants in human skin cells.



EPR Oral Session

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103. *Aqueous Sample in EPR Cavity: Field Distribution and Signal Intensity.*
Yu. E. Nesmelov and D. D. Thomas, University of Minnesota

Water is a major component of most biological samples and dominates their dielectric properties. At microwave frequencies, water has high values of both the dielectric constant and loss. The resulting effects on the distribution of fields in the EPR cavity and on the cavity quality factor *Q* are crucial for the sensitivity of biological EPR. Using the radial mode matching method, we have modeled microwave field distributions in a cylindrical EPR cavity with dewar and an aqueous sample. Cavity quality factor, filling factor, microwave magnetic and electric field intensity at the sample were found from calculated microwave field distribution. The dependence of signal intensity on aqueous sample size, temperature and conductivity was analyzed. Theoretical predications were verified quantitatively by experiment. Optimization of experimental parameters for maximum sensitivity of EPR measurement of non saturated and saturated aqueous samples is discussed and compared with previous work. *The support of University of Minnesota Supercomputing Institute is acknowledged.*

EPR Oral Session
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104. *Aqueous Flat Cells Perpendicular to the Electric Field for Use in Electron Paramagnetic Resonance Spectroscopy.*
Richard R. Mett and James S. Hyde, Medical College of Wisconsin

An analytic solution of the Maxwell equations for aqueous flat cells in rectangular TE_{102} cavities has led to the prediction of significant (3-6 times) X-band ESR signal improvement over the standard flat cell for a new sample configuration consisting of many flat cells oriented perpendicular to the electric field nodal plane. Analytic full wave solutions in the presence of sample and wall losses were carried out and then numerically evaluated using modern computational tools. Observation of the predicted fields lead to a classification of three distinct types of sample loss mechanisms, which, in turn inspired sample design that minimizes each loss type. The resulting ESR signal enhancement is due to the presence and centering of a tangential electric field node within each individual sample region. Samples that saturate with the available RF magnetic field and those that do not are considered. Signal enhancement appears in both types. These observations carry over to the uniform field[1-4] (UF) modes, a relatively new class of microwave cavities for use in EPR spectroscopy developed in this laboratory. Rectangular UF modes have an rf magnetic field magnitude that is uniform in a plane. Based on this analysis, a practical multiple flat cell design is proposed and is currently under construction in the authors' laboratory.

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[3] J. S. Hyde, R. R. Mett, and J. R. Anderson, Cavities with Axially Uniform Fields for Use in Electron Paramagnetic Resonance III. Re-entrant Geometries, *Rev. Sci. Instrum*. **73**, 4003-4009 (2002).

[4] J. S. Hyde and R. R. Mett, "Aqueous sample considerations in uniform field resonators for electron paramagnetic resonance spectroscopy," *Current Topics in Biophysics* **26**, 29-36 (2002).

EPR Oral Session
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EPR WEDNESDAY POSTER SESSIONS C & D **(Posters listed alphabetically by presenting author, J–Z)**

* Identifies recipients of Jules Stein Student Travel Awards † Identifies posters in the session dedicated to Larry Kevan

105. *Electron Spin Resonance Studies on Anthracite Coals and Soots.*
Yi Jin Jiang, Mark S. Solum, Ronald J. Pugmire and David M Grant, University of Utah

It was previously observed that the ESR spectrum of some anthracite coals such as LCNN and Jeddo, measured at 50mW microwave power, show two peaks with the same g value, one sharp and one broad, whereas other anthracite coals such as Harmony and Summit, only show the broad resonance when measured under the same conditions. Similar results have also been observed in soots formed from aromatic compounds such as anthracene and pyrene, with the soots formed at lower temperatures having only the one broad peak and soots formed at higher temperatures showing both peaks. A possible explanation for these observed differences is discussed in this poster. Previous measurements of the graphite factors of these four anthracite coals gave values of 0.15, 0.11, 0.02, and 0.01, for LCNN, Jeddo, Harmony and Summit, respectively. This result suggests

that samples with larger condensed ring formation are showing the two peaks. In addition, it has long been known that in solid state ESR the two major sources of line narrowing are electron spin exchange and delocalization of the unpaired electron in the molecule. One possible explanation of this observation is as follows: If the unpaired electron is on an aromatic π system, the larger the condensed ring system the more it can be delocalized. In this poster, the factors leading to the presence of the narrow resonance in the ESR spectra are explored using two stable free radicals, BDPA and DPPH. BDPA has a structure allowing extensive delocalization, whereas the unpaired electron is fairly localized in DPPH. The effect of the microwave power used on the presence of the second narrow peak will also be explored.

EPR Poster Session

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106. *ESR Study of γ-Irradiation on the Photosynthetic Biomembrane System.*

Y.S. Kang and D.K. Lee, Pukyong National University

The suppression of photosynthesis on the leaves of plant can be caused by radioactive irradiation. This is by the destruction of photosynthetic system on the leaves. The destroyed system has been studied with ESR. The prepared system has been identified with SEM and TEM images directly, and also identified with UV-vis and IR indirectly. The photosynthetic efficiency has been checked with ESR integration. After γ-Irradiation of samples, ESR signal intensity was rapidly decreased. The reason and mechanism has been studied with ESR spectra.
Supported by The Korean Ministry of Science and Technology (MOST) as a part of Nuclear R&D Program.

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EPR Poster Session

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107. *EPR and ENDOR Studies on the Effect of Bicarbonate on Copper Site and Free Radical Formation in WT and W32F Human and Bovine Copper, Zinc Superoxide Dismutase.*

Chandran Karunakaran, Hao Zhang, William Antholine and Balaraman Kalyanaraman, Medical College of Wisconsin; John Crow, University of Alabama-Birmingham, Joseph Beckman, Oregon State University;

Recently we reported the bicarbonate dependent peroxidase activity of human Cu,ZnSOD by EPR spin trapping and its aggregation with relevance to amyotrophic lateral sclerosis disease[1]. There is a controversy regarding whether bicarbonate protects it or deactivates the enzyme by increased consumption of hydrogen peroxide. In this study, we investigate the geometry and coordination of the Cu(II) active site as well as formation of free radicals during the peroxidase activity, using X-band CW EPR at liquid helium temperature and X-band CW ENDOR spectroscopy. EPR measurements on the time course of bovine SOD, W32F mutant and WT human SOD with hydrogen peroxide reveals that reduction and reoxidation of the Cu(II) active center by hydrogen peroxide also changes coordination from rhombic to tetragonal geometry. In the case of both WT and W32F human SOD, the reduction is slow due to possible reaction of hydrogen peroxide with a free sulfhydryl group. However, in the presence of bicarbonate, there is a totally different mechanism of reaction with the formation of tryptophan radical signal in the case of WT human SOD. Further, W32F behaves like bovine SOD in that there is no radical formation, so there is a back reaction of carbonate radical with the Cu(I) center leading to rapid reduction and oxidation[2]. In human SOD, the formation of a stable tryptophan radical prevents the back reaction. Further, we measured ^{1}H and ^{14}N ENDOR to gain insight into the ligand environment around the Cu(II) site during the peroxidase activity. ^{1}H and ^{14}N ENDOR reveal the disappearance of signal from HIS 118 in the bovine SOD. However, in the presence of bicarbonate, the ^{1}H and ^{14}N hyperfine couplings are not affected, indicating the protection of the active site by bicarbonate, which diffuses out as the carbonate anion radical. Thus, the oxidation of coordinated HIS ligands are thereby prevented. The mechanism of bicarbonate dependent peroxidase activity in relation to ALS will be discussed.

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[2] Liochev, S I *et al*, *Free Radic. Biol. Med*. 2003, 34(7), 908.

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108. *The Distances Between Electron Transfer Components in Photosystem II Studied by Spin Polarized ESEEM.*

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Spin polarized ESEEM has been observed in spinach photosystem II reaction center with the reconstituted quinone DBIMB reduced. By analysis of the observed ESEEM the distance between the laser induced triplet chlorophyll and the reconstituted acceptor quinone was estimated about 23 Å. The triplet state was assigned to one of the accessory chlorophylls based on angular dependence of triplet signal intensity. However, which chlorophyll in D1 and D2 proteins could be assigned has been undetermined.

Based on the recent X-ray data, the distance could be assigned to the chlorophyll in D1 protein. Similar result was observed in cyanobacterium *Synnechoccus vulcanus.* Therefore, the distance measurements have provided the functional information on the electron transfer chain in the photosystem II.

EPR Poster Session

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109. *Distance Measurement in RNA Molecules using EPR Spectroscopy.*

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As a basic model study for measuring distances in RNA molecules using continuous (CW) and pulsed EPR spectroscopy, site-directed spin labeled RNA duplexes (10 b.p.) with various inter-spin distances were examined. The distances between two nitrogen atoms of the nitroxide spin labels varied from 10Å to 30Å, which were estimated by modeling the duplexes using molecular dynamics simulations. Dipolar line broadening of the CW EPR spectrum is observed when the inter-spin distances are 10 - 21Å, and is not detected for distances over 25Å. The spin-spin distances were calculated by the Fourier deconvolution method[1], and these values match well with those measured from molecular modeling. For measuring distances over 25Å, PELDOR (pulsed electron electron double resonance) spectroscopy was tested. As an application of the distance measurement, the hammerhead ribozyme was spin labeled at the ends of stems I and II in order to investigate the folding pathway of this ribozyme, and spin-spin distances were calculated using PELDOR spectroscopy.

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110. *Characterization of External Surface Area of MFI Zeolites Using EPR.*

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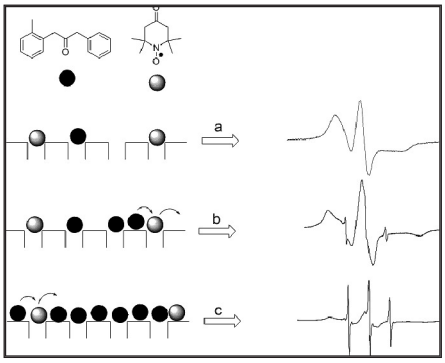
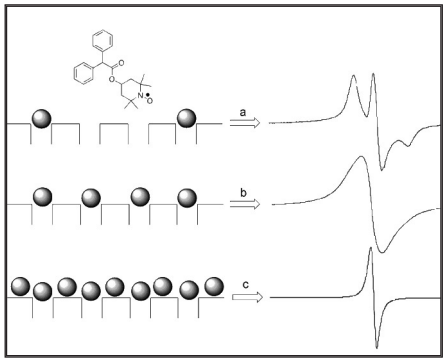
Electron Paramagnetic Resonance (EPR) of TEMPO derivatives as a probe has been employed to measure the absorption of ortho-methyldibenzyl ketone (oMeDBK) on the external surface of MFI zeolite crystals. The displacement of the adsorbed probe by coadsorbed oMeDBK leads to the conclusion that the adsorbate molecules first adsorb on stronger binding sites (holes on the external surface) which is characterized by slow motion of the probe and then the adsorbate molecules adsorb on weaker binding sites (external surface framework between holes) which is characterized by fast motion of the probe. The transition point from slow to fast motion is manifested by the change in TEMPO EPR spectra from broad to narrow lines and provides a means of ***quantitative*** characterization of the external surface area of zeolite crystals. Sequential competitive coadsorption of ^{14}N, and ^{15}N spin labeled TEMPO derivatives reveals the strength of adsorption on different adsorption sites. As an alternative method of quantitatively characterizing the external surface, the TEMPO probes were used as the sole adsorbate on the external surface. With increasing loading, the EPR line shape shows a progressive change of spectra: (1) characteristic of individual probe molecules with reduced mobility and minimal spin-spin interaction (3-line spectrum); (2) characteristic of closely positioned immobile probe molecules undergoing spin exchange through dipole-dipole interaction (broad 1 line spectrum): (3) characteristic of freely mobile probe molecules undergoing spin-spin exchange through collisions (sharp 1-line spectrum). The distances between probe molecules and the spin-spin exchange frequency can be obtained by simulations. The transition point from nearly zero to high spin-spin interaction provides a novel, simple and highly sensitive means of characterization of the external surface area of zeolite crystals. The EPR methods have been applied to a series of monodisperse MFI crystals to determine the validity and scope of the EPR methods as sensitive and structurally specific method for investigating external surface areas of zeolite crystals.





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111. *Notre Dame Radiation Chemistry Data Center, 2003 Status Report.*

Keith P. Madden, University of Notre Dame

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. Our current compilation activity is an update to the hydrogen atom section of "Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms, and Hydroxyl Radicals in Aqueous Solution"[1]. The preliminary data from this update is available at the RCDC web site, http://www.rcdc.nd.edu .

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EPR Poster Session

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112. *The Bonding in MCH_3 (M= Cd, Mg, Hg, Zn) Radicals Revealed by Neon Matrix Isolation EPR.*

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The radicals MCH_3 (M=Cd, Mg, Zn) have been generated by the reaction of the plume formed from laser ablation of the metal and a CH_3 precursor such as $(CH_3)_2CO$. The $HgCH_3$ radical has been generated from reaction of excited Hg atoms and a CH_3 precursor. These radicals have been isolated in neon matrices at 4 K and probed by EPR. The EPR spectra have been recorded and analyzed using an approach involving exact diagonalization of the spin Hamiltonian. This analysis has included the C-13 and D labeled isotopomers as well as the Cd-111 and Cd-113, Hg-199, Hg-201, Mg-25 and Zn-67 isotopomers. From the analysis of the spin Hamitonian parameters the electronic structure in these radicals has been derived and is compared with the results of DFT and CI ab initio calculations.

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113. *Spin Dependent Recombination of Deep Level Defects at Silicon Carbide — Silicon Dioxide Heterointerfaces.*

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Silicon carbide devices have great potential in high temperature and high power applications[1]. However, performance of silicon carbide devices has been limited by high numbers of deep level defects. The physical and chemical nature of these defects is largely unknown. In this study, we have utilized spin dependent recombination (SDR) to detect electron paramagnetic resonance of deep level defects in silicon carbide metal-oxide semiconductor field effect transistors (MOSFETs)[2]. SDR detection is particularly useful in studies of semiconductor devices as it offers sensitivities many orders of magnitude higher than that of conventional EPR (our sensitivity is of the order 1000 paramagnetic defects). Furthermore, since the SDR effect involves the measurement of electrical currents, the technique allows one to make a very direct connection between point defect structure and deep levels, which play important roles in device operation. We find a close correspondence between the SDR measurements and electronic measurements of the density of states of silicon carbide oxide interface traps. Preliminary results suggest that the paramagnetic centers involve unpaired electrons localized on interface or near interface carbon atoms back-bonded to three silicon

atoms. The size of the spin dependent recombination effect is very large; at room temperature, the EPR induced change in recombination current corresponds to several tenths of a percent.

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[2] Daniel J. Lepine, Phys. Rev. B, vol. 6, no. 2, pp. 436-441 (1972).

EPR Poster Session

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114. *ESR and ESEEM Study of Silver Clusters in ZK-4 Zeolites.*

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Silver exchanged Na-A and K-A zeolites (Si/Al =1) reduced chemically or radiolitically show unique ability to stabilize paramagnetic silver hexamers – Ag_6^{n+} in solidate cages[1-3]. In contrast, in ZK-4 zeolites isostructural to zeolite A we were able to observe only silver tetramers – Ag_4^{3+} even for the frameworks with small decrase of Al content (Si/Al =1.2). It proves that although the suitable framework cages are necessary for effective trapping of silver clusters the other factors as cation capacity and presence of adsorbates which control the location and migration of Ag cations and atoms affect significantly the nuclearity of stabilized clusters. Silver tetramers in ZK-4 are formed only in zeolite exposed to water and methanol before gamma irradiation. The ESEEM results clearly show that Ag_4^{3+} interacts with adsorbate molecules. In Ag-ZK-4 (Si/Al =1.2) Ag_4^{3+} and one H_2O molecule are located in the same solidate cage whereas in zeolite with Si/Al =2.4 silver tetramer coordinates two more distant H_2O molecules placed in two opposite hexagonal windows.

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[3] J. Michalik, L. Kevan, J. Amer. Chem. Soc., 1986, 108, 4247.

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115. *Electron Spin Resonance Studies of Manganese Ions in the Hammerhead Ribozyme.*

Matthew Vogt, Ayaluru Murali and Victoria J. DeRose, Texas A&M University

The Hammerhead (HH) ribozyme performs a site-specific cleavage of a phosphodiester bond. Both the structural and the catalytic properties of the hammerhead ribozyme are dependent on divalent metal ions. This report pertains to the ESR spectra of a single Mn^{2+} ion bound to the hammerhead ribozyme and discusses the symmetry and ligands around the Mn^{2+} ion. The sixth hyperfine line in the ESR spectra of Mn^{2+} bound to the HH shows a lineshape that appears different than that observed for Mn^{2+} in buffer. This difference in lineshape has been attributed to a single high affinity site in the HH. ESEEM and ENDOR studies on this system revealed the coordination of nitrogen and phosphate ligands to the manganese ion. In order to find the origin of the sixth line feature, the ESR spectra of model complexes have been studied to observe the effect of changing the symmetry of and ligands to the Mn^{2+} ion. The ESR spectra of Mn^{2+} coordinated to GMP, bipyridine, and GTP show broadened hyperfine lines in comparison with a Mn^{2+}-buffer standard. Moreover, the ESR spectra of a tetrahedral manganese compound (Mn^{2+} : LiCl in methanol) were also studied for comparison to the manganese site in the HH.

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116. *Relationships Among the Different Components of a CW EPR Spectrum.*

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A Continuous Wave (CW) EPR spectrum may be obtained in either the absorption mode or the dispersive mode. Because of the Zeeman or DC field modulation, running at a frequency that is typically anywhere from 1 KHz to 1 MHz, one may have a spectrum that is either in phase or quadrature to the driving modulation. Moreover, one may obtain signals at any harmonic of that modulation. We have solved the Bloch Equations of motion for a simple spin system subjected to the Zeeman modulation. We will show that the exact solution may be recast in terms of Bessel Functions. The Bessel functions are the basis for the technique of convolution of signals to obtain other signals. In particular, the Medical College of Wisconsin group has popularized the technique of pseudomodulation, by which one may demonstrate the effects of Zeeman modulation (or more typically over-modulation) on EPR spectra. Here, we show that similar techniques can be developed to relate the various components of

the EPR response to one another. The techniques may be generalized to saturation conditions. In particular we can show that the traditional STEPR spectrum (which is the second harmonic, out of phase absorption spectrum) is rigorously equivalent to its first harmonic counterpart at low modulation frequency, and is still rather good at higher modulation frequencies. This relation is demonstrated for experimental EPR spectra of nitroxide spin labels under STEPR conditions (i.e. strong rf and rotational times in the microsecond regime). This demonstrates that Zeeman modulation, under most conditions of interest to spectroscopists, is easily accounted for as a correction – after simulation – to any simulation that does not contain Zeeman modulation. The extent of modulated or over-modulation of the experimental spectrum is quantitatively simulated.

EPR Poster Session

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117. *Orientation of Stearic Acid in Magnetically Aligned Phosphatidylcholine Bilayers by X-band EPR Spectroscopy: Cholesterol, Chain Length and Temperature Effects.*

* Nisreen A. Nusair and Gary A. Lorigan, Miami University

Magnetically aligned phospholipid bilayers or bicelle discs have been successfully used to study the structural and dynamic properties of magnetically aligned disc-like phospholipid bilayers or bicelles using X-band EPR spectroscopy. This study has been performed with 5, 7, 12, and 16-doxylstearic acid spin-labels incorporated into a DMPC/DHPC phospholipid bilayer system. The orientational-dependent data provides a more complete picture about the chain conformation of the membrane system, high order and low motion for the hydrocarbon segment close to the carboxyl groups of the stearic acid and less order and more rapid motion toward the terminal methyl groups. Also, the influence of cholesterol and temperature on the hydrocarbon chain ordering in the DMPC/DHPC phospholipid bilayer discs was investigated. Cholesterol increased the order parameter of the phospholipid bilayers and decreased the number of degrees of freedom of motion of the hydrocarbon acyl chain region closer to the polar head groups in the phospholipid bilayer discs. The increase in the motional order in this region corresponds to a decrease in trans-gauche isomerization. Conversely, temperature decreased the orientational order of the hydrocarbon chains of the liquid-crystalline bilayers at various cholesterol concentrations due to the higher random motion of the acyl chain of the stearic acid. In addition, incorporation of cholesterol into phospholipid bilayers broadened the cooperative gel to liquid-crystalline phase transition significantly.

EPR Poster Session

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118. *EPR Study on Free Radicals Produced by Hydrogen Addition to Alknylsilanes at 77K.*

† Nobuaki Ohta, Hiroshima University

Radiolysis of alknylsilanes such as ethynyltrimethyl- and ethynyltriethy silanes at 77K produced alkyl radicals caused by C-H bond scission and vinyl radicals due to H-addition to carbon-carbon triple bonds. The vinyl radicals have large proton hyperfine coupling constants (>5mT) which are characteristic of organic σ-radicals in which unpaired electrons occupy sp^2 σ-orbitals. The large hfs 's may be due to the β-protons which are in the trans positions with respect to unpaired electron orbitals as the case of HC=CH2. The absence of the large hfs in deuteroethynyltrimethylsilane indicates that the addition of a hydrogen atom might occur in the cis position with respect to the unpaired electron orbital on the contrary to the H addition to acethylene. Radical structures and mechanisms of H-addition will be discussed in terms of ab intio Molecular-orbital calculations.

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119. *The Antisymmetric Part of the g-Matrix: Can It Be Observed?*

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The g-factor is usually presented in the form of a symmetric tensor. However, as mentioned in the books by Abragam and Bleaney and by Weil, Wertz and Bolton, the g-factor can have a skewed or anti-symmetric part. The results from conventional EPR spectral measurements can always be written in symmetric form. However, we find that the anti-symmetric part can appear during motional averaging and can affect lineshapes of exchange-coupled centers. Situations where an anti-symmetric g-matrix could arise in biological systems are discussed. *Supported by NIH GM61904.*

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120. *High Power Pulse Amplifiers for 250 MHz EPR.*
Richard W. Quine and Gareth R. Eaton, University of Denver

Two high power pulse amplifiers at 250 MHz were evaluated for use in a VHF EPR Pulsed Spectrometer. The first of these, from Tomco Electronics Pty LTD (Adelaide, South Australia.) was specified to be 500 Watts of peak power, rise and fall times of less than 30ns and a noise blanking feature that brings the output noise to a level of less than 10dB above thermal in less than 80ns. The second amplifier, from Communications Power Corp. (Brentwood, NY) was specified to be 400 Watts of peak power with similar rise and fall times and noise blanking. This amplifier is not yet in its final form, but preliminary tests have been completed. Engineering data from tests of both of these amplifiers will be presented.

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121. *Pulsed Proton ENDOR Spectroscopy of Gadolinium Complexes.*
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There are two types of manifestations of weak crystal field interaction (*cfi*) of high-spin transition ions in ENDOR spectra: (1) the ENDOR spectra show nuclear transitions (often overlapped) that belong to several different electron spin manifolds and (2) the transition lines for each manifold are distorted by the effect of *cfi*. The latter effect is the result of departures (different for different electron spin manifolds) of electron spin quantization axes from the direction of the external magnetic field caused by *cfi*. In this work we (1) analyze the spectral distortions caused by *cfi* and (2) show that two-dimensional Mims ENDOR technique can be used to disentangle the nuclear transitions that belong to different electron spin manifolds. The results of the analysis are applied to study the Gd^{3+} aquo complex and Gd^{3+}-based MRI contrast agents in frozen glassy water/methanol solutions. The distance between Gd and protons of the water ligands is found to be about 3.1 Å for all studied complexes.
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122. *Photoinduced Charge Separation of Organic Molecules in Chromium Containing Silicoaluminophosphate (SAPO-5) Microporous Materials at Room Temperature.*
† Koodali T. Ranjit and Larry Kevan§, University of Houston

The photoinduced charge separation of organic molecules such as N-methylphenothiazine, N,N,N'N'-tetramethylbenzidine and pyrene in chromium containing SAPO-5 materials with ultraviolet irradiation at room temperature was examined. Photoionization of these organic molecules results in the formation of cation radicals that are characterized by electron spin resonance (ESR) and diffuse reflectance spectroscopy (DRS). The ESR studies indicate that Cr acts as an electron acceptor. The photoyield and stability of the photoproduced cation radicals were found to depend on the pore size of the microporous material, concentration and the oxidation state of chromium ion. The photoyield is found to be higher in microporous CrAPSO-5 material than in mesoporous materials such as MCM-41 and SBA-15 investigated in our laboratory earlier. Such microporous materials with "in-built" transition metal ions stabilize the photoproduced radical ions and prolong their lifetime for weeks at room temperature. The study demonstrates the importance of Cr containing microporous SAPO-5 materials as potential candidates for photochemical conversion and storage devices.

§ Deceased June 4, 2002

EPR Poster Session
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123. *Design, Construction and Performance of a Large EPR Imaging Magnet for use at 250 MHz.*
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An air core magnet and gradient coil system for operation at 250 MHz was constructed to provide a large volume of homogeneity and relatively low inductance to allow rapid scanning, while minimizing the mass of copper. Design criteria included a main magnetic field to be swept about a central value of 0.009 T (90 G), a sphere of homogeneity of diameter 30 cm, homogeneity greater than 40 parts per million,

and open access to the working volume from axial and perpendicular directions. A four-coil eighth-order design was used for this magnet and is geometrically similar to that for a half-size version, which has been constructed and is presently being used in a fully operational imaging system. Thin foil windings, the width of the coils were used instead of square wire for ease of fabrication. As with the half-size magnet, the two smaller coils of the four-coil system are adjusted to correct for inhomogeneities introduced by winding and mounting irregularities. The table gives the scaling of the magnet parameters to achieve a constant surface area to power ratio for a magnet whose coil diameter is scaled by a factor of k. This results in the same operational temperature while scaling the magnet size. The table also gives the new parameters for a magnet scaled by a factor of k = 2.

	Scale up of factor, k	k = 2
Resistance	$R(k) = k^{-1/3}$	0.8
Current	$I(k) = k$	2
Power	$P(k) = k^{5/3}$	3.2
Weight	$W(k) = k^{7/3}$	5

In addition three-axis gradient coils provide a gradient with maximum value of 5 gauss per cm. The fully constructed magnet will be shown as well as the measurements of the extent to which the magnet satisfies the design criteria. *Support in part by NIH P41 RR12257 is gratefully acknowledged.*

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124. *On Redfield Theory: A Novel Relaxation Equation of Motion.*

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We present a tutorial on Redfield, or more completely Bloch-Wangness-Redfield, Theory (BWRT) that is in a representation independent, operator form. We feel that our approach is reasonably intuitive and of direct use to spectroscopists. The equations for the relaxation of observables follow directly from the general equation of motion. The novel form of the relaxation equation has fewer assumptions and approximations in it than traditional BWRT: There is no time restriction on the relaxation and Boltzmann Equilibrium appears quite naturally. We show that this new form gives results consistent with traditional BWRT and limits to BWRT when the additional restrictions and approximations of BWRT are applied to the new equation of motion. The new form shows how the usual equations for relaxation rates may be easily modified to include detailed balance and to avoid the long-standing problem that certain relaxation rates incorrectly become large when the lattice fluctuations become small; that is, the relaxation rates determined from this new approach avoid the BWRT "catastrophe". The new formulation leads to a more complete description of both longitudinal and transverse relaxation in magnetic resonance and takes into account the oscillatory nature of the relaxation of both transverse and longitudinal components in the slow motion regime. Two classic examples will be given: The dynamic averaging of two lines and the motionally narrowed nitroxide spectra for a molecule undergoing isotropic rotational Brownian motion.

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125. *Aqueous Sample Heating at X- and W-band: Towards a Microwave T-jump EPR Experiment.*

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It is well known that excessive microwave power in EPR experiments may result in undesirable heating of aqueous samples especially in continuous wave (CW) EPR saturation studies. One of the accounts of such a heating at X-band (9 GHz) was given in[1]. Using very accurate measurements of the temperature-dependent isotropic nitrogen hyperfine coupling constant of the dianion radical Fremy's salt, the heating of an aqueous sample of up to 15 ºC at incident microwave power of 128 mW was reported. Clearly, such a large heating could be a source of errors in, for example, dioxygen accessibility measurements carried out with CW saturation. From the other hand, once calibrated, microwave heating might be very useful for changing the sample temperature in EPR experiments quickly and reliably with minimum of additional accessories. Our particular interest is in developing microwave heating method for triggering conformational changes in biomolecules over a short period of time (microwave T-jump) and then monitoring re-equilibration kinetics with spin-labeling EPR. Here we describe our initial studies of microwave heating at steady-state conditions using CW X- and also W-band (95 GHz) EPR spectrometers. While at X-band any rapid T-jumps are limited by the sample size and available microwave power, at high magnetic fields the optimum size of aqueous samples decreases to ca. 50 nanoliters and this relaxes requirements for peak microwave power. On the way toward implementation of this method in HF EPR, we have measured microwave sample heating using a low power CW W-band spectrometer. We have found that the steady-state microwave heating of a miniature

capillary using a microwave source with only 30 mW incident power was rather modest (up to ca. 10 ^{o}C) and dependent upon the capillary diameter. We have also found, that the accuracy of magnetic field scanning at W-band was insufficient to track the changes in the nitrogen hyperfine coupling constant associated with such a modest heating. However, the changes in temperature can be monitored accurately and reliable using measurements of the isotropic g-factor of the nitroxide Tempone (perdeuterated 2,2',6,6'-tetramethyl-4-piperidone-1-oxyl). We also demonstrate that microwave sample heating can be used to trigger a phase transition in phospholipid membranes. *This work is supported by the North Carolina Biotechnology Center grant 2001-ARG-0033 to AIS.*

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126. *Metal Binding to Anthracis Repressor (AntR).*

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AntR is a transition metal ion activated repressor from Bacillus anthracis, the agent responsible for anthrax. AntR is a member of the Diphtheria Toxin Repressor (DtxR) family of proteins with less than 50% homology at the putative metal binding sites. It contains only a single domain rather than two seen in nearly all other DtxR homologues. Little is known about the mechanism of metal ion homeostasis in B. anthracis. Furthermore, the structural differences between AntR and DtxR suggest that the activation mechanism may differ in these two homologues. This effort focuses on characterization of metal binding and coordination environment by Electron Paramagnetic Resonance (EPR). Room temperature EPR studies on Manganese(II) ion, which is the most effective activator of AntR, showed that two cations bind per AntR molecule. The binding affinities for two sites are observed to be similar. Pulsed EPR methods are used to determine the coordination sphere of the bound cations and to characterize the nature of the residues that form the metal binding sites. The results are compared to metal coordination in DtxR.

EPR Poster Session

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127. *Experimental Limitations of High Spatial Resolution Multi-Site EPR Oximetry.*

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We previously have reported a new method and algorithm for data analysis that enhances the spatial resolution of multi-site EPR Oximetry[1]. This HSR MS EPR method is based on the use of magnetic field gradients with the same direction but different magnitudes and uses a convolution-based fitting algorithm to derive the Lorentzian EPR line width (LW) of each peak of the EPR spectrum. It corrects distortions of line shapes caused by the gradient and thus overcomes limitations of previous multi-site EPR oximetry methods[2] that restricted the ratio of the particle size to the distance between sites. The method is suitable for any shape of a solid paramagnetic material implanted in tissue and is applicable for any particulate EPR oxygen sensitive material. To enhance the utilization of this method we have developed software to determine the accuracy of HSR MS EPR under various practical conditions. The new algorithm and developed software improves the quality of the line shape analysis in data processing by incorporating additional intervals of fitting. Using the new software and several different phantoms we have found that the error in LW determination is proportional to noise-to-signal ratio (N/S) and does not exceed 8% at N/S=0.1. To have an accurate determination of LW the second magnetic field gradient should exceed 30% of the value of the first gradient. Overlap of adjacent sites can be neglected if the Splitting/LW$\geq$6. Such resolution can be achieved by increasing the field gradient but this can decrease sensitivity. Accuracy in LW determination decreases if the fitting interval is lower than 25% of the field sweep. We achieved an accuracy of about 20% in determination of the LW with up to 10 sites using two properly chosen gradients.

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128. *Deuterated OX-031: A Non-toxic Trityl Spin Probe With Significantly Narrower Spectral Lines for In-vivo Oximetry.*

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Trityl spin probes from Nycomed Innovations (Malmo SW) have enabled high resolution EPR imaging of oxygen concentrations in living animals. This is due to their stability, their narrow spectral lines, their simple one-line spectra, and their relative insensitivity to other aspects of the aqueous in-vivo solvent. Although deuterated variants of the symmetric trityl probes have been published showing extremely narrow spectral lines[1], these probes (in either natural abundance or deuterated forms) have been found to be toxic. Recent simplification of the synthesis of the trityls [2] have made it possible to synthesize partially deuterated versions of trityls that are both non-toxic and have the favorable spectral properties of the previously published trityls. This partially deuterated trityl is OX-031: methyl-tris[8-carboxy -2,2,6,6-tetrakis[(2-hydroxyethoxy)deutero-methyl]benzo[1,2-d:4,5-d']bis [1,3]dithiol-4-yl]-, trisodium salt , MW 1811.3. This deuterated version is also referred to as OX031D. The electron coupling to the ^1H in the CH_2-group of the natural isotope abundance OX31 dominates the spectral linewidth. Replacing these protons by deuterons substantially decreases the linewidth. We present a short discussion of the novel synthetic route for this molecule. Preliminary CW measurements indicate a reduction in the overall p-p linewidth reduction from 8.7 to 3.7 microTesla upon deuteration. Spin packet linewidths that will be compared with time domain measurements. *Support is gratefully acknowledged to NIBIB for P41-RR12257*

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129. *Distance Measurement by T_1 Enhancement.*

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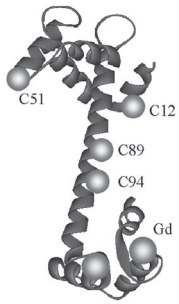
The enhancement of spin-lattice relaxation rate of spin label (nitroxide) in the presence of paramagnetic metal (Gd^{3+}) was used to measure the distances in labeled troponin complex, which is responsible for the regulation of muscle contraction. Gd^{3+} bound to the C domain of troponin C was used as a metal relaxant with spin labels placed on selected residues in both the C domain and N domain of troponin C: 94, 89, 51 and 12. The measured distances of this residues to Gd in isolated troponin C were 24Å, 25Å, 42Å and 35Å respectively, which were in good agreement with that observed in the crystal structure. The changes in these distances in reconstituted troponin ternary complex of TnC, TnI and TnT indicate the N domain moving towards the C domain in ternary complex (7 Å change in TnC 51) and no large rearrangement of the C-domain of TnC (1-2 Å changes in TnC 94 and 89). These results provide argument that the extended structure of isolated TnC observed in the crystal structure (See Fig.) is largely modified in a complex with TnI and TnT subunits. A similar domain argument was observed for homologous protein calmodulin in a complex with target peptide.



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130. *Rapid-Scan EPR.*

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Traversing a magnetic resonance line at rates that are fast relative T_1, and then processing the resultant spectrum to recover the undistorted line, is a well-known technique in NMR, where it has been called rapid-scan FT and rapid-scan correlation spectroscopy. The ringing or wiggles described by Jacobsohn and Wangness[1] are prominent only when T_1, T_2, and $1/\gamma\delta H$ are all greater than the interval spent at resonance during the modulation cycle, which is roughly $(H_m\omega_m\gamma T_2)^{-1}$. For certain conditions, rapid-scan NMR can achieve nearly the same improvement in signal-to-noise (S/N) per unit time as does pulsed FT NMR. We seek to determine whether rapid-scan EPR can improve S/N per unit time relative to "normal" phase-sensitive detection. In addition, there are situations, such as imaging of animals, in which certain frequencies interfere with CW EPR measurements. We seek to determine whether there are spectral acquisition rates that might beneficially avoid some of these problems. Scan-rate dependent spectra have been observed at X-band and at 250 MHz EPR for several samples, including the trityl radicals that are being used for in vivo imaging, and for lithium phthalocyanine radical that is being used for oxymetry. Rapid-scan EPR spectra acquired at various scan rates (G/s) are being simulated using the Bloch equations, and limitations imposed by resonator Q and detector system filtering are being explored to optimize the rapid scan EPR measurement. Further studies will explore the diverse parameter space of this non-steady-state technique, to achieve the best S/N per unit time and to optimize the post processing of the data for EPR imaging.

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EPR Poster Session

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131. *Saturation-Recovery at Q-Band.*

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A self-built Q-band multiquantum spectrometer was modified so that it could be used for pulse saturation-recovery (SR) experiments. The instrument was used for an extensive series of experiments measuring spin-lattice relaxation time (T_1) and oxygen transport parameters (oxygen diffusion-concentration product) in model saturated and unsaturated membranes as a function of the depth in the lipid bilayer. The T_1 and oxygen transport parameters were also evaluated for a spin-labeled protein, namely Arrestin K267C-MTSL. These are believed to be the first SR experiments on spin labels at Q-band. One advantage of this method is that the amount of the sample required is very small – less than one microliter. Another highly significant advantage is that the T_1 values of spin labels in membranes and proteins at Q-band in the absence of oxygen are longer than at X-band by a factor of ~50-75%. This increases the sensitivity for measurements of the collision rate between the nitroxide moiety of spin labels and molecular oxygen.

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132. *Lipid Raft Domains: EPR Discrimination by Oxygen Transport.*

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Rafts are lipid liquid-ordered domains rich in cholesterol and sphingolipids that are formed in the plasma membrane lipid-disordered environment. Detergent insolubility has been used to define rafts biochemically. However, such an approach is not useful for understanding the size, lifetime and dynamics of the raft constituent molecules and the raft itself in the membrane. To address these issues, we applied the pulse EPR spin labeling technique called discrimination by oxygen transport (DOT) for in situ studies of rafts in model membranes. The spin-lattice relaxation time of spin labels is long (1-10 μs), and membrane dynamics can be observed on this long time scale. The DOT method permits discrimination of different membrane domains because the collision rate between O_2 and the nitroxide moiety of spin labels (oxygen diffusion-concentration product) can be quite different. Additionally, membrane domains can be characterized by profiles of the oxygen diffusion-concentration product in situ without the need for separation. Preliminary data for phosphatidylcholine/cholesterol membranes and membranes made from raft-forming mixtures are presented.

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133. *Spin Probe Monitoring of Starch Gelatinisation in Bread Dough Modelled Using Wheat and Pea Starch.*
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The spin probes 1,1,3,3-tetramethylisoindolin-2-yloxyl (TMIO) and the sodium salt of the sulfonate derivative (NaTMIOS) are unreactive free radicals that have relatively sharp ESR lines. TMIO is only slightly soluble in water whereas NaTMIOS is very water-soluble and is insoluble in lipid. Here, these probes have been used to monitor the behaviour of dough during the baking process. Dough (~2g) was prepared by means of a computer-controlled 10g capacity minimixer, which imitates the action of a large commercial Chorleywood process mixer and gives a graphical output, logging the mixing behaviour. The spin probe TMIO was used to report simultaneously on the effect of heating on the aqueous (starch) phase and lipid phase of the dough: while NaTMIOS was used to give information on the starch component(s). Samples of dough were heated progressively from 30 ºC to 90 ºC, with spectra recorded at ~7 ºC intervals. Simulation of the experimental spectra using the computer program EWVOIGTN showed no apparent involvement of the lipids in the baking process. However, a change in the water-soluble components was found at temperatures above 50 ºC, consistent with starch gelatinisation. Purified starch granules from wheat, (with traces of lipid), and from pea, (lipid free), were mixed with TMIO, to mimic dough preparation and analysis. For both starch sources, heating above ~50 ºC produced an irreversible decrease of the mobility of TMIO in one of the environments sampled, confirming the behaviour in dough is associated with starch gelatinisation. A second environment, not previously noted using TMIO in flour, showed a reversible reduction in mobility with heating. From the similarity in the TMIO partitioning ratio (~1:3) between environments and the starch amylose: amylopectin ratio (~1:3) we ascribe these changes to amylose and amylopectin respectively. Funding from the BBSRC is gratefully acknowledged

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134. *EPR Measurements of Interspin Distances in Spin Labeled Myoglobin.*
Dmitriy Ulyanov, Bruce Bowler, Sandra S. Eaton and Gareth R. Eaton, University of Denver

Thirteen mutants of sperm whale myoglobin were designed by site-directed mutagenesis with cysteine at desired locations and modified with the spin label MTSL. The mutation sites provided a range of distances and orientations with respect to the magnetic axes of the heme iron. High spin and low spin samples of the metmyoglobins were prepared by addition of F- or CN- as the axial ligand. The interspin distances were determined in several ways. 1. Saturation recovery was used to measure the effect of the rapidly relaxing iron on the spin lattice relaxation rate of the MTSL spin label. 2. The effect of the iron on the minimum intensity of the two-pulse echo for the spin label in the temperature regime where the iron relaxation rate is comparable to the iron-nitroxyl dipolar interaction. 3. The temperature dependence of the shape of the two-pulse echo decay was analyzed. The distances measured by saturation recovery for high spin and low spin samples agree well. The saturation recovery data indicate that more than one conformation of the spin label is present in the samples of some mutants. The distances calculated from the minimum echo intensity measurements correlate well with the values obtained from the saturation recovery measurements, and reveal additional information about the spin label conformation. The distances measured by EPR will be compared to those calculated using the Insight II software to calculate the protein conformation.

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135. *Substrate and Cofactor Interactions With Lysine 2,3-aminomutase Studied by 35 GHz ENDOR.*
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Lysine 2,3-aminomutase (LAM) catalyzes the interconversion of L-Lysine and L-β-lysine. It is a member of the superfamily of enzymes in which a $[4Fe\text{-}4S]^{+}$ cluster with a unique, non-cysteinyl coordinated Fe, provides the electron to cleave S-adenosyl-L-methionine (SAM) and initiates radical catalysis by formation of the 5'-deoxyadenosyl radical. Expanding on our previous work on members of this family of enzymes, we have used ENDOR studies with labeled SAM to examine the geometry of interactions at the LAM active site. ^{2}H and ^{13}C Mims ENDOR experiments of $[4Fe\text{-}4S]^{+}$-LAM in the presence of SAM labeled at the methyl position show ^{2}H couplings (~ 0.7 MHz) as well as substantial ^{13}C couplings (0.7 MHz), indicating that SAM lies close to the cluster. Further, Davies ENDOR experiments with ^{17}O and ^{15}N labels on the methionine end of SAM demonstrate bidentate coordination to the unique iron site of the cluster. These results, in concert with a previous EXAFS study of the reaction of LAM with Se-adenosyl-L-selenomethionine leads us to postulate a mechanism by which LAM cleaves SAM to generate an intermediate where N, O and S of the methionine product are bound to the octahedrally coordinated unique Fe of the [Fe-S] cluster. We shall also report ENDOR measurements on intermediates formed during the reaction of LAM in the presence of substrate and substrate analogues. *Supported by NIH grants HL13531 (BMH) and DK28607 (PAF).*

EPR Poster Session
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136. *A Liquid-Solution EPR and ENDOR Study of Two 2,2-Diphenyl-1-monosulfo, Dinitrophenyl Hydrazyl Salts.*
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The electron paramagnetic resonance (EPR) and electron-proton double resonance (ENDOR) spectroscopic characterization of several stable and water-soluble paramagnetic salts of sulfonated (modified picryl ring) versions of the well-known free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) is presented herein. Liquid-solution room-temperature EPR spectra of the potassium (K^+) salts of both the ortho- and para- (to the carbon attached to N_1) sulfonated (−1) radical anions in solvents not previously studied have been measured and quantitatively analyzed. The EPR/ENDOR parameters obtained demonstrate that they are very similar to those of DPPH, and that, except for a few exceptions, the unpaired-electron probability population, primarily located at the two hydrazinic nitrogen nuclei, is relatively unaffected by the H-bonding and the polarizability capabilities of the organic solvents studied. However a significant shift of this unpaired-electron population does occur when these sulfonated hydrazyl salts are dissolved in water. Possible reasons for the observed effects are discussed.

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137. *Pulsed EPR Studies of Vanadium-Exchanged Zeolites.*
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The pulsed electron paramagnetic resonance (EPR) technique of hyperfine sublevel correlation (HYSCORE) was used to obtain structural information about vanadium exchanged zeolites. HYSCORE spectra were obtained for the vanadium exchanged ZSM-5 and mordenite samples before and after dehydration and after adsorption of ammonia. Proton couplings associated with water and ammonia ligands as well as nitrogen hyperfine and quadrupole coupling constants were determined from the spectra. The results were compared with density functional theory (DFT) calculations for model complexes.

EPR Poster Session
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138. *PELDOR Studies on the Spatial Properties of Trapped Radicals in Irradiated DNA.*
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The spatial properties of trapped radicals produced in heavy ion-irradiated solid DNA at 77K have been probed using pulsed Electron Paramagnetic Double Resonance (PELDOR) techniques. Salmon testes DNA hydrated to eighteen water molecules per nucleotide was formed into solid cylinders 4-5 nm in diameter, frozen in liquid nitrogen and then irradiated side-on with 36Ar ions of energy 100 MeV/nucleon and LET of approximately 400 keV/µ. Irradiated samples were maintained at cryogenic temperature at all times. Measurements were made on a Bruker ESP380E pulsed EPR spectrometer at 60K. PELDOR measurements were made using a refocused echo detection sequence that allowed the dipolar interaction between trapped radicals to be observed. The EPR spectrum is attributed to electron loss/gain DNA base radicals and neutral carbon-centered radicals that likely arise from sugar damage. Here we will focus on the general features of the free radical distribution in the particle tracks. We find a radical concentration of $13.5*10^{18}$ cm^{-3} in the tracks and a track radius of 6.79 nm. The cross section of these tracks is 144 nm^2 yielding a lineal radical density of 2.6 radicals/nm. Based upon the yields previously determined for particles having calculated LET values of 300 – 400 keV/µm and using our measured lineal density, we obtain an LET of 270 keV/µm, which is in good agreement with the calculated range of values. A portion of this research was performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory. Argon irradiations were performed at the National Superconducting Cyclotron Laboratory at Michigan State University. *Supported by the Structural Biology Program of the DOE OBER and by the NIH/NCI, grants CA45424 (MS) and CA80211 (JZ).*

EPR Poster Session
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139. *Insight into Structure and Function of Photosynthetic Reaction Centers from Time-resolved EPR Spectroscopy.*
Stephan G. Zech, Columbia University

Time-resolved (TR) EPR spectroscopy has been proved to be a powerful tool to study structural and functional properties of the Photosynthetic Reaction Centers. The wealth of structural information can be extracted from magnetic interaction tensors, i.e. the g-tensor, the dipolar electron spin-spin coupling within radical pairs and the hyperfine coupling tensors. In many cases, these information can be supplemented by by kinetic and dynamic parameters. The 'out-of-phase' electron spin echo modulation can be used to obtain the dipolar spin-spin coupling within charge separated states, thereby providing inter-cofactor distances. These can be helpful for the interpretation of structural models of low and intermediate resolution for large membrane proteins as obtained from X-ray crystallography or electron microscopy. Pulsed EPR experiments on single crystals of Photosystem I (PS I) are presented which allow the determination of the location of the quinone electron acceptor within the protein matrix. Multifrequency EPR data of charge separated states provide a detailed insight into the interaction between the quinone and the immediate protein environment. Furthermore, time-resolved EPR experiments on site-directed PS I mutants are used to address the question of directionality of electron transfer between the two symmetrically related branches of cofactors in PS I. *Supported by the Alexander-von-Humboldt Foundation.*

EPR Oral Session
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140. *95-287 GHz EPR Study of Radical Intermediates Formed in the Reaction of Myoglobin with H_2O_2.*
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Multifrequency EPR measurements were applied to characterize the peroxide intermediates in the reaction of equine myoglobin with hydrogen peroxide. Myoglobin (Mb) is a heme protein with a limited catalytic ability but it supports the H_2O_2-dependant oxidation of many substrates. The protein (globin) radical generated upon the reaction of Mb with H_2O_2 rapidly undergoes subsequent chemistry, reacting with oxygen to form the peroxyl radical, which exhibits the axial EPR signal with $g_{II} = 2.04$ and $g_{\perp} = 2.0$ at 9 GHz. To understand the origin of this radical and its location in the protein, we compared the EPR parameters of the radical produced in Mb treated with H_2O_2 with those of the radicals formed by oxidation of individual amino acids, namely, Tyr, Trp and His. The EPR spectra of the peroxyl radicals formed on different residues have similar g values at X-band. In contrast, at higher frequencies (95-287 GHz), it is possible to resolve the g-anisotropy of amino acid radicals and to distinguish them. The broadening of the g_X portion of the HF-EPR spectra allow better resolution of the g = 2 region and identification of the radicals superimposed at conventional fields. The initial tryptophanyl radical ($g_X = 2.00391$, $g_Y = 2.00298$, $g_Z = 2.00183$) and tyrosyl radical ($g_X = 2.00876$, $g_Y = 2.00471$, $g_Z = 2.00272$) were determined from the 287 GHz spectra of the Trp and Tyr peroxyl radicals, respectively. Two different radicals were determined for the oxidized His at 95-193 GHz. Possible sites for the peroxyl radical location in Mb are discussed.

EPR Oral Session
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141. *Rapid Freeze Quench EPR with Dead Times Below 100 Microseconds: Applications in High Frequency EPR.*
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The technique of Rapid Freeze Quench (RFQ) is used to quench molecular processes and stabilize short-lived kinetic intermediates, allowing their study using a variety of spectroscopic techniques. In general, the technique involves mixing two or more reagents in a mixing chamber and, after a predetermined time delay, injecting the mixture into a cryogen to freeze the sample. Typical commercially available RFQ apparatus employ cold liquid isopentane as the cryogen and Wiskind grids as mixers. These apparatus have RFQ dead times of approximately 5 ms and yield samples which are mixtures of the sample of interest frozen within isopentane. RFQ techniques have been particularly useful when combined with low frequency (X and Q band) EPR spectroscopy for the study of short-lived paramagnetic species. However, the extension of RFQ techniques to higher frequencies has been problematic: the sample frozen in isopentane is difficult to pack into the small capillary sample tubes used in the most common HFEPR resonators, particularly for pulsed High Frequency (HF) EPR experiments. Recently, a new ultra-fast microfluidic mixer and RFQ device was described which utilizes a 450 picoliter mixing chamber photolithographically etched into silicon (Y. Lin, G. Gerfen, D. Rousseau and S-R. Yeh, submitted for publication). The sample is frozen by injecting it onto rotating copper disks in

contact with liquid nitrogen. This design achieves very rapid freeze times (not possible by directly injecting the sample into liquid nitrogen) without dispersing the sample into isopentane. The resulting frozen sample can be readily packed into the capillary tubes and holders for use in High Frequency EPR resonators, either in fundamental TE_{011} cylindrical resonators or in overmoded TE_{11N} resonators. Moreover, the RFQ deadtime using the device has been measured to be 50 μsec, approximately two orders of magnitude better than can be achieved commercially. Descriptions of the apparatus and examples of RFQ HFEPR experiments will be presented.

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142. *High Resolution ESR Microscopy.*

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NMR microscopy is a well-established technique, which employs the methods of MRI with large gradients in high magnetic fields, to achieve images with micrometer resolution. The state-of-the-art of today's NMR microscopy has reached voxel resolution of ~ $[3.5\mu m]^3$ at 400 MHz, with ~30 h acquisition time [Ciobanu, L., Seeber, D. A., and C. H. Pennington, Journal of Magnetic Resonance, 158 (2002) 178-182.]. In contrast to NMR, ESR microscopy is still at its infancy. Most of the efforts with respect to ESR imaging are directed towards low resolution imaging of large biological objects to identify the radical and the oxygen concentration. The best result, with respect to ESR microscopy, was a resolution of ~ $[20\mu m]^3$ in a unique long T_2 organic conductor system, at 300 MHz, with ~ 12 h acquisition time [Feintuch, A., Alexandrowicz, G., Tashma, T., Boasson, Y., Grayevsky, A., and Kaplan, N. Journal of Magnetic Resonance, 142 (2000) 382-385]. Simple theoretical considerations show that both pulsed and CW ESR imaging methods should achieve voxel resolution better than 1×1×10 microns in several minutes of acquisition (at 35-60 GHz) for samples doped with trityl radical. These capabilities can be valuable for applications such as sub-cellular $[O_2]$ measurements, molecular imaging, which employs mobile spin probes targeted at specific molecules, functional imaging of plants, sub-cellular microviscosity measurements, exploration of radicals in materials science and other aspects addressed currently only by NMR microscopy. In view of the possible potential of this method, we recently initiated theoretical and experimental activities, directed at achieving micron resolution ESR imaging capability. As a test case we present our results in X-band CW imaging, which include the construction of a miniature dielectric resonator and a gradient coil set, enabling one to acquire 2D image in a resolution better than 10 microns. The resonator is based on a $SrTiO_3$ single crystal, machined to the appropriate shape. The unique miniature gradient coil set achieves gradients of 5 T/m/A and facilitates the examination of an "optical microscope-like" thin sample on a glass slide. The imaging is based on the CW-ESR modulated gradient method [Herrling, T., Klimes, N. Karthe, W., Ewert, U., and Ebert, B., Journal of Magnetic Resonance, 49 (1982) 203-211.]. Further issues, such as parallel image acquisition in CW-ESR imaging, choosing the optimal frequency of operation and CW vs. pulsed methods with respect to imaging, will be also discussed.

EPR Oral Session

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143. *Nanoparticulate Spin Probes for EPR Cell-Tracking and Oximetry.*

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The ability to non-invasively track cells in vivo provides valuable insights into the development of targeted cell therapy and tissue repair procedures. Particulates of superparamagnetic MRI contrast agents are currently being explored as probes for cell-tracking. Though the detection is indirect, the superior anatomic resolution of MRI enables the tracking by the internalized contrast particulates at the single cell level. We have developed paramagnetic crystalline particulates that can be used by EPR spectroscopy. The particles are lithiated derivatives of phthalocyanine macrocycles. The compounds can be prepared in a variety of sizes ranging from 0.1 – 60 um suitable for in vivo tagging. In addition, the particulates show highly desirable characteristics suitable for biological EPR oximetry. They exhibit large line-width sensitivity to oxygen, high spin density, linear response to oxygen over a wide range of pO_2, rapid response to changes in oxygenation, and long-term stability in tissues (> 5 months) without apparent toxicity. We have internalized these particulate probes into a variety of mammalian cells and studied their effect on the cell morphology, viability and oxygen consumption. In addition to oxygen measurements, these nanoparticulate probes offer the potential for paramagnetic-labeling of cells to study cell proliferation and migration. The micro- or nanoparticulate suspensions can also be used as EPR imaging probes. A wide range of applications of these EPR particulate probes in basic research and clinical applications including cell physiology, pulmonary and cardiovascular pathophysiology, and cancer is envisaged.

EPR Oral Session

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144. *Biological Correlates of EPR Oxygen Images: Preliminary Images of Response to Radiation Plus Adenovirus Delivered EGR-TNF Anti-cancer Therapy.*

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EPR imaging at 250 MHz imaging using trityl spin probes (Nycomed Innovations, Malmo SW) has been used to probe the oxygen physiology of a novel anti-cancer therapy. This involves the local injection of an viral vector into which has been inserted an early growth response (EGR) gene, a radiation responsive promoter sequence, upstream of a Tumor Necrosis Factor α (TNFα) gene. Upon the local administration of 10 Gy radiation, cells infected with this vector produce high local concentrations of TNFα, a potent anti-angiogenic peptide. Given the resistance to radiation conferred by hypoxia, the synergism between this vector and radiation was surprising. Near simultaneous images of the same tumor with T_1 weighted MRI of gadolinium washout show the effect of the therapy on the tumor blood volume and vascular permeability-area product. A total of five animals have successfully completed EPRI and MRI on days 0, 3 and 16 relative to therapy administration. Preliminary analysis of the EPRI demonstrates a reduction of the oxygen concentration in the tumor tissue 3 days post therapy. At 16 days post therapy there is a significant reduction in the tumor size. Tumor tissue remaining appears to have reoxygenated. Further analysis of the multimodality images, their correlation and the physiologic consequences of this therapy will be presented. *Support in part by DAMD17-02-1-0034 and NIH P41 RR12257 is gratefully acknowledged.*

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Luminescence • Monday Oral Sessions

145. *Two-Beam Fluorescence Cross-Correlation Spectroscopy for Discriminating Positive and Negative Ions in Continuous Flow Capillary Electrophoresis.*

Keir Fogarty and Alan Van Orden, Colorado State University

Single molecule, two-beam fluorescence cross-correlation spectroscopy (FCCS) is a non-invasive technique that allows for multicomponent analysis of complex samples in continuous flow capillary electrophoresis. In contrast to conventional CE, the single molecule technique allows detection on the microsecond to millisecond time scale which enables the monitoring of distinct species regardless of electrophoretic flow direction and without macroscopic separation. The speed and versatility of FCCS also make it an excellent candidate for high throughput analysis in the areas of clinical diagnostics, drug discovery, proteomics research, and environmental monitoring. As a demonstration of concept, a three component mixture of Rhodamine 6G, 5-carboxytetramethylrhodamine (TAMRA), and a 39 strand DNA oligomer labelled with TAMRA has been successfully differentiated, based on the species' different electrophoretic mobilities. The ability to monitor both positive (R6G) and negative (DNA, TAMRA) species simultaneously, and on millisecond timescales, opens the door to the study of ligand-receptor systems difficult to study using previously existing methods.

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146. *Lateral Diffusion Measurement on Cell Surfaces by Total Internal Reflection Fringe (TIRIF) Photobleaching Recovery.*

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Total internal reflection (TIR) techniques combine the sensitivity of previous interference fringe photobleaching (IF-FPR) methods with the cell surface selectivity afforded by traditional spot photobleaching recovery measurements. IF-FPR methods (Munnely *et al*., 1998, *Biophys. J*., **75**, 1131) employ a 3D fringe pattern to interrogate entire cells in lateral diffusion measurements and are especially useful for weakly-expressed membrane species (Song, *et al*, 2002, *Biochem*., **41**, 881). However, difficulties arise with GFP fusion proteins, or otherwise autofluorescent cells, since cytoplasmic species contribute to the recovery signal and distort measurements aimed at surface molecules. In TIRIF methods using an Olympus 1.65 NA objective, interfering laser beams are placed at the back focal plane periphery where the NA exceeds 1.38. This creates an interference pattern totally internally reflected at the coverslip-medium interface. Fluorescence excitation only occurs in the evanescent wave, ie, where the cell membrane is in contact with the coverslip. Contributions from cytoplasmic fluorescence are thus avoided. For GFP-epidermal

growth factor receptor (GPF-EGFr) expressed in CHO cells, spot FPR, IF-FPR and TIRIF-FPR yielded fluorescence signals of about 1160, 40000, and 4300 CPS, respectively. With these methods D was $9.4x10^{-10}$, $9.6x10^{-10}$, and $6.2x10^{-10}$ cm^2s^{-1} while mobility was estimated at 48%, 80%, and 37%, respectively. Cytoplasmic fluorescence distorts IF-FPR mobility estimates, while TIRIF-FPR provides accurate measurements with sensitivity improved over spot methods. *Supported in part by NSF grant MCB 98-07822 to BGB and NIH grant HD23236 to DAR.*

Luminescence Oral Session

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147. *Time-Resolved Fluorescence Studies of Sol-Gel Derived Nanocomposite Materials Suitable for Biosensor Applications.*

Gillian L. Goring and John D. Brennan, McMaster University

The entrapment of biomolecules within sol-gel derived organic/inorganic hybrid materials has been widely utilized for the development of biosensors. Hydrolysis and condensation of tetraalkoxysilanes can be done in the presence of either a dispersed additive such as an organic polymer, producing a Class I material, or along with an organosilane, leading to Class II materials with covalently anchored functional groups. Incorporation of both dispersed and anchored organic groups is also possible leading to Class I/II nanocomposite materials. Such materials can be designed to have a range of properties, including tunable polarity and porosity, which can be optimized to maintain the activity of entrapped biomolecules. However, at this time there is still limited knowledge regarding the effects organic precursors and additives on the nanoscale morphology of the resulting sol-gel derived material. This presentation will focus on how morphology on the nanometer to micrometer size scale is altered owing to phase separation upon the addition of organically modified silanes (ORMOSILs) and/or polymers to tetraethyl orthosilicate (TEOS) derived materials. Through the use of imaging techniques such as tapping mode atomic force microscopy, scanning electron microscopy and confocal fluorescence microscopy, it was possible to assess the macroscopic and microscopic features within both type I and type II nanocomposite materials. A model describing the phase segregation of hydrophobic additives within TEOS derived materials will be presented, and the implications of these findings for biosensor design will be discussed.

Luminescence Oral Session

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148. *Design and Applications of Highly Luminescent Metal Complexes.*

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Inorganic complexes show great promise as molecular probes and luminescence-based sensors. The majority of work uses Ru(II), Re(I), and Os(II) complexes with α-diimine ligands (e.g., 2,2'-bipyridine, 1,10-phenanthroline, and analogues). The rational design of practical systems requires 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. A convenient method for measuring diffusion coefficients of analytes in sensors will be presented. Photochemical results will demonstrate the unique role the polymer can play in the photostability of the sensor molecules.

Luminescence Oral Session

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149. *Single Pyrene Labeled Dendrimers: pH-Dependent Fluorescence Behavior.*

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We report the pH-dependent fluorescence behavior of the dendrimers functionalized with a single pyrene label in order to obtain information about the dependence of dendrimer order and branching on its molecular architecture. We utilized a wide variety of molecular (i.e., nitromethane, N,NN-dimethylaniline, and methyl iodide) and ionic (iodide and metal cations) fluorescence quenching agents toward the single, focally located pyrenyl-adduct of a series of asymmetric poly(amido) dendrimers possessing carboxylate moieties at their periphery to assess their relative structural permeabilities as a function of the pH of the environment. These experiments provided the information on the effect of pH on the chain segmental densities and diffusional behaviors as a function of generation number, further giving insight into the roles of size and electrostatics in the process. The effect of pH on the fluorescence emission behavior (i.e., intensity and band ratio) of pyrenyl-adducts was also

explored. Static fluorescence anisotropy is used as a tool to explore the segmental flexibility of the pyrenyl-adduct as the pH of the solution is changed. *Supported by Sandia-University Research Program (SURP).*

Luminescence Oral Session

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150. *On the Formation of Self-Assembled Aggregates within the Room-Temperature Ionic Liquid 1-ethyl-3-butylmethlylimidazolium bis (trifluoromeths ylsulfonyl)imide.*

Kristin A. Fletcher and Siddarth Pandey, New Mexico Institute of Mining and Technology

Room-temperature ionic liquids (RTILs) can be used as replacements for select organic solvents and have potential to act as environmentally-benign solvent media for many industrially important chemical applications. One important application yet to be thoroughly investigated is the formation of molecularly organized assemblies within RTILs. Towards this end, we have begun a systematic investigation of the behavior of select solvatochromic probes (Reichardt's betaine dye, pyrene, 1-pyrenecarboxaldehyde and 1,3-bis(1-pyrenyl)propane) as the concentration of surfactant solubilized within 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (emimTf_2N) is increased. The response of Reichardt's betaine dye did not change significantly as Brij-35, Brij-700, Triton X-100 or Tween-20 was added to emimTf_2N. Conversely, the addition of Brij-35, Brij-700, or Triton X-100 to emimTf_2N caused a considerable change in the response of pyrene (sensed a less dipolar environment) and 1,3-bis(1-pyrenyl)propane (the viscosity was shown to increase substantially) indicating possible aggregation of surfactant. We observed no apparent change in the microenvironment surrounding all probes as cetyltrimethylammonium bromide (CTAB) was added to emimTf_2N. The formation of reverse micelle-like structures was investigated in an Aerosol OT (AOT)-water-emimTf_2N ternary system. The response of pyrene as the concentration of AOT and water was increased showed the cybotactic region became increasingly non-polar, indicating the presence of hydrophobic regions. Further, the response of Reichardt's betaine dye indicates possible interactions between the dye and either surfactant or water as the concentration of AOT and water increase.

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151. *Solid-Matrix Luminescence Properties of Benzo[e]pyrene and Dibenzo[a,l]pyrene Diolepoxide-DNA Adducts.* Allison L. Thompson and Robert J. Hurtubise, University of Wyoming

Polycyclic aromatic hydrocarbons (PAHs) are known mutagenic and carcinogenic compounds with dibenzo[a,l]pyrene (DB[a,l]P) being the most carcinogenic PAH currently known. DP[a,l]P can be metabolically activated to dibenzo[a,l]pyrene-11,12-diol-13,14-expoxide (DB[a,l]PDE) which then is able to bind to DNA and form DNA adducts. Benzo[e]pyrene (B[e]P) was used as a model compound because its aromatic ring system is the same as DB[a,l]PDE. Thus, the solid-matrix luminescence properties for the two aromatic systems should be similar. Solid-matrix fluorescence (SMF) and phosphorescence (SMP) data were obtained for B[e]P and the DB[a,l]PDE-DNA adducts with and without the aid of the heavy-atom salts, thallium nitrate ($TlNO_3$) and sodium iodide (NaI). The data acquired as a function of the amount of $TlNO_3$ were SMF and SMP spectra, SMP intensity, and SMP lifetimes. The SMP spectra for the two systems showed that the spectra were similar with only slight red shifts for DB[a,l]PDE-DNA adducts compared to B[e]P. Generally, DB[a,l]DE-DNA adducts gave a much weaker SMF signal than B[e]P, which made it difficult to directly compare the SMF data. With SMP, both the DB[a,l]PDE-DNA adducts and B[e]P gave fairly intense signals even without a heavy-atom present. However, the DB[a,l]PDE-DNA adducts showed a greater enhancement in the SMP intensity in the presence of $TlNO_3$ compared to B[e]P. Also, the enhancement of SMP of B[e]P with $TlNO_3$ was much greater than with NaI. Thus, more emphasis was placed on $TlNO_3$ as a heavy-atom salt. The SMP lifetimes of the DB[a,l]PDE-DNA adducts and B[e]P were similar without $TlNO_3$. Also, the SMP lifetimes of B[e]P and DB[a,l]PDE-DNA adducts were found to be monoexponential without a heavy-atom salt present. However, the SMP lifetimes of B[e]P and DB[a,l]PDE-DNA adducts gave biexponential decay curves in the presence of $TlNO_3$.

Luminescence Oral Session

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152. *Optical Sensor Platforms for Quantifying Pollutant Emissions in Combustion Exhausts.*
James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103; Rodolfo Barron-Jimenez and Thomas N. Anderson, Dept. of Mechanical Engineering, Texas A&M University, College Station, TX 77843; Robert P. Lucht, School of Mechanical Engineering, Purdue University, West Lafayette, IN 47907; Sukesh Roy and Michael S. Brown, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Rd., Dayton, OH 45440-3638; Scott Stouffer, University of Dayton Research Institute, Dayton, OH 45469

Quantifying pollutants in the exhaust of a combustor is critically important for understanding and evaluating the performance of the combustor and/or tailored fuels and fuel additives. To this end, we have developed sensors for NO and CO based on line-of-sight absorption. The sensors use sum-frequency and difference-frequency mixing of solid-state lasers in nonlinear crystals to obtain the required resonant optical frequencies. The NO sensor relies on sum-frequency mixing of a single-mode, tunable, 10-mW, 395-nm external-cavity diode laser with the output of a 115-mW frequency-doubled, diode-pumped Nd:YAG laser in a BBO crystal. The CO sensor makes use of difference-frequency mixing of a single-mode, tunable, 70-mW, 860-nm external-cavity diode laser with the output of a 550-mW diode-pumped cw Nd:YAG laser in a PPLN crystal. Both sensors have been constructed on single breadboard platforms for robustness and portability. Construction and performance as well as application of these sensors for the detection of CO and NO in the exhaust stream of the well-stirred reactor at WPAFB will be discussed.

Luminescence Oral Session
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153. *Effects of Dynamic Strain on OH* and CH* Luminescence in Counterflow Diffusion Flames.*
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Passive flame-emission sensors have the potential to provide real-time feedback on combustion performance in a number of industrial and propulsion applications. Initial studies indicate that molecular flame emission, from OH* and CH* in particular, can be used to monitor the relative fuel/air ratio as flame in-flow conditions are varied. After proper calibration in a well-controlled laminar flame, this approach also shows promise for quantitative measurements of fuel/air ratios. The goal of the current work is to extend the applicability of this approach to spatially inhomogeneous flames that are subject to transient velocity gradients (i.e., dynamic strain). These gradients, which are typical in advanced combustors that rely on turbulence for stable and efficient operation, alter the local gas composition, temperature, and reaction rates. To evaluate the effects of such conditions on the performance of emission-based sensors, broadband and narrowband molecular flame-emission data have been collected in a repeatable, vortex-perturbed counterflow diffusion flame. The relationship of OH* and CH* luminescence to fuel/air ratio is examined as the flame is subjected to a range of transient velocity gradients for a variety of fuels.

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154. *Dual-Pump, Dual-Broadband Coherent Anti-Stokes Raman Scattering for Characterization of Liquid-Fueled Combustors.*
Sukesh Roy and Terrence R. Meyer, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638; Robert P. Lucht, Department of Mechanical Engineering, Purdue University, West Lafayette, IN 47907-1288; Vincent M. Belovich, Edwin Corporan, and James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

A dual-pump, dual-broadband coherent anti-Stokes Raman scattering (CARS) system has been developed for simultaneous detection of temperature and three species concentrations in reacting flows. In this CARS system, the rotational transitions of N_2/O_2 and the rovibrational transitions of N_2/CO_2 are probed. The CARS spectra of each molecule pair are observed within a distinct wavelength band, allowing two molecule pairs to be measured simultaneously using a detection system that includes two spectrometers and two cameras. Since nitrogen is a common species in each molecule pair, it can be used as a reference for normalizing species concentrations and for improving the accuracy and dynamic range of temperature measurements. Demonstration of this measurement technology has been accomplished in the exhaust of a liquid-fueled, swirl-stabilized CFM-56 combustor. These measurements were performed to investigate the exhaust-stream temperatures and CO_2 concentrations for various jet fuels over a range of equivalence ratios. The effects of fuel additives on these combustor parameters were explored as well.

Luminescence Oral Session
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155. *Energy Deposition in "Nonresonant" Transient Grating Thermometry.*
Michael S. Brown and Terrence R. Meyer, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638; Dale T. Shouse and James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

The reaction zone of a pressurized, liquid-fueled combustor presents a difficult environment for making in-situ, non-intrusive, spatially resolved temperature measurements. Transient grating thermometry provides one means of performing such measurements. Employing lasers that are not tuned to a specific molecular resonance, we have executed such measurements in a pressurized JP-8-fueled model combustor of interest to the Air Force. The acquired signals indicate that thermalization via absorption dominates signal generation. Candidates for "nonresonant" absorption include soot particles and polyaromatic hydrocarbons. Energy transfer to the surrounding gases appears to follow both fast and slow paths.

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156. *Quenching Studies of Highly Luminescent CdS Nanoparticles in the Presence of Sulfur Containing Compounds.*
Justyna Widera, James R. Gord and Christopher E. Bunker, Air Force Research Laboratory, Propulsion Directorate

Nanoparticles have recently attracted a great deal of scientific attention due to their small size, unusual electronic and optical properties, and their potential applications as sensors, catalysts, lightweight structures, and pharmaceuticals. Currently, we are using these materials to design sensors for chemical detection. CdS nanoparticles are synthesized using the reverse micelle method and then treated by a photoirradiation and vacuum-drying procedure resulting in highly luminescent particles with quantum efficiencies of ~35 percent. The nanoparticles are characterized by uniform size distributions (~3-5 nm diameters), high surface areas, and trap-state emissions. In this paper, we present data for the systematic investigation of the luminescence quenching of the CdS nanoparticles by different sulfur containing compounds. The system (CdS nanoparticles – quencher) was characterized by means of UV-vis absorption and steady-state and time-resolved luminescence spectroscopy. The results will be discussed within the context of both static and dynamic quenching processes.

Luminescence Oral Session
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157. *Solvatochromic Shifts of Pyrene in Supercritical Fuels.*
Donald K. Phelps, Christopher E. Bunker and James R. Gord, Air Force Research Laboratory, Propulsion Directorate

Aviation fuels serve as the primary coolant for all aircraft on-board heat sources. As such, the thermal stability of these materials is an important issue. Through the continued development of JP-8+100, JP-8+225, and JP-900, the Propulsion Directorate's Fuels Branch has invested in the design of thermally stable fuels and fuel additives for current and next-generation aircraft. Research in this area has been focused on obtaining a detailed understanding of the chemical and physical processes at work in high-temperature fuels. At high temperatures and pressures, these fuels exist as supercritical fluids that exhibit unique properties. To study these properties at a molecular level, we have been investigating spectral shifts in the excitation and emission spectra of fluorophores doped into supercritical aviation fuels and fuel surrogates. Experiments accomplished with steady-state absorption and fluorescence instruments have been modeled through calculations using Molcas, Gaussian 03, and Columbus *ab initio* QM codes and molecular mechanics simulations.

Luminescence Oral Session
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158. *HPLC/MS/MS Quantitative Bioanalysis of Drugs Used to Protect Against Chemical Warfare Agents.*
Shane Needham[1], Binying Ye[1], J. Richard Smith[2] and Benedict R. Capacio[2] [1]Alturas Analytics, Inc. 1282 Alturas Drive Moscow, Idaho [2]US Army Medical Research Institute of Chemical Defense, Aberdeen Proving Ground, Maryland

We have developed several bioanalytical HPLC/MS/MS methods for the analysis of drugs used to protect against chemical warfare nerve agents. Here we present the low-level GLP validation of an HPLC/MS/MS method for the determination of pyridostigmine bromide (PB) from guinea pig plasma. In addition, we will discuss the development of an HPLC/MS/MS method for the determination of atropine from monkey serum. PB is a pretreatment drug used to protect against chemical warfare nerve agents. By itself PB is not protective against chemical warfare nerve agent poisoning. However, when used as a pretreatment, PB might enhance the antidote effects of the standard atropine treatments used by the U.S. military for nerve agent poisoning. Atropine is used immediately upon exposure to nerve gas agents to counteract the effects of the cholinesterase inhibitors. Since the US Army continues to improve formulations, the low level quantitative analysis of these drugs in biological fluids is important. For PB, the guinea pig PK experiments required the use of less than 30 µL of plasma with quantitation limits near 500 pg/mL. For atropine, the monkey studies required limits of quantitation (LLOQ) near 10 pg/mL.

Here we report on the development of separate HPLC/MS/MS assays for the determination of PB from guinea pig plasma and atropine from monkey serum. To accelerate sample analysis, all sample preparation was done in 96 well plates. Deuterated internal standards were used for both assays. High-speed gradient HPLC pumps were used in tandem with a Sciex API3000. Multiple reaction monitoring was used to detect the drugs and internal standards. The LLOQ for the atropine assay was less than 10 pg/mL whereas the LLOQ for the PB assay was 100 pg/mL using only 25 µL of plasma. The run time for each assay was less than 2.0 minutes per sample. This presentation illustrates a rapid, selective and sensitive method for the determination of PB and atropine in guinea pig and monkey serum, respectively.

MS, GC/MS, LC/MS & Pharmaceutical Analysis Oral Session
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159. *Fourier Transform-Infrared Imaging of Aortic Tissue: A Novel Approach for the Study of Atherosclerosis.*
Manoj Mehta, Elaine Holmes and George E. Tranter, Imperial College London, Faculty of Medicine, London SW7 2AZ, UK;
Elaine McKilligin, GlaxoSmithKline, Medicines Research Centre, Stevenage, Hertfordshire, SG1 2NY, UK

Despite remarkable advances in medical therapeutics and technology over the last 40 years, cardiovascular disease remains the second most common cause of death worldwide, after infectious diseases, leading to almost 17 million deaths every year1. The aim of this study is to precisely locate and characterise major chemical constituents of aortic tissue from Watanabe Heritable Hyperlipidemic Rabbits (WHHL) and determine any correlations with age and disease state using the imaging technique Fourier transform infrared (FT-IR) microspectroscopy coupled with chemometric analysis. The results obtained here by FT-IR microspectroscopy coupled with Chemometric analysis are intended to show that this method can be applied to aortic tissue to confirm the presence of specific functional groups (such as amide –NH and C=O, and acyl CH2 and ester C=O) from specific biological materials (such as proteins and cholesterol esters). As well as detecting differences in the chemical composition, functional group mapping can establish, accurately and specifically, the spatial distribution of these materials within the aortic tissue, including the plaques. This approach seems extremely beneficial as an analytical tool in pathology as the visualisation potential, vital in histological protocols, is retained, whilst simultaneously broadening the diagnostic capacity of IR spectroscopy. This technique is spectroscopically 'information rich', rapidly generating vast amounts of data relating to the myriad of biochemical information within the aortic tissue. Analysing and appropriately interpreting the wealth of information offered by this technique still remains the greatest challenge.

[1] World Health Organisation: World Health Report 2000: Health Systems: Improving Performance, (2000). World Health Organisation, Geneva, Switzerland.

MS, GC/MS, LC/MS & Pharmaceutical Analysis Oral Session
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160. *Accurate Mass Measurement in Drug Stability Studies on an Enhanced Mass Resolution Triple Quadrupole Mass Spectrometer.*
Gary Paul, Thermo Electron Corporation

In this presentation, the accurate mass measurement and high performance quantitative capabilities of the TSQ Quantum triple quadrupole mass spectrometer product line will be discussed. The attainment of accurate mass measurement on an enhanced mass-resolution triple quadrupole mass spectrometer, the TSQ Quantum Ultra AM, will be described in detail, relative to the identification of an unknown impurity formed when the pharmaceutical cabergoline was dissolved in methanol. The successful identification of this impurity through accurate mass

measurement enabled the determination of a suitable solvent system for cabergoline storage. Drug stability studies of this nature are essential in order to achieve high performance quantitation. Comparison of the quantitative performance of cabergoline on the TSQ Quantum Discovery and TSQ Quantum Ultra AM instruments will also be addressed where the instrument features responsible for the high sensitivity and broad linear dynamic range observed will be discussed. Pertinent examples involving other drugs of interest will be included in this presentation to illustrate the unique blend of accurate mass measurement and quantitative capabilities provided by the TSQ Quantum Ultra AM.

MS, GC/MS, LC/MS & Pharmaceutical Analysis Oral Session
Gary Paul, Field Marketing Manager, Thermo Electron Corporation, Somerset, NJ, USA

161. *Composition of Pharmaceutical Production Equipment Materials.*
Don H. Miller, Ph.D.

Pharmaceutical production equipment is composed primarily of metals, plastics and rubbers. The evolution of high quality materials for pharmaceutical product contact has been underway for decades but in the last ten years materials with low extractables have become routinely available. This paper will examine the composition, both analytical and theoretical, of older materials often found in in-use pharmaceutical production equipment as well as more current materials which should be specified for new installations.

MS, GC/MS, LC/MS & Pharmaceutical Analysis Oral Session

162. *Structural Characterization of Organometallic Macrocomplexes Utilizing Electrospray Mass Spectrometry and Matrix-Assisted Laser Desorption Ionization Mass Spectrometry.*
Christina Sorensen and B.P.Sullivan, University of Wyoming

Electrospray ionization (ESI) and Matrix-Assisted Laser Desorption Ionization (MALDI) mass spectrometry provide complementary data to augment NMR and x-ray crystallography characterization of organometallic compounds, especially those of high nuclearity. Here we present and compare ESI-MS and MALDI data for a series of novel diphosphine bridged rhenium macromolecules containing up to five metal atoms. (e.g., the trimetallic ion $[Re(CO)_2PPh_3(bpy)(\mu_2\text{-dppene})Re(CO)_2(bpy)(\mu_2\text{-dppene})Re(CO)_2PPh_3(bpy)]^{3+}$ (where bpy is 2,2'-bipyridine and dppene is *(E)*1,2-bis(diphenylphosphino)ethylene)) Presented results are from experiments involving the variation of counterions, matrices, and solvents. Solvent and ionization characteristics were first optimized with ESI-MS, but subsequent MALDI analysis utilized these optimized conditions and confirmed the structural features implied by ESI-MS. Our data concerning preparations with different bridging ligands demonstrates the viability of MALDI for structural elucidation of large organometallic oligomers. *This work is supported by the National Science Foundation.*

MS, GC/MS, LC/MS & Pharmaceutical Analysis Oral Session
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163. *Fatty Acid Ethyl Ester Quantitation with a Novel Gas Chromatography Column and Automatic Injection System, and Correlation with Blood Ethanol Levels.*
Clark C. Kulig, Thomas P. Beresford and Gregory T. Everson, University of Colorado Health Sciences Center

Fatty Acid Ethyl Esters (FAEEs) are non-oxidative metabolites of ethanol present in serum at least 24 hours after ethanol ingestion. We sought to determine the precision of FAEE quantitation by GC/MS with a DB-1 column and automatic injection system. We also assessed for correlation between blood ethanol levels and FAEEs.

Methods: 500 pm ethyl heptadecanoate internal standard (IS) and 4 ml cold acetone were added to 0.5 ml serum samples, which were then vortexed and centrifuged. FAEE were extracted from the supernatant with 6 ml, then 2 ml hexane. Samples were injected into an Agilent 6890 gas chromatograph/ 5973 mass spectrometer using an automatic liquid sampling system after solid phase extraction (SPE) with aminopropyl silica columns. Ions 88.1 and 101.1 were monitored as the oven temperature increased from 150° to 250° C at 15°/min. A 30 m x 0.25mm DB–1 chromatography column was used. Standard curves, retention times and ion ratios were determined from FAEE commercial standards (Nu Chek Prep, Elysian, MN). Instrument precision was determined by three series of 10 injections from serum samples containing ethanol at concentrations of 25, 50, and 522 mg/dl. Linear regression was used to assess for correlation between blood alcohol level and FAEE concentration in 17 serum samples. **Results:** Instrument precision (CV) for three series of ten analyses is as follows: E 16:0, 0.7, 0.5, and 0.4%; E 18:1, 1.5, 0.8, and 0.6% and E 18:0, 1.2, 1.0, and 0.2%. Linear regression showed correlation between blood ethanol and serum levels of E 16:0, E 18:1, and E 18:0, r= 0.6, 0.57 and 0.56, respectively ($p<0.01$ for each). **Conclusion:** Measurement of FAEE via GC/MS equipped with a DB-1 GC column and automatic injection system offers excellent precision and increased time efficiency for FAEE quantitation. FAEE levels are correlated with serum ethanol levels.

MS, GC/MS, LC/MS & Pharmaceutical Analysis Oral Session
Clark C. Kulig, , University of Colorado Health Sciences Center, Denver, CO.

163b. *The Role of the AccuTOF Mass Spectrometer in Biochemical Analyisis.*
Adrian W. Pike, Zhanpin Wu and Chip Cody, JEOL USA Inc.

It has been a decade since the inception of the first ESI TOF MS. JEOL USA Inc., more recently announced a new generation LC-TOF MS using a continuous averager, ADC (Analogue to Digital Converter). For the first time, this has enabled a TOF mass spectrometer, the AccuTOF, to achieve a wider dynamic range than the conventional TOF, with high resolution and without compromising sensitivity.

This presentation will briefly discuss the principles of TOF MS, and the applications of the AccuTOF in biochemical analysis. Data will be presented utilizing the AccuTOF in trace analysis of such classes of compounds as peptides, oligonucleotides, pharmaceuticals, and environmental contaminants. Moreover, data will be presented demonstrating all functionalities of this instrument including in-source CID.

MS, GC/MS, LC/MS & Pharmaceutical Analysis Oral Session
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Nanotechnology • Monday Oral Sessions

164. *De Novo Design, Synthesis and Self-Assembly of Nanometer Scale Membrane Proteins.*
Krishna Kumar, Tufts University

The mechanisms for stabilizing the tertiary structures of water soluble globular proteins and membrane proteins are inherently different. While water soluble proteins are amenable to design via binary patterning, i.e. inside hydrophobic and outside hydrophilic, rigorous control of structure in designed membrane proteins is currently intractable. This lack of a simple binary patterning scheme has rendered membrane protein design a primitive science compared to water soluble proteins. This study describes a binary coding scheme that is suitable for use in the nonpolar lipid environment. The conceptual advance is the introduction of a third phase ('fluorous' phase), which is immiscible in both hydrocarbon and aqueous phases. Using this strategy, we have designed, synthesized and characterized proteins that fold into discrete structures within membranes. The self-assembly is envisioned as a two step process: first, the hydrophobic peptides partition into lipid bilayers. Second, due to phase separation properties of appropriately placed fluorinated amino acids, the peptides self-assemble within the lipid into predetermined structural ensembles. This is the first example of rational control of helix components in membranes and will pave the way for increasingly sophisticated membrane protein architectures.

Nanotechnology Oral Session
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165. *Lipid Nanotube Arrays for Biochip Applications.*
Alex I. Smirnov and Ali M. Alaouie, Department of Chemistry, North Carolina State University, Raleigh, NC 27606; Oleg G. Poluektov, Chemistry Division, Argonne National Laboratory, Argonne, IL 60431.

Combinatorial approach is becoming indispensable in biophysical and biomedical research. Together with DNA and protein biochips obtained by imprinting the molecules on planar substrates, pattering of phospholipid membranes on surfaces is considered as another promising biochip technology[1]. Here we report on an alternative approach to build patterned arrays of lipids and/or proteins, which is a departure from the methods currently in use. Our approach is based on the property of the phospholipids to self-assemble inside the nanopores into cylindrical nanoscale structures. We have already confirmed the existence of these structures, which we call lipid nanotubes, with spin labeling Electron Paramagnetic Resonance (EPR) technique. Being placed inside aligned through-film, rigid nanopores, these lipid nanotubes form arrays that are suitable for the combinatorial assay applications, especially if the pores are macroscopically homogeneous and uniformly packed as in Anodic Aluminum Oxide membranes (AAO). While dynamics of the lipids in the nanotubes confined by the AAO substrate appears somewhat more restricted, other properties, such as the main phase transition temperature and the oxygen permeability profile, were found to be essentially the same as for aqueous liposomes. The new lipid nanotube biochips have several advantages over the planar design, including much larger - at least by a factor of 100 - surface area and a better protection from surface contaminants. Preliminary results indicate, that lipid nanotubes are suitable for supporting membrane-associated proteins. *The work at NCSU is supported by the DOE Contract DE-FG02-02ER15354 and NATO (both to AS); ANL is supported by the DOE Contract W-31-109-Eng-38.*

[1] Kam L., and Boxer S. *J. Am. Chem. Soc.* 122: 12901-12902 (2000).

Nanotechnology Oral Session
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166. *Multi-functionalized Mesoporous Silica Nanosphere-Based Fluorescence Sensor and Controlled Release Delivery System.*
Victor S.-Y. Lin, Cheng-Yu Lai, Daniela R. Radu and Brian G. Trewyn, Iowa State University

Multi-functionalized Mesoporous Silica Nanosphere-Based Fluorescence Sensor and Controlled Release Delivery System. Victor S.-Y. Lin, Cheng-Yu Lai, Daniela R. Radu, Brian G. Trewyn, Iowa State University, Department of Chemistry, Ames, Iowa 50011-3111.

We have recently synthesized a series of multi-functionalized, MCM-41 type mesoporous silica nanosphere (MSN) materials[1,2]. The mesopore surface of these materials was derivatized with fluorescence sensor groups that can recognize and react with amino acid-based neurotransmitters. The exterior surface of the MSN materials was covalently coated with polylactides and polypeptides. The polylactide and polypeptide layers of these MSN sensors showed a unique "sieving" effect that regulates the rates of diffusion of different amino acids into the sensor mesopores of the material. The diffusion kinetics of various amino acid-based neurotransmitters was studied and the *in vitro* biocompatibility with neurons, astrocytes, and stem cells was also investigated. This type of MSN materials were also designed as controlled release delivery system[2] by using various *chemically removable caps*, such as surface-derivatized cadmium sulfide (CdS) nanocrystals and cell membrane permeable dendrimers, to encapsulate pharmaceutical drugs and neurotransmitters inside the organically functionalized mesopores. We studied the stimuli-responsive release profiles of several drug/neurotransmitter-loaded MSN systems by using various non-cytotoxic chemicals as *release triggers*. The biocompatibility and delivery efficiency of the MSN system with various neural cells *in vitro* were investigated. The molecules of interest were encapsulated inside the MSN by capping the openings of the mesopores with CdS nanoparticles or dendrimers to block the drugs/neurotransmitters from leaching out. Utilization of this MSN stimuli-responsive release system as a new gene transfer agent will also be demonstrated. *Supported by NSF CAREER Award (CHE-0239570) and DOE Ames Laboratory (MPC-PSI grant).*

1. Lin, V. S.-Y.; Lai, C.-Y.; Huang, J.; Song, S.-A.; Xu, S.; J. *Am. Chem.* Soc., **2001**, 123, 11510-11511.
2. Lai, C.-Y.; Trewyn, B. G.; Jeftinija, D. M.; Jeftinija, K.; Xu, S.; Jeftinija, S.; Lin, V. S.-Y. J. *Am. Chem. Soc.*, **2003**, 125, 4451-4459.

Nanotechnology Oral Session
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167. *Proton-Carrier Sol Gel Composites for High-Temperature PEM Applications.*
F. John Pern, J. A. Turner, National Renewable Energy Laboratory, Golden, CO 80401; and A.M. Herring, Department of Chemical Engineering, Colorado School of Mines, Golden, CO 80401.

In an effort to develop high-performance, high-temperature proton exchange membranes (PEM) for fuel cell applications in the 100°-150°C range, a number of proton-carrier composites were synthesized via a tetraethoxysilane (TEOS)-based sol gel approach using various silanes in acidic conditions. The proton-carrying component is either a Keggin-structured heteropoly silicotungstic acid ($SiO_2.12WO_3.26H_2O$, STA) or a sulfonic acid (SFA) that was chemically converted from a mercapto (-SH) group. The composites were characterized by diffusion-reflectance Fourier transform infrared (DRIFT), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), UV-vis absorption measurements, and ion exchange capacity (IEC) analysis before and after water extraction. The results show that the "bonding" level of STA on the silane-modified SiO_2 sol gels was strongly affected by the presence, and the functional group, of the silane. Without a silane, most of the STA on the sol gels was "free," i.e., only weakly adsorbed, and could be washed off. Higher bonding levels of STA were achieved when silanes with suitable functional groups were used. Furthermore, both of the SiO_2-based STA and SFA proton-carrier composites, after washing, show IEC results two to three times higher than that for Nafion 117 (0.9 meq/mol). Various composite-polymer membranes were made from the sol solutions or from the fine powders of the gels. The "free" STA was found to be largely retained by a glycidyl methacrylate copolymer matrix (PEMAGMA), with a small weight percentage loss even extracted in 85°C water bath. The composite membranes made of STA- and SFA-containing sol gels and PEMAGMA showed a broad endothermal peak in DSC and ~5% weight loss in TGA at ~150°C, presumably due to water loss. This is compared to the water loss from a blank SiO_2 sol gel at ~125°C in DSC. The proton conductivities of the STA- and SFA-containing membranes are currently under study. *This work was conducted at NREL under the Department of Energy contract number DE-FC02-0CH11088.*

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168. *Physical Characterization of Nanotechnology Materials.*
M.C. Pohl and R.B. Heninger, Horiba Instruments, Inc.

Nanotechnology has recently become an area of research that has taken the news headlines. While the formative ideas were expressed in 1959, the practical applications have just been realized in the last 5-10 years. These developments are affecting a wide range of industries from biotechnology to semiconductors to coatings to ceramics. While each technology has some unique challenges, there are many common areas of concern. Production of the nanoparticle involves the use of many manufacturing methodologies and so is difficult to understand. The physical characterization of the product materials on the other hand have many features in common with each other. These techniques would include particle size distribution, surface area determination, Zeta Potential measurement as well as other tests. These tests are performed routinely on many industrial samples every day. In the area of nanoparticles, these analyses become much more difficult as well as complex. The proper performance of these tests will form the basis for this paper. Emphasis will be placed on Particle Size Distribution measurements, as they are the most frequently cited numbers! Critical issues involved in sample preparation such as Bulk Sampling, Sample Dispersion and Sample Stabilization will be explored in detail. Possible methods of performing this analysis will be discussed with particular emphasis on Laser Light Scattering Methods. The use of this method for real-world samples will also be presented.

[1] NIST workshop on issues in characterization of sub-micron and nano-sized powders, October 4-5, 2001, Gaithersberg, MD.

Nanotechnology Oral Session
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169. *Probing the Electronic Structure of Cubane [Fe_4S_4]: Nature's Favorite Cluster for Electron Transfer and Storage.*
Xue-Bin Wang, Xin Yang, You-Jun Fu, Lai-Sheng Wang, W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352 and Department of Physics, Washington State University, 2710 University Drive, Richland, WA 99352; Shuqiang Niu, Toshiko Ichiye, School of Molecular Biosciences, Washington State University, Pullman, WA 99164; Christopher J. Pickett, Department of Biological Chemistry, John Innes Centre, Norwich, NR4 7UH (UK)

The cubane [Fe_4S_4] is the most common multi-nuclear metal center in nature for electron transfer and storage. Using electrospray, we produce a series of gaseous doubly-charged cubane-type complexes, $[Fe_4S_4L_4]^{2-}$, and probe their electronic structure with photoelectron spectroscopy and theoretical calculations. The photoelectron data confirm the two-layer model for the $[Fe_4S_4]^{2+}$ core, in which two ferromagnetic [Fe_2S_2] sub-layers are coupled antiferromagnetically to give a low-spin state. Reduction and oxidation are shown to occur on different sub-layers of the $[Fe_4S_4]^{2+}$ core. The current study provides intrinsic electronic structure information of the [Fe_4S_4] cluster and the molecular basis for understanding the protein and solvent effects on the properties of the [Fe_4S_4] active sites. We will also present a new experimental observation of symmetric fission of the doubly charged cubane in the gas phase: $[Fe_4S_4L_4]^{2-} \rightarrow 2[Fe_2S_2L_2]^{-}$, and its implication for cluster assembly and disassembly in Fe-S proteins.

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170. *Morphological Analysis of Sol-Gel Derived Nanocomposite Materials Suitable for Biosensor Applications.*
Gillian L. G. Goring and John D. Brennan, McMaster University

The entrapment of biomolecules within sol-gel derived organic/inorganic hybrid materials has been widely utilized for the development of biosensors. Hydrolysis and condensation of tetraalkoxysilanes can be done in the presence of either a dispersed additive such as an organic polymer, producing a Class I material, or along with an organosilane, leading to Class II materials with covalently anchored functional groups. Incorporation of both dispersed and anchored organic groups is also possible leading to Class I/II nanocomposite materials. Such materials can be designed to have a range of properties, including tunable polarity and porosity, which can be optimized to maintain the activity of entrapped biomolecules. However, at this time there is still limited knowledge regarding the effects organic precursors and additives on the nanoscale morphology of the resulting sol-gel derived material. This presentation will focus on how morphology on the nanometer to micrometer size scale is altered owing to phase separation upon the addition of organically modified silanes (ORMOSILs) and/or polymers to tetraethyl orthosilicate (TEOS) derived materials. Through the use of imaging techniques such as tapping mode atomic force microscopy, scanning electron microscopy and confocal fluorescence microscopy, it was possible to assess the macroscopic and microscopic features within both type I and type II nanocomposite materials. A model describing the phase segregation of hydrophobic additives within TEOS derived materials will be presented, and the implications of these findings for biosensor design will be discussed.

Nanotechnology Oral Session
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171. *Extensions of Solid-State NMR Methodology to Dipolar Field Effects in Solution.*
W. S. Warren, Motohiro Mizuno and Xiaoping Tang, Princeton University

Several years ago, we showed that dipolar couplings between distant spins produce additional peaks in the indirectly detected dimension in solution two-dimensional NMR experiments[1,2,3]. These peaks correspond to intermolecular multiple-quantum coherences (iMQCs) between widely separated molecules (typical separations are 10μm-10 mm). In the last few years, these effects have evolved from a curiosity into a wide range of applications in imaging and high resolution spectroscopy[4]. For example, it has been shown that solvent magnetization can be used as a highly efficient spin amplifier to boost signals from dilute species in solution[5]. However, *practical* exploitation of these approaches is often limited, because the (desired) solute-solvent dipolar couplings are overwhelmed by the (undesired) solvent-solvent dipolar couplings. We will discuss a new (in liquids) approach to overcoming this difficulty, the use of dipolar recoupling and magic angle spinning in solution. We will show that these methods, which are of course much easier in liquids than in solids, provide a robust method for dipolar signal enhancement.
This work is supported by the Center for Molecular and Biomolecular Imaging, and by the NIH under grant CA88683.

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NMR Oral Session
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172. *MRI Strategies for the Study of Permeable Media.*
Rudi Michalak and A. Ted Watson, Colorado State University, Dept. of Chemical Engineering and RMMR® Center

The study of properties of porous media is a rapidly developing field of research for both, academia and industry. Pore-size distributions, permeability distributions, and transport behaviors are key properties and have been widely studied by a number of methods. A variety of theoretical approaches have been developed for the simulation of quasi-homogeneous and heterogeneous cases and for single phase and multiple phase flow. MRI, as a truly microscopic and non-destructive method, increasingly plays the role of a key actor in the determination of these properties via diffusion, relaxivity, and flow field studies. Some developments are relatively recent and have not been brought to their fullest use yet. The MRI method is currently unsurpassed in its access to the critical length scales (sub-mm range) of porous media, a point where most competing methods fall short and have to resort to somewhat dubious up-scaling techniques and unrealistic homogeneity assumptions.

Biological tissues can be represented as permeable media. It has, therefore, recently been suggested that the methodological and analytical approaches available for the study of permeable media by MRI can be applied to the flow of fluids in biological media and contribute to a better understanding of fields of biomedical interest such as skin structure or bone and cartilage architecture. If successful, these new approaches may eventually contribute to find more effective treatments of diseases like osteoporosis or give insight into early stages of cancer development which are non-existent today and, at the same time, provide a microscopic tool for studying recovery processes.

In this contribution, we will present 3-dimensionally resolved MRI porosity-, relaxivity-, and flow distribution studies on single- and two-phase flow in porous rocks and outline the road of applicability of the MRI techniques used to the study of bio-materials.

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173. *Recent Developments in GARField Magnets for Broad-line Imaging.*
Peter J. McDonald, University of Surrey

Over the past 20 years, two classes of method each encompassing a range of sub-classes have been developed for the magnetic resonance microscopy of solids and other broad line systems: those which exploit line narrowing techniques and those which exploit large magnetic field gradients. Profiling using GARField design magnets developed out of our interest in stray field imaging with high field super-conducting magnets and falls into the second category (Glover et al., *J. Magn. Reson.,* 1999, 139, 90). GARField magnets are small permanent bench top magnets with curved pole pieces designed to yield a carefully tailored field profile. Spatial resolution of the order of 7 to 15 μm is routinely obtained using echo times of the order of 100 μs with temporal resolution of the order of 1 to 5 minutes. The method has certain advantages of quantitation, ease of interpreting relaxation contrast and experimental robustness. For profiling planar samples we find that, in many respects, GARField magnets out-perform their super-conducting parents and that they are allowing us to engage the attention of materials scientists for studies of, e.g., dispersion coatings. In this talk, I will describe the development of GARField magnets and explain how they can be used to overcome many of the inherent difficulties of conventional STRAFI including those of field curvature and sample levelling (Godward J et al., *J. Magn. Reson.* 2002, 155, 92). By way of application example, I will go on to describe the manner in which profiling with GARField magnets is offering fresh insight into the formation of structures akin to bi-liquid foams during the late stages of film formation from alkyd emulsions, when the emulsion is virtually dry (Gorce et al., *European Physical Journal* E 2002, 8, 421).

NMR Oral Session

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174. *High-temperature Rheological NMR of Polymer Melts.*
Antje Gottwald and Ulrich Scheler, Institute for Polymer Research Dresden

Knowledge of the flow properties of polymeric materials which are dominated by the viscoelastic properties is fundamental for an understanding of and design of the processing of these materials. Rheo NMR, in general NMR experiments under shear provides an insight on a molecular level. In a combination of NMR imaging and pulsed field gradient NMR molecular insight into the flow properties of material under study is gained and complex flow can be studied non-invasively. In a non-symmetric setup stable eddies are monitored. In addition a variety of NMR parameters like chemical shift an relaxation times is used to generate contrast in order to separate the flow patterns of individual components in a multi-component system for the study of mixing behaviour under shear. Integral measurements in addition permit the investigation of polymer dynamics under shear. Indirect detection in permits the measurement of J couplings in the molten polymers .

A high-temperature rheo NMR system operating up to 200 °C is demonstrated with examples of commercial PVC[1] and physically crosslinked polyamidines[2].

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[2] A. Gottwald, U. Scheler, Polymer preprints (in press)

NMR Oral Session

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175. *Imaging What We Eat to Maintain Quality and Ensure Safety.*
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Moisture plays a key role in the processing, stability and safety of foods. We are exploiting ^{1}H NMR imaging to quantify heat and mass transfer in foods during harvesting and processing. These traditional heat and mass transfer operations (cleaning, soaking, cooking) are operationally well established yet technically are often only casually analyzed. Understanding the transport and distribution of moisture permits us to engineer the food/process and ensure the safety and quality.

NMR Oral Session

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176. *Dynamics of Methane Combustion by In Situ NMR Spectroscopy Using High Density Xenon-129 Optical Pumping.*
Satyanarayana Anala, Galina E. Pavlovskaya, Prakash Pichumani, Todd J. Dieken, Michael D. Olsen and Thomas Meersmann, Colorado State University

Combustion studies by in-situ NMR have been successfully attempted using high density optical pumping of xenon-129. To the best of our knowledge, this is the first time that any kind of NMR has been employed for a direct analysis of a free combustion process. High-density optical pumping[1] is particularly promising for in-situ NMR of combustion and we were able to demonstrate the effect of temperature on the sensitive chemical shift for various xenon partial pressures. The high signal intensity obtained can be utilized in two-dimensional studies of the gas flow dynamics within a combustion process and for chemical shift selective hp-^{129}Xe magnetic resonance imaging (MRI) of specific combustion zones. In-situ NMR of high temperature reactions has a high potential value for the investigation of catalytic combustion processes, catalytic combustion technology and other high temperature applications of catalysts such as steam reforming or partial oxidation of hydrocarbons to produce feedstock chemicals.

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NMR Oral Session
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177. *Satellite-Transition MAS NMR of Quadrupolar Nuclei in Solids: New Techniques, Applications and Observations.*
Stephen Wimperis, University of Exeter

The satellite-transition MAS (STMAS) experiment offers an alternative approach to established methods such as dynamic angle spinning (DAS), double rotation (DOR) and multiple-quantum MAS (MQMAS) for obtaining high-resolution NMR spectra of half-integer quadrupolar nuclei. Unlike the better-known multiple-quantum experiment, STMAS involves two-dimensional correlation of purely single-quantum coherences; quadrupolar satellite transitions in t_1 (or F_1) and the central transition in t_2 (or F_2). STMAS is a relatively sensitive technique and we show that it can be used to obtain high-resolution 17-O (I = 5/2) spectra of very small amounts of material (~10 mg) made in a multi-anvil press and to obtain high-resolution natural abundance 25-Mg (I = 5/2) and 39-K (I = 3/2) spectra of minerals. The main drawback of the STMAS experiment is the need to adjust the spinning angle on the NMR probehead to the magic angle to an accuracy of ~0.002°. However, we present a new technique, SCAM-STMAS, that is self-compensated for this angle misset and we demonstrate that third-order quadrupolar and second-order quadrupolar-CSA effects are also refocussed. Finally, we show that STMAS is very sensitive to the presence of slow motions and that the method may thus be used as a novel probe of molecular reorientation in solids.

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178. *NMR Development of Functionalized ^{129}Xe as a Biosensor.*
E. Janette Ruiz, Sandra Garcia, Tom Lowery,* Seth M. Rubin,[1,*] David E. Wemmer*, and Alexander Pines, University of California at Berkeley, Department of Chemistry, Berkeley, CA 94720; Lawrence Berkeley National Laboratory, Materials Sciences and *Physical Biosciences Divisions, Berkeley, CA 94720; Nicolas Winssinger,[2] and Peter G. Schultz, The Scripps Research Institute, Department of Chemistry and the Skaggs Institute for Chemical Biology, 10550 North Torrey Pines Road, La Jolla, CA 92037; Thierry Brotin, and Jean-Pierre Dutasta, Stéréochimie et Interactions Moléculaires, École Normale Supérieure de Lyon, 69364 Lyon 07, France
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The encapsulation of xenon inside a protein-binding cage adds functionality to the noble gas atom, allowing it to act as a biosensor by specifically interacting with a target protein. Changes in both chemical shifts and relaxation rates of the functionalized ^{129}Xe upon binding of the complex to the protein serve as markers indicating the presence of the target protein. Xenon-based biosensors offer potential advantages over other sensors by capitalizing on both the chemical shift sensitivity of ^{129}Xe as well as the signal-to-noise enhancement made possible by hyperpolarization of ^{129}Xe. The possibility to multiplex by simultaneously detecting multiple analytes is promising based on results showing that even spatially distinct cage diastereomers can result in separate xenon chemical shifts. By varying cage structure, unique functionalized-xenon complexes can be used in a direct, one-shot multiplexed assay, which is potentially applicable to *in vitro* and perhaps, through the use MRI detection methods, also *in vivo* heterogeneous environments with no background. Recently, we have developed a water-soluble macromolecular construct consisting of biotin-derivatized cryptophane-A cage that binds avidin protein while encapsulating a xenon atom. We present an NMR characterization of the binding of encapsulated biotin-derivatized xenon to avidin along with a general description of the synthetic route to obtaining the biosensor molecule for xenon functionalization. Further enhancement of the biosensor signal-to-noise is sought by reducing linewidth of peaks attributable to protein-bound functionalized xenon. Towards this end, the properties of physical exchange and spin-lattice relaxation for both free and avidin-bound functionalized xenon were examined using ordinary and deuterated cryptophane-A cage. *This work*

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179. *Double-Quantum-Filtered STMAS and Magic-Angle Effect from Homonuclear Dipolar Coupling in Solid State NMR of Quadrupolar Nuclei.*

HyungTae Kwak, Parthasarathy Srinivasan, John Quine and Zhehong Gan, National High Magnetic Field Laboratory

Satellite Transition Magic-Angle Spinning (STMAS) offers an alternative to MQMAS technique to refocus second-order quadrupolar broadening. It is capable of measuring symmetric spin interactions such as Q-CSA cross-term and third-order quadrupolar effect. Satellite transitions are also more sensitive to fast molecular motion than MQ and central transitions. We will first present double-quantum and double-quantum-filtered STMAS experiments. Using a central-transition selective π-pulse, the new pulse sequences convert desired satellite transition single-quantum coherence to double-quantum with nearly 100% efficiency. The conversion allows the acquisition of double-quantum and double-quantum-filtered STMAS spectra by filtering out unwanted CT-CT diagonal and ST-CT peaks of outer satellite transitions. The picture of matrix representation for coherence transfer pathway is found particularly useful for transition-correlated experiments of quadrupolar nuclei. The picture can distinguish various coherences of the same order, for example all satellite and central transitions belong to single-quantum transition.

The second-half of the talk focuses on dipolar couplings among quadrupolar nuclei. Homonuclear dipolar interaction can recouple under magic-angle spinning affecting line width, spin-echo decay and polarization transfer. The recoupling with satellite transitions is very sensitive to magic-angle setting. Small changes of angle setting by as little as a few tenth of a degree can improve the resolution of MAS and MQMAS spectra. For transition-correlated spectra with significant homogeneous broadening, an orthogonal shearing scheme is proposed to avoid peak-shape distortion of non-orthogonal shearing.

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180. *High Field Solids NMR of Proteins and Nucleic Acids.*

Kurt W. Zilm, Eric K. Paulson, Rachel W. Martin, John D. Gehman and Corey R. Morcombe, Yale University

Rapid progress in high field solids NMR instrumentation and techniques has made solid state NMR (ssNMR) determination of small protein structures a reality. To become a widely adopted tool in biophysics, several important problems remain to be addressed. In this talk we discuss a number of the issues in ssNMR of proteins and nucleic acids and the solutions we have developed. Preparation of nanocrystalline protein is critical for obtaining optimal resolution in ^{13}C, ^{15}N or ^{1}H ssNMR spectra. A general rapid nanocrystalization protocol will be described in application to half a dozen different proteins, and the nanocrystals and their stability characterized by ^{13}C ssNMR, powder X-ray diffraction and scanning electron microscopy. A simple robust homonuclear dipolar recoupling technique will be described, along with its use in resonance assignments and in obtaining distance constraints. How one might extract distances from 2D dipolar exchange spectra using such recoupling methods in isotopically enriched proteins will be analysed, as well as the distance errors produced by finite signal to noise in such spectra. We also use this framework to compare the relative merits of different isotope enrichment patterns. The advances in high field solid state probe design that make such measurements routine on samples of only a few 100 nmoles, with an emphasis on temperature measurement and control and RF homogeniety, will also be discussed.

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181. *High Resolution Proton Solid-State NMR with Fast Magic-Angle Spinning: Exploring the Effects of Spin Dilution and Multiple Pulse Decoupling for Multidimensional Correlation Spectroscopy.*

Chad M. Rienstra, Donghua Zhou and W. Trent Franks, University of Illinois at Urbana-Champaign

Indirect detection of proton signals is a ubiquitous technique in solution NMR, but not yet commonly employed for magic-angle spinning (MAS) experiments. Recently several approaches to this problem have been presented, including very fast MAS[1,2], pulsed-spin locking[3], and high level deuteration with back-exchange of amide protons[4]. Here we present alternatives that employ some aspects of all these approaches. Specifically, we have prepared a series of partially deuterated samples, which have proton densities varying from 1% to 30% of their naturally occurring values. Extremely high resolution proton spectra can be acquired with MAS alone with at these levels of protonation. This has important implications for ^{1}H-detected HETCOR experiments; improvements of 3-5 in sensitivity and 5-10 in resolution are observed in model

compounds such as ^{15}N,^{13}C-Ala diluted in ^{2}H-Ala. For example, the directly acquired proton dimensions of a 10% diluted sample of Ala at 20-25 kHz have Hα and Hβ line widths of <0.4 ppm. We are in the process of integrating these ideas into 3D ^{15}N-^{13}C-^{1}H and ^{13}C-^{13}C-^{1}H experiments for chemical shift assignments and structure determination in proteins.

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182. *Real Examples of Catalysts Functionalized on the Nanometer Scale.*

James F. Haw, University of Southern California

A decade of NMR-intensive research on the chemistry of zeolites and related solid acids laid the background for the eventual elucidation of several reaction mechanisms in heterogeneous catalysis, most notably the conversion of methanol to light olefins. Building on the insight from that work we were soon able to rationally design and synthesize a variety of microporous materials with inorganic and/or organic modifiers, often through novel "ship-in-a-bottle" routes. Silico-aluminophosphates of the CHA and AEI topologies and certain aluminosilicates (e.g., FER) provide frameworks in which the chemist can attempt to control structure and properties on the nanometer scale to achieve useful catalytic results. As will be shown, NMR remains an essential component of these programs.

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183. *Magnetic Resonance Studies of Hierarchically Ordered Replicas of Wood Cellular Structures Prepared by Surfactant-Mediated Mineralization.*

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Hierarchically ordered positive and negative replicas of wood cellular structures prepared using surfactant templating methods under acidic and basic conditions have been studied by means of continuous flow hyperpolarized ^{129}Xe NMR, solid-state MAS ^{13}C, ^{29}Si, and 2D WISE NMR spectroscopic techniques. ^{129}Xe NMR data confirm a highly ordered and uniform structure with interconnected porosity in the positive silica wood replicas (SWR(+)) prepared under acidic conditions. In contrast, non-uniform porosity with irregular pore structures is inferred from similar data for negative silica wood replicas (SWR(-)) prepared under basic conditions. This contrasts with results from N_2 adsorption and TEM measurements that indicate regular nanoporous channels in both cases. From ^{13}C MAS NMR spectra, significant leaching of wood lignin was found to occur under acidic but was not evident for samples subjected to basic treatment. ^{29}Si MAS NMR spectra revealed higher hydroxylation levels for the silica replica prepared under acidic conditions compared to those observed in samples prepared under basic conditions. 2D WISE NMR experiments showed increased mobility of protons associated with the organic functional groups in cellulose after acidic treatment when compared with the dry and base-treated wood. Reported NMR data provide compelling evidence for the proposed mechanism of surfactant directed mineralization of wood cellular structures in acidic and basic solutions.

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184. *2D NMR and MRI Applications in Formation Evaluation.*
Boqin Sun and Keh-Jim Dunn, ChevronTexaco

Nuclear magnetic resonance and imaging technology has been widely used to measure mineralogy independent porosity, irreducible water saturation, and pore size distribution in porous media. Recent efforts have extended the NMR applications to *in-situ* fluid typing, oil viscosity measurements, and fluid mobility in core analysis and wireline logging. We have developed several NMR relaxation-encoded 2D and imaging techniques for characterization of rock samples. Combinations of NMR T_1/T_2 relaxation measurements with NMR diffusion measurements yield relaxation-diffusion 2D (RD2D) correlation distributions of fluid saturated rock samples that can distinguish oil, water, and gas. It also provides means to estimate fluid viscosity and wettability. T_1 relaxation or diffusion measurement in the magic angle spinning framework provides high resolution NMR spectrum and information of relaxation time or diffusion coefficients of imbibed fluids in rock samples. These can be used to identify the composition of oil, the difference between produced oil and that left behind, and the change of wettability. The combination of imaging with relaxometry/diffusion not only provides how the fluid is distributed within the core plug, but also provides a way to study the surface wettability in the spatial image of a core plug.

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185. *Xe NMR Studies in Cavities and Channels.*
Cynthia J. Jameson, University of Illinois at Chicago

We will consider the types of information that can be obtained from the NMR spectrum of Xe in porous materials and provide some examples of the interpretation of the observations by using a combination of quantum-mechanical calculations and Monte Carlo simulations. The overlap, exchange, and dispersion interactions of the Xe atom with the atoms constituting the pore evokes a shielding response that depends on the electronic structure of the pore. Both the shielding response and the potential energy of interaction play a role in determining the Xe NMR chemical shifts and lineshapes as a function of temperature and of loading. In confined geometries, the architecture of the pore determines the nature of the averaging that can take place. This is the basis for the relationship between the observed NMR lineshapes and the pore shapes.

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186. *Nitrogen-14 and Xenon-129 NMR Study of Trapped Gases in Microstructured Amorphous Carbohydrate Matrices.*
Eric Hughes, Mike MacInnes, Gilles Vuataz, Catherine Gretsch, Johan B. Ubbink, Annemarie Schoonman, Heribert J. Watzke, Nestlé Research Centre,

Many low molecular weight gases can be encapsulated in amorphous polymeric carbohydrate matrices. In this study we utilise ^{14}N and ^{129}Xe NMR to observe directly the nitrogen and xenon gas trapped in foamed amorphous powders consisting of maltodextrin and sodium caseinate. The effective pressure of the nitrogen gas in the closed pores of the foamed matrix can be obtained by measuring the ^{14}N spin-lattice relaxation times. The behaviour of the gas as a function of time and temperature was investigated in order to understand the release behaviour of the matrices. Samples loaded with xenon gas at various loading pressure show a linear chemical shift dependance and it can be shown that the effective pressure of the gas within the material is equal to the loading pressure over a range of 20 to 50 bar.

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187. *^{129}Xe and ^{131}Xe Nuclear Magnetic Resonance Studies of Carbon Nanotubes.*
Catherine F. M. Clewett, Tanja Pietraß and Kai Shen, New Mexico Tech

Carbon nanotubes have many interesting properties, but two of their most interesting properties furnishing potentially important applications. We are most interested in their ability to adsorb gases for use as storage media and their high susceptibility to changes in the electronic structure for use as sensor devices[1]. While the tube helicity intrinsically determines the conductive properties, adsorption of a small amount of O_2 can change a nanotube from semiconducting to metallic[2]. Many of these properties have been modeled or measured on single nanotubes with specific helicity[3], however the production of selected nanotubes has not been accomplished yet. In this regard we are interested in the bulk properties of the nanotubes using NMR spectroscopy as a means of characterization. ^{131}Xe NMR spectroscopy is employed to probe the electric field gradients produced at the tube surface, and we use multiple-quantum techniques to indirectly detect quadrupolar interactions[4]. Temperature dependent studies of ^{129}Xe, a non-quadrupolar nucleus, provides complementary information about pore size, pore accessibility, adsorption sites, and xenon adsorption energy on the carbon nanotubes[5].

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NMR Oral Session

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188. *Dynamical NMR: Filling in the Blanks?*

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In many of our recent efforts to use solid state NMR as a probe of dynamics, we have been frustrated by the limited perspective provided by standard NMR methods. Most commonly, we use ^{2}H NMR as a probe of dynamical flexibility in amorphous and semi-crystalline polymers from varied sources (both synthetic and bio-derived). Unfortunately, in many such systems the lineshape transition is between the full Pake pattern and a sharp, dynamically averaged component; no well-defined modes are observed, and the lineshape changes occur continuously over a broad temperature range. So we are forced to look to other tools; some spectroscopic, some based in molecular modeling, which help enlighten the observations derived from our magnetic resonance studies. We will review some of those efforts in this talk in reference to our studies of dynamics in nanocomposites and in silks.

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189. *Probing the Structural and Dynamic Properties of the Integral Membrane Protein Phospholamban Using Solid-State NMR Spectroscopy.*

Elvis K. Tiburu, Paresh C. Dave, Krishnan Damodaran and Gary A. Lorigan, Miami University

Phospholamban (PLB) is a 52-amino acid transmembrane protein that inhibits the Ca^{2+}-ATPase at submicromolar concentrations of Ca^{2+}. In order to understand these interactions, spectroscopy and molecular modeling techniques have been used to probe the structure and dynamics of the Ca^{2+}-ATPase and PLB in the cardiac sarcoplasmic reticulum and in reconstituted membranes. ^{2}H Solid-state NMR studies of leucine residues in the transmembrane domain of PLB provide information for understanding the rotational reorientation and dynamics of PLB in phospholipid bilayers. Specific PLB Leu residues (CD_3) were isotopically labeled with ^{2}H and reconstituted into 1-palmitoyl-2-oleyl-phosphatidylcholine (POPC) bilayers. ^{2}H solid-state NMR spectra were collected for each of the residues (Leu-28, Leu-39, and Leu-51) as a function of temperature. The ^{2}H lineshapes and quadrupole splittings will be used to probe the structural and dynamic properties of PLB inside POPC phospholipid bilayers. Additional aligned 15N experiments will be used to describe the topology of PLB with respect to the membrane.

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190. *Solid-State NMR Evidence For Entropy-Driven Miscibility in Macromolecules.*

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We present experimental evidence for increased local entropy in a high-molecular weight polymer upon blend formation with a second, *higher* T_g, polymer. Direct spectroscopic observation of conformational dynamics by 2D solid-state NMR reveals an increase in the absolute configurational entropy of a one-million molecular weight polymer, polyisobutylene (PIB), when miscible blends with head-to-head polypropylene (hhPP) or polyethylene-co-butene (PEB) are formed. Increased conformational dynamics for the low-T_g PIB are not observed in phase-separated blends. Static ^{2}H and ^{129}Xe NMR experiments support this conclusion. These results contradict traditional thermodynamic models, based on Flory-Huggins theory, in which the entropy of mixing for two macromolecules is assumed to be zero. Such models are inherently based on non-local polymer structures, and fail to account for specific dynamics at sub-R_g length scales. Our experimental results on saturated hydrocarbon blends, in which enthalpic interactions are small due to the identical chemical composition of polyolefins, indicate that the cumulative conformational entropy gains upon mixing can reach values up to $\mathbf{ln\ (3)}^N$, where N is the number of backbone bonds. Further, these results indicate that the characteristic glass-transition length scale is less than the polymer radius of gyration.

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191. *Sweeping and Burning in Fringe-field NMR Diffusometry: New Micro-slice Manipulations.*
Eric E. Sigmund, Northwestern University, Department of Radiology, Chicago, IL 60611; William P. Halperin, Northwestern University, Department of Physics, Evanston, IL 60208; Philip L. Kuhns, National High Magnetic Field Laboratory, CMP NMR, Tallahassee, FL, 32306; Arneil P. Reyes, National High Magnetic Field Laboratory, CMP NMR, Tallahassee, FL, 32306

^{1}H and ^{13}C NMR translational diffusion experiments on glass-forming liquids performed in the high stray field gradients of superconducting and resistive magnets will be presented. These experiments focused upon slow dynamics in glycerol and propylene carbonate, and resolved diffusivities as low as 10^{-10} cm^2/s. Gradients of 42 T/m from an 8 T superconducting magnet (Northwestern University), as well as 216 T/m from a 28 T resistive magnet (National High Magnetic Field Laboratory) were applied. In the resistive magnet, special measures were required to combat applied magnetic field instability. Using a helium-cooled inductive shield, the 60 Hz magnetic field ripple was suppressed by a factor of 20. The primary diffusion sequence used was the standard stimulated echo decay; however, the stray-field environment dictated novel data acquisition styles. First, the steady gradients allow a maximal slice selection of ~100 μm. Frequency jumping methods were developed to combat this spin count limitation. Namely, fresh spins from diffusively identical slices were detected during otherwise unused dead time, and averaged to enhance signal-to-noise. At the other extreme, hole-burning was employed as an alternate diffusometry mode. This refers to the labeling of micron-thick slices and subsequent monitoring of their diffusive broadening. In a new sequence termed the "hole-comb," a full diffusive evolution can be measured within a single transient. The dynamical range provided by these techniques allows study of dynamical crossovers[1] and heterogeneity[2] in glass-forming liquids. These effects in glycerol and propylene carbonate will be discussed in light of their different fragility. In particular, a previously unobserved crossover behavior in the diffusivity of glycerol is reported. Finally, potential extensions of these methods and results to other systems, such as biomedical imaging and porous media, will be discussed. *Support is acknowledged from the National Science Foundation through the Materials Research Center at Northwestern University, grant DMR-9632472.*

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NMR Oral Session

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192. *A Novel Method for Detecting Diffusion: Stimulated Echo/CPMG.*
Xiaoping Tang and Warren S. Warren, Princeton University

We will present a novel approach for detecting diffusion employing the pulse sequence "preparation rf pulse train - single rephasing 180° rf pulse – echo train ". A simple derivation of the evolution of the various coherence pathways, phase cycling schemes, and flip angle dependences will be described. This approach can be viewed as combining the Stimulated Echo method with the CPMG technique. The obvious advantages of this approach include (1) Our echo train is immune from the problem with the dead time after rf pulses and the imperfect rephasing pulse train crippling the CPMG sequence at times. (2) The time separations between two neighboring preparation pulses can now be different from each other. This enables one to design more elaborate experiments. (3) By varying the time between the pulse train and the rephasing 180° pulse, one can more decisively resolve the diffusion and spin relaxation effects and one can probe diffusion for different spin groups with different T_2. Our method can be further exploited (1) The CPMG-like echo train can be also acquired during the preparation pulse train. (2) The sequence "preparation pulse train – rephasing 180° pulse – echo train - rephasing 180° pulse – echo train - …" enables one to truly simultaneously probe diffusion at various time scales. Like the CPMG sequence, our sequences can be widely applied and be effective with pulsed field gradient, stray field gradient, and internal field gradient. We will also show its application for diffusion imaging. *Supported by NSF through the Grant Number MRSEC DMR-0213706 & NIH under grant CA88683.*

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193. *Zeolite Host / Guest Structure Determinations by High Resolution Solid-State NMR Spectroscopy.*

Colin A. Fyfe, Darren H. Brouwer, Andrew R. Lewis, J-S. Joseph Lee, Anix C. Diaz, Yi Feng and Hiltrud Grondey, University of British Columbia

Zeolites are open framework silicates and aluminosilicates often used as catalysts and for the separation of gases. They contain well defined channels and cavities which are of molecular dimensions and these give the frameworks a size and shape selectivity towards medium sized organic molecules. A complete understanding of this selectivity depends on the determination of the structures of the complexes of organic molecules and other intercalates with the frameworks. However, with a very few important exceptions, it is not possible to apply single crystal diffraction techniques because of the small dimensions (few microns) of these materials and powder techniques have insufficient data to properly define the complexes.

We will describe a general method for the determination of the structures of zeolite host/guest complexes by solid-state NMR spectroscopy alone which involves the assignment of the resonances of the ^{29}Si MAS spectra to specific sites in the framework by homonuclear connectivity experiments such as COSY and INADEQUATE and the location of guest species by measurements of the distance dependent heteronuclear dipolar couplings between the ^{29}Si nuclei in the framework and specific nuclei in the guests. For single atoms, eg ^{19}F, exact distances can be measured by CP, REDOR. For organic guests, all possible locations and orientations are tested for linear correlation between the Tcp values from CP or CP drain experiments and the calculated heteronuclear second moments. This has been automated and the final structure determined by machine calculation. The viability of the approach will be demonstrated for a known structure and by the prediction and subsequent verification of an unknown structure. Further examples will illustrate the robustness of the method, present a variety of predicted structures and describe possible complications from disordered structures.

Lastly, extensions of the method in the future to cases where diffraction techniques cannot be used and to mixtures of guests where NMR and different diffraction techniques can be used together will be outlined.

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194. *A Concept for Structure Determination of Small Membrane Proteins by 3D Magic Angle Spinning NMR and its Application to the α-spectrin SH3 Domain.*

Federica Castellani, Bart van Rossum, Anne Diehl, Kristina Rehbein, Ludwig Krabben, Jutta Pauli and Hartmut Oschkinat, Forschungsinstitut für Molekulare Pharmakologie, Robert-Rössle-Str. 10, 13125 Berlin, Germany; Chris Weise and Ferdinand Hucho, Freie Universität Berlin, Institut für Biochemie, Thielallee 63, 14195 Berlin, Germany; Alexander Arseniev, Shemyakin & Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences, 16/10 Miklukho, Maklaya str., V-437, Moscow, Russia; Marc Baldus, Adriaan van Gammeren, Jan Hollander and Huub de Groot, Solid State NMR Secretariat, Gorlaeus Laboratoria, Einsteinweg 55, 2300 RA Leiden, The Netherlands;

A concept for structure determination of proteins in the solid state using MAS NMR together with the structure of the α-spectrin SH3 domain as an example is presented. We have assigned the carbon and nitrogen resonances of the 62 residue SH3 domain with heteronuclear double and triple resonance MAS NMR techniques, whereby sequence specific assignments of backbone carbons and nitrogens were achieved by NCA, NCACO, NCO, and NCOCA experiments. A proton assignment was obtained using Lee-Goldburg techniques involving carbons or nitrogens. Three-dimensional MAS NMR techniques were applied to resolve ambiguities. 3D HNCA spectroscopy served for the assignment of amide protons. Several methods for the collection of distance restraints were tested and compared. This involved the preparation of samples using different labeling strategies, such as statistical dilution of carbons, biosynthetically directed labelling using glycerol, and uniform deuteration of non-exchangeable sites. Application of 3D-spectroscopy allowed the collection of a higher number of constraints than previously, and a refinement of the MAS NMR structure. The merits of various sample preparation concepts with regard to line width and spectral quality will be discussed with diagnostic spectra at hand. First attempts to the identification of amino acids in membrane protein spectra will be presented.

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195. *Local Order in Polycarbonate Glasses by REDOR.*

Robert D. O'Connor, Thomas K. Weldeghiorghis, Barbara Poliks (Binghamton University), Karen L. Wooley, and Jacob Schaefer, Department of Chemistry, Washington University, St. Louis, MO 63130.

Interchain packing in ^{13}C, ^{2}H, and ^{19}F-labeled polycarbonates has been characterized by $^{13}C\{^{2}H\}$ and $^{13}C\{^{19}F\}$rotational-echo double resonance (REDOR) NMR on a 1-2 nm distance scale. Differences in the REDOR dephasing rates of the centerband and spinning sidebands of the carbonyl-carbon resonance indicate local orientational order. The orientational angles are extracted directly from sideband intensities using collections of contour maps for the centerband and each sideband as a function of the REDOR evolution time. This approach is analogous to the use of the familiar Herzfeld-Berger maps to characterize chemical-shift tensors from sideband intensities. The attractive features of this REDOR experiment as a general method for determination of specific orientation in polymers are that it is: (i) one dimensional and hence high sensitivity; (ii) chemical-shift specific because of magic-angle spinning; (iii) accessible to any site that can be stable-isotope labeled; (iv) adaptable to clusters of two or more labels; and (v) suitable for simple spin counting for quantitative analysis. The $^{13}C\{^{19}F\}$REDOR experiments involved a blend of 1% CF_3-labeled polycarbonate (the isopropylidene has one CF_3 and one CH_3) with 99% ^{13}C(=O)-labeled polycarbonate. The observed dephasing is greater than 1% after less than 3 msec dipolar evolution, which indicates that every CF_3 has at least one carbonate label within 5 Angstroms. This result is consistent with local pair-wise order in chain packing for bisphenol-A polycarbonate, and inconsistent with random packing.

NMR Oral Session

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196. *Investigating Structural Changes in the Membrane Protein Bacteriorhodopsin by Solid State NMR.*

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Bacteriorhodopsin (bR) is a seven-transmembrane G-protein coupled receptor (GPCR) which undergoes a number of conformational changes during its photocycle. Many extensive studies have shown how the chromophore retinal rearranges at the different intermediate steps. Recent electron diffraction and x-ray structures of bR in different photointermediate states demonstrate how the helices also rearrange during the cycle. We are trying to characterise these helical rearrangements of bR in the *native purple membrane* using solid state NMR.

In a first step, we have used two different approaches to characterise some orientational and conformational constraints of the helices of bR in the ground state. One approach relies on static oriented methods such as PISEMA and HETCOR, while the other uses magic angle oriented sample spinning (MAOSS). Examples of how these methods can be applied to bR in the native purple membrane will be given. The applicability of these methods to characterize conformational changes of the photocycle intermediates of bR will be demonstrated in light of these results.

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197. *Characterization and Quantification of Acid Sites in Solid Acid Catalysts.*

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We report the methodology for discernment and quantification of acid sites in solid acid catalysts using solid-state ^{31}P MAS NMR of adsorbed phosphorous probe molecules[1-3] Detailed acidic features of solid acid catalysts, including their type, strength, concentration and location, can be deduced concurrently through analysis of ^{31}P NMR chemical shifts of various adsorbed probe molecules, namely trimethylphosphine oxides (TMPO) and tributylphosphine oxide (TBPO), in conjunction with data obtained from elemental analysis[4].

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198. *Solid State ^{19}F-NMR of Polypeptides in Oriented Membranes.*

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Solid state ^{19}F-NMR is a highly sensitive approach to resolve the conformation, alignment and dynamic behaviour of selectively fluorine-labelled peptides in biomembranes. The advantages and disadvantages of introducing certain non-natural amino acids such 4-fluro-phenylglycine, 4-CF_3-phenylglycine, and 3F-alanine will be compared both from a chemical and spectroscopic point of view. The structure analysis is based on measuring orientation-dependent ^{19}F chemical shifts and dipolar couplings of these side chains, once the peptide is reconstituted in macroscopically oriented membranes. The difficulties of accurate chemical shift referencing in such non-spheroidal samples will be illustrated, as it may be essential to avoid susceptibility-induced line-shifts and line-broadening. Several different fusogenic and antimicrobial peptides will be presented as biologically active examples. The observed changes in membrane-alignment and oligomerization state in response to the peptide concentration and lipid type may be relevant in interpreting their functional mechanism.

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199. *Solid State ^{17}O NMR of Amino Acids, High Precision Experiments and Calculation of Parameters.*

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^{17}O NMR is reported for the majority of amino acids and for some related compounds. Carbonyl and hydroxyl oxygens in amino acids have isotropic chemical shifts separated by typically 150 ppm, and have CQs of 8.15-8.55 and 7.60-7.35 MHz respectively. The sensitivity of ^{17}O NMR parameters to structure is very high, protecting an amino acid ready for incorporation in much larger molecules can change the carbonyl shift by > 25 ppm and the hydroxyl by 15 ppm. Because of the high measurement precision, different amino acids can be readily distinguished, and usually all oxygen sites can be readily resolved in the MAS spectrum. Assignment in cases where the shifts and quadrupole parameters are similar e.g. alanine or the two carbonyls of glutamic acid, has been carried out by a combination of high speed double resonance (^1H–^{17}O) DOR (to determine the spatial proximity of the nearest hydrogen atoms) and calculation utilizing a recently developed periodic DFT method using pseudopotentials[1-3]. Both calculation and experimental data agree, for example, on the assignment of the two carbonyls in glutamic acid whose shifts differ by only ~ 7 ppm and CQs by < 0.15 MHz. Further evidence of the reliability of calculation is given by the fact that the calculated shift and quadrupole tensors and their relative orientation produce accurate multi-field simulations of static spectra of e.g. glycine.

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NMR Oral Session

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200. *Solid State NMR Studies of Membrane-Associated HIV-1 and Influenza Viral Fusion Peptides.*

Jun Yang, Rong Yang, Paul D. Parkanzky, Christopher M. Wasniewski, Michele L. Bodner and David P. Weliky, Michigan State University

For many viruses including HIV-1 and influenza, a key step in infection is fusion between viral and target cell membranes. Fusion is catalyzed by viral fusion peptides, which are twenty-residue apolar domains of larger viral envelope proteins. The interaction of fusion peptides with cellular and viral membranes is believed to underlie fusion catalysis. We are using solid state NMR to study HIV-1 and influenza fusion peptides in membranes and are developing structural and functional models for these peptides. One advantage of solid state NMR for these systems is the similarity between the conditions used for NMR sample preparation and those used for functional fusion assays. Chemical shift, 2D exchange, and REDOR measurements show that the peptides have significant structural plasticity which is modulated by peptide:lipid ratio and by the lipid headgroup and cholesterol composition of the membrane. However, in membranes whose lipid and cholesterol composition is close to that of the target cells of the viruses, the peptides are predominantly non-helical. Additional REDOR measurements on samples containing mixtures of ^{13}C-carbonyl labeled peptide and ^{15}N-labeled peptide demonstrate that the non-helical structure has a large fraction of beta strand oligomers with roughly equal populations of parallel and antiparallel strand arrangements. For the parallel-strand oligomers, the

REDOR data also show that the strands fray apart near their C-termini. We also studied cysteine cross-linked fusion peptides because their oligomeric topology should be close to that found for the peptides in the whole virus. These cross-linked peptides are more fusogenic than their non-cross-linked analogs, and in one structural model, this enhanced fusogenicity can be explained with a preference for parallel arrangement of peptide strands. Progress will be reported on solid state NMR experiments which test this model and on experiments to assign U-^{13}C, ^{15}N labeled fusion peptides in membranes.

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201. *Structure of Silk Fibroins Studied with Solid-State NMR.*

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Silk fibroin from Bombyx mori silkworm is an Ala/Gly-rich protein, which is spun from aqueous solution at room temperature to produce fibers with exceptional strength and high toughness. Synthetic materials with comparable properties must be processed at much higher temperatures and/or from less benign solvents. Hence it is most intriguing to resolve the molecular conformation of silk fibroin before (Silk I) and after spinning (Silk II) and to characterize the structural transition in the process on fiber formation. The Silk I structure has been determined as repeated type II β-turn with solid state NMR (2D spin diffusion NMR, REDOR and chemical shift constraint)[1,2]. On the other hand, Silk II takes heterogeneous structure which has been also determined with similar analytical technique[3,4]. The transition from Silk I to Silk II has been examined with MD method by taking into account several external forces in the silk gland of the silkworm. The similar approarch has been applied to the structure determination of silk fibroin from a wild silkworm, Samia cynthia ricini[5-7].

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NMR Oral Session

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202. *Cell-Wall Complexes of Vancomycins in Whole Cells of S. Aureus.*

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Cross-polarization magic-angle spinning and rotational-echo double resonance (REDOR) experiments have been performed to investigate the effects of vancomycin on cell wall synthesis in *Staphylococcus aureus*. Vancomycin (at therapeutic levels) interrupts peptidoglycan synthesis in *S. aureus* by interference with transglycosylation. REDOR experiments involving a fluorinated vancomycin analogue (LY329332) have provided data to illustrate how the drug binds to the peptidoglycan of ^{13}C and ^{15}N-labeled whole cells. The drug binds homogeneously, without forming dimers or membrane anchors (*Biochemistry 41,* 6967, 2002*)*. Recent results using distance and orientation information obtained from site-specific REDOR experiments have enabled the construction of a higher resolution model involving atomic-level detail of the peptidoglycan. This model will inevitably aid in gaining insight into how the dramatic interruption of transglycosylation is achieved.

NMR Oral Session

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203. *Towards a Complete Structural Model of Alzheimer's ß-Amyloid Fibrils by Solid State NMR.*

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Building upon our experimentally based model of the full length Alzheimer's β-amyloid fibrils (Petkova et al., PNAS, 99:16742-16747, 2002), we have utilized recent advances in fibril formation, uniform ^{13}C,^{15}N labeling and solid state NMR techniques to produce a new, refined structural model of the $A\beta_{1-40}$ fibrils. We use chemical shift assignments from 2D ^{13}C-^{13}C and ^{15}N-^{13}C correlation spectra of fibrils with uniform ^{13}C,^{15}N labeling of 31 of the 40 residues (5-7 per sample) and subsequent backbone torsion angle estimates from the TALOS database. Long distance constrains provided from frequency selective REDOR and rotational resonance measurements elucidate non-sequential inter-residue sidechain-sidechain salt bridge and hydrophobic interactions. Electron microscopy of $A\beta_{1-40}$ fibrils (TEM and STEM mass-per-length data) is essential in determining the arrangement of filaments within the fibrils.

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NMR • Thursday Oral Sessions

204. *NMR and Quantum Information Processing.*

R. Laflamme, University of Waterloo and Perimeter Institute for Theoretical Physics

Advances in computing are revolutionizing our world. Present day computers advance at a rapid pace toward the barrier defined by the laws of quantum physics. The quantum computation program short-circuits that constraint by exploiting the quantum laws to advantage rather than regarding them as obstacles. Quantum computer accepts any superposition of its inputs as an input, and processes the components simultaneously, performing a sophisticated interference experiment of classical inputs. This "quantum parallelism" allows one to explore exponentially many trial solutions with relatively modest means, and to select the correct one. This has a particularly dramatic effect on factoring of large integers, which is at the core of the present day encryption strategies (public key) used in diplomatic communication, and (increasingly) in business. As demonstrated approximately five years ago, quantum computers could yield the most commonly used encryption protocol obsolete. Since then, it was also realized that quantum computation can lead to breakthroughs elsewhere, including simulations of quantum systems, implementation of novel encryption strategies (quantum cryptography), as well as more mundane applications such as sorting. I will describe recent work done in quantum computation, in particular I will give a critical review of the NMR implementation.

NMR Oral Session

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205. *NMR Quantum Information Processing with a Single-Crystal Solid.*

Garett Leskowitz and Leonard J. Mueller, University of California, Riverside

NMR is now by far the most well developed test bed for quantum information processing (QIP). To date, NMR quantum information processing has been demonstrated in liquids, in liquid crystals, and in powdered solids under MAS conditions. There are significant advantages, however, to performing QIP in static single crystal solids, which stem from the retention of orientation-dependent dipolar couplings. Specifically, through-space dipolar couplings allow greater flexibility in the design of spin-spin coupling networks than do scalar couplings, which fall off sharply with the number of bonds separating nuclei. Dipolar couplings are also stronger than scalar couplings, and so gate times (which are inversely proportional to the couplings) are correspondingly faster. Provided spin-spin relaxation can be controlled, solid-state NMR methods could improve scalability in the number of qubits, to perhaps 30 by some accounts, which is beyond the limit where such systems can be simulated on today's classical computers. There are also practical advantages to single crystal solids, which include compatibility with low temperatures and solid-state chip implementations. While there have been ambitious proposals for advanced NMR quantum computing systems in crystals, to our knowledge there have been no published accounts of experiments. Here we report three-qubit NMR quantum information processing in a static single-crystal of isotopically labeled glycine ($H_2{}^{15}N{}^{13}CH_2{}^{13}COOH$). We illustrate innovations specific to oriented crystals for pseudopure state preparation and gate manipulations. In particular, concurrent cross-polarization of both the ^{13}C and ^{15}N spins from proton magnetization enhances and equalizes populations on these nuclei in a single step. Also, proton decoupling is switched off to dephase unwanted coherences during preparation of pseudopure spin states. This "relaxation averaging" (or T_2 averaging) is an alternative to spatial averaging, which requires special hardware and large gradient strengths for small crystals. Finally, we introduce quantum gates based on small-amplitude *J*-pulses for homonuclear systems. These pulses circumvent difficulties with quantum gates based on selective pulses in both solid- and liquid-state NMR.

NMR Oral Session

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206. *Quantum Information Processing With Solid State NMR.*
Chandrasekhar Ramanathan, Massachusetts Institute of Technology

NMR continues to be an important experimental test bed for quantum information processing. Liquid state NMR techniques have enabled the implementation of gates with very high fidelities, the experimental demonstration of algorithms and exploration of the important issues of control, decoherence and error correction in small quantum systems. Solid state NMR allows us to address a different set of questions than those that have been studied with liquids. In this talk, I will start by discussing the creation of highly polarized spin states using low temperature dynamic nuclear polarization. The increased polarization allows us to explore a larger number of qubits, and also allows us to prepare the system in close to a pure state. I will go on to discuss the design and control of qubit systems in the solid state, as well as the challenges to implementing multi-qubit gates with high fidelity. Using solid state NMR techniques, we obtain control over a much larger Hilbert space, and using the dipolar interaction, it should be possible to implement a large number of operations before the spins decohere. Finally I will conclude with a discussion of some recent results from our experiments on spin dynamics. The long spin lattice relaxation times make solid state NMR a very useful tool to study quantum many body dynamics. In the short-time, few-spin limit we have studied spin dynamics using novel multiple quantum coherence techniques while in the long-time, many-spin limit we have measured the spin diffusion rates of Zeeman and dipolar order in a single crystal of calcium fluoride.

NMR Oral Session

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207. *Spin Processor.*
Anatoly Khitrin, Kent State University

Ability of spin systems to process information is discussed from a spectroscopic point of view. Clusters of coupled spins with unresolved spectra can be manipulated to store a large amount of information and for implementing algorithms with cascades of parallel bitwise operations. This is made possible by using a new type of coherent collective response signals. The processing speed is determined by strength of time-independent internal interactions and information can be processed much faster than flips of individual spins.

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NMR Oral Session

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208. *The Rational Reduction Algorithm for Off-Period Observations of Periodic Hamiltonians.*
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Many solid-state NMR simulations take advantage of the periodicity of the underlying Hamiltonian to simplify the computations. Most of the methods used, however, require the time step between observations to be some integer or reciprocal-integer multiple of the period, thereby restricting the observation bandwidth. Calculations of off-period observations are often reduced to brute force, direct methods resulting in many demanding matrix operations (multiplications and exponentiations). For large spin systems, these matrix operations become the limiting step. We present a simple method that can dramatically reduce the number of matrix multiplications required to calculate the time evolution propagators when the observation time step is some rational fraction (n/m, where n and m are integers greater than 1) of the period of the Hamiltonian. The algorithm implements two different optimization routines. One uses pattern matching and additional memory storage, while the other recursively generates the propagators via time shifting and little or no additional memory storage. The net result is a significant speed improvement for some types of time domain calculations. This algorithm can be applied to the calculation of the propagators for any density matrix time evolution problem where off-period observations are desired.

NMR Oral Session

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209. *SPINEVOLUTION: A Powerful Tool for the Simulation of Solid and Liquid State NMR Experiments.*
Mikhail Veshtort and Robert G. Griffin, Massachusetts Institute of Technology, Francis Bitter Magnet Laboratory and Department of Chemistry, 77 Massachusetts Ave, Cambridge, MA 02139, USA

Exact numerical simulations of NMR experiments are commonly required for the engineering of new techniques and for the extraction of structural and dynamic parameters from the spectra. The calculations can be very demanding, especially in the case of solid-state problems. We propose a number of new algorithms that drastically improve the efficiency of these calculations. Among the most important ones are the integration of the equation of motion via Chebyshev expansion of the matrix exponential, explicit utilization of the sparsity of the Hamiltonian in large spin

systems, advanced optimization and data fitting methods, time evolution and powder averaging with the generalized γ-COMPUTE algorithm. We also present SPINEVOLUTION, a highly optimized computer program developed based on these advanced techniques and intended as a powerful and easy to use tool for the simulation and data fitting of general NMR experiments. Performance of SPINEVOLUTION was compared with that of SIMPSON, a recently developed and widely popular NMR simulation package. Benchmarked on a series of examples, SPINEVOLUTION was consistently found orders of magnitude faster. The program has been successfully used to simulate numerous solid-state NMR experiments, both for the purposes of the extraction of structural information from the spectra and for methods development. It also served as the main instrument in the development of a family of high-performance selective excitation pulses. We believe that SPINEVOLUTION should be of great utility to people working in NMR for the design and optimization of new experiments, theoretical research, data fitting, and other purposes.

NMR Oral Session

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NMR • Monday and Tuesday Poster Sessions

210. *Solid-State ^{13}C-^{75}As TRAPDOR NMR Spectroscopy Studies of Organo-Arsenic Compounds.*

Todd M. Alam, Sandia National Laboratories

Despite the high natural abundance of ^{75}As (100%), there have been a limited number of solid-state NMR investigations involving arsenic. Previous NMR investigations for this quadrupolar nuclei (I = 3/2) have involved either the direct detection of ^{75}As in very symmetric environments using either static or MAS NMR, or the observation of quadrupolar coupled ^{13}C or ^{11}B MAS NMR line shapes for a few select compounds. This laboratory has recently investigated the use of solid-state {^{1}H-CP} ^{13}C-^{75}As TRAPDOR NMR experiments as a method for the identification of organo-arsenic compounds. For example, dimethyl arsenic acid (DMA V), also known as cacodylic acid, was shown to have a very strong ^{13}C-^{75}As double resonance effect. The magnitude of this TRAPDOR signal was investigated as a function of spinning speed and ^{75}As irradiation offset for DMA V. Investigations of other organo-arsenic compounds with different binding motifs are presently in progress to determine the utility of the TRAPDOR method. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.*

NMR Poster Session

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211. *Vanadium-51 Solid State NMR Spectroscopy: Homonuclear Dipolar Couplings in Inorganic Solids.*

Becky Gee, Long Island University

Dipolar dephasing of the magnetization following a Hahn spin echo pulse sequence potentially provides a quantitative means for determining the dipolar second moment in solids. In this work, the possibility of employing Hahn spin echo decay spectroscopy to obtain quantitative ^{51}V-^{51}V dipolar second moments is explored. Theoretical spin echo response curves are compared to experimental ones for a collection of crystalline vanadium-containing compounds. This work suggests that ^{51}V dipolar second moments can be obtained by selectively exciting the central m = 1/2 -> -1/2 by a Hahn echo sequence for vanadate compounds with line broadening no greater than approximately 220 ppm. For vanadates with greater broadening of the central transition due to chemical shift, second order quadrupolar, and dipolar interactions, off-resonance effects lead to an oscillatory time dependence of the spin echo. Experimentally determined second moments of the nomalized echo decay intesities lie within 10-33% of the calculated values, if the second moments are extrapolated to zero evolution time due to the time scale dependence of spin exchange among neighboring vanadium nuclei. Alternatively, the second moments can be obtained to within 10-25% of the calculated values, if the broadening of the central transition due to chemical shift and second order quadrupolar effects can be estimated.

NMR Poster Session

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212. *Simultaneous Frequency-selective Solid-state NMR Analysis of Internuclear Distances and Through-bond Connectivities in the Presence of Quadrupolar Nuclei.*

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In solid-state NMR spectroscopy, the potential of rotational echo double resonance (REDOR) for deriving distance information is well documented in the literature for isolated pairs of spin-1/2 nuclei. Several extensions of REDOR to more complex spin-1/2 systems have been proposed. Herein, we investigate the feasibility of the frequency-selective REDOR (FS-REDOR) approach to a multispin system SI_n, where S spin is a quadrupolar nucleus. In addition, we describe the effect of scalar couplings J_{SI} on these measurements and use this result to study through-bond connectivities between ^{27}Al and ^{31}P in VPI_5. In order to extract this through-space and through-bond information, we use simple formulae taking into account simultaneously the internuclear distances and the homo- and hetero-J couplings.

We also present a new frequency-selective (FS-J-RES) method that allows determining the number of I nuclei directly bonded to the S species under observation, so that their corresponding J_{SI} couplings.

NMR Poster Session

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213. *^{17}O NMR of Phosphate and Borophosphate Glasses.*

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Results of ^{17}O NMR and double resonant NMR experiments involving ^{17}O are presented for sodium phosphate and sodium borophosphate glasses. For sodium phosphate glasses it is shown that both high field NMR and high B_1 fields are required to excite the quadrupole pattern of the bridging oxygen sites uniformly. If these conditions are not met, severely distorted patterns are measured. Furthermore, ^{17}O-^{31}P REDOR experiments are presented for the non-bridging oxygens which allow both the determination of the oxygen-phosphorus distance and the relative orientation between the quadrupole and dipole tensors in a one-dimensional NMR-experiment. For borophosphate glasses and depending upon the sample compositions, up to five different oxygen sites have been found by MQMAS and have been assigned. Furthermore, connectivities between borate units and phosphate groups have been investigated by ^{11}B-^{31}P HETCOR NMR experiments. C.J. and M.Z. acknowledge financial funding by the Otto-Schott-Glas-Fonds, Schott, Mainz.

NMR Poster Session

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214. *A High-Field ^{27}Al and ^{29}Si MAS NMR Investigation of Portland Cement Hydration in the Presence of Sodium Aluminate.*

Morten Daugaard Andersen, Hans J. Jakobsen, and Jørgen Skibsted, University of Aarhus

The principal binding phase responsible for the strength development in hydrated Portland cements is a poorly crystalline calcium-silicate-hydrate (C–S–H) phase. The C–S–H phase is formed by hydration of the calcium silicates alite (Ca_3SiO_5) and belite (Ca_2SiO_4). Alite, belite, and the C–S–H phase contain metal-ion impurities such as Mg^{2+}, Fe^{3+}, and Al^{3+} where the latter can substitute for Si^{4+} in the chains of SiO_4 tetrahedra of the C–S–H phase. This work presents a ^{29}Si MAS and high-field ^{27}Al MAS NMR investigation of the hydration of white Portland cement (wPc) in water and in a 0.3 M solution of $NaAlO_2$ at 5 °C and 20 °C. ^{29}Si MAS NMR spectra, following the hydration for up to two years, reveal that $NaAlO_2$ accelerates the hydration of alite and belite in wPc. Furthermore, hydration of wPc in a $NaAlO_2$ solution results in an increase of the average chain length for the SiO_4 tetrahedra in the C–S–H phase and in an increase of Al incorporated in the C-S-H structure. The high-field (14.1 and 21.1 T) ^{27}Al MAS NMR spectra demonstrate that the resonance from tetrahedral Al incorporated in the C–S–H phase can be distinguished from the resonances for the Al guest-ions in the anhydrous alite and belite phases. Moreover, the spectral region for octahedrally coordinated Al shows separate resonances from ettringite, monosulphate, and a third aluminate hydrate phase[1]. The latter phase has not been observed in earlier ^{27}Al MAS NMR studies of Portland cement hydration and the composition and structure of this phase have been investigated in detail by ^{27}Al MAS and $^{27}Al\{^1H\}$ CP/MAS NMR. From these experiments the third aluminate hydrate phase is tentatively assigned to a less-crystalline aluminate hydrate or calcium aluminate hydrate phase.

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215. *NMR Structural and Ion Binding Studies of the Domain V from Group II Self-splicing Intron RNA.*
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Group II introns, which are believed to share similar catalytic machinery as pre-mRNA splicing, consist of six domains radiating from central wheel. An attractive feature of these ribozymes is that individual domains can be transcribed and used as a model system to study RNA splicing. Of the six domains, domain V (D5), a 34-nucleotide hairpin, is critical for the splicing. We use the intron of the large ribosomal subunit of *Pylaiella littoralis* (PL) brown algae mitochondria as a model to study the conformation of the catalytically essential D5 by NMR methods. Our solution structure is different from the X-ray crystal structure of another model from yeast al5gama intron (ai5γ). Our study found that the two structures are mainly different in the bulge region. D5-ai5γ has a U9-G26 base pairing whereas D5-PL has U9-A24 base pairing. Our preliminary structural model of D5-PL indicates that D5 has binding and chemistry surface that lie on opposite faces of the molecule, which is in agreement with previous biochemical and mutagenetic studies. The structural implications for catalysis and the role of the interaction of Mg^{2+} ions with the conserved catalytic AGC triad and tetraloop region will be presented.

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216. *1D and 2D ^{13}C CPMAS NMR Study of PMAA/PVAc Miscible Blends.*
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The miscibility of poly(methacrylic acid) (PMAA) and poly(vinyl acetate) (PVAc) blends was investigated by one and two-dimensional (1D and 2D) ^{13}C CPMAS NMR methods. The observed $T_{1\rho}{}^{H}$ values from the blends revealed that the PMAA/PVAc blends are homogeneous on a scale of 2-5nm for PMAA-rich compositions. For PMAA-poor compositions, the blends are heterogeneous on the scale, while those are homogeneous on a scale of 20-50nm[1]. The 1D ^{13}C CPMAS NMR spectra in the blends showed that PMAA carboxyl group interacts with PVAc carbonyl group: the interaction is hydrogen bonding. From an analysis of the peak area ratio, we estimated that the interaction is occurred at [MAA]:[VAc]=3:2 for whole blends[1]. Furthermore, the natural abundant 2D ^{13}C-^{13}C exchange NMR reveals the specific close proximity of 0.37 nm between the carboxyl carbon of PMAA and carbonyl carbon of PVAc at the interacted region. On the basis of the value, molecular mechanics calculation showed that the distance between the hydrogen of carboxyl group of PMAA and oxygen of carbonyl group of PVAc is within ca. 0.2 nm. This value supports the strong hydrogen bonding interaction.

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217. *Domain Selective Solid-State Flourine NMR Spectroscopy of Fluoropolymers — The Direct DIVAM Experiment.*
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Domain selection methods for fluoropolymers primarily consist of relaxation, selective dephasing and dipolar filtering techniques, where in most cases only pure amorphous spectra can be obtained. Crystalline domain spectra are almost invariably contaminated with residual amorphous signal. Recently the Discrimination Induced by Variable Angle Minnipulses (DIVAM) experiment was developed which is capable of selecting for either just the amorphous or just the crystalline domain. A series of small angle pulses are applied to the protons at short intervals until a phase difference of 90^{o} has accumulated between those protons in the amorphous and crystalline domain. The fluorine signal is observed upon cross-polarization from those protons that are in phase with the spin locking field. If one were to perform the DIVAM experiment directly on the fluorine nuclei, off-resonance effects will interfere with the selection process. A new pulse sequence is presented which uses a series of spin-echoes to compensate for these effects allowing for domain selection directly on fluorine. Sample spectra of PVDF and simulations are shown.

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218. *Natural Abundance ^{17}O NMR.*
S. E. Ashbrook and I. Farnan, University of Cambridge

Oxygen is a major component of many systems of biological, geochemical and industrial interest. Owing to the low sensitivity and low natural abundance (0.037%) of the only NMR active isotope, ^{17}O, NMR studies have been relatively few in number. The majority of work has involved the use of costly ^{17}O isotopic enrichment. In addition, the quadrupolar nature of ^{17}O (I = 5/2) results in solid-state NMR spectra that are often broad and featureless, and techniques to enhance resolution such as magic-angle-spinning (MAS) or multiple-quantum MAS (MQMAS) may be required. However, the relatively large chemical shift range and the strong correlation of ^{17}O quadrupolar and chemical shift parameters with the local environment offer great potential for the extraction of structural information. In many cases, ^{17}O isotopic enrichment is too costly or, for naturally-occurring systems such as minerals, is impossible to achieve. Our aim is to determine the viability of the study of ^{17}O at natural abundance level in a range of different systems, utilising combinations of sensitivity enhancement methods currently in the literature. We demonstrate conventional ^{17}O NMR is possible when the quadrupolar interaction is small. We then consider systems with larger quadrupole interactions and demonstrate rotor-assisted population transfer (RAPT) and cross polarization (CP) techniques provide substantial signal enhancements. Additionally, we discuss the use of the Carr-Purcell-Meinboom-Gill (CPMG) approach for ^{17}O NMR. We demonstrate through NMR of boehmite (AlO(OH)), brucite ($Mg(OH)_2$) and forsterite (Mg_2SiO_4) that one or all of these techniques may be employed to acquire natural abundance ^{17}O spectra. Finally, we show that these approaches may be utilized to obtain natural abundance ^{17}O NMR spectra of two zircons ($ZrSiO_4$), one of which displays damage from natural radioactive decay of the small amounts of Uranium and Thorium it contains. These systems provide important information on the effect of radiation damage.

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219. *The Effects of Cholesterol on Acyl Chain Dynamics of Magnetically Aligned Phospholipid Bilayers.*
Junxia Lu, Marc A. Caporini and Gary A. Lorigan, Miami University

Cholesterol is a major component of cell membranes. Solid-state deuterium NMR spectroscopy is used to study the effects of cholesterol in magnetically aligned phospholipid bilayers (bicelles) as a function of temperature for both chain perdeuterated DMPC and a partially deuterated (α-[2, 2, 3, 4, 4, 6-$^2H_6$] cholesterol. The results of our studies demonstrate that cholesterol is incorporated into the bicelle discs. The segmental order parameters of individual methylene and methyl group are extracted directly from the ^2H quadrupolar splittings of the chain perdeuterated DMPC. The order parameter shows high order and low motion for the hydrocarbon segments close to the carboxyl groups of DMPC acyl chain and less order and more rapid motion toward terminal methyl groups. EPR spectroscopy is also carried out utilizing a cholestane spin-label incorporated into magnetically aligned phospholipid bilayers to provide a complementary picture about the ordering and dynamics of the membrane system. Both methods clearly indicate an increased overall degree of ordering of the acyl chains in the presence of cholesterol. However, as the temperature of the bicelle samples increased, the corresponding order parameters decreased due to higher random motions of the phospholipid acyl chains of DMPC.

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220. *Using ^{129}Xe NMR to Probe the Void Structure of a Series of Periodic Mesoporous Organosilicas.*
A. J. Baer, K. Landskron, H. Grondey and G. A. Ozin, University of Toronto

A series of periodic mesoporous organosilicas (PMOs) have been produced containing organic groups in the framework structure. These materials have been characterized using a variety of methods including solid-state NMR spectroscopy and powder X-ray diffraction. The presence of the bridging organic groups was investigated using solid-state NMR spectroscopy. Using ^{129}Xe NMR spectroscopy with natural abundance Xe gas on a standard solid-state NMR spectrometer, the pores of these materials have been probed. The focus of these experiments were to characterize the internal nature of the pores as well as to obtain information on the homogeneity of the pores themselves. Preliminary results of these experiments in ^{129}Xe NMR spectroscopy will be reported.

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221. *Quadrupolar Coupling Constants and Chemical Shifts in Zeolites A Investigated by ^{27}Al MQMAS and ^{29}Si MAS-NMR.*
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Zeolites A, the typical alumino-silicates with the ratio Al/Si = 1 contain cations, mostly sodium, which neutralize the negative electric charge of the alumino-silicate framework[1]. Sodium cations can be easily exchanged by other mono and divalent cations, but it is known that properties of zeolites strongly depend on the type of cation[2]. Multiple-quantum magic-angle spinning ^{27}Al NMR and ^{29}Si MAS-NMR techniques were applied in the high field of 14.1 T to the study of zeolites A fully exchanged with mono and divalent cations having different ionic radii. A monotonic correlation between the isotropic value of the ^{27}Al chemical shift and the ^{29}Si chemical shift could be found for zeolites with monovalent cations. Also the dependence of the ^{27}Al chemical shift on the ionic radii of monovalent cation was found. Combination of data obtained from NMR on both nuclei give detailed information about structural changes in the zeolites A caused by the exchange of sodium cations by the divalent cations such as Ca^{2+} or Ba^{2+}. MQMAS NMR technique, which is a valuable tool in the investigation of quadrupolar nuclei [3], was used to obtain values of the ^{27}Al quadrupolar coupling constants. They show strong dependence on the ionic radii of the charge-compensating cations.

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222. *Simple Signal Enhancement Schemes for ½-Integer Quadrupolar Nuclei.*
Larry W. Beck, Kathryn J. Hughes and Mark V. Wilson, University of Michigan

The NMR signal strength of quadrupolar nuclei in solids is known to depend on the relative strengths of the quadrupolar splitting frequency and the excitation field, ν_q/ν_{rf}. In most cases the quadrupolar interaction is large and the resulting anisotropic line width exceeds the maximum rf-field strength which means that only a small fraction of total spins contribute to the observable magnetization. Here three methods are discussed for enhancing the detectable signal for quadrupolar nuclei under MAS conditions. The three pulses schemes discussed here enhance the central transition signal intensity by changing the polarization of the unobserved satellite transitions. These three sequences are very simple to apply, have less demanding hardware requirements, and are much easier to optimize for the maximum signal enhancement, than the related DFS and RAPT methods recently reported. In one scheme two pulses are used, the first pulse is applied off-resonance saturates the satellite transitions followed by solid-selective (on-resonance) pulse to create the enhanced central transition magnetization. This scheme is optimized when the 1st pulse offset $\nu_{off} = \nu_q/4$ and the power of the pulse $\nu_{rf} = \nu_q/40$ (I=3/2), which maximizes the saturation of the satellites. In the second scheme a pair of anti-phase pulses $\{\pi/2(x), \pi/2(-x)\}$ can be applied prior to a solid-selective $\pi/2$ pulse to observe the same signal enhancement. In this scheme the rf-field strength of the first two-pulses is optimized at $\nu_{rf} = \nu_q/4$, and is independent of frequency offset. In the third method signal enhancement can also be achieved by a rotational resonance polarization transfer mechanism as has been recently described for creating multiple-quantum coherence states (FASTER). We demonstrate that under the appropriate cross-polarization conditions central transition enhancement, when $\nu_{rf} = \nu_{off}$ and $\nu_r > 2\,(I+1/2)\,\nu_{rf}$, or complete suppression, when $\nu_{rf} + \nu_{off} = \pm n\cdot\nu_r$ (n=1,2), is observed.

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223. *Through-Bond and Through Space characterisation of AP_2O_7 Phosphates.*
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Many members of the AM_2O_7 compounds show interesting specific properties like negative thermal expansion. The exact room temperature structure of AP_2O_7 compounds may become very complex and can only be resolved by the combined use of cutting-edge diffraction techniques and solid state NMR multidimensional experiments that enable the enumeration of the different non-equivalent P sites. In this family of phosphorus based materials, T_2 relaxation times are long enough to enable the use of J-based experiments as well as of the more classical dipolar based recoupling techniques (C7 and evolutions). We show that increased resolution can be obtained using INADEQUATE DQ/SQ experiments, allowing the description of more than 100 different P sites in some of the AP_2O_7 compounds. *Supported by EEC HPRI 1999-00042 contract.*

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NMR Poster Session

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224. *Investigation of Cinnamic Acid as a Powder and Single-Crystal: ^{1}H and ^{13}C Spectra and Simulations.*

Marko Bertmer, Ryan C. Nieuwendaal, Alexander B. Barnes and Sophia E. Hayes, Washington University

Cinnamic acid is being investigated as a model compound for photocyclization reactions. In addition to the assignment of resonances using static and magic angle spinning (MAS) NMR, we hope to gain information on structure and dynamics in powder samples, together with simulations using the SIMPSON[1] program. Single crystals of cinnamic acid show characteristic lineshapes for ^{1}H measurements, and ^{13}C spectra exhibit narrow lines typical for single crystals. Information on the CSA and dipolar tensors has been obtained by varying the orientation of the sample with respect to the external magnetic field.

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225. *Solid-state NMR Characterization of Oxygen Sites in Organically Modified Aluminosilicate Xerogels.*

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Solid-state NMR characterization hybrid alumino-silicate xerogels, by ^{17}O magic angle spinning (MAS) and triple quantum magic angle spinning (MQMAS) techniques, evidences Si-O-Si and Si-O-Al oxygen sites signatures, spectrally separated in MQMAS experiments. Inversion of the MQMAS spectra allows to measure quadrupolar parameters, isotropic chemical shifts, distribution of chemical shift, and to discuss the mobility of the structural units. *Supported by EEC HPRI 1999-00042 contract*

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226. *Temperature Dependence, Structural Plasticity, and Resonance Assignment of Selectively and Uniformly Labeled HIV-1 Fusion Peptides Associated with Membranes.*

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The HIV-1 viral fusion peptide serves as a biologically relevant model for viral/target cell membrane fusion and in this study, the structure of the membrane-associated peptide was probed by solid state NMR MAS ^{13}C chemical shift measurements. Solution NMR studies have shown that the peptide is predominantly helical in detergent micelles and this was correlated with solid state NMR ^{13}C chemical shifts in frozen detergent. Similar chemical shifts were observed for the peptide in a phosphocholine/phosphoglycerol lipid mixture, which indicates that the peptide has significant helical character in this mixture. Large shift changes (2-4 ppm) were observed for the peptide in a mixture whose lipid headgroup and cholesterol composition reflects the target T cells of the virus. In this more biologically relevant composition, the chemical shifts are consistent with predominant non-helical structure. Future studies will investigate whether these differences in peptide structure can be correlated with differences in peptide fusogenicity in the different compositions. In a second set of experiments, NMR spectra were compared at –50 ^{o}C and at 20 ^{o}C. Similar peak chemical shifts were observed at both temperatures, which indicates that cooling the sample does not significantly change the peptide structure. Relative to –50 ^{o}C, the 20 ^{o}C signals were narrower and had lower intensity, which is consistent with greater motion at higher temperature. Finally, $^{13}C/^{13}C$ correlation experiments were performed on a sample in which the peptide was U-$^{13}C/^{15}N$ labeled over three sequential residues. The resulting 2D spectra were used to assign all of the ^{13}C chemical shifts in the labeled residues. The high signal-to-noise of the 2D spectra suggests that membrane-associated fusion peptides with longer sequences of labeled amino acids can also be assigned with 2D and 3D methods and that it may be possible to apply solid state NMR methods to obtain a high-resolution structure.

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227. *Structural Study of Yttrium Silicate Compounds by ^{89}Y and ^{29}Si MAS-NMR Spectroscopy.*
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The whole set of $Y_2Si_2O_7$ and Y_2SiO_5 polymorphs has been synthesised following the ceramic, sol-gel and hydrothermal methods. ^{29}Si and ^{89}Y MAS-NMR single pulse spectra have been obtained for all the polymorphs. The ^{29}Si chemical shifts of these compounds follow the same trend with Si partial charge as that found for a wide set of silicates by Janes and Oldfield *(J. Am. Chem. Soc. 107 (1985) 6769*). Likewise, we have found a correlation between the ^{89}Y chemical shift and the partial charge on the yttrium atom for all the $Y_2Si_2O_7$ and Y_2SiO_5 polymorphs analysed. Finally, ^{89}Y MAS-NMR spectra have helped determining the definitive structural arrangement of some $Y_2Si_2O_7$ polymorphs which were controversial in the literature. *Supported by EEC HPRI 1999-00042 contract*

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228. *Quantitative GIAO Prediction of Nuclear Shielding Anisotropies and Tensor Components via Extrapolation to the Complete Basis-Set Limit.*
Teobald Kupka, Branko Ruscic and Robert E. Botto, Argonne National Laboratory

The nuclear shielding anisotropy and shielding tensor components calculated using the hybrid density functional B3PW91 are reported for a set of model compounds: N_2, NH_3, CH_4, C_2H_4, HCN, CH_3CN. An estimation of the density functional theory (DFT) and Hartree-Fock (HF) Complete Basis Set Limit (CBS) NMR parameters from the 2 (3) point exact fit vs. least-squares fit (NLLSQ) was obtained with the cc-pVxZ and aug-cc-pVxZ basis sets (x = D, T, Q, 5, 6). Both HF- and DFT-predicted CBS shielding anisotropies and tensor componenets of the model molecules were in reasonable agreement with available experimental data. The utility of extrapolating low-zeta basis sets to the CBS limit for calculating accurate nuclear shielding parameters of larger molecules is proposed. *Work performed in part under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, Biosciences and Geosciences, U. S. Department of Energy, under contract no. W-31-109-ENG-38.*

NMR Poster Session
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229. *Circularly Polarized NQR With a Surface Coil Array.*
J. B. Miller and A. N. Garroway, Naval Research Laboratory

Circularly-polarized RF fields are a more efficient way of exciting and detecting magnetic resonance than the more commonly used linearly-polarized fields. Circularly-polarized fields are generally produced with pairs of orthogonal, "crossed", coils when the application calls for the use of surface coils. Such crossed surface coils can produce reasonable circularly-polarized fields in two dimensions, acceptable for high field NMR experiments, but generally inadequate for NQR experiments. Here we describe a surface coil array suitable for use in NQR. We show simulations and measurements of coil parameters as well as N-14 NQR data obtained with the coils.

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230. *Fate of Nerve Agent Simulants on Concrete Substrates.*
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The nerve agent VX (O-ethyl S-[2-(diisopropylamino)ethyl]methylphosphonothiolate) has been shown to decompose in contact with concrete surfaces[1]. We have previously shown that ^{31}P NMR can be employed to study 1) the adsorption of VX into concrete; 2) the decomposition kinetics; and 3) detect decomposition products[2]. Recently reported results show a dramatic effect of the VX decomposition kinetics on droplet size, with 0.01 μL droplets reacting within a few hours[3] in contrast to months observed for VX drop sizes on the order of several μL.[2] In the present study, ^{31}P NMR results will be presented for the decomposition of nerve agent simulant DMMP (dimethyl methylphosphonate) on concrete as a function of droplet size.

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231. *Applications of Solid NMR Techniques for Liquid Samples.*

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In the intermolecular multiple-quantum coherences (iMQCs) experiments, the distant-dipolar field (DDF) gives inhomogeneous broadening in the f2 dimension and limits the data acquisition time. We show that solid-state NMR techniques can be applied to iMQCs experiments in order to obtain high-resolution spectra. Magic angle spinning (MAS), which is frequently employed in solid NMR, is expected to suppress DDF and inhomogeneous broadening. However, suppression of DDF makes it difficult to observe iMQCs signal concurrently, since iMQCs signal is generated by DDF. We propose MAS and multiple-pulse dipolar recoupling in iMQCs experiments. This pulse sequence reintroduces DDF by multiple pulses synchronized with MAS while the iMQCs signal is being generated.

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232. *40 Tesla ^{27}Al MAS NMR and ^{1}H and ^{17}O NMR of Methylaluminoxane (MAO).*

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Methylaluminoxane, a co-catalyst for a new generation of single site polyolefin catalysts, is a remarkably difficult sample for characterization by ^{27}Al NMR[1]. In addition to its high reactivity with air, all aluminum sites have large quadrupolar coupling constants (>15 MHz), necessitating the use of high magnetic fields, typically 19.6 T, and 40 T in one run. The ^{27}Al MAS NMR spectra do not resolve individual sites, yet provide useful constraints on the local site structure, for example, limiting the number of 4-member $(AlO)_2$ rings present in this amorphous, multi-component substance. The ^{17}O data show 3-coordinate sites dominate and the ^{1}H T_1 values show the presence of two methyl sites, interpreted as a distribution of terminal and bridging methyl sites. DOSY NMR shows an interesting correlation between cluster molecular weight and the abundance of bridging methyls in that cluster. In the absence of resolved NMR spectra, NMR parameters derived from calculations of putative MAO structures are extremely useful. To better explore all possible MAO structures, simulations are underway of the synthesis of MAO from trimethylaluminum and water. New tools for reaction simulation on parallel supercomputers are being developed. *Supported by NSF CHE-9977124.*

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233. *^{1}H-^{15}N Correlation Spectroscopy of Nanocrystalline Protein.*

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A key ingredient in solution phase protein NMR studies is the ^{1}H-^{15}N shift correlation map. Dispersion in this spectrum is key to sequential assignment and obtaining most NOE distance constraints. Applications of solid state NMR to protein structure would also benefit from high quality ^{1}H-^{15}N shift correlation spectra. We investigate the limits of the resolution that can be obtained in ^{1}H-^{15}N 2D NMR spectroscopy for an isotopically enriched nanocrystalline protein. In attempt to reduce ^{1}H homonuclear couplings, combinations of frequency switched Lee Goldberg (FSLG) decoupling, fast magic angle sample spinning (MAS) and isotopic dilution via deuteration are investigated. Heteronuclear decoupling of ^{15}N from the ^{1}H resonances is also studied. Using human ubiquitin as a model system, the best resolution is obtained using a ^{15}N-^{2}H enriched and back-exchanged sample, MAS at ~20kHz, and WALTZ-16 decoupling of the ^{15}N nuclei. The combination of these techniques results in ^{1}H lines which are only ~ 0.15 ppm full width at half maximum. In this particular crystal form, two sets of ^{15}N and ^{1}H resonances are observed, and are attributed to two magnetically inequivalent molecules in the unit cell. The resolution in deuterated samples is sufficient that the ^{1}H dimension now has potential for providing useful resolution of heteronuclear NMR signals in multidimensional NMR studies of solid proteins. *Supported by W.M. Keck Foundation (Yale), National Institute of Health (NCI), and Natural Sciences and Engineering Research Council of Canada (CRM).*

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234. *Material Characterization with High Speed Solid-State ^{1}H MAS and Double Quantum NMR.*

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High speed magic angle spinning (MAS) ^{1}H NMR in combination with double quantum (DQ) ^{1}H NMR spectroscopy has opened the doors to utilizing the abundant protons in the study of solid materials. Routine MAS ^{1}H NMR at spinning frequencies that approach or exceed the ^{1}H-^{1}H homonuclear dipolar coupling provides ^{1}H NMR spectra with excellent resolution. Dipolar re-coupling pulse sequences, such as BABA, can be used to re-introduce the ^{1}H-^{1}H homonuclear dipolar coupling. Investigations of the proton environments of a variety of materials were investigated. For example, the charge carrying moieties of fuel cell polymer electrolyte membrane materials were investigated. DQ-filtered MAS provided a means to identify the mobile, proton conducting sulfonic acid groups. Furthermore, a novel spin diffusion technique utilizing a DQ-filter was used to explore the domains present in these materials. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.*

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235. *Environmental Weathering of Aluminosilicate Clay Minerals: Solid-State NMR Studies of Transformations Leading to Radionuclide Sequestration.*

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Mobilities of radionuclides (such as ^{137}Cs and ^{90}Sr) are governed by their interactions with natural soil particles in the saturated and unsaturated zones at Department of Energy sites (e.g. Hanford Site, Savannah River Site). High surface area aluminosilicate clay minerals are a component of the natural soils beneath the leaking waste tanks at these sites, and serve as possible radionuclide sorbents. However, due to the characteristics of the contaminant medium (high pH, high Al, and high ionic strength), clay minerals are susceptible to transformations during exposure to tank waste leachates. To gain a better understanding of fundamental processes taking place in the vadose and saturated soil environments in these polluted areas, we are currently studying the transformation of clays under specific chemical conditions that mimic the composition of the contaminant solutions. In these studies, specimen clay samples are reacted for varying time periods (up to one year) with simulated tank waste leachate (STWL) solutions containing fixed concentrations of (non-radioactive) Cs and Sr (at levels of 10^{-3}, 10^{-4}, and 10^{-5} M). Mineral dissolution and transformation are followed with solution analysis, x-ray diffraction, solid-state NMR, and a number of other analytic methods. We report here results from ^{27}Al MAS NMR at variable magnetic field strengths (up to 18.8 T), ^{29}Si MAS NMR, and $^{1}H/^{29}Si$ CPMAS NMR, and evaluate these results along with those of other parallel analytic studies. A number of neophases are identified through these analyses, and solid-state NMR results are used to quantify the reaction kinetics. As neophases are formed, Cs and Sr sequstration varies and one additional question of interest is the location of the Cs and Sr species within the original clays or neophases. Results of initial double resonance experiments incorporating Cs (and possibly Sr) nuclides will be reported. *The Department of Energy EMSP program currently supports this work via grant DE – FGO7-99ER15012.*

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236. *Quantification of Difficult Pharmaceutical Ingredients by NMR Spectroscopy.*

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Active pharmaceutical ingredients are frequently composed of in addition to the drug substance. Many of these counter ions and solvates are difficult to quantify by chromatography because they lack UV chromophore or require laborious sample preparation. Even in cases where a chromatographic or titration assay exists, an orthogonal technique will be immensely useful for validation or investigation of the release method. In support of a recent drug candidate under development, proton NMR spectroscopy was applied to measure the concentration of lysine, the counterion of the active pharmaceutical ingredient (API). In addition, this particular API also contained a significant amount of ethanol that impacted the corrected purity calculation. Two different proton NMR methods were developed; the first utilizing an internal standard, and the second utilizing a standard addition technique. The NMR parameters of relaxation, signal to noise, and data table size have been explored and optimized. The accuracy, precision and sensitivity of both methods have been determined. A discussion of the relative merits and liabilities of each method will also be presented. These studies extend the applicability of quantitative proton NMR to the assay of active pharmaceutical ingredients allowing methods, consistent with cGMPs and cGLPs, to be developed.

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237. *Uniform-sign Cross-peak Double-Quantum-Filtered Correlation Spectroscopy in Solids.*
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Recently, we introduced a novel through-bond solid state correlation method that is a variant of the popular double-quantum-filtered correlation spectroscopy (2QF COSY) experiment in liquids (*J. Am. Chem Soc*., **124,** 9360-9361 (2002)). This experiment maintains the many advantages of the 2QF COSY experiment, but is also robust for solids by providing in-phase diagonal and cross-peaks. We call this variant the *u*niform-sign *c*ross-peak (UC) 2QF COSY. Despite two relatively long (1/2*J*) refocusing periods, we find good efficiency in a number of organic and inorganic solids. Applications from our laboratory include establishing through-bond connectivity in the protonated Fullerene cation HC_{60}^+ and the assignment of uniformly labeled organic and inorganic molecules. Here we present several novel applications and variations of the original UC2QF COSY, including natural abundance ^{13}C correlation spectroscopy, which is used to refine the crystal structure of vitamin-D_3.

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238. *^{31}P and ^{2}H Solid-State NMR Spectroscopic Studies of the Transmembrane Domain of the Membrane-Bound Protein Phospholamban.*
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Phospholamban (PLB) is a 52-amino acid integral membrane protein that regulates the flow of Ca^{2+} ions in cardiac muscle cells. In the present study, the transmembrane domain of PLB (24-52) was incorporated into phospholipid bilayers prepared from 1-Palmitoyl, 2-Oleoyl-*sn-glycero*-phosphatidylcholine (POPC). The interaction between the lipid bilayers and phospholamban was investigated using ^{31}P and ^{2}H NMR spectroscopy at temperatures ranging from 30 to 60^{o}C. Also, the peptide concentration was varied from 0 to 6 mol% with respect to POPC. Solid-state ^{31}P NMR spectroscopy is a valuable technique to study the different phases formed by model phospholipid membranes. The ^{31}P NMR line shapes are very characteristic of the different lipid phases as well as the size of the membranes. ^{31}P NMR results suggest that the transmembrane protein phospholamban is incorporated into the bilayer and the effects are observed in the lipid lamellar phase. Simulations of the ^{31}P NMR spectra were carried out to reveal the formation of different sizes of the vesicles upon PLB insertion. The bilayer vesicles fragmented into small size vesicles by increasing the concentration of PLB with respect to POPC. Additionally, different proportions of bilayer species were observed as the temperature was increased. Finally, order parameters were calculated by performing ^{2}H solid-state NMR studies when the PLB peptide was inserted into chain per deuterated (sn-1 chain) POPC phospholipid bilayers.

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239. *A ^{13}C CP/MAS and ^{31}P NMR Study of the Interactions of Dipalmitoylphosphatidylcholine with Respirable Silica and Kaolin.*
David K. Murray, Yau-Hsin Wang, Joel C. Harrison and William E. Wallace, National Institute for Occupational Safety and Health

The interaction of silica and kaolin with dipalmitoylphosphatidyl choline (DPPC) has been studied using ^{13}C and ^{31}P solid state NMR spectroscopy. These studies explore the molecular interactions of these respirable dusts with a model lung surfactant species to characterize silica toxicity in mixed systems. DPPC's choline head group was found to remain mobile on kaolin, in sharp contrast to immobile head groups on silica. Further, glycerol carbon intensities were greatly diminished relative to that of choline carbons, a result attributed to broadening effects caused by their interaction with aluminum sites. These preliminary findings suggest that silica toxicity may not be related to choline mobility as previously noted [J. Colloid Interface Sci. 172, 536-538, (1995)].

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240. *Solid-State NMR of Membrane Proteins in Phospholipid Bicelles.*
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Multidimensional solid-state NMR is a powerful tool for structural studies of membrane proteins reconstituted into fully hydrated phospholipid bilayers. Our approach takes advantage of the simplifications that result from spontaneous uniaxial orientation of phospholipid bicelles in the static magnetic field. This model membrane system offers some practical advantages compared to mechanically aligned bilayers on glass plates, such as ease in maintaining sample hydration and allowing the use of solenoid-coil NMR probes. When bicelles spontaneously orient with their normal perpendicular to the magnetic field, the order parameter, determined by the angle between the bilayer normal and the magnetic field, is $S_{zz} = -1/2$. Therefore, the ^{15}N chemical shift frequency range is decreased by a factor 2, and inverted with respect to the

parallel orientation (S_{zz} = 1), while dipolar couplings are scaled down by a factor 2. It is shown here that two-dimensional solid-state NMR spectra display resolved resonances in both chemical shift and dipolar coupling dimensions, demonstrating that bicelles can be used to obtain structural information. Spectra from several uniformly and selectively ^{15}N-labeled proteins are used to illustrate the method. *Supported by NIH 1F32 GM65833-1.*

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241. *^{1}H Detected ^{1}H–^{15}N Correlation Spectroscopy in Deuterated Nanocrystalline Ubiquitin.*

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Enhancement of sensitivity by detection of the ^{1}H signals instead of the ^{15}N signals in ^{1}H–^{15}N correlation spectroscopy is demonstrated experimentally on a deuterated, ^{1}H back-exchanged, ^{15}N-labeled protein in a nanocrystalline state. ^{1}H detection is complicated by the presence of a large water signal in the spectrum, but as demonstrated, this signal can be largely suppressed by a combination of pulse-sequence-based and numerical techniques. In addition to deuteration, fast magic angle sample spinning and decoupling of the ^{15}N nuclei were used to narrow the ^{1}H signals. The increased sensitivity and resolution of this approach make a variety of 3D experiments more practical for distance measurements in solid proteins, some of which are examined.

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242. *Carbon-Protonation of 2,4,6-Triaminopyrimidines: NMR and Quantum Chemical Study.*

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The pyrimidine system is an essential structural motif in a number of natural products of biological importance. There is a large class of pharmacologically important substituted 2,4-diaminopyrimidines acting as dihydrofolate reductase inhibitors (pyrimethamine, thrimethoprim) as well as hexaalkyl-2,4,6-triaminopyrimidines coupled to 21-aminosteroids showing iron-dependent lipid peroxidation inhibitory effect (tirilazad). The site of protonation has been extensively investigated in solution and gas phase for simple aminopyrimidines; those studies indicated that protonation occurs at the pyrimidine ring nitrogen [N(1) and/or N(3)][1-7]. We have recently demonstrated by detailed NMR studies that, in addition to the expected N(1) protonation, hexamethyl-2,4,6-triaminopyrimidine could also be protonated at the C(5) position in water[8]. Moreover, a stable σ-complex was isolated in a special case. In the present paper, we investigate the scope and limitations of C-protonation in structurally close 2,4,6-triaminoaminopyrimidine analogues by NMR protonation studies. The observed protonation characteristics are interpreted in terms of electronic and geometrical factors and analyzed by quantum chemical computations on the B3LYP/cc-pVDZ level. The calculated gas phase N- and C-protonation energies of 2,4,6-triaminopyrimidine are 1030 and 1018 kJ-mol, respectively, almost the same.

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243. *Colors in Silver Exchanged Zeolites: ^{109}Ag Solid State NMR Study.*
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A series of silver exchanged zeolites have been studied by solid state NMR methods in their hydrated and dehydrated states. Zeolite X changed its color from white to lemon yellow upon vacuum dehydration at 673K. Originally grey colored Zeolite A changed its color from yellow to orange as the dehydrating temperature was varied from 473K to 673K. These color changes were also reflected in the chemical shift of silver. Zeolite X exhibited a paramagnetic shift which is indicative of a shortening of the AgO coordination bond formed between silver cations and oxygens of the zeolite framework. Zeolite A showed progressive diamagnetic shift with temperature which is indicative of the AgO bond lengthening and a different dynamics of silver cations upon dehydration. Based on our NMR data, we also found no evidence of metallic species present in the dehydrated materials, and the observed color changes are explained by the electronic transitions occurred between lone pairs of oxygens of the zeolite framework and 5s level of silver, or Ligand-to-Metal-Charge-Transfer. This study demonstrates the efficiency of ^{109}Ag solid state NMR methods in elucidating dynamics of silver cations in porous materials.

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244. *Fitting of Wide-line Deuterium Spectra Using Simulated Annealing and Spectral Libraries.*
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Simulated annealing has previously been suggested as a method for fitting wide-line deuterium spectra (Aliev and Harris, Magn. Reson. Chem. 36:855, 1998). We are interested in fitting deuterium spectra to study the dynamics of benzene associated with natural organic matter. In this case up to three different motional models (large-angle wobble, small-angle wobble, and isotropic) may be detected simultaneously, as already reported for the Ca-montmorillonite/benzene system (Xiong and Maciel, J. Phys. Chem. B 103:5543, 1999). Preliminary tests of simulated annealing for fitting a polynomial indicate that the traditional exponential cooling schedule (Kirkpatrick, Gelatt, and Vecchi, Science 220:671, 1983) works well, but only if the step size in annealing is reduced according to the goodness of fit, not according to the control parameter. Further tests with polynomials of two to eight variables show that for two variables a random walk accepting only downhill steps is faster than simulated annealing, while for more than two variables simulated annealing is comparable to or faster than the downhill method. The benzene motional models have 30 or 32 sites, and the time required to obtain a single spectrum makes calculation of a spectrum at each step in simulated annealing impractical. Instead, we simulate a large library of spectra for each motional model with a range of kinetic parameters prior to the fitting calculation, and select spectra from these libraries at each fitting step. Simulated annealing and downhill random walks are compared, and the practical threshold for detecting a small percentage of one motional model in the presence of another is considered.

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245. *Improvement of 3QMAS Using Shaped Pulses For I=5/2 Nuclei.*
Jun Gu and William P. Power, University of Waterloo

Improvement of 3QMAS Using Shaped Pulses For I=5/2 Nuclei. Jun Gu and William P. Power, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1

The main drawback of MQMAS is the low sensitivity, which is due to the low efficiency in MQ excitation and MQ-to-1Q conversion that depends strongly on the magnitude of the quadrupolar interaction. Of these, the low efficiency in conversion to observable single-quantum magnetization is the main culprit. Most of the strategies proposed to deal with inefficient conversion have been for I=3/2 nuclei, not for I=5/2 nuclei such as ^{27}Al. It has been demonstrated by Vega[1] that pure adiabatic population transfer between the |3/2> and |1/2> states of I=5/2 does not occur during CW irradiation in rotating samples. Hence, the direct coherence transfer sequence FAM-II[2] yields a significant sensitivity enhancement in 3QMAS of I=5/2 nuclei. In this work, two pulse sequences with exponential-shaped-pulses as conversion pulses were studied, and the results showed that they can efficiently convert the triple quantum coherence to single quantum coherence in 3QMAS of I=5/2 nuclei, specifically ^{27}Al in yttrium aluminum garnet (YAG) and andalusite. These sequences are less sensitive to the magnitude of the quadrupolar interactions, and they provide more accurate quantitative site information over a broad NQCC range (0.6 MHz ~15.3 MHz). Both perform better than the FAM-II pulse sequence, with one of the two sequences in particular providing slightly better performance overall.

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246. *Fast ^{1}H-MAS NMR studies of Water on coated Silica-Nanoparticles.*

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SiO_2 nanoparticles with a diameter of 100nm and a special surface membrane coating that allows the formation of pores on top of the silica with a diameter of 2nm and various wall structures were prepared and studied by NMR techniques. After initial characterization of the sample coating by ^{13}C, and ^{1}H-solid state NMR spectroscopy the samples were treated with different amounts of water and water/tyrosine solution. The amounts of water were selected in such a way that a partial or complete coverage of the surface of the nano-spheres is achieved. Employing fast ^{1}H-MAS-NMR we were able to characterize the different water phases on the membrane coated surface and analyze the exchange dynamics of the different surface sites.

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247. *Detection of the Degradation of Perfluoropolyethers Adsorbed on Solid Surfaces.*

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Perfluorinated compounds are recognized as an environmental concern due to their persistence and potential toxicity, and these global contaminants have been found in the environment from the Arctic to the Antarctic. In our current experiments, two common perfluoropolyethers (PFPEs) have been deposited on solid surfaces, and their degradation is being investigated through a combination of nuclear magnetic resonance (NMR), matrix-assisted laser desorption-ionization (MALDI) mass spectrometry, and other analytic techniques. The PFPEs are adsorbed onto alumina, MCM-41, and a silica sol-gel; these high-surface area materials serve as models for minerals, pores, and reactive surfaces in the environment. One degradation method attempted involves thermal treatments of the samples, and other planned experiments include photodegradation studies. Through the use of various NMR techniques, such as liquid-state ^{19}F NMR, high-speed ^{19}F MAS-NMR, and ^{27}Al MAS-NMR, the degradation of these fluorinated polymers is examined. In parallel experiments, MALDI mass spectrometry identifies changes in mass of the fluorinated polymer. In preliminary results, fluorine-containing degradation products are detected on the PFPE-coated aluminas after heating to 300˚C; this is evidenced by the appearance of fluoride resonances in the NMR as well as lower mass degradation products in MALDI experiments. Further studies will be reported and examined for links to environmental pollution and remediation efforts.

NMR Poster Session

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248. *A Structural Study of the V_2O_5-WO_3 System by MAS and Static Vanadium-51 NMR.*

Becky Gee, Long Island University

Solid state NMR spectra showing single quantum excitation of the vanadium-51 (I=7/2) central and six satellite transitions were obtained for polycrystalline V_2O_5 and x % V_2O_5 – (100 – x %) WO_3, (10 mol% ≤ x ≤ 40 mol%), solids by magic angle spinning (MAS) and static NMR spectroscopies. All MAS spectra show full spinning sideband manifolds resulting from incomplete averaging of the chemical shift and quadrupolar interaction anisotropies. Chemical shift parameters (δ_{iso}, δ_{aniso}, η_{cs}) and quadrupolar parameters (C_Q, η_Q) were obtained by simulation of both MAS and static spectra. A single vanadium site was observed in the nominally 40 mol% V_2O_5 – 60 mol % WO_3 and 30 mol% V_2O_5 – 70 mol % WO_3 compositions. Interpretation of NMR spectral parameters suggests that the vanadium in this single site resides in a square pyramid-like oxygen coordination environment. Three sites were observed for the nominally 20 mol% V_2O_5 – 80 mol % WO_3 and 10 mol% V_2O_5 – 90 mol % WO_3 compositions. The spectral parameters for the three sites are consistent with the presence of vanadium(V) in (1) square pyramid-like, (2) distorted tetrahedral, and (3) spherically symmetric oxygen coordination environments. A distribution of ^{51}V quadrupolar coupling parameters may be present and may suggest a distribution of second or higher order atomic environments.

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249. *Influence of Hydration the Slow and Fast Dynamics of Collagen: A Solid-state NMR Study.*

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Molecular processes play an important role in the understanding of biologic activity in proteins. These biopolymers commonly exhibit a wide distribution of dynamic parameters like motional rates and amplitudes. The present paper is focused on the medically relevant molecule Collagen. It is an substantial ingredient of cartilage and is believed to determine its mechanical properties. The latter in turn is determined by the dynamic properties of the molecular at the molecular level where in particular slow processes are believed to contribute to the mechanical properties. Solid- State NMR in principle provides tools for the investigation of dynamic processes in solids at molecular resolution. Since isotopic labeling is unfeasible for such materials, a prerequisite for the investigation are methods that are able to work in natural isotopic abundance. In this paper we present preliminary results from investigations aimed to the determination dynamic parameters of both fast and slow processes. The former are conveniently investigated by methods that observe the partial averaging of anisotropic interactions while the latter are approached by novel 1D-MAS exchange methods. All these methods provide detailed information about motional amplitudes for all molecular segments that can be resolved in the MAS-NMR spectrum. We will discuss the applicability of different methods and demonstrate this approach for the investigation of the molecular mobility in the Collagen at different degrees of hydration. The data reveal that hydration has an much larger effect on the amplitude of the molecular processes as temperature. In particular, the γ carbon of the Hyp residues exhibits a strong dependence of the amplitude of motion. This could be correlated to the effect of hydration on the hydrogen bounding structure for which this residue is known to play a crucial role. Perspectives for a more detailed characterization of the dynamic processes will be discussed.

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250. *A Ferroelectric Resonator Insert Used for Increasing the Sensitivity of NMR Method.*

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Up to now a common model of a send-receive coil in NMR and MRI spectroscopy remains a birdcage resonator. However, it is difficult to find an optimal L/C - relation for the capacities and inductivities at frequencies above 300 MHz. A fully ceramic resonator without discrete network elements to substitute usual resonator was developed recently[1]. To avoid engineering changes and to increase the sensitivity of NMR method we suggest to insert a ferroelectric resonator, like it was done in EPR[2], into cavity. The ferroelectric resonator is made from single-crystal potassium tantalate with hole of 1 mm in diameter for introduction capillary with sample. The sizes of this resonator are 6x6x7 mm^3. A ferroelectric resonator significantly increases signal-to-noise ratio in hydrogen NMR spectra. Occasionally, it becomes necessary to eliminate the signal from one constituent of sample. An example is an unwanted water signal which overwhelms the signal from the desired constituent. The differences in T_1 (or saturation) can be used to eliminate the signal from water. A ferroelectric resonator insert can be used to eliminate signal from water (for example) if located under the active zone.

[1] P.Daleiden, et al., Biomed Tech. (Berl.), 47 Suppl 1 Pt 2,758-761 (2002).

[2] I.N. Geifman, et al., Ferroelectrics 234, 81-88 (1999).

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251. *Phase Separation and Hydrogen Bonding in Polymer Blends and Complexes.*

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Blends and complexes containing poly(acrylic acid) have been investigated. Bulk poly(acrylic acid) exhibits a high concentration of acrylic acid dimers. These are manifested in the ^{13}C chemical shifts in CPMAS spectra[1]. Due to their strong hydrogen bonds, they are easily detectable in proton high- resolution solid-state NMR spectra under high-speed MAS or CRAMPS. Double quantum proton spectra in addition to the chemical shift proof the close proximity of two acid protons. In comparison in complexes and blends of poly(acrylic acid) and poly(amide) and in a complex with poly(ethyleneoxide) this dimer structure breaks down. The majority of the acid protons is isolated as seen in the ^{13}C spectra. In the case of the blend with poly(amide) hydrogen bond are indicated in the proton spectra. However, the double quantum spectra reveal, that these are between the amide and the acid protons and not in dimers of acid protons.

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252. *NMR Studies of Confined Molecules in Porous Al_2O_3 Films.*
R.E. Gerald II, D.N. Sears, K.J. Ruscic, R.J. Klingler and J.W. Rathke, Argonne National Laboratory

Porous anodic aluminum oxide (AAO) films were formed on aluminum disks by an established electrochemical process. The AAO-coated aluminum disks were incorporated into our coin cell NMR detector as the inductor element of the radiofrequency probe circuit. The AAO films have nano-size pores and micron-size depth, and are formed uniformly across the aluminum surface; the channel axes are oriented normal to the metal surface. The highly uniform pores provide an anisotropic environment for detailed molecular confinement studies. Multinuclear NMR experiments were conducted on various organic polymers confined in the oxide pores. *This work was 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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253. *DANTE-based, Frequency-Selective REDOR: Methodology and Applications.*
Oshrat Cabri, Osnat S. Lipson, Lilia Kaustov and Asher Schmidt, Technion 32000

In this work, the development and application of a new pulse sequence, *DANTE-Based, Frequency-Selective REDOR (dbFSR),* is presented. This pulse sequence, being a combination of the REDOR experiment with the frequency-selective DANTE pulse sequence, enables us to recouple nuclei within a pre-chosen chemical shift range. First, its performance is evaluated using [4-^{13}C,^{15}N]asparagine as a model compound (diluted in natural abundance). Following, the application of dbFSR in the context of structure-function studies of bio-macromolecules will be demonstarted; it will be shown that in such systems dbFSR is capable to delineate specific interactions within uniformly ^{15}N-labeled enzyme in ternary complex with substrate and inhibitor, and to minimize natural abundance ^{13}C bacground dephasing. Finally, a tailored version of dbFSR for spectral editting and assignment in molecular crystals will be shown.

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254. *Measuring Distance, Angle Distributions and Correlations in Oxide Glasses with RAPT-Enhanced O-17 DAS.*
Philip J. Grandinetti, Ted M. Clark, Ohio State University, 100 W. 18th Ave., Columbus, OH, 43210; Pierre A. Florian, CNRS, 1D Av. de la Recherche Scientifique, 45071 Orléans Cedex 2, France; Jonathan F. Stebbins, Stanford University, Stanford, CA 94305-2115; Jeffrey L. Yarger, University of Wyoming, Laramie, WY 82071.

Ab initio quantum chemistry calculations and comparisons with experimental O-17 solid-state NMR investigations were used to obtain analytical expressions relating O-17 quadrupolar coupling constant and asymmetry parameter values of bridging oxygen to their T-O-T angle and average T-O distance. These expressions were then used to analyze the RAPT-enhanced two-dimensional O-17 MAS-detected DAS spectra of silica and germania glass. From the two-dimensional distribution of quadrupolar coupling parameters extracted from the spectra, the two-dimensional distribution correlating the T-O-T angles to T-O distances were obtained for both glasses. The average Si-O distance and Si-O-Si angles in silica glass obtained with this approach are consistent with recent high energy X-ray experiments of Neuefeind and Liss with a mean Si-O distance of 1.58Å and mean Si-O-Si angle of 146.6°, although the distribution width for both parameters was narrower than that predict by Neuefeind and Liss, and significantly narrower than the often cited Si-O-Si angle distribution of Mozzi and Warren. Additionally, we observed an unusual correlation between Si-O distance and Si-O-Si angle in silica glass in which the Si-O distance decreases with decreasing Si-O-Si angle: a trend that is opposite for crystalline silicates. The O-17 results on germania show that the Ge-O-Ge angle distribution peaks near 135°, lower than silica, as expected, given the larger Ge radius. It also shows a similar trend with decreasing Ge-O distance as the Ge-O-Ge angle decreases, except around 140° the trend reverses with Ge-O distance increasing with decreasing Ge-O-Ge angle. The implication of these results on current models of glass structure will be discussed.

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255. *Structure and Dynamics of Peptides Controlling Cell Signaling Using Solid State NMR.*
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The development of material interfaces that control cell behavior is a central challenge for the fields of diagnostics, drug screening, biomaterials, biosensors, and tissue engineering. In bone and teeth, proteins control cell behavior during mineral formation and regeneration, but the interactions that are necessary for cell recognition are not well understood. Recently, we have shown that a designed peptide can

signal cell recognition, and then activate cellular pathways. The peptide design was based on the fusion of a known biomineralization protein found in saliva with cell recognition sequences found in osteopontin and collagen I, giving the following sequences, respectively, DpSpSEEKFLRRIGRFGPGRGDS and DpSpSEEKFLRRIGRFGPDGEA. We have also shown that solid state NMR is a very powerful tool in determining the secondary structure of biomineralization proteins as well as aiding in the determination of the interaction of the protein with the mineral surface. Currently, we are utilizing the capabilities of SSNMR to understand the relevance of secondary structure and amino acid composition in the cell signaling process, along with proteomic protein identification techniques to assess the extent to which cellular pathways have been triggered. These effects are being studied as a function of peptide sequence and surface type to provide insight into the effect on cell recognition and cell signaling. Initial results on the dynamics of the protein indicate that the binding region is mobile on the NMR time scale, suggesting it is positioned away from the surface, perhaps allowing for better access to cells. Further studies on the structure of the cell signaling peptides vs the control peptides and with and without cell-simulant sequences bound is currently under way.

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256. *Resource for Solid-state NMR of Proteins.*

Christopher. V. Grant, Chin. H. Wu and Stanley. J. Opella, University of California, San Diego

Developments in instrumentation and methods at the Resource for Solid-State NMR of Proteins at the University of California, San Diego will be presented. The Resource is dedicated to the advancement of solid-state NMR spectroscopy for the study of proteins that defy analysis by the traditional techniques of structural biology, solution NMR spectroscopy and X-ray crystallography. The development of instrumentation is focused on the implementation of high magnetic fields, low temperature operation, and on the development of double and triple resonance probes capable of handling the high power irradiations demanded by biological applications of solid-state NMR. The Resource has magnets ranging from 400 MHz to 900 MHz with bore sizes that range from 89 mm to 52 mm and probes that have been constructed for these bore sizes will be described. In addition to applications of static and MAS double and triple resonance NMR techniques, much of the recent focus is on the development of pulse sequences derived from the PISEMA experiment optimized for the study of magnetically and mechanically oriented samples of membrane and viral proteins in lipid bilayers. The application of this technology to selected examples of membrane proteins will be presented. *The Biomedical Technology Resource for Solid-State NMR of Proteins is supported by grant P41RR09789 from the National Center for Research Resources, National Institutes of Health.*

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257. *A Metabonomic Study of Interspecies Variation Following Acute Exposure to Mercury.*

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Mercury is one of the most toxic metals in the environment and continues to cause environmental and human toxicology problems[1,2]. However, the influences of nutritional state and life stressors on mercury toxicity are poorly understood. NMR based metabonomics[3] can be employed to detect, identify and quantify multivariate metabolic changes in integrated biological systems and is an appropriate tool to model complex metabolic responses to metal toxicity. Such metabolic changes can be catalogued by producing a metabolic profile based on time-related changes detected by NMR. This study aims to compare the responses of wild and laboratory mammals to both organic and inorganic mercury, and to characterize the different mechanisms of toxicity for these two forms. Studies carried out to date in which the metabolism of Hg^{2+} dosed bank voles (*Clethrionomys glareolus*), a common rodent in the UK, and laboratory mice were compared using biofluid, tissue solution and solid state NMR analysis have demonstrated significant metabolic differences between the two rodent species in the response to toxic insult. Changes in TCA cycle intermediates identified by metabonomics suggested mitochondrial dysfunction in both species, but this was more severe in the bank vole. Furthermore, NMR spectroscopy coupled with multivariate chemometric analysis indicates that laboratory animal toxicology is not indicative of responses in wild species.

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[2] WHO (1991) *EHC 118 – Inorganic mercury*, WHO: Switzerland.

[3] Nicholson *et al*., *Nat. Rev. Drug Dis.*, 2002, 1, 153-161.

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258. *^{13}C-^{2}H REDOR: A Universal Dipolar Dephasing Curve and Applications.*
Terry Gullion, West Virginia University

Deuterium has a rich history in solid-state NMR, but its application in determining structures has been limited. The measurement of ^{13}C–^{2}H dipolar interactions by ^{13}C-observe REDOR can be hampered by the deuterium quadrupolar interaction since it is difficult to irradiate the wide deuterium powder pattern efficiently with modest radio-frequency pulse power. A composite excitation pulse overcomes this problem, and we show that the ^{13}C–^{2}H REDOR experiment can be described by a simple universal dipolar dephasing curve similar to that found for REDOR experiments of spin-1/2 pairs. Applications of ^{13}C–^{2}H REDOR to determining local structure in silk peptides and in polymer blends will be presented.

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259. *Application of Carr-Purcell-Meiboom-Gill (CPMG) Experiments to Characterize NMR Powder Patterns in Solids.*
Renée Siegel, Roderick E. Wasylishen and Thomas T. Nakashima, University of Alberta

The CPMG experiment was originally designed to minimize errors associated with measuring transverse relaxation times, T_2's, in liquid samples (H.Y. Carr and E.M. Purcell, *Phys. Rev.*, **1954**, *94*, 630 and S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, **1958**, *29*, 688). Later, Garroway (*J. Magn. Reson.*, **1977**, *28*, 365) and others (e.g., R.G. Bryant and co-workers, *J. Magn. Reson.*, **1986**, *69*, 531; J.T. Cheng and P.D. Ellis, *J. Phys. Chem.*, **1989**, *93*, 2549; B.A. Cowans and J.B. Grutzner, *J. Magn. Reson.*, **1993**, *105*, 10) demonstrated that application of the CPMG pulse-sequence leads to "spikelets" which mimic the lineshape of a stationary powder sample. The technique has found wide-spread application in solid-state NMR investigation of the 2 :-2 transition for non-integer spin quadrupolar nuclei (F.H. Larsen, H.J. Jakobsen, P.D. Ellis, and C.N. Nielsen, *J. Phys. Chem. A*, **1997**, *101*, 8597) in non-spinning samples. The resulting quadrupolar CPMG (QCPMG) spectra of the central transition in these systems can be readily calculated and compared with experiment to yield the magnitudes and relative orientation of electric-field gradient and magnetic shielding tensors. Sensitivity gains on the order of 30 have been realized using the QCPMG experiment. Here we have revisited applications of the CPMG experiment to characterize magnetic shielding tensors of spin-2 nuclei. While our studies have focused on the advantages of applying the experiment to spin-2 nuclei with relatively large shielding anisotropies (spans), we have also investigated some of the limitations of the CPMG experiment, for spin-2 nuclei and for quadrupolar nuclei where the spectra are broadened by the first-order quadrupolar interaction.

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260. *Structures of Vanadium Ions in Monolithic Vanadia-Silica Composite Gels.*
Oc Hee Han, Solid State Analysis Team, Daegu Branch, Korea Basic Science Institute and Department of Industrial Chemistry, Kyungpook National University, Daegu, 702-701, Korea; Sunha Kim, Sang Guel Lee, Solid State Analysis Team, Daegu Branch, Korea Basic Science Institute, Daegu, 702-701, Korea; Young-Uk Kwon, Department of Chemistry and BK-21 School of Molecular Science, Sungkyunkwan University, Suwon, 440-746, Korea

Decavanadate $[V_{10}O_{28}]^{6-}$ polyoxometalate (POM) ions in water decompose into smaller POM ions or monomeric $H_2VO_4^-$ when pH is raised to higher than 6. In this report, we have found that silicate ions can kinetically stabilize decavanadate ions for up to 8 h at pH 12 conditions. Gelation of these solutions by lowering the pH to 4-5 followed by aging produced monolithic vanadia-silica composite gels with a wide range of vanadium contents. Solid state 51V NMR and infrared spectroscopic data show that the vanadium species is predominantly $[V_{10}O_{28}]^{6-}$ when the vanadium content is V/(V+Si) < 32 %. Upon further drying and aging, $[V_{10}O_{28}]^{6-}$ ions in the sample with 2.3 % of V/(V+Si) appeared to decompose to smaller POM and monomeric vanadium ions. The first characterization of the structure of the monomeric vanadium ions embedded in silicate structure by multinuclear solid state NMR and XRD will be discussed, which may become the guideline of the characterization of nanocomposite materials in this kind.

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261. *Effects of T_2-Relaxation in MAS NMR Spectra of the Satellite Transitions for Quadrupolar Nuclei: A ^{27}Al MAS NMR Study of $KAl(SO_4)_2 \cdot 12H_2O$ (Alum).*
Jørgen Skibsted, Morten Daugaard Andersen, Hans J. Jakobsen, University of Aarhus, Denmark.

Asymmetries in the manifold of spinning sidebands (ssbs), observed for the satellite transitions in MAS NMR spectra of quadrupolar nuclei, may originate from (*i*) chemical shift anisotropy, (*ii*) a small deviation from exact magic-angle setting, or (*iii*) rf offsets caused by filters or improper cable lengths either between the probe and the preamplifier or for the λ/4 cable in the duplexer of the preamplifier. Thus, a careful

setup of the experimental conditions is required in order to observe reliable ssb manifolds. In this work asymmetries in the manifold of ssbs for the ^{27}Al satellite transitions are observed in ^{27}Al MAS NMR spectra of $KAl(SO_4)_2 \cdot 12H_2O$ (alum) recorded at temperatures in the range -50 °C to 80 °C, with the largest effects observed at lowest temperature. The asymmetries reflect the fact that the ssbs possess different line widths, showing that the T_2 relaxation times for the two inner ($m = 1/2 \leftrightarrow m = 3/2$ and $m = -1/2 \leftrightarrow m = -3/2$) transitions are different and similarly that the T_2 values are different for the two outer ($m = 3/2 \leftrightarrow m = 5/2$ and $m = -3/2 \leftrightarrow m = -5/2$) transitions. This is confirmed by the determination of the T_2 relaxation times from spin-echo ^{27}Al NMR experiments for a single crystal at -50 °C. The spin-echo NMR spectra were recorded using high-power ^1H decoupling in order to suppress modulations of the spin-echo decay by ^1H-^{27}Al dipolar interactions. For an arbitrary orientation of the crystal, the T_2 relaxation times of 0.99 ms and 2.08 ms are determined for the two inner transitions while T_2 values of 0.76 ms and 3.53 ms are obtained for the corresponding two outer transitions for one of the four magnetically inequivalent Al sites in alum. A similar variation in T_2 relaxation times are observed for the other Al sites.

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262. *WISE NMR Characterization of Nanoscale Heterogeneity and Mobility in Supercontracted Nephila Clavipes Spider Dragline Silk.*

Gregory P. Holland, University of Wyoming, Department of Chemistry, Laramie, WY, 82071-3838; Randolph V. Lewis, University of Wyoming, Department of Molecular Biology, Laramie, WY, 82071-3944; Jeff L. Yarger, University of Wyoming, Department of Chemistry, Laramie, WY, 82071-3838

Exposing spider dragline silk to water results in isochoric supercontraction where the fiber shrinks to half its length and swells in diameter[1]. The $^1H \rightarrow ^{13}C$ CP-MAS NMR spectrum of water-saturated *Nephila Clavipes* dragline silk decreases in total intensity compared to the spectrum of native silk. This has been interpreted to result from molecular motion that averages the dipole interactions that facilitates the cross-polarization process[2]. Two-dimensional WISE NMR can be implemented to correlate ^{13}C chemical shifts with mobility by observing the corresponding ^1H line shapes and linewidths[3]. The WISE NMR spectrum of the native silk displays ^1H linewidths that are ~44 kHz for all carbon environments characteristic of a rigid organic system. In contrast, the water-saturated case shows a component of the proton line that is narrowed to ~5 kHz for the glycine C_α and carbonyl environments while the alanine C_α and C_β remain broad. The spider silk morphology can be best described as crystallites embedded in an amorphous matrix[4]. The crystallites are composed of polyaniline with a β–sheet structure. A delay time is added to the WISE NMR pulse sequence to monitor spin diffusion between the amorphous, mobile region and the crystalline domains. The time required for spin diffusion to reach spatial equilibrium is related to the size of the crystallites. This technique is used to measure domain sizes that are on the nanometer length scale in solvated spider dragline silk.

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[2] Jelinski et al., J. Amer. Chem. Soc., 2000, 122, 9019.

[3] Schmidt-Rohr et al., Macromolecules, 1992, 25, 3273.

[4] Vollrath et al., J. Microscopy, 1997, 189, 64.

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263. *Measurement of Diffusion Coefficients by ^1H NMR Spectroscopy for the Investigation of Protein-ligand Binding.*

Eleni Skordi, John C. Lindon and Jeremy K. Nicholson, Imperial College London

A ^1H NMR spectroscopic study is presented for the investigation of protein-ligand binding using the measurement of molecular translational diffusion coefficients. A series of carboxylate compounds are compared with respect to their binding capacity to human serum albumin (HSA), using a term defined as log (ratio of ligand to HSA) required to give 50% of the ligand bound. This term can provide information on protein-ligand interactions without the need to determine the number of binding sites and their individual dissociations constants. HSA is a principal transport protein in blood plasma that binds extensively many drugs and hence it is a major determinant in their disposition and biological activity *in vivo*. It is therefore of great interest to understand the binding of drug ligands to HSA. The diffusion-based approach is advantageous over other NMR methods in that it eliminates the necessity to derive error-prone values for bound-ligand chemical shifts, linewidths or relaxation times. The approach may find widespread application in the construction of quantitative structure activity relationships (QSARs), as well as in drug design studies.

[1] Liu et al., Analytical Communications, 1997, 27, 225.

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264. *Restricted Water Diffusion Through Silica Sol-Gel Made Particles Measured by Pulsed-Field Gradient NMR.*
Susanne Veith, Sotiris E. Pratsinis, Particle Technology Laboratory, ETH Zurich, CH-8092, Switzerland; Eric Hughes, Gilles Vuataz, Nestlé Research Centre, Vers-chez-les-Blanc, CH-1000 Lausanne 26, Switzerland; Matthias Perren, Nestlé Product Technology Centre, Kemptthal, Switzerland.

Porous sol-gel particles can act as an encapsulation matrix for different biological and chemical species. Applications for the latter can be found as controlled release systems in the pharmaceutical and food industry or as biocatalysts and biosensors. The kinetic response of these biocatalysts depends on the species diffusion through the porous matrix. Furthermore, the release kinetics of the entrapped chemical molecules are governed by their diffusion through the porous matrix. Therefore the knowledge of the restricted diffusion in these porous systems is important to understand the transport of molecules .The restricted diffusion coefficient of water through porous silica is measured by Pulsed Field Gradient (PFG) NMR and a model, at complete wetting, is developed to describe molecular self-diffusion through the sol-gel made particles. To further characterize the materials, the diffusion of water and its NMR relaxation properties in the sol-gel made silica particles at different degrees of filling of is examined. The results are discussed in terms of the different regions of the silica/water adsorption isotherm as determined by gravimetric and NMR methods.

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265. *Probing the Dynamics and Side Chain Motion of Leucine Residues in Phospholamban Using ^2H Solid-State NMR Spectroscopic Techniques.*
Elvis K. Tiburu, Paresh C. Dave, Krishnan Damodaran and Gary A. Lorigan*, Miami University

Active calcium transport into the sarcoplasmic reticulum of cardiac muscle is catalyzed by the Ca^{2+}-ATPase and regulated by phospholamban (PLB). PLB is a 52-amino acid transmembrane protein that inhibits the Ca^{2+}-ATPase at submicromolar concentrations of Ca^{2+}. In order to understand these interactions, spectroscopy and molecular modeling techniques have been used to probe the structure and dynamics of the Ca^{2+}-ATPase and PLB in the cardiac sarcoplasmic reticulum and in reconstituted membranes. ^2H Solid-state NMR studies of leucine residues in the transmembrane domain of PLB provide information for understanding the rotational reorientation and dynamics of PLB in model phospholipid bilayers. Specific PLB Leu residues (CD_3) were isotopically labeled with ^2H and reconstituted into 1-palmitoyl-2-oleyl-phosphatidylcholine (POPC) bilayers. ^2H solid-state NMR spectra were collected for each of the residues (Leu-28, Leu-39, and Leu-51) as a function of temperature. At –25 ºC, the NMR spectrum of the PLB Leu-51 sample revealed a quadrupolar splitting of 36 kHz which due to methyl group rotations (40 kHz). The quadrupolar splittings of Leu-39 and Leu-28 were slightly smaller than Leu-51 at the same temperature. At higher temperatures (0, 25, 45, 60 ºC), the deuterium line shapes of the three leucines vary due to motional averaging. The ^2H lineshapes and quadrupole splittings will be used to probe the structural and dynamic properties of PLB inside POPC phospholipid bilayers.

NMR Poster Session

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266. *Quantitative Measurements of Quadrupolar Nuclei.*
Kathryn J. Hughes and Larry W. Beck, The University of Michigan

Acquiring quantitative NMR measurements of quadrupolar nuclei in the solid state is difficult due to large quadrupolar coupling interactions. Most NMR studies of quadrupolar nuclei in solids are not quantitative, and instead focus on qualitative interpretation of the quadrupolar interaction. Previous studies have shown that low power, short pulses can be used to acquire quantitative spectra in the solid-selective regime. However, if υ_{rf} or υ_{MAS} are on the same order of magnitude as υ_Q, the populations of different spin states will mix, resulting in non-quantitative spectra. Here we demonstrate that other anisotropic interactions, such as CSA or dipolar coupling can also limit our ability to obtain quantitative information. We will show that for samples where the static central transition linewidth is on the order of υ_Q, spectra are only qualitative. Quantitative measurements of quadrupolar nuclei should be referenced to an aqueous solution of known concentration. Prior quantitative interpretations (particularly for high aluminum zeolites as NaY and LTA) may need to be re-addressed. Simple nutation experiments should be used to determine if samples fall completely within the solid-selective regime prior to quantitative analysis.

NMR Poster Session

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267. *Solid and Solution-State Investigation of The Dynamics and Structure of Aluminum Tris (Quinoline-8-olate).*
Marcel Utz, University of Connecticut, Institute of Materials Science and Department of Physics, Storrs CT06269; Changqing Chen, University of Connecticut, Department of Chemistry, Storrs CT06269; Martha Morton, University of Connecticut, Department of Chemistry, Storrs CT06269; Magesh Nandagopal, University of Connecticut, Institute of Materials Science, Storrs CT06269; Mathew Mathai, University of Connecticut, Institute of Materials Science, Storrs CT06269; and Fotios Papdimitrakopoulos, University of Connecticut, Institute of Materials Science and Department of Chemistry, Storrs CT06269;

We present a detailed structural and dynamic NMR study, using both ^{1}H solution-state exchange spectroscopy as well as ^{27}Al solid-state NMR, of Aluminum tris (quinoline-8-olate) (Alq_3). Alq_3 is an organometallic complex of great importance in the context of organic light-emitting diodes (OLEDs). While substantial experimental effort has been invested into the optimization of Alq_3 based electronic devices, systematic studies into the fundamental properties of the Alq_3 molecule have only appeared recently. Alq_3 is an octahedral chelate complex, with three identical quinoline ligands. While a meridianal and a facial isomer are conceivable, only the former has been positively identified in solution and in the solid state so far. Using 2D proton exchange NMR, we have characterized the exchange dynamics of the three inequivalent ligands in meridianal Alq_3 in solution as a function of temperature. The results can be interpreted by a simple first-order kinetic model, and the relevant activation parameters have been determined. The exchange rate between the two enantiomers of meridianal Alq_3 in solution has been determined as a function of temperature using a chiral paramagnetic shift reagent. ^{27}Al solid-state NMR results will be presented that demonstrate that the recently discovered δ-polymorph of Alq_3 is composed of the facial isomer, whereas the previously described α-phase contains the meridianal form. The implications of these NMR results for the processing, transport properties, and operating lifetime of Alq_3 – based devices will be discussed.

NMR Poster Session
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268. *Complete Ring Assignment of the ^{13}C Signals of Bacterial Cellulose.*
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NMR has widely been used to study cellulose and its derivates. The assignment of the various carbon signals to the carbon sites in the crystalline structure was possible using specifically labelled glucose and glycerol for the biosynthesis. It is also known that most carbon signals possess two resonances in cellulose I and II. However, the structural assignment of these lines to the two anhydrous rings has not been done so far. This lack of information is crucial as this piece of information is important for understanding the hydrogen bonding system and, also, for cross checks with theoretical simulations. Furthermore, cellulose has always amorphous parts. These can be recognized by broad C4 and C6 signals which are shifted from those of the crystalline regions. However, the signals of C1, C2, C3 and C5 superimpose with their crystalline counterparts making it impossible to determine both the mean isotropic shifts and their distribution widths. These problems have been solved using fully ^{13}C-labelled bacterial cellulose consisting of the polymorphs I_α and I_β in conjunction with RFDR and Double Quantum NMR techniques.

NMR Poster Session
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269. *Universal Curves for Internuclear-distance Determination from REAPDOR Dephasing Curves for Quadrupolar Nuclei With Spin 1, 3/2, or 5/2.*
Amir Goldbourt, Shimon Vega, Weizmann Institute of Science, Chemical Physics Department, Rehovot 76100, ISRAEL; Eric Hughes, Terry Gullion, West Virginia University, Department of Chemistry, Morgantown, West Virginia 26506; and Alexander J. Vega, DuPont Central Research and Development, Experimental Station, P.O. Box 80356, Wilmington, Delaware 19880-0356.

A universal function is proposed to describe dipolar dephasing curves of REAPDOR experiments involving dipolar recoupling between an observed nucleus and a quadrupolar nucleus of spin 1, 3/2, or 5/2. Previous work has shown that, in contrast to REDOR, the shape of the REAPDOR dephasing curve depends on a large number of parameters including the quadrupolar coupling constant and asymmetry parameter, the sample rotation speed, the rf amplitude, and the relative orientations of the quadrupole tensor and the internuclear vector. Here we demonstrate by numerical simulations that the actual dispersion of REAPDOR phasing curves is quite small, provided the rotation speed and the rf amplitude applied to the quadrupolar nucleus satisfy an adiabaticity condition. The condition is practically achievable for virtually any compound containing $S \geq 1$ nuclei with small-to-moderate QCC such as ^{2}H, ^{11}B, ^{14}N, ^{17}O, ^{23}Na, ^{27}Al. This allows the REAPDOR curves to be approximated by analytical universal gaussian-type functions, comparison of which with experimental data yields internuclear distances with less than 4% error. Examples of applications of the S = 1 universal curve are given for $^{2}H/^{13}C$ and $^{14}N/^{13}C$ in alanine and of the S = 5/2 universal curve for $^{67}Zn/^{13}C$ in Zn-acetate and $^{17}O/^{13}C$ in L-tyrosine.

NMR Poster Session
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270. *Solid State NMR Studies of Zeolite Catalysts.*
Conrad Jones, Donald Stec and Sarah Larsen, University of Iowa

Solid state magic angle spinning (MAS) NMR has been used to investigate reactions of labeled urea on ZSM-5 and the structure of nanocrystalline zeolites. In this study, ^{13}C and ^{15}N MAS NMR spectra of labeled urea on FeZSM-5 (Fe/Al =0.11) and HZSM-5 revealed the formation of CO_2 and NH_3 after heating to 250 ºC. ^{15}N MAS NMR spectra of FeZSM-5 with labeled urea and unlabeled NO indicated that nitrogen is formed at elevated temperatures. In addition, solid state MAS NMR was used to characterize framework silicon and aluminum in nanocrystalline zeolites. The linewidth in the ^{29}Si and ^{27}Al MAS NMR spectra increased as the zeolite particle size decreased suggesting an increase in lattice strain with decreasing crystal size.

NMR Poster Session
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271. *$^{47,49}Ti$ Wideline and ^{31}P and ^{13}C MAS NMR Study of GD Reactions With TiO_2 and Titanium.*
G. W. Wagner, L. R. Procell, U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, 21010-5424; Shekar Munavalli, Geo-Centers, Inc., Aberdeen Proving Ground, MD 21010-5424

Reactions of nerve agent GD with TiO_2 (anatase and rutile) and titanium metal powder have been examined by $^{47,49}Ti$ wideline and ^{31}P and ^{13}C MAS NMR. GD hydrolyzes on TiO_2 to yield a titanium phosphonate species with its pinacolyl group intact as detected by ^{31}P and ^{13}C MAS NMR. GD reacted with titanium metal mixed with TiO_2 results in the dissolution of the titanium metal and/or TiO_2 to form the identical titanium phosphonate species. ^{31}P MAS NMR spectra indicate the structure of the titanium phosphonate species is complex, possessing at least three different P-sites. $^{47,49}Ti$ NMR wideline spectra of this species and a synthesized titanium phosphonate model compound were obtained and compared to further characterize the structure.

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272. *^{17}O MQMAS and CP/MAS Studies on Non-Crystalline Aluminophosphate and Calcium Aluminosilicate Glass.*
K. Kanehashi and K. Saito, Nippon Steel Corporation

Structural investigations of the amorphous aluminophosphate and calcium aluminosilicate were done using ^{17}O MQMAS and CP/MAS. For the aluminophosphate, two oxygen sites are resolved in the ^{17}O MQMAS spectrum, that assigned to the species containing Al-O bond (Al-O-Al, Al-O) and P-O bond (P-O-P, P-O-Al, P-O) by the $^{31}P \rightarrow {}^{17}O$ CP/MAS spectrum. On the other hand, three peak tops were observed in the $^{17}O \rightarrow {}^{31}P$ CP/MAS spectrum, that was thought to be the Q^2, Q^3 and Q^4 unit. For the calcium aluminosilicate, three cross sections were observed in ^{17}O 3QMAS, those are considered to correspond to the bridging sites (Si-O-Al and small amount of Si-O-Si) and the non-bridging sites (Ca---O). The Al-O-Al peak was not observed because of its stoichiometry. Assignment of the bridging oxygen and non-bridging oxygen in the calcium aluminosilicate was confirmed by the $^{27}Al \rightarrow {}^{17}O$ CP/MAS experiment.

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273. *High Temperature and Ambient Temperature NMR Investigation of Metal Selenophosphate Syntheses.*
Christian G. Canlas, Mercouri G. Kanatzidis and David P. Weliky, Michigan State University

Many different metal selenophosphate compounds can be synthesized in high temperature (400 – 600 ºC) melts and these compounds contain a rich variety of metal selenophosphate anions. In order to understand better the chemistry which occurs in these melts, syntheses have been carried out in situ in the NMR spectrometer and ^{31}P NMR has been applied to identify and quantify reactants, intermediates, and products over the time course of the reactions. For example, in a melt containing Ag:P:Se in a 2:1:3 mol ratio, there are two distinct ^{31}P signals which can be tentatively assigned to the PSe_4^{3-} and $P_2Se_6^{4-}$ anions, and which correlate with the final ambient temperature products, Ag_7PSe_6 and $Ag_4P_2Se_6$, respectively. The observed signals are relatively broad, which could be diagnostic of chemical exchange in the melt or of solid precipitation in the melt. For the PSe_4^{3-} signal, MAS narrows the lineshape, which suggests that this anion exists in some solid or at least slowly-rotating form at high temperature. In a parallel study, ambient temperature ^{31}P NMR has been applied to the solid metal selenophosphate product compounds, and a correlation was observed between the ^{31}P chemical shift and the presence or absence of a P–P bond in the selenophosphate anion. This correlation will be useful in anion identification in the high-temperature melts. In addition, ^{31}P spin-lattice relaxation times were measured at ambient temperature and showed a surprisingly large range (20 – 3000 s) among the different compounds. Two of the compounds which demonstrate fast relaxation were also shown to have detectable ESR signals. Although these compounds are not paramagnetic per se,

they appear to contain paramagnetic impurities whose chemical identity is currently under investigation. Overall, NMR has been shown to be a promising technique for understanding the mechanisms of high temperature syntheses of metal selenophosphates.

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274. *Caesium Motion in Potential Ceramic Radioactive Waste Host Phases From ^{133}Cs NMR Experiments at High Temperature.*

L. Le Pollès, K. R. Whittle and I. Farnan, University of Cambridge

NMR is a powerful technique to study motion and diffusion in solids as a function of temperature. We have developed a high–temperature static probe operating between ambient temperature and 1200ºC. This temperature range is interesting for the study of mineral compounds: their phase transitions, the different mobility regimes of the cations. We use this high temperature probe for the study of pollucite, a caesium aluminosilicate. Pollucite $CsAlSi_2O_6$ has been proposed as a storage medium for ^{135}Cs and ^{137}Cs active nuclear wastes. The centre–line temperature of nuclear waste storage cannisters containing fission products is ~ 300˚C. The ^{133}Cs room temperature spectrum exhibits a first-order quadrupolar lineshape (central and a set of three satellite transitions) with Cq = 120kHz. At nuclear waste storage temperature (~ 300˚C), this spectrum remains similar to that at room temperature with no indication of significant Cs motion on the NMR time scale. Above 500˚C, the spectra show a narrowing of the central transition and the 'averaging in' of the satellite transitions, indicating a substantial caesium motion. In the fast motion regime (500˚C – 900˚C K), the analysis of the line shape as a function of the temperature allows us to calculate the rate of Cs motion and the activation energy and self-diffusion pre-factor. These are essential data for the modelling of the long-term behaviour of Cs ceramic host materials if the Cs loss is diffusion-controlled. Some preliminary results about caesium motion have also been obtained on compound of the Hollandite family which is another possible host for radioactive cesium.

NMR Poster Session

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275. *Obtaining Structural Clues in Non-Ideal Solids via Dipolar Coupling NMR Spectroscopy.*

Erin Wilson and Larry W. Beck, University of Michigan

Recently Shimon Vega and coworkers have successfully applied dipolar coupling solid-state NMR techniques to determine structure in rigid, well-crystallized systems. Here we will demonstrate the application of these techniques to less ideal systems, such as the non-covalent interactions between guest molecules in a host lattice and defect-rich deproteinated bone crystallites. X-ray diffraction analysis of these systems is difficult due to low-occupancy of species of interest and the challenge of growing crystals of sufficient size for single-crystal studies. In such X-ray opaque systems, dipolar coupling techniques such as CP, LG-COSY, LG-HETCOR, and 2D LG-CPMAS make it possible to extract structural information. Guest-guest interactions between *para*-fluorinated aromatic molecules and PABA in a zeolite host are examined by ^{19}F–^{13}C and ^{1}H–^{13}C 2D LG-CPMAS for evidence of dipole order of the guest molecules inside the host lattice. Carbonate-containing bone material is investigated via ^{1}H Bloch decay and LG-COSY, ^{1}H–^{13}C CP, and ^{1}H–^{31}P LG-HETCOR and 2D LG-CPMAS for clues to the location and role of carbonate ions and water molecules at lattice defects.

NMR Poster Session

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276. *Multi-scale NMR Characterization of Mesostructured Materials Using ^{1}H-^{13}C Through Bond Polarisation Transfer, Fast MAS, and 1H Spin Diffusion.*

B.Alonso and D. Massiot, CRMHT - CNRS, France

A robust and simple to implement multi-scale NMR characterisation of materials is presented. It combines the selection of ^{1}H–^{13}C pairs by a through-bond polarisation transfer (INEPT in the case presented here) and the exploration of larger distances by the introduction of ^{1}H spin diffusion. This strategy of characterisation is well adapted to the highest MAS rates and takes benefits of it. The effect of ^{1}H dephasing on the efficiency of the $^{1}H \rightarrow {}^{13}C$ through-bond polarisation transfer is determined which allows consecutively the quantification of signals. Mesostructured spherical silica-based particles containing CTA^+ cations were characterised by this strategy. Contrasted spin diffusion curves were found and qualitatively explained by differences in terms of mobility and spatial distributions. Preliminary lattice calculations facilitate the description of the initial rates. *Supported by EEC HPRI 1999-00042 contract*

[1] B.Alonso, D.Massiot, "Multi-scale NMR characterization of mesostructured materials using 1H-13C through bond polarisation transfer, fast MAS, and 1H spin diffusion.", J. Magn. Reson., (published on JMR web site).

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277. *Simple Central Transition Enhancement and Quadrupolar Coupling Constant Estimation of Spin — 3/2 and 5/2 Quadrupolar Nuclei via MAS NMR.*

Mark V. Wilson and Larry W. Beck, University of Michigan

A two-pulse method for enhancement of the central transition of spin-3/2 and 5/2 nuclei will be presented. Utilizing the effect of fast sample spinning on the transition frequencies of crystallites in a polycrystalline sample, a single off-resonance pulse can be used to selectively saturate the satellite transitions of a quadrupolar nucleus. This leads to a maximum theoretical enhancement of I + 1/2 at $\nu_q/2$. Enhancement drops to unity (no enhancement) again at ν_q (for spin-3/2) or $2\nu_q$ (for spin-5/2). Because of this, obtaining an enhancement profile with respect to offset can give an accurate estimation of the quadrupolar splitting frequency. Both of these uses have been previously demonstrated using adiabatic sweeps and, recently, RAPT and Gaussian-RAPT. Compared to those experiments, the current method is not hardware limited, and is easier to implement and optimize. As has been noted elsewhere, the method of adiabatic sweeps requires specialized equipment, whereas the current method does not. RAPT, on the other hand, introduces a phase-alternating pulse train to implement and requires optimization of this RAPT modulation frequency (ν_m) in addition to the parameters that must be optimized in the current experiment. In addition, the maximum ν_m is limited by the hardware of a given system. Since optimal enhancement occurs at $\nu_m = C_q/4$, this limits the range of compounds for which maximum enhancement can be achieved. Maximum enhancements obtained, conditions for optimization, accuracy of ν_q estimation, and possibilities for further investigations will be discussed.

NMR Poster Session

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278. *Heteronuclear Correlations Involving Quadrupolar Nuclei, a Through Bond Approach Using J-couplings.*

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Heteronuclear correlation involving quadrupolar can be established using through bond dipolar interaction (CP), but also using isotropic J-coupling (INEPT, HMQC), providing long enough T'2 coherence life times. We demonstrate that the through bond approach can be very fruitful, providing significant signal enhancement, and can be combined with high resolution encoding of the quadrupolar nucleus spectrum (MQMAS). We show applications to a variety of alumino-phosphate molecular sieves or Zeolite structures. *Supported by EEC HPRI 1999-00042 contract.*

[1] D. Massiot, F. Fayon, B. Alonso, J. Trebosc, J.P. Amoureux, " Chemical bonding differences evidenced from J coupling in solid state NMR experiments involving quadrupolar nuclei.", J. Magn. Reson., (in press).

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279. *NMR Detection of Dynamics in Metallic Supercooled Liquids and Glasses.*

Lilong Li and Yue Wu, University of North Carolina

NMR is a local probe of atomic structures and dynamics and is an important complementary tool to diffraction measurements, especially in the study of disordered systems. Here we present an NMR study of metallic glasses and supercooled liquids. The nature of glass transition remains an open question. It has been predicted that rattling motions of atoms within cages surrounded by neighboring atoms show a critical behavior at a temperature T_c significantly above the glass transition temperature T_g. Above T_c the dynamics is liquid-like and below T_c the system becomes solid-like on microscopic scales. Such rattling motion is represented by local density fluctuations. We will show both theoretically and experimentally that Knight shift is a perfect tool for detecting such local density fluctuations capturing fluctuations on all timescales. This is very different from motional narrowing which is caused by atomic diffusion. Our experiments show clearly a transition in local density fluctuation at a temperature region above T_g in PdNiCuP metallic supercooled liquid.

NMR Poster Session

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280. *Characterization of Guest-Ions in Cement Minerals and in the Calcium-Silicate-Hydrate Phase by High-Field Solid-State NMR Spectroscopy.*
Jørgen Skibsted, Morten Daugaard Andersen, Michael Ryan Hansen and Hans J. Jakobsen, University of Aarhus, Denmark

The calcium silicates alite (Ca_3SiO_5) and belite (Ca_2SiO_4) are the main hydraulic components in Portland cements responsible for strength development during hydration. Metal-ion impurities incorporated into their crystal lattices during manufacture may stabilize different crystal forms of alite and belite. Thus, their presence can greatly affect the physical and chemical properties of cements. This work demonstrates that valuable structural information about the quantity and mechanism for the incorporation of aluminum and boron guest-ions in these calcium silicates can be obtained by ^{11}B, ^{27}Al, and ^{29}Si MAS NMR. It is shown that ^{27}Al MAS NMR spectra, recorded at high magnetic fields (14.1 and 21.1 T), provide unique information about the incorporation of aluminum in the calcium-silicate-hydrate (C-S-H) phase, resulting from Portland cement hydration. The combination of these results with those obtained from ^{29}Si MAS NMR of the same hydrated samples is found to be particularly useful for characterization of the structure/composition of the C-S-H phase and for determination of the degree of Al incorporation in the C-S-H structure. The present ^{29}Si and ^{27}Al MAS NMR results are in agreement with a defect tobermorite-like structural model for the C-S-H phase. Furthermore, it is shown that small quantities of boron stabilize the β-form of belite, however, ^{11}B MAS NMR demonstrates that only a small fraction of boron is incorporated into the silicate framework by substitution for Si. The greater boron part is present as trigonal boron, most likely as a separate phase of B_2O_3. Finally, the effects of boron on the hydrational reactivities for alite and belite have been investigated by ^{11}B and ^{29}Si MAS NMR for a Portland cement containing a large quantity of boron and with belite as the dominant calcium silicate phase.

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281. *Insight into Structure and Function of Proteins and Protein-ligand Complexes from Solid-State-NMR Spectroscopy.*
Stephan G. Zech and Ann E. McDermott, Columbia University

We present CP-MAS data on the transition state analogon immunicillin-H which inhibits the enzyme purine nucleoside phosphorylase (PNP). These enzymes specifically catalyze the C-N bond cleavage between ribose sugars and purine bases. In humans, PNP inhibition induces apoptosis in activated T-cells, suggesting a clinical means to improve disorders linked to T-cell proliferation. The ionization state of immucillins bound to the PNP enzyme can be established using multidimensional Solid-State NMR methods. Analysis of free and bound immucillins indicated that in the protein-inhibitor complexes, mimicry of transition state features, such as the ionization state, is a dominant force for the tight binding to the enzyme. A more general goal of Solid-State NMR is to obtain structural constraints on proteins which eventually facilitate the ab-initio determination of the three-dimensional protein structure.

A number of methodologies has been developed which allow a site-specific assignment of Solid-State NMR spectra and have recently been applied to small proteins like SH3 domain or ubiquitin. However, long-range structural information is crucial to obtain the three-dimensional structure of a protein. Different recoupling methods are presented to study tertiary contacts between amino acids in microcrystallin ubiquitin. Labeling schemes involving selectively 13C labeled glycerol as carbon source can suppress the dominant one-bond couplings observed in uniformly labeled samples and allow the observation of long range carbon-carbon couplings. Initial results appear promising for extension of these approaches to more challenging targets such as membrane proteins. *Supported by Alexander-von-Humboldt Foundation.*

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