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41st Rocky Mountain Conference on Analytical Chemistry

Abstract

Final program, abstracts, and information about the 41st annual meeting of the Rocky Mountain Conference on Analytical Chemistry, co-sponsored by the Colorado Section of the American Chemical Society and the Rocky Mountain Section of the Society for Applied Spectroscopy. Held in Denver, Colorado, August 1-5, 1999.

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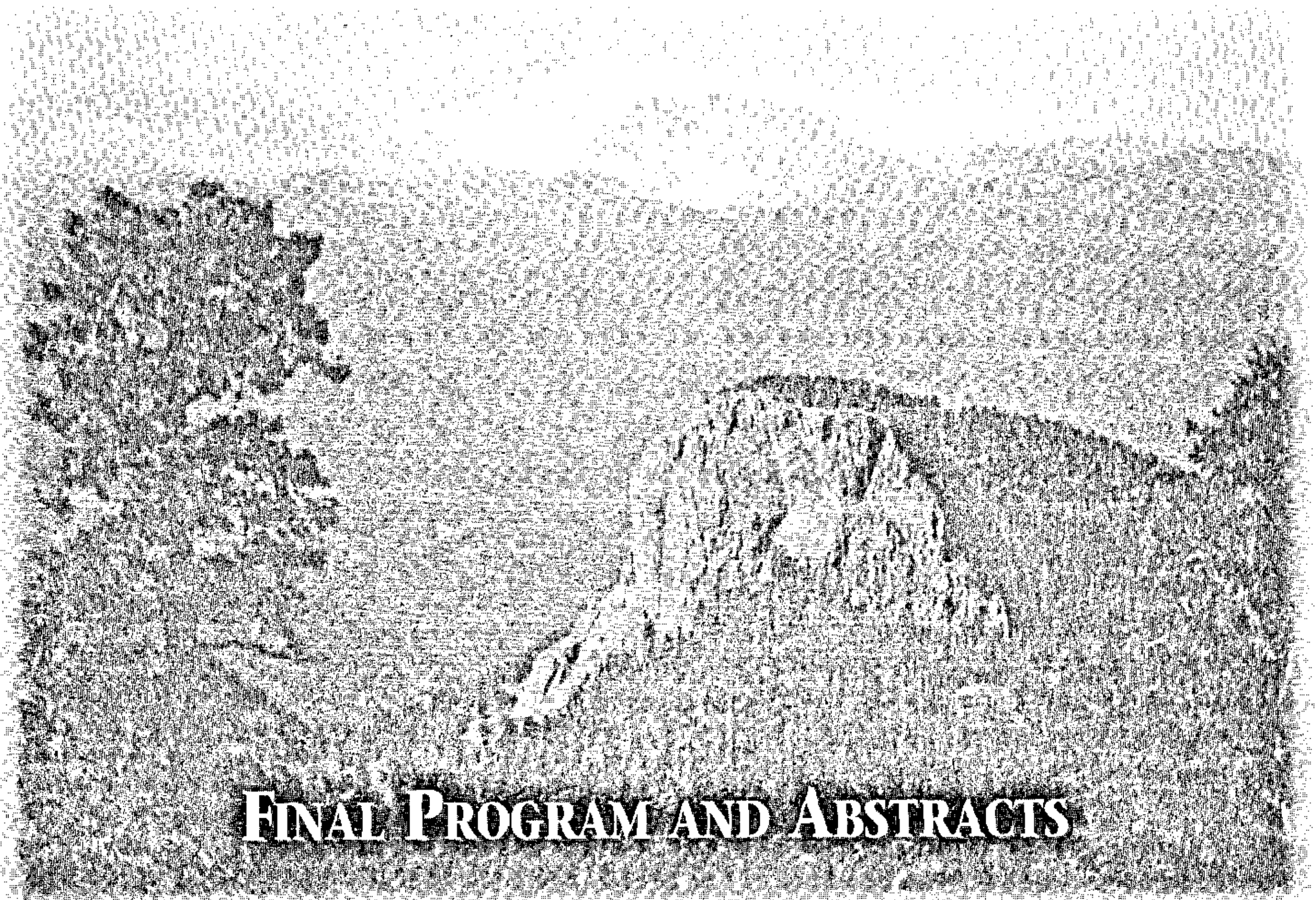
Publication Statement

41st ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY



FINAL PROGRAM AND ABSTRACTS

August 1-5, 1999
Hyatt Regency Denver
Denver, Colorado

Sponsored by:
Rocky Mountain Section Society for Applied Spectroscopy
Colorado Section American Chemical Society

Rocky Mountain Conference on Magnetic Resonance, Vol. 41 [1999], Art. 1

41ST ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

Denver, Colorado

August 2-4, 1999 (Exhibition) * August 1-5, 1999 (Symposia)

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Symposia Schedule:

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Supercritical Fluids—Theory & Applications

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ROCKY MOUNTAIN CONFERENCE INFORMATION

Poster Sessions
Conference-wide Plenary Lecture from M. Bonner Denton, University of Arizona
Short Courses
Technical Sessions
Vendor Exhibits
Vendor Workshops

Exhibition Hours

Monday, August 2 10:00 a.m. - 7:00 p.m.

Tuesday, August 3 9:00 a.m. - 5:00 p.m.

Wednesday, August 4 9:00 a.m. - 2:00 p.m.

Location

Hyatt Regency Denver
1750 Welton Street
Denver, CO 80202
Technical sessions and the exhibition will be held at the Hyatt Regency Denver

Registration

Admission to all technical sessions and the exhibition is included with your registration. You may pick up your credentials at the Rocky Mountain Conference on Analytical Chemistry registration desk at the Hyatt anytime Sunday, August 1 through Thursday, August 5, between 8:00 a.m. and 5:00 p.m. Admission to the exhibits-only is $15.00.

Message Center

Messages will be accepted and posted on the message board located near the Rocky Mountain Conference on Analytical Chemistry registration desk. Call (303) 690-3233 to leave messages.

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OTHER EVENTS AND INFORMATION

General Posters

Monday, August 2 and Tuesday, August 3
Authors present August 3, 3:00 p.m.–5:00 p.m.

Plenary Lecture

Join in Tuesday, August 3 at 1:30 p.m. for a conference wide Plenary Lecture from M. Bonner Denton, Professor, University of Arizona. Topic is Advances in the Application of Array Detectors for Improved Chemical Analysis from X-ray to IR. (Admission is complimentary with any registration to the Symposium)

Social Programs

Registration Mixer, Sunday, August 1, 4:00 p.m.–8:00 p.m. A cash bar will be open in the Imperial Ballroom Foyer of the Hyatt. Plan to meet and network with other attendees.

Symposium Reception, Monday, August 2, 5:00 p.m.–7:00 p.m. All attendees are cordially invited to join in for cocktails and hors d'oeuvres in the Imperial Ballroom of the Hyatt.

EVENT INFORMATION

Milestone Presentations, LLC
4255 South Buckley Road, #118• Aurora, CO 80013
Phone: (303) 690-3233• Toll Free: (800) 996-3233 • Fax: (303) 690-3278
E-mail: milestone@bod.net• Web: www.milestoneshows.com/rmcac

ROCKY MOUNTAIN CONFERENCE-AT-A-GLANCE

	Rooms	Sunday, August 1		Monday, August 2		Tuesday, August 3		Wednesday, August 4		Thursday, August 5	
		A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
Atomic Spectroscopy	Royal			▨							
Electrochemistry	Royal				▨						
Environmental Chemistry	Far East			▨	▨						
EPR Lectures	Grand Ballroom			▨	▨	▨		▨	▨	▨	
EPR Posters	Grand Foyer			▨	▨	▨	▨	▨	▨	▨	
Exhibition	Imperial Ballroom			▨	▨	▨	▨	▨	▨		
General Posters	Imperial Ballroom			▨	▨	▨	▨				
ICP-MS	Royal					▨					
Lasers, Materials and Surfaces	Parisienne			▨	▨						
Luminescence	Pavilion				▨	▨					
MS, GC/MS, LC/MS/ Pharmaceutical Analysis	Far East							▨	▨		
NMR Lectures	Moulin Rouge			▨	▨	▨		▨	▨	▨	
NMR Posters	Imperial Ballroom			▨	▨	▨	▨	▨	▨	▨	
Plenary Lecture	Grand Ballroom						▨				
Quality Assurance/ Pharmaceutical Analysis	Parisienne					▨					
Radiochemistry	Florentine			▨	▨	▨					
SAS Short Course	Parisienne	▨	▨								
Supercritical Fluids— Theory & Applications	Vista			▨	▨						
Speaker Prep	Gold	▨	▨	▨	▨	▨	▨	▨	▨	▨	

EXHIBITORS & SPONSORS FOR THE 1999 ROCKY MOUNTAIN CONFERENCE

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(as of July 14, 1999)

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Special thanks to Broadband Power Technology, JEOL, USA, Inc. and Varian Associates, Inc. for their conference-wide sponsorships

SAS Short Course

Sunday, August 1, 1999
8:00 a.m. - 5:00 p.m. (lunch will be served)
Hyatt Regency—Denver

GENERAL INFORMATION

The Society for Applied Spectroscopy is pleased to offer a course designed to introduce both bioscientists and spectroscopists to the rapidly expanding use of IR in the biosciences. It will enable bioscientists to ascertain if IR can provide solutions to their biological problems and help them learn how to use IR for their experiments. The course will aid spectroscopists in finding out what biological experiments are possible or needed, how to handle biological samples, and what techniques and accessories yield the most biological information.

Course Outline

STRUCTURAL BIOLOGY AND THE ROLE OF SPECTROSCOPIC TECHNIQUES

—Vibrational spectroscopies (IR, Raman, etc.): advantages and disadvantages
—Biological structures (proteins, nucleic acids, lipids)
—Biologically relevant important vibrational modes
—Vibrational Theory with protein examples

IR INSTRUMENTATION

—FTIR principles, methods and advantages
—Advanced techniques (Time-resolved, polarization modulation (VCD), Imaging)

SAMPLING TECHNIQUES

—Transmission
—Reflectance (diffuse, ATR.)
—IR microscopy
—Demonstration of sampling accessories

DATA MANIPULATION AND DATA INTERPRETATION

—Subtraction (buffer, water vapor, matrix)
—Deconvolution / Derivatives (resolution enhancement)
—Quantitative secondary structure analysis
—Formulation analysis

APPLICATION EXAMPLES

—Pharmaceuticals formulation (liquid, powder, ...)
—Protein secondary structure determination
—Nucleic acid conformations
—Membranes and constituents
—Biological Tissues

INSTRUCTORS

Rina Dukor, Ph.D. is a Research Scientist / Product Manager at Vysis, Inc. (formerly AMOCO Technology Company). She is responsible for the design and implementation of new products based on IR spectroscopy. She has extensive experience using spectroscopic methods (IR, CD and VCD) for the study of proteins, peptides and nucleic acids. She has co-authored about 20 peer-reviewed papers and has presented her work at many international meetings. In the past year, she has provided hands-on training on biological infrared spectroscopy at many leading pharmaceutical and biotechnology companies.

Timothy A. Keiderling is Professor of Chemistry at the University of Illinois at Chicago and has spent more than 25 years of his professional career developing new infrared and other spectroscopic techniques, applying them to biomolecular structural problems. He is the author of more than 170 publications which include a number of invited reviews and book chapters.

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41ST ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

Technical Program

Symposium on Atomic Spectroscopy

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Monday, August 2, 1999

Geoff Coleman presiding

8:30 1. *ATOMIC FLUORESCENT MERCURY ANALYSIS USING A METHOD 1631 COMPLIANT INSTRUMENT.* Keith W. Ballantyne, Brian N. Radford, Genesis Laboratory Systems, Inc.

8:55 2. *DISTRIBUTION OF INORGANIC MERCURY IN SACRAMENTO RIVER WATER AND SEDIMENTS USING ATOMIC FLUORESCENCE SPECTROMETRY.* D.A. Roth, H.E. Taylor, U.S. Geological Survey

9:20 3. *FIELD SCREENING MEASUREMENT OF CR AND PB IN SOILS: A NEW TECHNOLOGY.* A.J.R. Hunter, L.G. Piper, M.E. Fraser, S.J. Davis, Physical Sciences, Inc.

9:45 4. *SENSITIVITY ENHANCEMENT OF METALS USING A CONCOMITANT HYDRIDE GENERATOR WITH ICP-AES.* Tina R. Harville, Albert Brennsteiner, Agnes Cosnier, Instruments S.A. Inc., JY Emission/HORIBA Group

10:10 Break

10:25 5. *DETERMINATION OF LEAD IN A CALCIUM CARBONATE MATRIX BY GFAA.* G.R. Dulude, D.L. Pfeil, G.N. Coleman, Thermo Jarrell Ash

10:50 6. *COMPUTER SIMULATIONS OF ATOMIC AND MOLECULAR SPECIES WITHIN A GRAPHITE FURNACE ATOMIZER.* Gary D. Rayson, Kowit Sae-tueng, New Mexico State University

11:15 7. *TRACE ANALYSIS OF TUNGSTEN BY DIRECT CURRENT PLASMA SPECTROMETRY.* R. Starek, G.N. Coleman, Thermo Jarrell Ash

11:40 8. *A COMPARISON OF METHODS FOR DETERMINATION OF DETECTION LIMITS.* Greg W. Johnson, Jude O. Proctor, Virginia H. Houlding, Matheson Gas Products

Symposium on Electrochemistry

Symposium Chair:

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Monday, August 2, 1999

1:15 9. ***DETECTION OF SURFACE BOUND BIOMOLECULES AT ATTOMOLE CONCENTRATIONS USING A UNIQUE COMBINATION OF ELECTROCHEMISTRY, CAPILLARY ELECTROPHORESIS, AND LASER INDUCED FLUORESCENCE.*** Lorna Pehl Hunter, Guoying Chen, Daniel A. Buttry, University of Wyoming; Shauna Hiley, Missouri Western State

1:40 10. ***FTIR SPECTROSCOPIC INVESTIGATION OF LONG-CHAIN ALKYL THIOL DERIVATIVES AND THE RELATIONSHIP TO INTERFACIAL CAPILLARY ELECTROPHORESIS.*** Richard C. Martoglio, Daniel A. Buttry, Guoying Chen, University of Wyoming

2:00 11. ***ROTATING RING-DISK ELECTROCHEMICAL STUDY OF ION TRANSPORT IN POLY(PYRROLE) FILMS.*** Corey A. Salzer, C. M. Elliott, Colorado State University

2:20 12. ***NEW POLYMER ELECTROLYTES BASED UPON POLYVINYLACETATE BLENDS.*** Radha Pyati, Shane Karnik, University of Colorado

2:50 Break

3:10 13. ***DYNAMICS OF CHARGE COMPENSATION IN REDOX PROCESS OF POLY(ANILINE-CO-N-PROPANESULFONIC ACID ANILINE), (PAPSAH) IN ORGANIC MEDIA.*** Hamilton Varela, Roberto M. Torresi, Universidade de São Paulo; Daniel A. Buttry, University of Wyoming

3:30 14. ***NOVEL V_2O_5 COMPOSITES FOR SECONDARY LITHIUM ION BATTERY APPLICATIONS.*** Kevin C. White, Daniel A. Buttry, University of Wyoming

4:00 15. ***NMR SPECTROSCOPY AND IMAGING OF AN ELECTROCHEMICAL CELL WITH A CARBON WORKING ELECTRODE.*** Rex E. Gerald II, Giselle Sandí, Robert J. Klingler, Jerome W. Rathke, Argonne National Laboratory

Symposium on Environmental Chemistry

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Financial Support provided by Hewlett Packard Chemical Analysis Group

Monday, August 2, 1999

Morning, Edward T. Furlong presiding

8:30 Opening Remarks

8:35 *INVITED SPEAKER IN ENVIRONMENTAL MASS SPECTROMETRY—Sponsored by Hewlett Packard Chemical Analysis Group*

16. ***MOLECULAR TRACERS OF ORGANIC MATTER SOURCES TO DRINKING WATER SUPPLIES.*** Standley, L.J., Kaplan, L.A., Stroud Water Research Center; Smith, D., South Central Connecticut Regional Water Authority

9:35 17. ***ANALYSIS OF SULFONYLUREA, IMIDAZOLINONE, AND SULFONAMIDE HERBICIDES IN WATER SAMPLES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY/ELECTROSPRAY IONIZATION-MASS SPECTROMETRY.*** P.M. Gates, S.L. Werner, E.T. Furlong, M.R. Burkhardt, National Water Quality Laboratory, U.S. Geological Survey

9:55 18. ***CONTINUING EFFORTS TO REMOVE MTBE FROM A DRINKING WATER RESERVOIR.*** M.W. Tikkanen, R.G. Sykes, East Bay Municipal Utility District

10:15 Break

10:35 19. ***DEVELOPMENT OF A SPARGING TECHNIQUE FOR ANALYSIS OF CHLORINATED HYDROCARBONS IN INDUSTRIAL WASTEWATER USING ATR-FTIR SPECTROSCOPY.*** Fiona Regan, Ambrose Hayden, Limerick Institute of Technology; Peter McLouglin, Waterford Institute of Technology

10:55 20. ***ELEMENTAL ANALYSIS OF AMBIENT WATER USING A MAGNETIC SECTOR ICP-MS.*** Rob Henry, Dagmar Koller, VG Elemental

11:15 21. ***MULTI-CLASS PESTICIDE RESIDUE ANALYSIS BY SOLID-PHASE EXTRACTION AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY/ELECTROSPRAY IONIZATION-MASS SPECTROMETRY.*** Stephen L. Werner, Bruce D. Anderson, Laura J. Coffey, Mark R. Burkhardt, Edward T. Furlong, National Water Quality Laboratory, U.S. Geological Survey

11:35 22. ***PHOTOOXIDATION OF ORGANIC CHEMICALS USING SEMICONDUCTOR NANOCLUSTERS.*** J.P. Wilcoxon, Sandia National Labs

12:00 Lunch

Afternoon, Maria Tikkanen presiding

1:30 Opening Remarks

1:35 23. ***INVITED SPEAKER IN ENVIRONMENTAL CHEMISTRY—SPECIATION OF ARSENIC IN DIETARY SOURCES.*** E. D. Pellizzari, Q. Akinbo, R. Fernando, J. Raymer, Research Triangle Institute

2:35 24. ***IS DISSOLVED URANIUM IN THE LITTLE COLORADO RIVER OF NATURAL OR MINING/MILLING ORIGIN: A $^{234}U/^{238}U$ STUDY.*** M.E. Ketterer, S.C. Szechenyi, Northern Arizona

2:55 25. ***ADVANTAGES OF DUAL-VIEW OPTICS FOR ICP ANALYSIS OF ENVIRONMENTAL SAMPLES.*** R.L. Stux, G. Kunselman, R.W. Foster, G.R. Dulude, G.N. Coleman, Thermo Jarrell Ash Corporation

3:15 Break

3:35 26. ***AFFINITIES AND CAPACITIES OF METAL ION BINDING TO DATURA INNOXIA UNDER MULTIELEMENT- EXPOSURE CONDITIONS.*** Patrick A. Williams, Gary D. Rayson, New Mexico State University

3:55 27. ***ENVIROGEOCHEMICAL EXPLORATION FOR ANTHROPGENIC URANIUM DISTRUBANCES: A LEAD ISOTOPES APPROACH.*** M.E. Ketterer, D.A. Lane, J.A. Jordan, D.L. Hudson, S.C. Szechenyi, Northern Arizona University

4:15 28. ***A UNIVERSAL ICP-OES METHOD FOR ENVIRONMENTAL ANALYSES.*** Zoe A Grosser, Lee Davidowski, John Latino, Douglas Sears, Randy Hergenreder, Perkin Elmer Corporation

4:35 29. To be announced

Symposium on EPR

Symposia Chairs:

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Financial Support provided by—Sponsor: Bruker Instruments, Inc., EPR Division; Contributors: JEOL; Resonance Instruments, Inc.; Wilmad Glass Research Specialties; and Scientific Software Services

Sunday, August 1, 1999

Bruker Pulsed EPR Workshop at the University of Denver, Olin Hall

The Workshop will be tutorial and non-mathematical. No background in pulsed EPR is assumed. For further details and downloadable registration form go to www.du.edu/~seaton/eprsym.html

Open House at the University of Denver EPR Laboratory

5:45 Meet in hotel lobby for bus transportation (for those who do not attend the workshop).

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

Monday, August 2, 1999

Session I, Recognition of International EPR Society award winners, J. R. Pilbrow presiding

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

8:35 Comments on the contributions of William B. Mims, 1998 Silver Medal awardee

8:40 30. J. Peisach, Albert Einstein College of Medicine.

9:10 31. *PROBING RADICAL INTERMEDIATES IN ENZYME CATALYSIS.* J. McCracken, V. Singh, R. B. Muthukumaran, V. L. Davidson, Z. Zhu, S. W. Ragsdale, and C. Furdui, Michigan State University, University of Mississippi Medical Center, and University of Nebraska.

9:40 32. *LONG-RANGE DISTANCES IN SPIN LABELED NUCLEOSOMES BY EPR.* M. K. Bowman, A. M. Tyryshkin, V. Burnett, J. Marx, and D. L. Springer, Pacific Northwest National Laboratory.

10:10 Break

10:40 33. *MIMS ENDOR INVESTIGATION OF A SUBSTRATE-BASED RADICAL INTERMEDIATE IN ETHANOLAMINE AMMONIA LYASE,* R. Lobrutto, V. Bandarian, and G. H. Reed, Arizona State University and University of Wisconsin.

11:00 34. *MIMS PULSED ENDOR AND ESEEM OF METALLOENZYMES: WHERE HAS BILL MIMS LED US?* R. Davydov, P. E. Doan, B. M. Hoffman, V. Kofman, H. I. Lee, S. Smoukov, R. Song, and D. L. Tierney, Northwestern University.

11:30 35. *DIRECT AND INDIRECT DETECTION OF ECHOES—EXPERIMENTS INSPIRED BY BILL MIMS.* H. Thomann, Exxon Research.

12:00 Lunch

Session II, Metal Ions, M. K. Bowman presiding

1:30 36. *A NEW ELECTRON SPIN RESONANCE METHOD TO IDENTIFY TRANSITION METAL ION INCORPORATION INTO MOLECULAR SIEVES.* A. M. Prakash and L. Kevan, University of Houston.

DOI: https://doi.org/10.56902/RMCMR.1999.41.1

2:00 37. *PULSED ENDOR AT 95 GHZ: NEW OPPORTUNITIES IN STUDIES OF S=5/2 METAL IONS.* D. Goldfarb, P. Manikandan, T. Shane, R. Carmieli, A. J. Gilboa, and D. Arieli, Weizmann Institute of Science, Israel.

2:25 38. *EPR AND ENDOR STUDIES ON SYNTHETIC MACROMOLECULE-METAL COMPLEXES.* G. Jeschke, Max-Planck Institute for Polymer Research, Mainz, Germany.

2:50 39. *^{1}H, ^{15}N, ^{2}D HYSCORE SPECTROSCOPY OF METAL ION COMPLEXES IN DISORDERED SYSTEMS.* A. Pöppl, W. Böhlmann, R. Böttcher, L. Ihlo, and R. Kirmse, Universität Leipzig, Germany.

3:15 **Break**

3:45 40. *A CW AND PULSE EPR AND ENDOR INVESTIGATION OF OXYGENATED CO(II) CORRIN COMPLEXES.* S. Van Doorslaer and A. Schweiger, ETH Zurich, Switzerland.

4:10 41. *EPR INVESTIGATIONS OF COPPER-EXCHANGED ZEOLITES.* P. J. Carl and S. C. Larsen, University of Iowa.

4:35 42. *POSSIBLE SPIN-FRACTON RELAXATION IN THE POLYMER RESIN P4VP DOPED WITH KRAMERS IONS Co^{2+}, Nd^{3+}, Yb^{3+}.* J. Pescia, S. Misra, and M. Zaripov, Laboratoire de Magnétisme et d'éléctronique quantique, France, and Concordia University, Canada.

5:00 **Conference Mixer and Instrument Exhibit**

Tuesday, August 3, 1999

Session III, In vivo EPR, H. M. Swartz presiding

8:30 43. *POTENTIAL MEDICAL (CLINICAL!!) APPLICATIONS OF EPR (ESR): OVERVIEW AND PERSPECTIVES.* H. M. Swartz, Dartmouth Medical School.

9:00 44. *EPR IN CANCER: PHYSIOLOGY, DIAGNOSIS, AND RESPONSE TO TREATMENT.* H. J. Halpern, University of Chicago.

9:30 45. *FREE RADICAL INTERMEDIATES OF DRUGS.* L. J. Berliner, and H. Fujii, Ohio State University and Tokyo Metropolitan Institute of Medical Science, Japan.

10:00 **Break**

10:30 46. *PHARMACEUTICAL APPLICATIONS OF IN VIVO EPR.* B. Gallez and K Mäder, Université Catholique de Louvain, Belgium and Freie Universität of Berlin, Germany.

11:00 47. *STABLE NITROXIDE FREE RADICALS AS ANTIOXIDANTS, RADIO-PROTECTORS, AND IMAGING AGENTS.* J. B. Mitchell, M. C. Krishna, P. Kuppusamy, J. A. Cook and A. Russo, National Cancer Institute and Johns Hopkins University.

11:30 48. *IN VIVO EPR - INSTRUMENTAL CHALLENGES AND POTENTIAL SOLUTIONS.* T. Walczak, Dartmouth Medical School.

12:00 **Lunch**

1:30 49. *ROCKY MOUNTAIN CONFERENCE PLENARY LECTURE.* M. Bonner Denton, University of Arizona

2:30 **Break**

Session IV, Posters, S. S. Eaton presiding

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

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

(Posters are listed alphabetically by presenting author, A-K)

A 50. *ANALYSIS OF ADRENOLUTIN AND ADRENOCHROME: OXIDATIVE METABOLITES OF CATECHOLAMINES USING HPLC, SPECTROFLUOROMETRY AND ELECTRON PARAMAGNETIC RESONANCE ANALYTICAL TECHNIQUES.* S. I. Baskin, R. J. Schafer, G. S. Behonick, and C. M. Arroyo, U.S. Army Medical Research Institute of Chemical Defense and Oak Ridge Institute of Science and Education Research.

B 51. *REFOCUSED PRIMARY ESE: A ZERO DEAD TIME DETECTION OF THE ELECTRON SPIN ECHO ENVELOPE MODULATION.* A. V. Astashkin, J. H. Enemark, A. Pacheco, and A. M. Raitsimring, University of Arizona.

A 52. *MULTIFREQUENCY ESEEM OF THE FERRIHEME CENTERS IN PROTEINS.* A. V. Astashkin, A. M. Raitsimring, and F. A. Walker, University of Arizona.

B 53. *MULTI-FREQUENCY ELECTRON SPIN ECHO ENVELOPE MODULATION (ESEEM) SPECTROSCOPIC STUDIES OF CYTOCHROME c.* N. I. Avdievich and J. Peisach, Albert Einstein College of Medicine.

A 54. *EPR PROBEHEADS FOR FAST SAMPLE SPINNING AT VARIABLE ANGLES.* C. Bauer, M. Hubrich, D. Hessinger, G. Jeschke, and H. W. Spiess, Max-Planck-Institute for Polymer Research, Mainz, Germany.

B 55. *W-BAND PULSE PROBEHEAD CONSTRUCTION—THE QUEST FOR MINIMUM LOSS AND MAXIMUM Q_L.* C. Bauer, G. Jeschke, and H. W. Spiess, Max-Planck-Institute for Polymer Research, Mainz, Germany.

A 56. ***AN X-BAND EPR STUDY ON ASCORBYL FREE RADICALS GENERATED IN RAT HEARTS IN THE PRESENCE OF DIFFERENT TYPES OF ROS SCAVENGERS.*** A. M. Bobst, J. W. Lee, E. V. Bobst, Y.-G. Wang, and M. Ashraf, University of Cinncinnati.

B 57. ***MOLECULAR DYNAMICS SIMULATIONS OF LOCAL SPIN-LABEL MOTIONS AND HIGH-FIELD EPR SPECTRA.*** R. Satyamurti, N. Nguyen, and D. E. Budil, Northeastern University.

A 58. ***LARGE MOLECULAR WEIGHT NITROXIDE CONJUGATES AS RADIOPROTECTORS AND/OR ANTIOXIDANTS.*** A. J. Carmichael, M. W. Hamilton, Y. N. Vaishnav, and T. M. Seed, Armed Forces Radiobiology Research Institute.

B 59. ***EPR SPIN LABELING MEASUREMENTS OF NUCLEAR, CHEMICAL AND BIOLOGICAL AGENT-INDUCED ALTERATIONS OF THE INSULIN RECEPTOR IN RED BLOOD CELL MEMBRANES: A POSSIBLE BIOLOGICAL MARKER FOR DOSE ASSESSMENT.*** F. C. Music, T. L. Hadfield, J. A. Centeno, L. Steel-Goodwin, R. E. Sweeney, W. F. Blakeley, P. G. S. Prasanna, R. C. Sine, C. M. Arroyo, and A. J. Carmichael, Armed Forces Institute of Pathology and Armed Forces Radiobiology Research Institute.

A 60. ***A STABLE LITHIUM-CONTAINING ALUMINUM CENTRE IN CRYSTALLINE QUARTZ.*** R. F. C. Claridge, N. S. Lees, W. C. Tennant, C. J. Walsby, and J. A. Weil, University of Canterbury, New Zealand, and University of Saskatchewan, Canada.

B 61. ***INVESTIGATION OF DANGLING BOND CONTENT IN PULSED LASER DEPOSITED AMORPHOUS SILICON CARBIDE THIN FILMS BY ELECTRON SPIN RESONANCE.*** T. Christidis, M. Tabbal, S. Isber, M. A. El-Khakani, and M. Chaker, American University of Beirut and INRS-Energie et Matériaux, Canada.

A 62. ***SPIN-TRAPPING STUDIES OF THE REACTION OF OZONE WITH ALKENES, PHENOLIC, AND SULFUR COMPOUNDS IN SOLUTION.*** D. F. Church, M. McAdams, and G. Cuadra, Radical Technologies and Louisiana State University.

B 63. ***CHARACTERIZATION OF CHAR MICROPARTICLES BY MEANS OF ADVANCED MAGNETIC RESONANCE TECHNIQUES.*** B. M. Odintsov, V. A. Atsarkin, R. L. Belford, P. J. Ceroke, V. N. Demidov, Z. Sh. Idiyatullin, A. N. Temnikov, R. Sh. Vartapetian, and R. B. Clarkson, University of Illinois and Russian Academy of Sciences.

A 64. ***A TWO-DIMENSIONAL ESR STUDY OF AGGREGATION OF GRAMICIDIN IN MEMBRANES.*** P. Borbat, R. H. Crepeau, M. Ge, and J. H. Freed, Cornell University.

B 65. ***HYSCORE STUDIES OF NO SYNTHASE AND MODEL COMPOUNDS.*** D. C. Gilbert, D. C. Doetschman, S. Dikanov, D. J. Stuehr, L. Huang, and J. A. Smieja, Binghamton University, Institute of Chemical Kinetics and Combustion, Russia, The Cleveland Clinic Research Institute, and Gonzaga University.

A 66. ***MAGNETIC RESONANCE STUDIES OF PHENALENYL-ALKALI CATION COMPLEXES IN SOLIDS AND SOLUTIONS.*** D. W. Dwyer, D. C. Gilbert, M. F. Ciraolo, D. P. Cheswick, and D. C. Doetschman, SUNY Brockport and Binghamton University.

B 67. ***COMPETITIVE BINDING OF WATER ANALOGS TO THE OEC IN PHOTOSYSTEM II PROBED BY THREE-PULSE ESEEM.*** M. Evanchik, K. Clemens, and R. D. Britt, University of California, Davis

A 68. ***ESR AND SPIN TRAPPING STUDY OF THE FLUORESCENT DYE, 2'7'-DICHLOROFLUORESCEIN AND ITS IMPLICATIONS FOR OXIDATIVE STRESS MEASUREMENTS.*** Y. C. Fann, E. Marchesi, C. Rota, C. Chignell, and R. P. Mason, National Institutes of Environmental Health Sciences.

B 69. ***HIGH-FREQUENCY EPR SPECTROSCOPY OF BIRADICAL TOAC AND MTS SPIN-LABELED PEPTIDES: ANALYSIS OF DIPOLAR AND EXCHANGE INTERACTIONS.*** C. T. Farrar, R. G. Griffin, J. McNulty, G. Millhauser, W. Xiao, and Y.K. Shin, MIT, University of California Santa Cruz, and University of California Berkeley.

A 70. ***HIGH-FREQUENCY PULSED EPR AND ENDOR STUDIES OF THE HYDROGEN BONDING ENVIRONMENT OF THE Y_z TYROSYL RADICAL OF PHOTOSYSTEM II.*** C. T. Farrar, R. G. Griffin, D. A. Force, B. A. Diner, K. A. Campbell, J. M. Peloquin, and R. D. Britt, MIT, E.I. Dupont de Nemours & Co., and University of California Davis.

B 71. ***η/4 ANTENNA COUPLING TO A DIELECTRIC RESONATOR: TIME RESOLVED NUMERICAL ELECTROMAGNETIC FIELD CALCULATIONS.*** J. Keller, J. Forrer, A. Schweiger, R. Schuhmann, and T. Weiland, ETH Zurich, Switzerland and Technische Hochschule Darmstadt, Germany.

A 72. ***PHARMACOLOGICAL MODIFICATIONS OF THE PARTIAL PRESSURE OF OXYGEN IN MURINE TUMORS: EVALUATION USING IN VIVO EPR OXIMETRY.*** B. Gallez, B. Jordan, C. Baudelet, and P.D. Mission, Université Catholique de Louvain, Belgium.

B 73. ***DIRECT AMPLIFICATION LOW FREQUENCY CW EPR SPECTROMETER.*** V. E. Galtsev, E. D. Barth, B. B. Williams, and H. J. Halpern, University of Chicago.

A 74. ***IMPROVEMENT OF EPR SENSITIVITY BY USE OF A FERROELECTRIC RESONATOR—TE_{011} STRUCTURE.*** I. N. Geifman, and I. S. Golovina, Institute of Physics of Semiconductors, Ukraine.

B 75. ***COMPUTER SIMULATION OF RANDOMLY ORIENTED EPR SPECTRA EMPLOYING HOMOTROPY.*** M. P. Griffin, K. E. Gates, G. R. Hanson, C. Noble, and K. Burrage, University of Queensland, Australia.

A 76. ***FLOW VELOCITY-SWEEP METHOD TO FOLLOW SUBMILLISECOND REACTION KINETICS OF CHEMICALLY EVOLVING FREE RADICAL SYSTEMS.*** V. M. Grigoryants, A. V. Veselov, and C. P. Scholes, SUNY at Albany.

B 77. ***MULTI-PHOTON RESONANCES IN PULSE EPR.*** I. Gromov and A. Schweiger, ETH Zurich, Switzerland and Kazan State University, Russia.

A 78. ***INFORMATION CONTENT IN RADIOFREQUENCY EPR SPECTRAL-SPATIAL IMAGES OF TUMORS IN LIVING MICE.*** B. Williams, G. V. R. Chandramouli, E. D. Barth, V. Galtsev, and H. J. Halpern, University of Chicago.

B 79. ***SYNTHESIS AND RADIOPROTECTION OF NOVEL POLY(ETHYLENE GLYCOL) CONJUGATE OF PBN.*** M. M. Hamilton, Y. N. Vaishnav, R. F. Brady, B. J. Spargo, A. J. Carmichael, and T. M. Seed, Armed Forces Radiobiology Research Institute and Naval Research Laboratory.

A 80. ***REFINEMENT OF THE EPR PARAMETERS FOR THE HIGH SPIN FE(III) CENTER IN A SWEET POTATO PURPLE ACID PHOSPHATASE - THE INFLUENCE OF STRAIN BROADENING.*** G. R. Hanson, C. J. Noble, C. L. Boutchard, G. Schenk, S. E. Hamilton, and J. DeJersey, University of Queensland, Australia.

B 81. ***ENHANCEMENT OF SIGNAL INTENSITY FOR SAMPLES WITH SLOW ELECTRON SPIN RELAXATION BY OUT-OF-PHASE DETECTION.*** J. R. Harbridge, G. Rinard, S. S. Eaton, and G. R. Eaton, University of Denver.

A 82. ***NOVEL SPIN REAGENTS FOR IN VIVO ESR: ACYL-PROTECTED HYDROXYLAMINES.*** O. Itoh, H. Yokoyama, M. Aoyama, H. Obara, H. Ohya, and H. Kamada, Yamagata Technopolis Foundation, Japan.

B 83. ***DRESSED ELECTRON SPIN RESONANCE.*** G. Jeschke, Max-Planck Institute for Polymer Research, Mainz, Germany.

A 84. ***W-BAND FT-EPR AND PULSED ENDOR STUDIES WITH THE BRUKER ELEXSYS E680 SPECTROMETER.*** A. Kamlowski, P. Höfer, and D. Schmalbein, Bruker Analytik GmbH, Germany.

B 85. ***PULSED EPR STUDIES OF 3-DIMENSIONAL STRUCTURE OF ELECTRON TRANSFER COMPONENTS IN PHOTOSYSTEM II.*** A. Kawamori, H. Hara, T. Yoshii, and A. V. Astashkin, Kwansei Gakuin University, Japan, and University of Arizona.

A 86. ***SPIN-TRAPPING STUDIES OF RADICAL INTERMEDIATES IN AZOESTER HYDROLYSIS: IN SEARCH OF NEW DNA-CLEAVING COMPOUNDS.*** V. Srinivasan, R. Hopson, S. V. Kolaczkowski, and D. E. Budil, Northeastern University.

B 87. ***220 GHz EPR STUDIES OF TRIPLET STATES IN THE BACTERIAL PHOTOSYNTHETIC REACTION CENTER.*** S. V. Kolaczkowski, R. Zheng, and D. E. Budil, Northeastern University.

A 88. ***EFFECT OF SOLVENT ON RELAXATION AND STRUCTURE OF MANGANESE(II) CENTERS BY MULTIFREQUENCY EPR AND CW ENDOR.*** R. I. Konda, Y.-M. Xia, R. B. Clarkson, and R. L. Belford, University of Illinois.

B 89. ***330-670 GHZ EPR STUDIES OF CANTHAXANTHIN RADICAL CATION STABILIZED ON A SILICA-ALUMINA SURFACE.*** T. A. Konovalova, J. Krzystek, P. J. Bratt, J. van Tol, L.-C. Brunel, and L. D. Kispert, University of Alabama and National High Magnetic Field Laboratory.

Tuesday evening - EPR Symposium dinner. All attendees are invited

Wednesday, August 4, 1999

Session V, Distance Measurements By EPR, L. J. Berliner, presiding

8:30 90. ***MEASUREMENT OF INTRA- AND INTERMOLECULAR DISTANCES.*** A. H. Beth, Vanderbilt University.

9:00 91. ***SIMULATION OF THE EPR SPECTRA OF DIPOLAR COUPLED NITROXIDES.*** E. J. Hustedt, Vanderbilt University.

9:30 92. ***DISTANCE MEASUREMENTS IN PROTEINS AND RNA USING SPIN LABELING EPR.*** Y.K. Shin, University of California Berkeley.

10:00 **Break**

10:30 93. ***IDENTIFICATION OF PROTEIN FOLDING PATTERNS USING SITE-DIRECTED SPIN LABELING.*** H. S. Mchaourab, Medical College of Wisconsin.

11:00 94. ***DISTANCES BETWEEN COFACTORS AND COFACTOR POSITIONS IN PHOTOSYNTHETIC REACTION CENTERS FROM PULSED EPR.*** S. G. Zech, W. Lubitz, and R. Bittl, Technische Universität Berlin, Germany.

11:30 95. ***PROGRESS IN MULTIPLE-QUANTUM ESR SPECTROSCOPY: POWERFUL TOOL FOR DISTANCE MEASUREMENTS.*** P. P. Borbat and J. H. Freed, Cornell University.

12:00 **Lunch**

Session VI, Distance Measurements by EPR, A. H. Beth, presiding

1:30 96. ***INTERRADICAL DISTANCES IN DIRADICALS AND IN IONIC CLUSTERS OF IONOMERS FROM DOUBLE ELECTRON ELECTRON RESONANCE.*** H. W. Spiess, M. Pannier, and G. Jeschke, Max-Planck-Institut for Polymer Research, Mainz, Germany.

1:55 97. ***ORIENTATION OF THE TETRANUCLEAR MANGANESE CLUSTER AND TYROSINE-Z IN THE OXYGEN EVOLVING COMPLEX OF PHOTOSYSTEM II: AN EPR STUDY OF THE*** $S_2Y_{Z\cdot}$ ***STATE IN ORIENTED ACETATE-INHIBITED PHOTOSYSTEM II.*** G. W. Brudvig, K. V. Lakshmi, S. S. Eaton, and G. R. Eaton, Yale University and University of Denver.

2:15 98. ***EPR STUDY OF THE MOLECULAR AND ELECTRONIC STRUCTURE OF THE $Q_A^{-}\cdot Q_B^{-}\cdot$ STATE OF THE PHOTOSYNTHETIC REACTION CENTER IN RB. SPHAEROIDES R26 AT 35 AND 94 GHz.*** R. Calvo, W. Hofbauer, F. Lendzian, W. Lubitz, M. L. Paddock, E. C. Abresch, R. A. Isaacson, M. Y. Okamura, and G. Feher, FBCB&INTEC, Argentina, Technical University, Berlin, Germany and University of California, La Jolla.

2:35 99. ***NEW LOOK INTO THE CHEMISTRY OF STABLE NITROXIDE RADICALS.*** L. Volodarsky, N.Y.

3:00 Break

Session VII, Posters, S. S. Eaton presiding

3:00–4:00 Authors Present for Posters Labeled C

4:00–5:00 Authors Present for Posters Labeled D

(Posters are listed alphabetically by presenting author, L-Z)

C 100. ***SITE-DIRECTED SPIN LABELING OF THE MYOSIN REGULATORY LIGHT CHAIN: COORDINATION OF EPR SPECTROSCOPY AND COMPUTER MODELING.*** L. E. W. LaConte, M. Enz, W. Smith, W. Meland, and D. D. Thomas, University of Minnesota Medical School.

D 101. ***PARAMAGNETIC DEFECTS AND OXIDE LEAKAGE CURRENTS.*** P. M. Lenahan, J. Mele, M. Fattu, R. K. Lowry, and D. Woodbury, Pennsylvania State University and Harris Semiconductor.

C 102. ***NOTRE DAME RADIATION CHEMISTRY DATA CENTER, 1999 STATUS REPORT: THE NDRL/NIST SOLUTION KINETICS DATABASE, VERSION 3.*** K. P. Madden, University of Notre Dame.

D 103. ***SPIN DYNAMICS STUDY IN DOPED POLYANILINE BY CW AND PULSED EPR.*** C. J. Magon, R. R. de Souza, A. J. Costa-Filho, E. A. Vidoto, R. M. Faria, and O. R. Nascimento, Universidade de São Paulo, Brazil.

C 104. ***SOLID STATE AND AQUEOUS SOLUTION CHEMISTRY OF PARENT AND HETEROATOM-CONTAINING SYMMETRIC AND ASYMMETRIC BIS(ACETYLACETONATE) OXOVANADIUM(IV) DERIVATIVES.*** K. Cryer, M. Mahroof-Tahir, S. S. Amin, B. Zhang, S. K. Mondal, A. R. Khan, L. Yang, O. P. Anderson, S. M. Miller, and D. C. Crans, Colorado State University.

D 105. ***W-BAND ENDOR SPECTRAL ANALYSIS OF THE MANGANESE-BINDING SITE OF CONCANAVALIN A: FROZEN SOLUTION AND SINGLE CRYSTAL SPECTRA.*** P. Manikandan, T. Shane, R. Carmieli, A. J. Kalb (Gilboa), and D. Goldfarb, Weizmann Institute of Science, Israel.

C 106. ***DETECTION OF A PAKE FUNCTION IN THE BROADENING OF TWO NITROXIDE SPIN LABELS COUPLED THROUGH DIPOLAR INTERACTION.*** N. Menhart, L. Cherry, and L. W-M. Fung, Loyola University of Chicago.

D 107. ***SINGLE-CRYSTAL EPR STUDIES OF Cr(III), Fe(III), Mn(II), AND Ni(II) AT 250 GHz.*** S. K. Misra, S. I. Andronenko, K. A. Earle, and J. H. Freed, Concordia University, Canada and Cornell University.

C 108. ***EPR STUDIES OF DOMAIN FORMATION IN THE PLASMA MEMBRANES OF LISTERIA MONOCYTOGENES.*** P.D. Morse, B. J. Wilkinson, and S. Jones, Illinois State University.

D 109. ***PARTITIONING AND MOTION OF HYDROCARBON SPIN LABELS IN LARGE UNILAMELLAR VESICLES OF DIPALMITOYLPHOSPHATIDYLCHOLINE/-DIPALMITOYLPHOSPHATIDYLGLYCEROL.*** P. D. Morse, J. Ruggaber, and S. R. Hitchcock, Illinois State University.

C 110. ***AN EPR STUDY OF THE PHASE TRANSITION BEHAVIOR OF BINARY MIXTURES OF NON-MESOMORPHIC SOLUTES IN MESOMORPHIC SOLVENTS.*** M. A. Morsy, G. A. Oweimreen, and J. S. Hwang, King Fahd University of Petroleum and Minerals, Saudi Arabia.

D 111. ***THE ELECTRONIC STRUCTURE OF HYDROXYETHYLTHIAMIN PYROPHOSPHATE RADICAL—A CATALYTIC INTERMEDIATE OF PYRUVATE:FERREDOXIN OXIDOREDUCTASE.*** R. B. Muthukumaran, J. McCracken, C. Furdui, and S. W. Ragsdale, Michigan State University and University of Nebraska.

C 112. ***STUDY OF CYTOCHROME-c AND MEMBRANES BY CW-EPR OF IRON HEME.*** M. R. Zucch. I. L. Nantes, A. Faljoni-Alário, and O. R. Nascimento, Universidade de São Paulo, Brazil and Universidade de Mogi das Cruzes, Brazil.

D 113. ***DIPOLAR RELAXATION IN A MANY-BODY SYSTEM OF ELECTRON SPINS: FROM MOTIONAL NARROWING TO THE RIGID LIMIT.*** A. A. Nevzorov and J. H. Freed, Cornell University.

C 114. ***LOW-NOISE AMPLIFIERS AND OTHER MEANS TO IMPROVE PERFORMANCE OF CW AND PULSED HIGH-FIELD EPR SPECTROMETERS.*** M. J. Nilges, A. I. Smirnov, R. B. Clarkson, and R. L. Belford, University of Illinois.

D 115. ***COMPUTER SIMULATION OF PULSED ELECTRON PARAMAGNETIC RESONANCE SPECTRA FOR A GENERALISED SPIN HAMILTONIAN AND ARBITRARY PULSE SEQUENCE.*** C. J. Noble, G. R. Hanson, K. E. Gates, and K. Burrage, University of Queensland, Australia.

C 116. ***MOLECULAR DIFFUSION AND OXYGEN RESPONSE IN AQUEOUS CHAR SUSPENSIONS.*** B. M. Odintsov, R. L. Belford, P. J. Ceroke, Z. Sh. Idiyatullin, A. N. Temnikov, and R. B. Clarkson, University of Illinois and Russian Academy of Sciences.

D 117. ***USING SPIN LABELS TO PROBE THE SURFACES OF COLLOIDAL GOLD NANOPARTICLES.*** A. E. Ostafin, H. Miyoshi, O. Makarova, and J. R. Norris, Jr., University of Chicago.

C 118. ***LABEL PROPERTIES EXPLAIN DIFFERENCES IN LOCAL ENVIRONMENTS SENSED BY SPECTROSCOPIC LABELS DURING PROTEIN-PROTEIN INTERACTION.*** R. Owenius, M. Österlund, M. Lindgren, M. Svensson, P.-O. Freskgård, O. H. Olsen, E. Persson, and U. Carlsson, Linköping University, Sweden and Tissue Factor/Factor VII Research, Sweden.

D 119. ***EPR OF DISORDERED SYSTEMS.*** J. R. Pilbrow and S. C. Drew, Monash University, Australia.

C 120. ***NITRIC OXIDE ADSORPTION COMPLEXES IN ZEOLITES: AN ESR AND PULSED-ENDOR STUDY.*** A. Pöppl, T. Rudolf, and D. Michel, Universität Leipzig, Germany.

D 121. ***PULSED ELECTRON-ELECTRON DOUBLE RESONANCE OF PARAMAGNETIC CENTERS WITH LARGE G-VALUE SEPARATION.*** A. V. Astashkin, J. H. Enemark, V. V. Kozlyuk, J. McMaster, and A. M. Raitsimring, University of Arizona.

C 122. ***OPTIMIZATION OF THE ESEEM ACQUISITION USING HIGH-SPEED DIGITIZING TECHNIQUE.*** A. V. Astashkin and A. M. Raitsimring, University of Arizona.

D 123. ***THE INFLUENCE OF Al_2O_3 CODOPANT ON PHASE AND SPIN-LATTICE RELAXATION OF Nd^{3+} IONS INCORPORATED IN VITREOUS SILICA.*** S. Orlinskii, R. Rakhmatullin, and S. Sen, Kazan State University, Russia and Corning, Inc., N. Y.

C 124. ***A THREE DIMENSIONAL ELECTRON SPIN DENSITY EQUATION FOR ALKENE CATION RADICALS GENERATED BY GAMMA-IRRADIATION AND OTHER OXIDATION METHODS.*** S. Shih , Yuan-Ze University, Taiwan

D 125. ***MOVEMENT OF ISP EXTRINSIC DOMAIN IN THE BC1 COMPLEX MONITORED BY SDSL EPR.*** M. Guergova, R. Kuras, A. R. Crofts, and A. I. Smirnov, University of Illinois.

C 126. ***PROBING LOCAL EVENTS OF PROTEIN FOLDING BY SDSL EPR.*** A. I. Smirnov, S.-W. Norby, R. B. Clarkson, and R. L. Belford, University of Illinois.

D 127. ***MAGNETIC FIELD ORIENTED CRYSTALLIZATION OF CuTPP.*** W. K. Subczynski, W. E. Antholine, M. Pasenkiewicz-Gierula, and J. S. Hyde, Medical College of Wisconsin and Jagiellonian University, Poland.

C 128. ***MOLECULAR ORGANIZATION AND DYNAMICS OF DIMYRISTOYLPHOSPHATIDYL-CHOLINE BILAYERS CONTAINING CHARGED AND UNCHARGED FORMS OF A TRANSMEMBRANE α-HELICAL PEPTIDE.*** W. K. Subczynski, J. S. Hyde, and A. Kusumi, Medical College of Wisconsin, Jagiellonian University, Poland, and Nagoya University, Japan.

D 129. ***CAN FIELD MODULATION INFLUENCE SPIN EXCHANGE IN WOOD CHARS?*** O. Y. Grinberg and H. M. Swartz, Dartmouth Medical School.

C 130. ***PARAMAGNETIC DEFECTS IN OXYGEN-DEFICIENT TiO_2/RUTILE.*** A. M. Tyryshkin, M. K. Bowman, M. A. Henderson, and G. C. Dunham, Pacific Northwest Laboratory and Institute of Chemical Kinetics and Combustion, Russia.

D 131. ***Q-BAND ENDOR OF THE BINUCLEAR HEME-COPPER CENTER IN CYTOCHROME bo_3 FROM ESCHERICHIA COLI.*** A. V. Veselov, C. P. Scholes, J. O. Osborne, and R. B. Gennis, SUNY at Albany and University of Illinois.

C 132. ***Q-BAND ENDOR STUDY OF THE UBISEMIQUINONE CENTER IN CYTOCHROME bo_3 FROM ESCHERICIA COLI.*** A. V. Veselov, C. P. Scholes, J. O. Osborne, and R. B. Gennis, SUNY at Albany and University of Illinois.

D 133. ***SITE-DIRECTED SPIN-LABELING OF THE CATALYTIC SITES AND OF SUBUNIT B YIELDS INSIGHT INTO THE STRUCTURE OF F_0F_1-ATP SYNTHASE OF ESCHERICHIA COLI.*** M. Kersten, C. Motz, G. Kraft, D. T. McLachlin, S. D. Dunn, J. G. Wise, and P. D. Vogel, Universität Kaiserslautern, Germany and University of Western Ontario, Canada.

C 134. ***POLARONS AND BIPOLARONS IN CONDUCTING POLYMERS OBSERVED FROM THE WIDTH OF THE ESR LINE.*** M. S. Sercheli, C. Rettori, L. Walmsley, A. A. Correa, L. O. S. Bulhões and E. C. Pereira, Universidade Estadual de Campinas, Universidade Estadual Paulista, and Universidade Federal de São Carlos, Brazil.

D 135. ***ASYMMETRICAL PENETRATION OF MICROWAVE IN A CONDUCTING MEDIA AND DETERMINATION OF THE MICROWAVE CONDUCTIVITY FOR VERY THIN SAMPLES*** A. C. Seridonio and L. Walmsley, Universidade Estadual Paulista, Brazil.

C 136. ***Q-BAND EPR AND ENDOR STUDIES OF CU^{2+} ION BINDING TO DENDRIMER MOLECULES.*** T. J. Wasowicz, M. Zhao, R. M. Crooks, and V. J. DeRose, Texas A&M University.

D 137. ***A 1-HYDROGEN 2-LITHIUM CENTRE AND MULTIPLE-HYDROGEN CENTRES IN CRYSTALLINE QUARTZ.*** R. F. C. Claridge, N. S. Lees, W. C. Tennant, C. J. Walsby, and J. A. Weil, University of Canterbury, New Zealand, and University of Saskatchewan, Canada.

C 138. ***MINIMIZATION OF DATA ACQUISITION TIMES FOR 3D SPECTRAL-SPATIAL IMAGING OF LIVING MOUSE TUMORS.*** B. R. Williams, E. D. Barth, V. Galtsev, and H. J. Halpern, University of Chicago.

D 139. ***SPIN DYNAMIC OF THE PHOTOEXCITED TRIPLET STATE OF PENTACENE AT LOW FIELD AND LEVEL ANTI-CROSSING REGION.*** T.-C. Yang, D. J. Sloop, S. I. Weissman, and T.-S. Lin, Washington University.

C 140. ***EPR INVESTIGATION OF THE INTERACTION OF TRAPPED EXCITED METASTABLE HE ATOMS WITH SOLID RARE-GAS MATRICES.*** R. A. Zhitnikov and Y. A. Dmitriev, A. F. Ioffe Physico-Technical Institute, Russia.

D 141. ***INTERSPIN DISTANCES IN MYOGLOBIN VARIANTS DETERMINED BY PULSED EPR.*** Y. Zhou, B. Bowler, S. S. Eaton, and G. R. Eaton, University of Denver.

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

Thursday, August 5, 1999

Session VIII, New Techniques and Instrumentation, J. Weil presiding

8:30 142. ***A MULTIFREQUENCY ESR APPROACH TO STUDY THE COMPLEX DYNAMICS OF BIOMOLECULES.*** Z. Liang and J. H. Freed, Cornell University.

9:00 143. ***220 GHZ EPR STUDIES OF SPIN-LABELED DNA.*** D. E. Budil, S. V. Kolaczkowski, A. Perry, C. Varaprasad, F. Johnson, and P. R. Strauss, Northeastern University and SUNY Stonybrook.

9:25 144. ***SUCCESSFUL OBSERVATION OF ALLOWED EPR TRANSITIONS IN HIGH SPIN (S=2) IRON(II): HFEPR OF A REDUCED RUBREDOXIN MODEL.*** J. Krzystek, M. J. Knapp, D. N. Hendrickson, and L.-C. Brunel, Florida State University and University of California San Diego

9:50 145. ***INFLUENCES OF THE MICROWAVE COUPLING ELEMENTS ON OVERCOUPLED PULSE EPR RESONATOR.*** J. Forrer, J. Keller, A. Schweiger, R. Schuhmann, and T. Weiland, ETH Zurich, Switzerland and Technische Hochschule Darmstadt, Germany.

10:15 Break

10:30 146. ***USE OF AN ENDOR PROBEHEAD FOR LONGITUDINAL DETECTION OF AMPLITUDE MODULATED EPR.*** J. Granwehr and A. Schweiger, ETH Zurich, Switzerland.

10:55 147. ***THE CHEMISTRY OF MOLECULES ENCAPSULATED IN NANOBUBBLES AS PROBED BY CW-EPR AND CW-TREPR.*** M. Jäger, O. Makarova, A. E. Ostafin, J. R. Norris, Jr., and D. Meisel, University of Chicago and University of Notre Dame.

11:20 148. ***PULSED EPR OF THE PENTACENE PHOTOEXCITED TRIPLET AT LOW AND ZERO FIELD WITH FAST MAGNETIC FIELD SWITCHING.*** T. C. Yang, D. J. Sloop, S. I. Weissman, and T.-S. Lin, Washington University.

11:55 Closing Remarks, S. S. Eaton

General Poster Symposium

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149. ***PHOTOCHEMICAL REACTION: APPLICATION OF LIQUID CHROMATOGRAPHIC POST-COLUMN PHOTOLYSIS TO THE ENHANCED CONDUCTIVITY DETECTION OF FOUR FENICOLS.*** Steve A. Gonzales, Allen P. Pfenning, José E. Roybal, Sherri B. Turnipseed, U.S. Food and Drug Administration

150. ***ADVANCES IN COMBUSTION TOTAL ORGANIC CARBON ANALYSIS.*** Don Harrington, Ken O'Neal, Brian T. Wallace, Maria Theresa Lee-Alvarez, Tekmar-Dohrmann

151. ***CLEANING VALIDATION BY TOTAL ORGANIC CARBON ANALYSIS: INSTRUMENTAL TECHNOLOGY CONSIDERATIONS.*** Don Harrington, Ken O'Neal, Brian Wallace, Tekmar -Dohrmann

152. ***DETECTION OF CHROMIUM AND CHROMIUM PICOLINATE IN DIETARY SUPPLEMENTS AND HERBAL PRODUCTS BY FLAME AAS AND BY LC-UV.*** Jeffrey A. Hurlbut, Kevin S. Ewing, Metropolitan State College of Denver; Susan B. Clark, Doug W. Rowe, Sherri B. Turnipseed, U.S. Food and Drug Administration

153. ***THE DEVELOPMENT OF AN IN-LINE NEAR INFRARED SYSTEM FOR TESTING FAT AND PROTEIN IN MILK AND RELATED PRODUCTS.*** Avril O'Sullivan, Dr. Barry O'Connor, APT Group; Desmond Brennan, National Microelectronics Research Centre

154. ***DETERMINATION OF RESIDUES OF AZAMETHIPHOS IN SALMON TISSUE BY LC/FLUORESCENCE.*** Allen P. Pfenning, José E. Roybal, Sherri B. Turnipseed, Steve A. Gonzales, Jeffrey A. Hurlbut, U.S. Food and Drug Administration

155. ***A METHOD FOR THE DETERMINATION OF FOUR FLUOROQUINOLONES IN MILK BY LIQUID CHROMATOGRAPHY.*** José E. Roybal, Allen P. Pfenning, Sherri B. Turnipseed, Calvin C. Walker, Jeffrey A. Hurlbut, U.S. Food and Drug Administration

156. ***FATTY ACID PROFILING OF HERBAL AND BIOLOGICAL MATRICES.*** John B. Atwater, Paul F. Smith, Hauser, Inc.

157. ***RESIDUAL SOLVENT IDENTIFICATION LIMITS FOR PHARMACEUTICAL PRODUCTS USING A GAS CHROMATOGRAPHY/MASS SELECTIVE DETECTOR (GC/MSD).*** Pauline Chow, Geneva Pharmaceuticals, Inc.

158. ***DEVELOPMENT OF A SELECTIVE RP-HPLC METHOD FOR THE ANALYSIS OF LEUPROLIDE ACETATE.*** Michele R. Gehring, Steven F. Volker, Atrix Laboratories, Inc.

159. ***A NOVEL SYNTHETIC ROUTE TO THE DOPAMINE AUTORECEPTOR ANTAGONIST (+) UH232.*** Zachary S. Jones, Justin G. Schiro, Christopher K. Murray, Scott A. Peterson, John X. Rizzo, Michael P. Scannell, Lalith R. Jayasinghe, Hauser, Inc.

160. ***RAPID IDENTIFICATION OF PHARMACEUTICALS AND METABOLITES BY HPLC/MS/MS.*** Shane Needham, Patrick Jeanville, Mark J. Cole, Pfizer Inc.

161. ***COMPARISON STUDY OF DISSOLUTION PROPERTIES FOR METALS IN SOILS UNDER THE VARIOUS EXTRACTING CONDITION.*** Kang-Sup Chung, Byung-In Choi, Sang-Yeon Kim, Duk-Young Song, Kun-Han Kim, Hak-Je Seong, Korea Institute of Geology

162. ***AN INVESTIGATION INTO THE DIFFUSION OF CHLORINATED HYDROCARBONS INTO POLYMER FILMS USING ATTENUATED TOTAL REFLECTANCE FOURIER TRANSFORM INFRARED SPECTROSCOPY.*** Rhona Howley, Dr. Peter McLoughlin, Waterford Institute of Technology; Dr. Fiona Regan, Limerick Institute of Technology

ICP-MS

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Tuesday, August 3, 1999

Al Meier presiding

8:00 163. ***HIGH RESOLUTION ICP-MS, THE FIRST DECADE (1989-1998).*** C.B. Douthitt, Finnigan MAT

8:25 164. ***OPTIMIZED SAMPLE INTRODUCTION FOR HIGH-SENSITIVITY AND HIGH-RESOLUTION ICP-MS.*** D. Weiderin, Elemental Scientific

8:50 165. ***SEMICONDUCTOR GRADE CHEMICAL ANALYSIS USING HIGH RESOLUTION ICP-MS.*** R. Henry, VG Elemental

9:15 166. ***AN IMPROVED SAMPLE INTRODUCTION SYSTEM AND OPTIMIZED SCANNING TECHNIQUES FOR PRECISE ISOTOPE RATIO MEASUREMENTS USING SINGLE COLLECTOR SECTOR-FIELD ICP-MS.*** C.B. Douthitt, M. Hamester, W. Kerl, J. Willis, Finnigan MAT; D. Wiederin, Elemental Scientific

9:40 167. ***THE DETERMINATION OF TRACE METALS IN SEA WATER USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY.*** J. Gluodenis, E. Bakowska, S. Wilbur, Hewlett Packard Company

10:05 Break

10:20 168. ***EXPANDING ICP-MS APPLICATIONS USING REVOLUTIONARY ION OPTICS IN A QUADRUPLE MASS SPECTROMETER.*** R. Henry, J. Batey, M. Liezers, VG Elemental

10:45 169. ***NEW WAVELENGTHS, NEW OPTICS AND MORE PRECISE CONTROL EXPAND THE APPLICATIONS OF LASER ABLATION ICP-MS.*** R. Henry, F. Keenan, VG Elemental

11:10 170. ***METHODS AND PROCEDURES USED IN ASSESSING TRACE METAL CONCENTRATIONS IN VEGETATION FROM AN ARTIFICIAL WETLAND USING ICP-MASS SPECTROMETRY.*** D.B. Peart, H.E. Taylor, T.I. Brinton, D.A. Roth, R.C. Antweiler, U.S. Geological Survey

11:35 171. ***DISTRIBUTION AND TRANSPORT OF SELECTED TRACE METALS DETERMINED BY ICP-MS IN THE SACRAMENTO RIVER.*** D.A. Antweiler, H.E. Taylor, U.S. Geological Survey

Symposium on Lasers, Materials and Surfaces

Symposium Chair: Nancy E. Levinger
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Monday, August 2, 1999

Alan Van Orden presiding

8:15 **Welcome and Opening Remarks,** Nancy E. Levinger

8:20 172. ***EVOLUTION OF ORIENTATION IN MONO- AND MULTILAYER SURFACE FILMS: MICROSCOPIC INTERPRETATIONS OF MACROSCOPIC MEASUREMENTS.*** Garth J. Simpson, University of Colorado

8:40 173. ***ATOMIC LAYER DEPOSITION OF TUNGSTEN USING BINARY REACTION SEQUENCE CHEMISTRY.*** Stephen J. Ferro, University of Colorado

9:00 174. ***SURFACE INTERACTIONS OF CF_2 RADICALS IN HEXAFLUOROPROPYLENE OXIDE PLASMAS.*** Carmen I. Butoi, Colorado State University

9:20 175. ***ATOMIC LAYER CONTROLLED GROWTH OF SiO_2 AND Al_2O_3 ON BN PARTICLES USING SEQUENTIAL SURFACE REACTIONS.*** John D. Ferguson, University of Colorado

9:40 176. ***PHOTOSENSITIZATION OF TIN SULFIDE SINGLE CRYSTAL BY SQUARAINE DYES.*** Norihiko Takeda, Colorado State University.

10:00 **Break**

10:20 177. ***MOLECULAR ORIENTATION AND REORIENTATION IN NANOSCALE REGIONS OF THIN FILM MATERIALS USING NEAR-FIELD SCANNING OPTICAL MICROSCOPY.*** Daniel A. Higgins, Kansas State University

11:00 178. ***AN INTEGRATED NSOM/AFM FOR THE STUDY OF NANOPARTICLE OPTICAL PROPERTIES.*** Peter C. Andersen, University of Colorado

11:20 179. ***SCANNING TUNNELING MICROSCOPY INVESTIGATION OF THE ORDERED STRUCTURES OF SQUARAINE DYE MOLECULES ADSORBED ON TWO DIMENSIONAL SUBSTRATES.*** Michele E. Stawasz, Colorado State University

11:40 180. ***THE EFFECT OF THIN WATER FILMS ON FORCE MICROSCOPY MEASUREMENTS.*** Dana Sedin, University of Colorado

12:00 **Lunch**

Nancy E. Levinger presiding

1:30 181. ***SPECTROMETRY FOR THE MASSES: NEW APPROACHES AND NEW APPLICATIONS.*** Richard N. Zare, Stanford University

2:30 182. ***USE OF ATOMIC FORCE MICROSCOPY TO STUDY THE GAS-SOLID REACTIONS OF OZONE WITH CARBONACEOUS NANOPARTICLES.*** Amy E. Michel, University of Colorado

2:50 183. ***INVESTIGATION OF THE DYE-TiO_2 (ANATASE) INTERFACE: DYE COVERAGE AND CRYSTAL FACE EFFECT ON SENSITIZATION EFFICIENCY OF TiO_2 (ANATASE) NATURAL SINGLE CRYSTALS.*** Akiko Fillinger, Colorado State University

3:10 184. ***ATOMIC LAYER DEPOSITION OF TUNGSTEN FILMS STUDIED USING AUGER ELECTRON SPECTROSCOPY.*** Jeffrey W. Elam, University of Colorado

3:30 **Break**

3:50 185. ***DIRECT EVIDENCE FOR OZONE OXIDATION OF A SELF-ASSEMBLED ALKANETHIOL MONOLAYER DURING EXPOSURE TO UV LIGHT.*** Matthew M. Ferris, University of Colorado

4:10 186. ***SOLIDS, LIQUIDS, AND AEROSOLS FOR ON-LINE MALDI SAMPLE INTRODUCTION.*** Kermit K. Murray, Emory University

4:50 187. ***COUPLED PLASMON-WAVEGUIDE RESONANCE (CPWR) SPECTROSCOPY: A NEW TOOL FOR CHARACTERIZING ANISOTROPIC THIN FILMS, INCLUDING BIOLOGICAL MEMBRANES.*** G. Tollin, University of Arizona

5:10 188. ***A SINGLE MOLECULE FLUORESCENCE IMAGING TECHNIQUE FOR ULTRA-HIGH THROUGHPUT DNA FRAGMENT SIZE ANALYSIS IN FLOW CYTOMETRY.*** Alan Van Orden, Colorado State University

5:30 189. ***BIOABSORBABLE POLYMER MATERIALS FOR MEDICAL DEVICE AND DRUG DELIVERY APPLICATIONS.*** Newton K. Seitzinger, Atrix Laboratories, Inc.

5:50 **Closing Remarks**

Luminescence

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Monday, August 2, 1999

James R. Gord presiding

1:30 Opening Remarks

1:35 190. ***ADVANCES IN THE DESIGN AND APPLICATIONS OF SENSORS BASED ON LUMINESCENT TRANSITION METAL COMPLEXES.*** J.N. Demas, Wenying Xu, Kristi Kneas, University of Virginia; B.A. DeGraff, James Madison University

1:55 191. ***OPTICAL DIAGNOSTIC TECHNIQUES FOR CHARACTERIZING VORTEX-FLAME INTERACTIONS.*** James R. Gord, Air Force Research Laboratory; Gregory J. Fiechtner, Keith D. Grinstead, Jr., Campbell D. Carter, Innovative Scientific Solutions, Inc.; Paul-Henri Renard, Juan Carlos Rolon, Laboratoire d'Énergétique Moléculaire et Macroscopique, Combustion, École Centrale Paris

2:15 192. ***THE USE OF LUMINESCENT SPECIES FOR PRESSURE MEASUREMENTS.*** Patricia B. Coleman, Ford Motor Company

2:35 Break

2:55 193. ***CAPTURING GAS TURBINE SPARK IGNITION THROUGH ULTRAFAST IMAGING.*** Keith D. Grinstead Jr., Gregory J. Fiechtner, Innovative Scientific Solutions, Inc.; James R. Gord, Charles Tyler, Air Force Research Laboratory; Michael Cochran, John R. Frus, Unison Industries

3:15 194. ***STUDYING THE SOLVENT-DEPENDENT SPECTROSCOPY OF IR-125 THROUGH ASYNCHRONOUS OPTICAL SAMPLING.*** Christopher E. Bunker, Idaho National Engineering and Environmental Laboratory; James R. Gord, Air Force Research Laboratory; Keith D. Grinstead, Jr., Gregory J. Fiechtner, Innovative Scientific Solutions, Inc.

3:35 195. ***OPTICAL DETERMINATION OF ADDITIVES IN AVIATION FUEL.*** Donald K. Phelps, Christopher E. Bunker, James R. Gord, Air Force Research Laboratory

Tuesday, August 3, 1999

Robert J. Hurtubise presiding

8:55 Opening Remarks

9:00 196. ***FLUORESCENCE INVESTIGATION OF PYRENE, TETROLS, AND TETROLS WITH DNA IN METHANOL: WATER SOLVENTS.*** Robert J. Hurtubise, University of Wyoming; Paul B. Steinbach, Stephen F. Austin State University

9:20 197. ***ROOM-TEMPERATURE PHOSPHORESCENCE QUENCHING TO STUDY OXYGEN DIFFUSION THROUGH ORAL BIOFILMS.*** J.A. Ekhoff, K.L. Rowlen, University of Colorado

9:40 198. ***SOLID-MATRIX LUMINESCENCE OF HETEROCYCLIC AROMATIC AMINES IN GLUCOSE GLASSES PREPARED FROM A GLUCOSE MELT.*** Shaun D. Mendonsa, Robert J. Hurtubise, University of Wyoming

10:00 Break

10:30 199. ***SOLID-MATRIX LUMINESCENCE OF HYDROXYL AROMATIC METABOLITES ON WHATMAN 1PS PAPER.*** Barry W. Smith, Robert J. Hurtubise, University of Wyoming

10:50 200. ***LUMINESCENCE-BASED OXYGEN SENSORS: FLUORESCENCE MICROSCOPY AS A PROBE OF SENSOR HETEROGENEITY.*** Kristi A. Kneas, J.N. Demas, Ammasi Periasamy, University of Virginia; B.A. DeGraff, James Madison University

11:10 201. ***SPECTROSCOPIC STUDIES OF PHOTO AND THERMAL STABILITIES OF VARIOUS EVA ENCAPSULANTS FOR PHOTOVOLTAIC APPLICATIONS.*** S.H. Glick, F.J. Pern, National Renewable Energy Laboratory

11:30 202. ***MULTI-DIMENSIONAL FLUORESCENCE FOR THE INVESTIGATION OF DIETARY HABITS OF FREE-RANGING HERBIVORES.*** Gary D. Rayson and Timothy L. Danielson, New Mexico State University; Dean M. Anderson, R. Estell, E. L. Fredrickson, K. M. Havstad, USDA Jornada Experimental Range

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Symposium on MS, GC/MS, LC/MS

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Symposium on Pharmaceutical Analysis

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Wednesday, August 4, 1999

Morning, Shane Needham presiding

8:40 Welcome and Introductory Remarks

8:45 203. *SAMPLE PREPARATION REQUIREMENTS FOR HIGH-THROUGHPUT AND HIGH-SENSITIVITY HPLC-MS.* Ronald F, Majors, Hewlett-Packard

9:15 204. *A NOVEL APPROACH FOR RAPIDLY DEVELOPING AN EFFICIENT SOLID PHASE EXTRACTION METHOD.* Jianmei Ding, Parnela Ireneta, Uwe Neue, Waters Corporation

9:45 205. *OPTIMIZED STATIONARY PHASES FOR THE ANALYSIS OF BASIC PHARMACEUTICALS BY HPLC/MS.* S.R. Needham, Pfizer Central Research; P.R. Brown, University of Rhode Island; Dave Bell, K.J. Duff, Restek Corporation

10:15 Break

10:30 206. *REFLECTIONS ON CHIRALITY; A RAPID AND INTUITIVE METHODS DEVELOPMENT STRATEGY FOR THE SEPARATION OF ENANTIOMERIC COMPOUNDS.* S.J. Brunet, Beckman Coulter

11:00 207. *ON-COLUMN REFRACTIVE INDEX DETECTOR FOR FLASH COLUMN CHROMATOGRAPHY.* Sarah G. Westerbuhr, Kathy L. Rowlen, University of Colorado

11:20 208. *QUANTITATIVE ANALYSIS OF COATING THICKNESS AND ACTIVE INGREDIENTS IN PHARMACEUTICAL TABLETS BY FT-NIR SPECTROSCOPY.* Qian Wang, Steve Dejesus, Basil Desousa, Sameer Londhe, Bruker Optics

12:00 Lunch

Afternoon, Robert K. Lantz presiding

1:30 Welcome and Introductory Remarks

1:35 209. *FAST LC/MS-TOF ANALYSIS.* Craig M. Whitehouse, Erol Gulcicek; Bruce Andrien, Shida Shen, Analytica of Brandford, Inc.

2:05 210. *LC/MS CONFIRMATION OF ANIMAL DRUG RESIDUES FOR REGULATORY USE.* Sherri B. Turnipseed, Steve A. Gonzales, Allen P. Pfenning, Jose B. Roybal, Animal Drugs Research Center, Food and Drug Administration (ADRC/FDA)

2:35 211. *COLUMN SWITCHING APPROACHES IN LC/MS/MS FOR HIGH THROUGHPUT BIOANALYSIS OF PHARMACEUTICALS.* Vince Gao, PE Biosystems

3:05 212. *IDENTIFICATION OF AN UNKNOWN DEGRADANT IN A PHARMACEUTICAL DRUG FORMULATION BY LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY (LC/MS).* Pauline Chow, Michael Bray, Geneva Pharmaceuticals, Inc.;David Manley, 3M Pharmaceuticals

3:30 Break

3:45 213. *LARGE SCALE QUANTITATIVE ANALYSIS OF PHARMACEUTICALS VIA LC-MS AND LC-MS/MS WITH AN ION TRAP MASS SPECTROMETER.* Jack Cunnift, Dieter Drexler, Rohan Thakur, Finnigan Corporation

4:15 214. *A BENCHTOP TIME-OF-FLIGHT MASS SPECTROMETER FOR ROUTINE ACCURATE MASS LCMS MEASUREMENTS.* Jeffrey W. Finch, Brian Williamson, Terry Kehoe, PE Biosystems

Symposium on NMR

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Monday, August 2, 1999

8:25 Opening Remarks and Welcome, Jeffrey A. Reimer

Session I, Applied NMR, Steve Sinton presiding

8:30 215. *RECENT DEVELOPMENTS IN TOROID CAVITY NMR SPECTROSCOPY, RHEOLOGY AND IMAGING.* Klaus Woelk, Peter Trautner, University of Bonn; Rex E. Gerald II, Robert J. Klingler, Jerome W. Rathke, Argonne National Laboratory

9:00 216. *MAGNETIC RESONANCE OUTSIDE THE LABORATORY.* B.H. Suits, A.N. Garroway, J. B. Miller, Naval Research Laboratory

9:30 217. *LANDMINE DETECTION BY NUCLEAR QUADRUPOLE RESONANCE.* G.A. Barrall, D. Gregory, R. Matthews, S.A. Vierkötter, Quantum Magnetics, Inc.; A.D. Hibbs, Information Systems Laboratories, Inc.

10:00 Break

Session II, Methods I, Clare Gery presiding

10:30 218. *SOME NEW ASPECTS CONCERNING THE ANALYSIS OF LOCAL ORDER AND DISORDER IN SOLIDS CONTAINING QUADRUPOLAR NUCLEI.* Jean-Paul Amoureux, Université des Sciences et Technologies de Lille; Marek Pruski, Iowa State University

11:00 219. *FAST RF AMPLITUDE MODULATION IN MQMAS-NMR SPECTROSCOPY.* Amir Goldbourt, P.K.Madhu, Lucio Frydman, Shimon Vega, Weizmann Institute of Science

11:25 220. *DETERMINATION OF INTERNUCLEAR DISTANCES FROM SOLID-STATE NMR: DIPOLAR TRANSFORMS AND REGULARIZATION METHODS.* Frederick G. Vogt, David J. Aurentz, James M. Gibson, Karl T. Mueller, The Pennsylvania State University

11:50 Lunch

1:30–2:30
Session III, Poster Session A, Lucio Frydman presiding
Session IV, Polymers, Yue Wu presiding

3:30 221. *HOMONUCLEAR DOUBLE-QUANTUM NMR STUDIES OF CONFORMATION AND PACKING IN DISORDERED POLYMERS.* Hironori Kaji1, Kyoto University; Matthew G. Dunbar, Douglas J. Harris, Klaus Schmidt-Rohr, Jörg Rupp, University of Massachusetts; Herbert Zimmermann, Max-Planck-Institut für Medizische Forschung

4:00 222. *FLUORINE AND CARBON SOLID-STATE NMR FOR THE CHARACTERIZATION OF FLUOROPOLYMERS.* Ulrich Scheler, Institute for Polymer Research Dresden

4:25 223. *THE EFFECT OF SOLUTION PROCESSING ON SOLID-STATE STRUCTURE: MAS NMR STUDY OF POLYANILINE FILM.* Matthew Espe, Tanya Young, University of Akron; Dali Yang, Benjamin Mattes, Santa Fe Science and Technology

4:50 Dinner Break

7:30–9:00
Session V, Vendor Carnival, Lucio Frydman presiding

Tuesday, August 3, 1999

Session VI, Applied NMR II, Yue Wu presiding

8:30 224. *SOLID STATE NMR STUDIES OF ENVIRONMENTAL CATALYSTS.* Jianjun Wu, Alexander Panov, Russell Larsen, Vicki Grassian, Sarah Larsen, University of Iowa

9:00 225. *MULTINUCLEAR SOLID-STATE NMR STUDIES OF TIN COMPOSITE OXIDE ANODE MATERIALS.* G. R. Goward, L. F. Nazar, W. P. Power, University of Waterloo

9:30 226. *NONDESTRUCTIVE DETERMINATION OF STRUCTURAL FEATURES BY COUPLED NMR-ACOUSTIC INSPECTION.* S. W. Sinton, J. H. Iwamiya, J. Bellin, E. Olsen, Lockheed Martin Missiles and Space

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9:55 227. *COMPARATIVE STUDY OF LI-ION MOBILITY IN SWOLLEN IONOMERS AS MEASURED BY 7LI MAS LINESHAPE, T1R, 7LI DIFFUSION AND CONDUCTIVITY.* A. J. Vega, E. F. McCord, M. Doyle, M. G. Roelofs, DuPont Central Research and Development

10:20 Break

Session VII, Metal Atoms, Steve Sinton presiding

10:30 228. *SOLID-STATE NMR INVESTIGATION OF COMPLEXES OF LEAD (II) DIHALIDES WITH ORGANIC LIGANDS.* A. Glatfelter, C. Dybowski, University of Delaware; G. Neue, Universitaet Dortmund; D.L. Perry, M. Blake, University of California Berkeley

10:55 229. *SOLID-STATE ^{25}MG, ^{27}AL AND ^{29}SI NMR INVESTIGATIONS OF MG (II), AL (III) AND SI (IV) CHEMICAL ENVIRONMENTS AND ORDERING IN VARIOUS MONTMORILLONITE CLAY CHEMICALS.* John J. Fitzgerald, South Dakota State University; Don Eisenhour, American Colloid Company; Herman Lock, Gary E. Maciel, Colorado State University

11:20 230. *NMR OF PARAMAGNETIC LANTHANIDE GLUTARATES.* Joseph R. Sachleben, The Ohio State University; Anthony Cheetham, University of California; Gérard Férey, Thomas Luxbacher, Fabien Serpaggi, Université de Versailles Saint-Quentin-en-Yvelines

11:45 231. *ONE AND TWO-DIMENSIONAL SOLID-STATE ^{93}Nb NMR SPECTROSCOPY OF INORGANIC NIOBATES.* J. S. Shore, S. Prasad, P. Zhao, J. Huang, J. J. Fitzgerald, South Dakota State University

12:10 Lunch

1:30 232. *ROCKY MOUNTAIN CONFERENCE PLENARY LECTURE*—M. Bonner Denton, University of Arizona

1:30–3:00
Session VIII, Poster Session B, Lucio Frydman presiding
Session IX, Methods II, Clare Grey presiding

3:00 233. *MULTIPLE-PULSE SOLID-STATE NMR: SYSTEMATIC DESIGN, MAGNITUDES AND ORIENTATION OF ANISOTROPIC INTERACTION TENSORS.* Nielsen Chr. Nielsen, Morten Hohwy, Mads Bak, Jimmy T. Rasmussen, Flemming H. Larsen, Hans J. Jakobsen, University of Aarhus; Malcolm H. Levitt, Stockholm University; Paul D. Ellis, Pacific Northwest Laboratory

3:30 234. *MAXIMUM ENTROPY INVERSION OF MQMAS SPECTRA.* T. Charpentier, J. Virlet, CEA Saclay

3:55 235. *STRUCTURAL ANALYSIS OF NEW ALUMINOPHOSPHATE MATERIALS USING HIGH RESOLUTION SOLID-STATE NMR.* Marek Pruski, Iowa State University; Alain Bailly, Jean-Paul Amoureux, Université de Lille; L. Delmotte, Ecole Nationale Supérieure de Chimie de Mulhouse

4:20 236. *A STUDY OF THE CROSS RELAXATION POLARIZATION TRANSFER PATHWAY FROM LASER POLARIZED XENON TO SURFACE SPECIES.* Ernesto MacNamara, Jay Smith, Charles V. Rice, Daniel Raferty, Purdue University

4:45 Dinner Break

Wednesday, August 4, 1999

Session X, R. W. Vaughan Session, Jeffrey A. Reimer presiding

8:25 237. Jeffrey A. Reimer

8:30 238. *R. W. VAUGHAN PLENARY LECTURE: "SCATTERING AND MAGNETIC RESONANCE SPECTROSCOPY"* Professor Hans W. Spiess

9:30 239. *SOLID STATE NMR OF PEPTIDES AND PROTEINS.* Oleg Antzutkin, John Balbach, Francisco Blanco, Yoshitaka Ishii, Carl Michal, David Weliky, Robert Tycko, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health

10:10 Break

10:40 240. *USE OF THE "b" SINE-CORRELATION TECHNIQUE TO MEASURE WEAK DIPOLAR INTERACTIONS IN ORDERED SOFT CONDENSED MATTER.* P.T. Callaghan, Massey University; E.T. Samulski, University of North Carolina

11:20 241. Huub de Groot

12:00 Lunch

Session XI, Inorganic materials, John Hanna presiding

1:30 242. *ASPECTS OF STRUCTURE AND DYNAMICS IN DISORDERED MATERIALS BY SOLID STATE NMR.* Hellmut Eckert, Joern Schmedt auf der Guenne, Guido Regelski, Sylvia Kaczmarek, Michael WitschasWestfaelische Wilhelms-Universitaet Muenster

2:00 243. ***HIGH RESOLUTION SOLID-STATE NMR : A POWERFUL TOOL FOR DESCRIPTION OF STRUCTURE AND DYNAMICS IN INORGANIC SOLIDS AND LIQUIDS, FROM ROOM TEMPERATURE UP TO VERY HIGH TEMPERATURE.*** Dominique Massiot, Thomas Vosegaard, Pierre Florian, Catherine Bessada, Frank Fayon, Jean-Pierre Coutures, CRMHT–CNRS

2:30 244. ***NTERMEDIATE RANGE ORDER IN BORON OXIDE GLASS: THE FRACTION OF RINGS FROM ANISOTROPY-CORRELATED TWO-DIMENSIONAL NMR.*** C. G. Joo, U. Werner-Zwanziger, J. W. Zwanziger, Indiana University

2:55 Break

3:25 245. ***^{17}O MQMAS AND DOR NMR STUDIES OF POROUS MATERIALS IN THE HIGH FIELD.*** Dieter Freude, Dieter Michel, Ulf-Torsten Pingel, Universität Leipzig; Ago Samoson, Institute of Chemical Physics; Jean-Paul Amoureux, Université des Sciences et Technologies de Lille.

3:55 246. ***NMR OF QUADRUPOLAR NUCLEI IN SOLIDS: CROSS-POLARIZATION AND ^{17}O MULTIPLE-QUANTUM MAS.*** Stephen Wimperis, University of Oxford

4:25 247. ***MULTIPLE QUANTUM MAS NMR EXPERIMENTS ON I=5/2 NUCLEI.*** M.E.Smith, R. Dupree, T. Mildner, University of Warwick; E.R.H. van Eck, University of Kent; S.C. Kohn, University of Bristol

4:50 248. ***USING ^{31}P{^{1}H} CROSS POLARIZATION MAS NMR TO PROBE THE SURFACE DISSOLUTION OF PHOSPHATE GLASSES.*** Todd M. Alam, David P. Lang, Sandia National Laboratories

5:15 Dinner Break

Thursday, August 5, 1999

Session XII, Biological/Organic Systems, Gina Hoatson presiding

8:30 249. ***LYSOZYME DYNAMICS.*** Richard Wittebort, University of Louisville

9:00 250. ***NMR STUDIES OF REARRANGEMENT PATHWAYS IN SOLIDS.*** Zeev Luz, Weitzmann Institute of Science

9:30 251. ***2D NMR INVESTIGATIONS OF BACTERIAL CELLULOSE AND CELLULOSE II.*** Christian Jäger, Stephanie Hesse, Thomas Heinze, Friedrich Schiller University Jena; Hans-Peter Schmauder, Forschungszentrum für Medizintechnik und Biotechnologie e.V.,

10:00 Break

10:25 252. ***IDENTIFICATION OF HISTIDYL AND LYSYL RESIDUES AT A POTENTIAL ALLOSTERIC SITE OF RIBULOSE 1,5-BISPHOSPHATE CARBOXYLASE/OXYGENASE.*** Lynda M. McDowell, Matthew E. Merritt, Jacob Schaefer, Washington University; Joe S. Schriner, Karinne Cortes, Delbert D. Mueller, Kansas State University

10:50 253. ***SOLID STATE NMR STUDY OF POLYMORPHISM AND NONCLASSICAL PHASE TRANSFORMATION IN 3MEDNBP.*** Asher Schmidt, Shifra Kababya, Michael Appel, Mark Botoshansky, Soliman Khatib, Yoav Eichen, Technion

11:15 254. ***TESTING THE SURROGATE PROBE STRATEGY USING SOLID-STATE ^{67}Zn NMR.*** Andrew S. Lipton, Paul D. Ellis, Pacific Northwest National Laboratory

11:40 255. ***SEGMENTAL DYNAMICS IN DRY AND SWOLLEN ELASTOMERS AS FUNCTION OF CROSS-LINK DENSITY AND FILLER CONTENT STUDIED BY THE NMR DIPOLAR-CORRELATION EFFECT.*** Winfried Kuhn, IIC Innovative Imaging Corp.; Farida Grinberg, Rainer Kimmich, Universität Ulm; Maciej Garbaczyk, Stefan Jurga, Uniwersytet Im. Adama Mickiewicza w Poznaniu

12:05 Concluding Remarks, Jeffrey A. Reimer

Poster Sessions

A 256. ***USING 31P{1H} CROSS POLARIZATION MAS NMR TO PROBE THE SURFACE DISSOLUTION OF PHOSPHATE GLASSES.*** Todd M. Alam and David P. Lang, Sandia National Laboratories

B 257. ***LOCATION OF PROTONS IN ANHYDROUS KEGGIN HETEROPOLYACIDS BY USING 1H<->31P REDOR AND MOLECULAR MODELING.*** Alain Bailly, Jean-Francois Paul, Jean-Paul Amoureux, Michel Fournier, Michel Guelton, Université des Sciences et Technologies de Lille; Subramanian Ganapathy, University of Pune

A 258. ***CHARACTERIZATION OF BRONSTED ACID SITES IN ZEOLITES BY MQ-REDOR NMR.*** Subramanian Ganapathy, University of Pune; Laurent Delevoye, Alain Bailly, Jean-Paul Amoureux, Université des Sciences et Technologies de Lille

B 259. ***RECENT DEVELOPMENTS OF CP MAS BETWEEN QUADRUPOLAR NUCLEI AND SPIN 1/2.*** Jean-Paul Amoureux, Alain Bailly, Université des Sciences et Technologies de Lille; Marek Pruski, Iowa State University

A 260. ***CHEMICAL SHIFT TENSORS OF POLYCYCLIC AROMATIC MOLECULES DETERMINED BY MAGIC ANGLE TURNING.*** Dewey H. Barich; A. M. Orendt; J. Z. Hu; R. J. Pugmire; D. M. Grant; University of Utah

B 261. *A ^{2}H AND ^{13}C EXPERIMENTAL SOLID-STATE NMR AND THEORETICAL STUDY OF ZEISE'S SALT, K[PtCl$_3$(C$_2$H$_4$)]•H$_2$O.* Guy M. Bernard; Roderick E. Wasylishen, Dalhousie University

A 262. *STRUCTURE DETERMINATION OF PEPTIDES AND PROTEINS USING SOLID STATE NMR.* Peter V. Bower, Joanna R. Long, Nathan A. Oyler, Gary P. Drobny, University of Washington

B 263. *MAGNETIC RESONANCE MICROIMAGING (MRM) OF PETROLEUM COKE.* Eric B. Brouwer, Yves Deslandes, Institute for Chemical Process and Environmental Technology (ICPET); Igor Moudrakovski, John A. Ripmeester, Steacie Institute for Molecular Sciences (SIMS); Keng H. Chung, Edmonton Research Centre

A 264. *EXPERIMENTAL ^{9}Be SOLID-STATE NMR STUDY OF Be(acac)^2 AND THEORETICAL STUDIES OF ^{9}Be ELECTRIC FIELD GRADIENT AND CHEMICAL SHIELDING TENSORS. THE FIRST EVIDENCE FOR ANISOTROPIC BERYLLIUM SHIELDING.* David L. Bryce; Roderick E. Wasylishen, Dalhousie University

B 265. *REMOTE ACCESS TO NMR SPECTROMETERS AT THE EMSL DOE USER FACILITY.* Sarah Burton; Andrew Lipton, PNNL

A 266. *INVESTIGATION OF LOCAL STRUCTURE ENVIRONMENT IN GLASSES BY ^{17}O, ^{23}Na AND ^{27}Al MQ-MAS NMR.* F. Angeli, T. Charpentier, P. Faucon, J.-C. Petit, J. Virlet, Service de Chimie Moléculaire, CEA Saclay

B 267. *^{13}C NMR STUDIES OF THE SELECTIVE OXIDATION OF n-BUTANE ON VANADIUM PHOSPHORUS OXIDE CATALYSTS.* Bin Chen, Eric J. Munson, University of Minnesota

A 268. *NMR STUDIES OF ^{129}Xe DIFFUSION IN ETHYLENE-PROPYLENE COPOLYMERS.* Naira M. da Silva, Maria Ines B. Tavares, Instituto de Macromoléculas Prof. Eloisa Mano, Universidade Federal do Rio de Janeiro; Hanna Gracz, E. O. Stejskal, North Carolina State University

B 269. *NMR SPECTROSCOPY AND SOLID PHASE SYNTHESIS: POLYMER SIGNAL SUPPRESSION VIA ISOTROPIC MIXING IN ^{1}D GEL PHASE ^{1}H NMR.* Michael J.T. Ditty, R.M.E. Mainville and W.P. Power, University of Waterloo; H.N. Hunter, Brantford Chemicals Inc.

A 270. *SOLID-STATE NMR CHARACTERIZATION OF ^{93}NB, ^{19}F SPIN PAIRS IN NIOBIUM FLUORIDES AND OXYFLUORIDES.* Lin-Shu Du, Robert W. Schurko, Kwang Hun Lim and Clare P. Grey, SUNY at Stony Brook

B 271. *Se NMR MEASUREMENTS ON EXCEPTIONAL Se-As GLASSES.* Birgit Effey, D. A. Drabold, R. L. Cappelletti, Ohio University; J. R. Sachleben, Ohio State University

A 272. *PHOSPHORUS CHEMICAL SHIFT TENSORS FOR TETRAMETHYLDIPHOSPHINE DISULFIDE - A ^{31}P SINGLE CRYSTAL NMR, DIPOLAR-CHEMICAL SHIFT NMR AND Ab INITIO STUDY.* Myrlene Gee, Roderick E. Wasylishen and Klaus Eichele, Dalhousie University; James F. Britten, McMaster University

B 273. *APPLICATIONS OF TOROID CAVITY NMR DETECTORS TO METALS, POLYMERS, RADIOACTIVE MATERIALS, AND SUPERCRITICAL FLUIDS.* Rex E. Gerald II, David E. Fremgen, Luis H. Nuñez, Donald T. Reed, Robert J. Klingler, Jerome W. Rathke, Argonne National Laboratory; Klaus Woelk, University of Bonn

A 274. *DISTRIBUTION OF CRYSTALLINE AND AMORPHOUS POLYMER ELECTROLYTE IN AN ELECTROCHEMICAL CELL.* Rex E. Gerald II, Edward T. Chainani, Robert J. Klingler, Jerome W. Rathke, Argonne National Laboratory

B 275. *ROTATIONAL SIDEBAND SEPARATION AT HIGH SPINNING SPEEDS: APPLICATIONS TO ^{207}Pb, ^{139}La AND ^{93}Nb NMR.* James M. Gibson, Frederick G. Vogt, David J. Aurentz, Alan J. Benesi, Karl T. Mueller, Pennsylvania State University

A 276. *TIN COMPOSITE OXIDE ANODE MATERIALS AS PROBED BY MULTINUCLEAR NMR, DIFFRACTION AND X-RAY ABSORBTION SPECTROSCOPY.* Gillian R. Goward, Linda F. Nazar, and William P. Power, University of Waterloo; Fabrice Leroux, Université Blaise-Pascal; Wojtek.Dmowski and Takeshi.Egami University of Pennsylvania

B 277. *PASSIVE-SHIMMING DESIGNS OF TOROID CAVITY PROBES USING SPECTRAL DISTORTION PARAMETERS.* Eric Growney, Rex Gerald II, Robert Klingler, Jerome Rathke, Argonne National Laboratory; Gary Friedman, University of Illinois at Chicago

A 278. *SOLID STATE NMR STUDY OF MOLECULAR MOTION IN HEXAKIS(TRIFLUOROMETHYL)BENZENE.* Edward W. Hagaman and David K. Murray, Oak Ridge National Laboratory

B 279. *SOLID-STATE NMR ANALYSIS OF SEMICONDUCTOR CLUSTERS AND THIN FILMS.* S.E. Hayes, L. Dinh, M. Balooch, Lawrence Livermore National Laboratory; J.A. Reimer, UC Berkeley

A 280. *SURFACE AND DEFECT CHARACTERISATION BY ^{27}Al NMR AND PALS OF INTERMEDIATE PHASES FORMED DURING CALCINATION OF GIBBSITE, Al(OH)$_3$, TO CORUNDUM, α-Al$_2$O$_3$.* Anita J.Hill, Timothy J.Bastow and Steven Celotto, CSIRO Manufacturing Science and Technology

B 281. *STOCHASTIC WIDELINE NMR SPECTROSCOPY—ADVANTAGES, PROBLEMS AND SOLUTIONS.* Ole Hirsch, Friedrich Schiller University Jena, Institute for Optics and Quantum Electronics; Frank Weingarten, Rheinisch-Westfälische Technische Hochschule Aachen, Institute of Technical and Macromolecular Chemistry

A 282. ***SOLID-STATE ^{25}Mg AND ^{93}Nb NMR STUDIES OF THE FORMATION OF LEAD MAGNESIUM NIOBATE $Pb(Mg_{1/3}Nb_{2/3})O_3$.*** J. Huang, S. Prasad, J. Shore and J.J. firzgerald, South Dakota State University; H. Lock and G.E. Maciel, Colorado State University

B 283. ***SOLID-STATE ^{13}C NMR INVESTIGATION OF RING-FLIPPING DYNAMICS OF BENZYL-ETHER DENDRITIC MACROMOLECULES.*** Joseph S. H. Huang and Christopher A. Klug, Stanford University

A 284. ***SOLID-STATE ^{1}H AND ^{29}Si NMR STUDIES OF HYDROGEN-LOADED AND ULTRAVIOLET-IRRADIATED OPTICAL FIBER MATERIALS.*** Margaret Hubbard, Erin Gill, and Sarah Gilbert, National Institute of Standards and Technology; Jincheng Xiong, Herman Lock, and Gary E. Maciel, Colorado State University

B 285. ***DEVELOPMENT OF VARIABLE-TEMPERATURE ISOLATED FLOW AND LARGE SAMPLE VOLUME MAS NMR PROBES FOR HETEROGENEOUS CATALYSIS STUDIES.*** Lauren E. Kaune, Paul K. Isbester and Eric J. Munson, University of Minnesota

A 286. ***SOLID-STATE NMR STUDIES OF TRI-P-TOLYLAMINE/POLYCARBONATE BLENDS.*** Brian Kesling, Eric Hughes, and Terry Gullion, West Virginia University

B 287. ***^{87}Rb MAS AND MQMAS NMR STUDIES OF HIGH TEMPERATURE PHASE TRANSITIONS IN $LiRbSO_4$.*** Hae Jin Kim, Marek Pruski, Jerzy W. Wiench, Iowa State University; Sung Ho Choh, Korea University

A 288. ***SOLID-STATE ^{19}F NMR STUDY OF MOLECULAR DYNAMICS OF PFPE LUBRICANT FILMS ON AMORPHOUS CARBON SURFACES.*** Yoojin Kim and Christopher A. Klug, Stanford University

B 289. ***A 380 MHZ GYROTRON-BASED DNP SPECTROMETER.*** K.E. Kreischer, C.T. Farrar, R.G. Griffin, R.J. Temkin, J.R. Vieregg, MIT

A 290. ***SOLID-STATE NMR STUDY OF EXCHANGED ZEOLITES.*** Theresa A. Lalain, Karl T. Mueller, James R. Fehlner, The Pennsylvania State University; D.E.W. Vaughan, Exxon Research and Engineering Company

B 291. ***USING ^{27}Al, ^{31}P MAS AND ^{31}P/^{27}Al TRAPDOR NMR SPECTROSCOPIES TO STUDY SODIUM ALUMINOPHOSPHATE GLASSES.*** David P. Lang and Todd M. Alam, Sandia National Laboratories

A 292. ***SOLID-STATE VANADIUM-51 NMR STUDIES OF DIOXOVANADATE(V) COMPLEXES.*** Man-Ho Lee, Kyungpook National University; Shigenobu Hayashi, National Institute of Materials and Chemical Research

B 293. ***TOWARDS AN EXACT SOLUTION TO THE DIFFICULTIES IN REDOR FOR MULTIPLY COUPLED HETERONUCLEAR SPIN SYSTEMS.*** Oskar Liivak, David B. Zax, Cornell University

A 294. ***ANALYSIS OF THE MULTIPLE QUANTUM CROSS POLARIZATION NMR EXPERIMENT FOR ^{19}F/^{23}Na AND ^{1}H/^{27}Al SPIN SYSTEMS IN SOLIDS.*** Kwang Hun Lim and Clare P. Grey, SUNY Stony Brook

B 295. ***EXPERIMENTAL INVESTIGATION OF THE POSSIBLILITIES OPEN BY RECENT SENSITIVITY IMPROVEMENTS OF THE QUADRUPOLAR MQ-MAS EXPERIMENT.*** Thomas Vosegaard, Pierre Florian, Valérie Montouillout, and Dominique Massiot; CNRS-CRMHT

A 296. ***DETERMINATION OF INTERNUCLEAR DISTANCES FROM SOLID-STATE NMR: APPLICATIONS OF MONTE CARLO ERROR ANALYSIS TO REDOR DATA.*** Sue M. Mattingly, Fredrick G. Vogt and Karl T. Mueller, The Pennsylvania State University; Leonard J. Mueller, University of California at Riverside

B 297. ***IDENTIFICATION OF HISTIDYL AND LYSYL RESIDUES AT A POTENTIAL ALLOSTERIC SITE OF RIBULOSE 1,5-BISPHOSPHATE CARBOXYLASE/OXYGENASE.*** Lynda M. McDowell, Matthew E. Merritt, Jacob Schaefer, Washington University; Joe S. Schriner, Karinne Cortes, Delbert D. Mueller, Kansas State University

A 298. ***HETERONUCLEAR 2D LOCAL FIELD NMR SPECTROSCOPY UNDER FAST MAS: PRINCIPLES AND APPLICATIONS TO ORGANIC SOLIDS.*** Dan McElheny, Enrico DeVita and Lucio Frydman, University of Illinois at Chicago

B 299. ***DISTANCE MEASUREMENTS TO THE PHOSPHOSDIESTER BACKBONE OF NUCLEIC ACIDS USING SOLID-STATE NMR.*** Matthew E. Merritt, Gary A. J. Meints, Snorri Th. Sigurdsson, Gary P. Drobny, University of Washington

A 300. ***A SOLID-STATE DEUTERIUM NMR STUDY OF DNA METHYLTRANSFERASE BINDING SITES: EFFECTS OF METHYLATION ON BACKBONE AND FURANOSE RING DYNAMICS.*** Gary A. J. Meints, Gary P. Drobny, University of Washington; Karen B. Geahigan, 3M Chemicals; Mary E. Hatcher-Skeers, Claremont Colleges

B 301. ***FINITE PULSE WIDTHS AND INFINITE LINEWIDTHS: ECHO SHAPES AND RELATIVE INTENSITIES.*** Joel B. Miller, Naval Research Laboratory

A 302. ***^{109}Ag NMR STUDIES OF SILVER-EXCHANGED ZEOLITES.*** Igor L. Moudrakovski, Christopher I. Ratcliffe, John A. Ripmeester, Steacie Institute for Molecular Sciences (SIMS)

B 303. ***QUANTIFICATION OF PHOSPHORUS-CHALCOGEN BONDING PREFERENCES IN TERNARY PHOSPHORUS-SULFUR-SELENIUM GLASSES BY MULTIPLE-PHASE ^{31}P AND HIGH-TEMPERATURE ^{77}Se NMR.*** Paul F. Mutolo, University of California at Santa Barbara; Hellmut Eckert, Institut für Physikalische Chemie, WWU

A 304. ***^{207}Pb AND ^{27}Al SOLID STATE NMR STUDIES OF LEAD-EXCHANGED ZEOLITES.*** Heiko G. Niessen, Jeffrey A. Reimer, Alexis T. Bell, University of California Berkeley; C. Dybowski, University of Delaware; David R. Corbin, DuPont Company

B 305. ***DYNAMIC NUCLEAR POLARIZATION IN AQUEOUS CHAR SUSPENSIONS AT 9.4 GHz.*** B.M.Odintsov, R.L.Belford, R.B.Clarkson, P.J.Ceroke, Illinois EPR Research Center; V.A.Atsarkin, V.N.Demidov, Institute of Radioengineering and Electronics

A 306. ***SPIN-LATTICE RELAXATION AND NMR SPECTROSCOPY IN AQUEOUS CHAR SUSPENSIONS.*** B.M.Odintsov, R.L.Belford, P.J.Ceroke, R.B.Clarkson, Illinois Research EPR Center; Z.Sh.Idiyatullin; A.N.Temnikov, State Technological University

B 307. ***SOLID-STATE ^{27}A1 MAS NMR INVESTIGATIONS OF AION POWDERS AND CERAMICS.*** Tom Offerdahl and John J. Fitzgerald, South Dakota State University; Steven F. Dec, Colorado School of Mines and Technology; Gary E. Maciel, Colorado State University

A 308. ***DETERMINATION OF THE ORIENTATION OF THE GLYCINE-ALPHA CARBON CSA TENSOR IN THE DIPEPTIDE AG.*** Nathan A. Oyler, John Stringer, and Gary P. Drobny, University of Washington

B 309. ***COMPARISON ^{13}C CP/MAS NMR AND POWDER X-RAY DIFFRACTION FOR ANALYZING SOLID ORGANIC COMPOUNDS.*** Brian E. Padden, Mark T. Zell, Zedong Dong, David J.W. Grant, Eric J. Munson, University of Minnesota; Steve A. Schroeder, The Monsanto Company

A 310. ***INVESTIGATIONS OF TITANOSILICATE MATERIALS BY SOLID-STATE ^{29}Si AND ^{47,49}Ti NMR SPECTROSCOPY.*** R.L. Peterson and J.J. Fitzgerald, South Dakota State University

B 311. ***SOLUTION ^{13}C, ^{47,49}Ti AND ^{93}Nb NMR STUDIES OF TITANATE AND NIOBATE ALKOXIDE SOL-GEL PRECURSORS TO ELECTRONIC MATERIALS.*** J. Qi, J. Huang and J.J. Fitzgerald, South Dakota State University

A 312. ***NMR OF PARAMAGNETIC LANTHANIDE GLUTARATES.*** Joseph R. Sachleben, The Ohio State University; Anthony Cheetham, University of California Santa Barbara; Gérard Férey, Thomas Luxbacher, Fabien Serpaggi, Université de Versailles Saint-Quentin-en-Yvelines

B 313. ***ANILINE OLIGOMERS AS A MODEL FOR POLYANILINE: A SOLID-STATE NMR STUDY.*** P. Michael Schmeida, Matthew Espe, University of Akron

A 314. ***EXAMPLES OF SODIUM AND GALLIUM CHEMICAL SHIELDING ANISOTROPY.*** Robert W. Schurko, Clare P. Grey, SUNY at Stony Brook; Roderick E. Wasylishen, Dalhousie University; Anthony Bielecki, Bruker Instruments, Inc.

B 315. ***CHARACTERISATION OF STRUCTURE AND DYNAMICS IN NANOCRYSTALLINE OXIDES BY SOLID STATE NMR.*** I.J.F. Poplett, M.E. Smith, University of Warwick; A.V. Chadwick and J.H. Strange, University of Kent

A 316. ***MULTIPLE QUANTUM MAS NMR EXPERIMENTS ON I=5/2 NUCLEI.*** M.E.Smith, R. Dupree and T. Mildner, University of Warwick; E.R.H. van Eck, University of Kent; S.C. Kohn, University of Bristol

B 317. ***SOLID-STATE NMR INVESTIGATION OF LEACHED LAYERS IN SODIUM-ALUMINOSILICATE GLASSES.*** Natia Tsomaia, James Hamilton, Karl T. Mueller, Penn State University

A 318. ***COMPARATIVE STUDY OF LI-ION MOBILITY IN SWOLLEN IONOMERS AS MEASURED BY ^{7}Li MAS LINESHAPE, T1p, ^{7}Li DIFFUSION, AND CONDUCTIVITY.*** A. J. Vega, E. F. McCord, M. Doyle and M. G. Roelofs, DuPont Central Research and Development

B 319. ***DYNAMICS OF POLARIZATION TRANSFER IN HIGH SPEED CPMAS EXPERIMENTS.*** Vladimir Ladizhansky and Shimon Vega, Weizmann Institute of Science

A 320. ***RESIDUAL DIPOLAR COUPLINGS BETWEEN QUADRUPOLAR NUCLEI IN SOLID STATE MQMAS NMR SPECTRA.*** Sungsool Wi and Lucio Frydman, University of Illinois at Chicago

B 321. ***MEASUREMENTS OF CONNECTIVITIES BETWEEN PO_4 UNITS IN ZINC PHOSPHATE GLASSES.*** Jerzy W. Wiench, Marek Pruski, Brad Tischendorf, Joshua Otaigbe, Iowa State University

A 322. ***DEUTERIUM WIDE-LINE NMR STUDIES OF LOCAL MOTION OF BENZENE ADSORBED ON Ca-MONTMORILLONITE.*** Jincheng Xiong, Union Carbide Corp.; Gary Maciel, Colorado State University

B 323. ***PROBING ELECTRONIC AND PROTONATION STATES IN A POLYMER: A ^{15}N SSNMR STUDY OF POLYANILINE.*** Tanya Young, Matthew Espe, University of Akron; Dali Yang, Benjamin Mattes, Santa Fe Science and Technology

A 324. ***INVESTIGATION OF POLY(LACTIDE) STRUCTURE USING SOLID-STATE NMR SPECTROSCOPY.*** Mark T. Zell, Brian E. Padden, Amanda J. Paterick, Marc A. Hillmyer, Eric J. Munson, University of Minnesota; Khalid A.M. Thakur, Robert T. Kean, Cargill Incorporated

Symposium on Quality Assurance

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Tuesday, August 3, 1999

8:30 325. ***THE ROLE OF INTERNET APPLIANCES IN THE MODERN ANALYTICAL LABORATORY.*** Brian N. Radford, Keith W. Ballantyne, Genesis Laboratory Systems, Inc.

9:00 326. ***CLEANING VALIDATIONS: DEVELOPMENT, VALIDATION AND TRANSFER OF ANALYTICAL TEST METHODS.*** David E. Nadig, Johnson & Johnson Merck Consumer Pharmaceuticals Company

9:30 327. ***SELECTION AND USE OF DEFENSIBLE REFERENCE MATERIAL STANDARDS FOR CALIBRATION, VALIDATION AND QUALIFICATION OF UV/VIS ABSORPTION SPECTROPHOTOMETERS.*** Kathy McLain, Aron Shultz, Jerry Messman, SpectroStandardsTM Analytical

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Radiochemistry

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Monday, August 2, 1999

Morning, Karen Schoendaller presiding

8:55 **Welcoming Remarks,** Ann Mullin, U.S. Geological Survey

9:00 328. *"RAMPSCAN—A PORTABLE GAMMA-RAY ANALYSIS SYSTEM FOR MONITORING AIR FILTERS.*
Colin G. Sanderson, and Norman Latner, U.S. Department of Energy, Environmental Measurements Laboratory

9:30 329. *PROPOSED RADIOCHEMICAL TECHNIQUE FOR RADIUM-224 IN DRINKING WATER SAMPLES.*
D.E. McCurdy, A.D. Banavali, J.M. Raimondi, Duke Engineering & Services

10:00 330. *COMPARISON OF MEASUREMENTS OF "FALLOUT" LEVELS OF Pu AND Am IN SEDIMENTS.*
Pamela Greenlaw, U.S. Department of Energy, Environmental Measurements Laboratory

10:30 **Break**

10:45 331. *EXTRACTION CHROMATOGRAPHY: PRINCIPLES AND THE ACHIEVEMENT OF SEPARATION AND SELECTIVITY.*
E. Philip Horwitz and Lawrence Jassin, Eichrom Industries, Inc.

Afternoon, Catherine Klusck, presiding

1:00 332. *STATISTICAL COMPARISON OF GROSS ALPHA AND GROSS BETA PARTICLE ACTIVITY IN WATER ANALYZED USING TWO ANALYTICAL METHODS.* Roy C. Bartholomay, U.S. Geological Survey, INEEL

1:30 333. *MARLAP,* Stan Morton, U.S. Department of Energy

2:00 **Break**

2:15 334. *INTRODUCTION OF EICHROM SR RESIN CARTRIDGES: Sr-90 ANALYSIS.*
Anil Thakkar, Lawrence Jassin, Michael Fern, Eichrom Industries

2:45 335. *UPDATE ON NELAC.* Donivan R. Porterfield

3:15 336. *CANBERRA INDUSTRIES ANALYTICAL ROLE IN THE ENVIRONMENTAL RESTORATION AND DECONTAMINATION AND DECOMMISSIONING OF ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE.*
Larry Umbaugh, Canberra Industries

Tuesday, August 3, 1999

Morning, Pam Greenlaw presiding

8:30 337. *A METHOD VALIDATION SOP AT EPA'S NATIONAL AIR AND RADIATION ENVIRONMENTAL LABORATORY.*
Mary Wisdom, U.S. EPA NAREL

9:15 338. *ADAPTATION OF EMPORE™ TECHNOLOGY TO FIELD SAMPLING AND ANALYSIS.*
David C. Seely, 3M Filtration Products

10:00 **Break**

10:15 339. *A QA CHEMIST GOES TO THE CENTER OF THE MEASUREMENT UNIVERSE: MY WEEK AT NIST.*
Mary Wisdom, U.S. EPA NAREL

10:45 340. *A COMPARISON OF Ra-224 AND Ra-226 BY ALPHA SPEC AND GAMMA SPEC.*
David Kappleman, U.S. EPA NAREL

Biological Infrared Spectroscopy Short Course Presented by the Society for Applied Spectroscopy

Symposium on Supercritical Fluids—Theory & Applications

Symposium Chair:

Frank G. Baglin
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Monday, August 2, 1999

8:50 Welcome and Introductory Remarks

9:00 341. *HOW DO LONG-LENGTH-SCALE SOLVENT DENSITY FLUCTUATIONS AFFECT SOLUTE DYNAMICS IN COMPRESSIBLE SUPERCRITICAL FLUIDS?* G. Goodyear, S. C. Tucker, University of California Davis (Invited Speaker)

10:00 342. *THE USE OF INTEGRAL EQUATION AND MONTE CARLO TECHNIQUES TO UNDERSTAND THE LIGHT SCATTERING DENSITY PROFILES OF SUPERCRITICAL BINARY MIXTURES.* Frank G. Baglin, Wayne T. Stanbery, tasha E. Palmer, University of Nevada

10:30 Break

10:45 343. *A NOVEL APPROACH IN DETERMINATION OF MOISTURE CONTENT IN PLUTONIUM DIOXIDE UTILIZING SUPERCRITICAL CARBON DIOXIDE EXTRACTION AND FOURIER TRANSFORM INFRARED DETECTION.* William K. Hollis, Aaron M. Martinez, Stephen Trujillo, James B. Rubin, Craig M. V. Taylor, Los Alamos National Laboratory (Invited Speaker)

11:45 Lunch

1:15 344. *THE USE OF SUPERCRITICAL FLUIDS IN ASYMMETRIC CATALYSIS TO TUNE PRODUCT ENANTIOSELECTIVITY AND ISOLATION.* Dolores C. Wynne, Philip Jessop, University of California Davis (Invited Speaker)

2:15 345. *SUPERCRITICAL CO2-ASSISTED NEBULIZATION AND BUBBLE DRYING FOR THE PRODUCTION OF MICRON-SIZED DRY POWDERS OF PHARMACEUTICALS FOR INHALATION DRUG THERAPY.* S.P. Sellers, K.D. Kusek, G.S. Clark, B.J. Korte, R.E. Sievers; University of Colorado, Cooperative Institute for Research in Environmental Science

2:45 346. *EXTRACTION AND DETERMINATION OF MOISTURE AND ORGANICS FROM PLUTONIUM DIOXIDE USING SUPERCRITICAL CARBON DIOXIDE EXTRACTION AND FOURNIER TRANSFORM INFRARED SPECTROSCOPY.* Aaron M. Martinez, William K. Hollis, James B. Rubin, Craig M. V. Taylor, Michael N. Jaspersona, Joseph B. Rodrigueza, Los Alamos National Laboratory

3:15 Break

3:30 347. *ALKYLATION OF AROMATICS AT SUPER-CRITICAL CONDITIONS; A PARAMETRIC AND In Situ SPECTROSCOPIC INVESTIGATION.* Daniel M. Ginosar, Christopher E. Bunker, Robert V. Fox, Kyle Coates, Idaho National Engineering & Environmental Laboratory

4:00 348. *NMR DETECTION AND IMAGING OF GAS PHASE MICELLES.* Daivd E. Fremgen, Rex E. Gerald II, Robert J. Klingler, Jerome W. Rathke, Argonne National Laboratory

4:30 Closing remarks and adjournment

349. *SUPERCRITICAL CARBON DIOXIDE PROCESSING CONSIDERATIONS TO PRODUCE CEMENT-BASED, CHEMICALLY BONDED CERAMICS.* Roger H. Jones, the Supramics Company (Poster Only)

DOI: https://doi.org/10.56902/RMCMR.1999.41.1

Plenary Lecture

Tuesday, August 3, 1999
1:30 p.m.

Presented by Professor M. Bonner Denton, University of Arizona

ADVANCES IN THE APPLICATION OF ARRAY DETECTORS FOR IMPROVED CHEMICAL ANALYSIS FROM X-RAY TO IR.

Today's increasing demands for greater sensitivity, enhanced selectivity, improved accuracy and higher sample throughput provide a strong incentive for continued developments in spectroscopic instrumentation. The impact of recent technological breakthroughs in array detectors, optical components and new geometries of optical systems will be discussed. Application of a number of these technological advances and how they are and will be used to provide improved spectroscopic capabilities will be the major topic of this presentation. Atomic spectroscopy has benefited from new capabilities and acquisition of complex databases, providing improved accuracy and sensitivity. Innovative applications of array detectors are solving significant problems in Laue x-ray crystallography and promise to provide complete crystallographic structures in minutes. Raman spectroscopy has benefited from tremendous advances in sensitivity. Imaging spectroscopies employing fluorescence, absorption and Raman are providing entirely new insights into real world chemical systems. Each of these areas will be discussed and data will be presented showing recent advances.

Biographical Information

M. Bonner Denton, Professor, University of Arizona, has research interests that include applying the latest technological advances in electronics, physics, optics, astronomy, acoustics, mechanical engineering and computer science in developing new and improved methods of chemical analysis and automation. A multifaceted but strongly interlocking program ranging from new frontiers of mass and plasma emission spectrometry through intelligent instrumentation is currently being conducted by an eighteen-member research group. Emphasis is placed both on gaining improved fundamental knowledge and on the application of theoretical concepts for improved analysis of real world samples. Research projects currently underway include selective single photo ionization of complex real world mixtures, studies of new modes of radio frequency only quadruple mass spectrometry operation, new hollow anode cathode discharges as spectroscopic sources, use of charge injection array detectors in new classes of intelligent instrumentation, charge-coupled array detectors in rapid scan and low photon flux spectroscopy, studies of fundamental excitation phenomena in inductively coupled plasma discharges as a function of pressure, element selective detection in both gas and liquid chromatography and new modes of automation utilizing improved sample handling methods.

Professor Denton received a Bachelor of Science degree in Chemistry and a Bachelor of Arts degree in Psychology from Lamar University in Beaumont, Texas. He then attended the University of Illinois Champaign-Urbana where he worked for Howard Malmstadt conducting a variety of research in flame spectroscopy, automation and instrumentation. Upon receiving his Ph.D. degree in Analytical Chemistry, he moved to the University of Arizona, Tucson, Arizona, where he attained full professorship in 1980. He has received a variety of honors, including an Alfred P. Sloan Research Fellowship, Outstanding Young Men of America Award, the 1989 ACS Division of Analytical Chemistry Award in Chemical Instrumentation, the 1991 Society for Applied Spectroscopy's Lester Strock Award, and the 1998 Pittsburgh Spectroscopy Award of the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, and has served as tour speaker for the American Chemical Society for Applied Spectroscopy.

41ST ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

Abstracts

1. *ATOMIC FLUORESCENT MERCURY ANALYSIS USING A METHOD 1631 COMPLIANT INSTRUMENT.* Keith W. Ballantyne, Genesis Laboratory Systems, Inc., P.O. Box 1484, Palisade, CO, 81526; Brian N. Radford, Genesis Laboratory Systems, Inc.

The introduction of a new EPA Method (1631) allowing mercury determination by atomic fluorescence will enable significant advances in reportable detection limits. These advances will push required method detection limits far below the levels of currently available instruments. This paper describes the new method and provides information about implementing method 1631 at your laboratory. It includes data gathered from GLSIís new mercury analyzer that was developed specifically for use with method 1631.

Atomic Spectroscopy Oral Session—Keith Ballantyne, Genesis Laboratory Systems, Inc., 385 Hill View Drive, Grand Junction, CO, 81503, (970) 241-0889, fax: (970) 245-9593, HYPERLINK mailto: keith@gj.net keith@gj.net.

2. *DISTRIBUTION OF INORGANIC MERCURY IN SACRAMENTO RIVER WATER AND SEDIMENTS USING ATOMIC FLUORESCENCE SPECTROMETRY.* D.A. Roth, H.E. Taylor, U.S. Geological Survey

No abstract.

3. *FIELD SCREENING MEASUREMENT OF CR AND PB IN SOILS: A NEW TECHNOLOGY.* A.J.R. Hunter, Physical Sciences, Inc., 20 New England Business Center,œAndover, MA 01810-1077, L.G. Piper, M.E. Fraser, S.J. Davis, Physical Sciences, Inc.

A quantitative on-site monitor has been developed for the measurement of metals in soils usingœspark-induced breakdown spectroscopy (SIBS). The method uses direct excitation of the soilœsurface with a robust electrically generated spark. The plasma creates excited states of the metalsœwithin the sample, and subsequently, the fluorescence from these states is used to identify the metals. The measurement is made quantitative by the application of standard addition analysis. We will report on the use of this method and technology on a variety of soil types, includin cross-checks with independent analytical laboratories and standard reference materials.

Atomic Spectroscopy Oral Session—Amy J. R. Hunter, Physical Sciences, Inc., 20 New England Business Center, Andover, MA 01810-1077, (978) 689-0003, fax: (978) 689-3232, hunter@psicorp.com

4. *SENSITIVITY ENHANCEMENT OF METALS USING A CONCOMITANT HYDRIDE GENERATOR WITH ICP-AES.* Tina R. Harville , Instruments S.A. Inc., JY Emission/HORIBA Group, 3880 Park Ave. Edison, NJ 08820; Albert Brennsteiner , Instruments S.A. Inc., JY Emission/HORIBA Group, 3880 Park Ave. Edison, NJ 08820; Agnes Cosnier, JY Emission/HORIBA Group, 16-18 Rue du Canal, Longumeau Cedex FRANCE

Elemental analysis by inductively-coupled plasma atomic emission spectrometry (ICP-AES) is used in many different types of applications, ranging from environmental to industrial. For many applications trace analysis is preferred for determining contamination levels, with detection limit requirements reaching lower and lower levels. A patented hydride generator allows sensitivity improvement by a factor of 20-30, and unlike other hydride generators it allows the analysis of all other elements (non hydride-forming) in the same analysis. In terms of sample preparation, no acidification prior to the analysis is required. The influence of acid concentration and other parameters will be shown, as well as detection limits for many elements of interest such as Hg, As, and Se in various matrices. The effect of the initial oxidation state on hydride generation efficiency will also be discussed.

Atomic Spectroscopy Oral Session—Tina Harville, Instruments S.A. Inc. JY Emission/HORIBA Group, 3880 Park Ave. Edison, NJ 08820, (732) 494-8660, fax: (732) 494-8796, Tina_Harville@isainc.com

5. *DETERMINATION OF LEAD IN A CALCIUM CARBONATE MATRIX BY GFAA.* G.R. Dulude, D.L. Pfeil, G.N. Coleman, Thermo Jarrell Ash

No abstract.

DOI: https://doi.org/10.56902/RMCMR.1999.41.1

6. *COMPUTER SIMULATIONS OF ATOMIC AND MOLECULAR SPECIES WITHIN A GRAPHITE FURNACE ATOMIZER.* Gary D. Rayson and Kowit Sae-tueng, Department of Chemistry and Biochemistry, New Mexico State University, Box 30001 MSC 3C, Las Cruces, NM

Graphite furnace atomizers enable the detection of parts per trillion concentrations of metals in microliter aliquots. However, these atom reservoirs are often problematic when using atomic absorption detection. Chemical matrix modifiers are routinely used to alleviate these difficulties but their selection and implementation can be time-consuming and frustrating for the analyst. In an effort to better understand the chemical interaction occurring within the gas phase of the graphite furnace atomizer, a theoretical model for the analyte species density inside the furnace has been developed. It is based on the existence of local gaseous chemical equilibrium with kinetic controlled graphite surface interactions with diffusion and convection mass transport mechanisms. Within the simulation, a Massman-style furnace atomizer is divided into 247 isothermal spatial zones that are assumed to be at local thermodynamic equilibrium during short (10 ms) time increments. The interactions of gaseous oxygen and the analyte with the graphite surface are treated as kinetically controlled processes. Because of the large number of zones and the small time increment within the simulation, it is possible to incorporate the impact of spatial and temporal temperature gradients. Specific parameters of this simulation and the comparison of its output with experimentally measured absorbance profiles will be described. The application of this tool to the understanding of the impact of sample matrix concomitants on the measured atomic absorbance signal will be discussed.

Atomic Spectroscopy Oral Session—Gary D. Rayson, New Mexico State University, Box 30001 MSC 3C, Las Cruces, NM 88003, (505) 646-5839, fax: (505) 646-2649, garayson@nmsu.edu

7. *TRACE ANALYSIS OF TUNGSTEN BY DIRECT CURRENT PLASMA SPECTROMETRY.* R. Starek, G.N. Coleman, Thermo Jarrell Ash

No abstract.

8. *A COMPARISON OF METHODS FOR DETERMINATION OF DETECTION LIMITS.* Greg W. Johnson, Matheson Gas Products, 1861 Lefthand Circle, Longmont, CO 80501; Jude O. Proctor, Matheson Gas Products, 1861 Lefthand Circle, Longmont, CO 80501; and Virginia H. Houlding, Matheson Gas Products, 1861 Lefthand Circle, Longmont, CO 80501.

Matheson Gas Products is a world leader in the specialty gases industry. Matheson Gas Products Branch 196 in Longmont, Colorado, is the worldís leading producer of the highest quality Tungsten Hexafluoride available. As a minimum, every production lot of product is routinely subjected to the most rigorous chemical analyses. One of these analyses is an examination of the metals composition of residue samples resulting from WF6 evaporation. In addition, several other Matheson Gas Products gases are examined at Branch 196 for metals content as one of several quality assurance tests run on them. As a procedure performed each year, the metals lab determines the Method Detection Limits (MDLís) exhibited by the instrumentation used for these analyses. Analysis techniques, instrumentation models, and manufacturers used in the metals lab are as follows: Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) using a model PQI manufactured by VG Elemental; Flame Atomic Emission done on a model 8100 Zeeman Corrected Atomic Absorption Spectrophotometer manufactured by Hitachi; Graphite Furnace Atomic Absorption (GFAA) performed on the Hitachi instrument; and ICP/Optical Emission Spectrometry equipped with an UltraSonic Nebulizer (ICP/OES-USN). The ICP/OES unit is a model PS1000 manufactured by Leeman Labs while Precision International (PI) manufactures the ultrasonic nebulizer used with it. Collectively, the instrumentation provides the capability of detecting concentrations of over sixty elements in aqueous solution at the sub part per billion ((g/L) level. The MDLís are determined using accepted Semiconductor Equipment and Materials International (SEMI) protocol. For the first six years the MDLís were determined in our lab, SEMI C10-94 protocol was used. SEMI C10-94 uses Ordinary Least Squares (OLS) regression statistics for computations. Within the last fourteen months, SEMI C10-0698 has been available for MDL determination. Weighted Least Squares (WLS) regression statistics form the computational basis of the more recent method. With the advent of SEMI C10-0698, the SEMI C10-94 designation has been changed to SEMI C10-94.1. For our most recent MDL determination, SEMI C10-0698 was used. The MDLís were found to improve for over eighty percent of the elements, with new record low MDLís noted for over fifty elements. Some of the improvements were factors of more than thirty, with our lowest MDL to date noted for U at 0.004 (g/L. The purpose of the presentation is to present the MDLís determined using OLS versus WLS, and discuss some of the reasons behind the improvements we have observed using the WLS statistics.

Atomic Spectroscopy Oral Session—Greg W. Johnson, Matheson Gas Products, 1861 Lefthand Circle, Longmont, CO 80501, phone 303-678-0700 extension 312, fax 303-442-0711, e-mail either HYPERLINK mailto:gjohnson@mathesongas.com

9. *DETECTION OF SURFACE BOUND BIOMOLECULES AT ATTOMOLE CONCENTRATIONS USING A UNIQUE COMBINATION OF ELECTROCHEMISTRY, CAPILLARY ELECTROPHORESIS, AND LASER INDUCED FLUORESCENCE.* Lorna Pehl Hunter, University of Wyoming, Department of Chemistry, P.O. Box 3838, Laramie, WY 82071; Shauna Hiley, Missouri Western State College, 4525 Downs Drive, St. Joseph, MO 64507; Guoying Chen, University of Wyoming, Department of Chemistry, P.O. Box 3838, Laramie, WY 82071; Daniel A. Buttry, University of Wyoming, Department of Chemistry, P.O. Box 3838, Laramie, WY 82071

Our laboratory is developing a unique approach to detecting biomolecules at low concentrations. A monolayer with a functional tail group is immobilized from solution on the surface of a gold microelectrode. Fluorescently labeled biomolecules are chemically attached to the self-

assembled monolayer. The electrode is inserted in a specially designed electrochemical cell, which allows the source end of a capillary in a capillary electrophoresis system to be positioned directly over the electrode. Once the capillary is correctly positioned the biomolecules are electrochemically desorbed and, since the distal end of the capillary is lower than the source end, the molecules are hydrodynamically swept into the source end of the capillary. The capillary is then moved to the source vial and capillary electrophoresis performed. The biomolecules are detected at the distal end of the capillary using laser induced fluorescence.

Electrochemistry Oral Session—Lorna Pehl Hunter, University of Wyoming, Department of Chemistry, P.O. Box 3838, Laramie, WY 82071, (307) 766-3041, fax: (307) 766-2807, lhunter@uwyo.edu

10. *FTIR SPECTROSCOPIC INVESTIGATION OF LONG-CHAIN ALKYL THIOL DERIVATIVES AND THE RELATIONSHIP TO INTERFACIAL CAPILLARY ELECTROPHORESIS.* Richard C. Martoglio, University of Wyoming, Department of Chemistry, Laramie, WY 82071; Daniel A. Buttry, University of Wyoming, Department of Chemistry, Laramie, WY 82071; Guoying Chen, University of Wyoming, Department of Chemistry, Laramie, WY 82071

The focus of our research entails the coupling of a gold microelectrode to capillary electrophoresis (CE) instrumentation. The microelectrode supports a monolayer of long-chain alkyl thiols that can be modified with a fluorescent species. The microelectrode electrochemically desorbs small amounts of the fluorescent molecule. The molecules are then immediately introduced to the CE device for analysis and quantification. In these studies the thiol is most often adsorbed to the gold surface prior to the chemical modification (coupling chemistry). The coupling chemistry typically involves a series of synthesis procedures to obtain the desired molecular configuration. Exploring the nature of the coupling chemistry is essential when interpreting experimental results. By duplicating the coupling chemistry on a macro scale and employing FTIR reflectance spectroscopy a better understanding of the chemistry that is involved in these CE experiments has been achieved.

Electrochemistry Oral Session—Richard C. Martoglio, University of Wyoming, Department of Chemistry, Laramie, WY 82071, phone 307-766-3041, fax 307-766-2807, ricardo@uwyo.edu

11. *ROTATING RING-DISK ELECTROCHEMICAL STUDY OF ION TRANSPORT IN POLY(PYRROLE) FILMS.* Corey A. Salzer and C. M. Elliott, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

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

Electrochemistry Oral Session—Corey A. Salzer, Colorado State University, Department of Chemistry, Box 102, Fort Collins, CO, 80523, phone 970-491-5435, fax 970-491-1801, salzec@lamar.colostate.edu

12. *NEW POLYMER ELECTROLYTES BASED UPON POLYVINYLACETATE BLENDS.* Radha Pyati and Shane Karnik, University of Colorado at Colorado Springs, Department of Chemistry, Colorado Springs, CO 80933-7150.

The need for solid and semi-solid polymer electrolytes for batteries has driven the exploration of various polymers as possible solvent systems. To this end, new polymer electrolytes based upon polyvinylacetate blends have been developed, characterized and optimized. Voltammetry and conductivity studies of these materials will be presented. Optimization of the blends for the best conductivity will be discussed. The effects of temperature, plasticizer and electrolyte concentration will be shown.

Electrochemistry Oral Session—Radha Pyati, University of Colorado at Colorado Springs, Department of Chemistry, Colorado Springs, CO 80933-7150, (719) 262-3229, fax: (719) 262-3047, rpyati@mail.uccs.edu.

13. *DYNAMICS OF CHARGE COMPENSATION IN REDOX PROCESS OF POLY(ANILINE-CO-N-PROPANESULFONIC ACID ANILINE), (PAPSAH) IN ORGANIC MEDIA.* Hamilton Varela and Roberto M. Torresi, Universidade de Sao Paulo, Instituto de Quimica de Sao Carlos, Caixa Postal 780 - 13560-970 Sao Paulo - SP, Brazil; Daniel A. Buttry, Department of Chemistry, University of Wyoming (UW), Laramie, Wyoming 82071-3838, USA

The study of the dynamics of charge compensation in redox process of modified electrodes with PAPSAH was carried out using an electrochemical quartz crystal microbalance (ECQM) associated with cyclic voltametry (CV) and electrochemical impedance spectroscopy (EIS). The incorporation of the side groups to polyaniline has enhanced its solubility and changed its physico-chemical properties. In this case we used the (CH2)3SO3H group linked to the polymer chain. PAPSAH was characterized using elemental analysis, UV-vis and FTIR. The cation participation in the redox process was estimated as an essential feature for rechargeable lithium battery. The films were obtained by solvent evaporation and the results were compared with electropolymerized polyaniline films. The experiments were carried out in propylene carbonate (PC) and acetonytrile (ACN), using LiClO4, NaClO4 and [(C4H9)4N]ClO4 as electrolytes. The results show that the cation par-

ticipation was enhanced in order of 1.4 times in comparison with Pani films, in addition, the solvent influence was estimated and indicates that the swelling process is more important in PC that in ACN solutions. By the using of EIS, we can analyze the capacitance effect observed in conducting polymers in terms of an ionic relaxation mechanism. Part of the ions involved in the charge compensation process exhibit a relatively short relaxation time. They can follow the low frequency ac signal and they are responsible for the capacitance effect. Another part of the doping ions appears to be deeply trapped in the polymer chain. They do not follow the ac signal and have not any contribution to the capacitance. We can divide the process in two contributions: one arising from ions deeply trapped in the polymer chain, called "capacitive current", and other called "non capacitive current" arising from ions shallowly trapped in the polymer chain giving a large hysteresis. Supported by FAPESP, CNPq (Brazilian agencies) and NSF.

Electrochemistry Oral Session—Hamilton Varela, Universidade de Sao Paulo, Instituto de Quìmica de Sao Carlos, Caixa Postal 780 ñ 13560-970 Sao Paulo SP, Brazil; fax: 55-16-2739952, varela@iqsc.sc.usp.br

14. *NOVEL V2O5 COMPOSITES FOR SECONDARY LITHIUM ION BATTERY APPLICATIONS.* Kevin C. White, University of Wyoming, Department of Chemistry, P.O. Box 3838, Laramie, WY 82071-3838; Daniel A. Buttry University of Wyoming, Department of Chemistry, P.O. Box 3838, Laramie, WY 82071-3838

The facilitation of lithium cation intercalation into metal oxide hosts represents the major impetus for studies concerned with the improvement of these materials for use as cathodes in rechargeable battery systems. Our research focuses on manipulating the morphology of vanadium pentoxide (V2O5) in an attempt to understand the relationship between layer spacing and the diffusion rate of Li+ in the system. This lamellar material is attractive due to its ability to reversibly intercalate Li+ into its matrix during reduction of the vanadium sites. Unfortunately the rate at which Li+ diffuses in V2O5 is very slow and this adversely affects the charge and discharge characteristics of a battery system using V2O5 as the cathode. We propose the diffusion rate of the Li+ ions in the system can be increased by controlling the distance between the layers of the V2O5 matrix by the insertion of molecular pillars. Desired traits for these pillars include minimal contribution to mass, charge storage capability in the voltage range of interest, n-type doping upon intercalation to electrostatically accommodate Li+ and the ability to control the amount of intercalated pillaring material in the V2O5 matrix. Cyclic voltametric data indicate a remarkable improvement in the Li+ intercalation/expulsion response for V2O5 intercalated with poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]} indicating it may be a viable candidate for a secondary lithium ion battery cathode material. A discussion of the characterization of this composite by electrochemistry, infrared spectroscopy, and UV-Vis spectroscopy will be presented along with testing of this material in half and full cells representative of actual battery applications

Electrochemistry Oral Presentation—Kevin C. White, University of Wyoming, Department of Chemistry, P.O. Box 3838, Laramie, WY 82071-3838, (307)766-3041, fax: (307)766-2807, whitek@uwyo.edu

15. *NMR SPECTROSCOPY AND IMAGING OF AN ELECTROCHEMICAL CELL WITH A CARBON WORKING ELECTRODE.* Rex E. Gerald II, Giselle Sandì, Robert J. Klingler, Jerome W. Rathke, Chemical Technology and Chemistry Divisions, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439-4873, USA

An electrochemical cell of cylindrical geometry was incorporated into a toroid cavity nuclear magnetic resonance (NMR) detector for in situ electrochemical studies. A cylindrical rod composed of glassy carbon was used as the working electrode located at the center of the cell. An insulated conductor placed along the center of the carbon rod served as the NMR detector element. A strip of lithium metal in contact with a platinum coil was used as the counter electrode. One molar LiPF6/(EC+DEC) was used as the electrolyte. The combined electrochemical cell/NMR detector apparatus was used to investigate the different 7Li NMR signals observed for the cell. Prior to charging the cell, the 7Li NMR spectrum showed four peaks: A, 0.0 ppm; B, 3.6 ppm; C, 15.1 ppm; D, 285†ppm. After passing incremental amounts of charge through the cell two additional Li peaks were observed to grow in: E, 267 ppm; F, -10.2 ppm. The application of the toroid cavity detector as a near-electrode imager provided the spatial disposition of the different peaks in the NMR spectrum. Thus, the following peak assignments were made: peak A, Li+ next to the surface of the carbon electrode; peak B, Li+ in the center of the cell; peak C, Li+ near the platinum electrode; peak D, Li-metal strip; peak E, dendritic Li-metal on the surface of the carbon electrode; peak F, Li+ near the platinum electrode and extending toward the center of the cell. The glassy-carbon cell was designed as the control cell for a series of experiments that will compare different carbon electrodes, including graphitic carbon and several synthesized carbons. We will describe the NMR methodology that was used to make the spatial assignments for the different lithium chemical shifts that were observed in the Li-NMR spectrum. We will also discuss the utility of this approach for investigations of Li+ intercalation into carbon materials. 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.

Electrochemistry Oral Session—Rex E. Gerald II, Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439-4873, phone (630) 252-4214, fax (630) 972-4458, gerald@cmt.anl.gov

16. *MOLECULAR TRACERS OF ORGANIC MATTER SOURCES TO DRINKING WATER SUPPLIES.* Standley, L. J., Kaplan, L. A. Stroud Water Research Center, Avondale, PA., and Smith, D., South Central Connecticut Regional Water Authority

Sources of organic matter (OM) to ground and surface waters are of concern to the drinking water industry for several reasons. The presence of organic matter in drinking water supplies may promote regrowth of pathogenic microorganisms in distribution systems and be transformed into toxic byproducts during disinfection. Thus, this industry is interested in promoting best management practices in source watersheds to reduce use of disinfectants and improve quality of their drinking water supplies.

For this project, we investigated the utility of various compounds for use as molecular tracers of OM sources in drinking water supplies. Sources of interest included waste water treatment plants (WWTP), agricultural/feed-lot runoff, urban/suburban runoff, and nature (i.e. wildlife). After analysis of tracers in source materials by mass spectrometry, we selected the following tracers: fecal steroids, laundry detergent fragrances, caffeine, nonylphenols (NPs), polycyclic aromatic hydrocarbons (PAH), n-alkanes, and the unresolved complex mixture (UCM). Results were then correlated with measures of land-use obtained through surveys of drinking water utilities.

Samples (4L) were filtered and then extracted using C-18 disks. Tracers were quantified using gas chromatography/mass spectrometry, with selected ion monitoring to improve sensitivity.

Tracers associated with WWTP effluent, including 5b/[b+a]-cholestan-3b-ol, fragrances, and caffeine, correlated well with each other, as did groups of molecular tracers targeted for other sources. Tracers also correlated with land-use values associated with their target source. For example, WWTP molecular tracers correlated with variables such as waste water discharge and combined-sewer overflows. Urban tracers such as UCM correlated with transportation and other urban measures.

When the twenty watersheds were ranked according to increasing urban and agricultural influence using their molecular tracers, the influence of natural sources decreased, as would be expected where anthropogenic activity is greater. Key Words: molecular tracers, natural organic matter, fecal steroids, land-use, mass spectrometry

Environmental Chemistry Oral Session—Laurel J. Standley, Stroud Water Research Center, 970 Spencer Road, Avondale, PA 19311, 610-268-2153 (ext. 229), fax: 610-268-0490, ljstandley@stroudcenter.org

17. *ANALYSIS OF SULFONYLUREA, IMIDAZOLINONE, AND SULFONAMIDE HERBICIDES IN WATER SAMPLES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY/ELECTROSPRAY IONIZATION-MASS SPECTROMETRY.* P.M. Gates, S.L. Werner, E.T. Furlong, and M.R. Burkhardt, U.S. Geological Survey, National Water Quality Laboratory, Methods Research and Development Program, Box 25046 Federal Center, MS 407, Denver 80225-0046

Sulfonylurea (SU), imidazolinone (IMI), and sulfonamide (SA) herbicides, postemergent herbicides used in the Midwestern United States, affect both weed and crop species at concentrations of about 100 ng/L (nanograms per liter) or greater in soil and water. The solubility of these herbicides in water suggests a potential for long-range transport in surface water and ground water. The isolation and detection of these compounds represent a substantial challenge, because they are labile, very polar, and applied at low rates, at about 0.01 compared to 0.20 kg per hectare for atrazine. A two-cartridge, solid-phase extraction method was developed to preconcentrate 12 SU, 3 IMI, and 1 SA herbicides from environmental water samples. Isolated analytes were identified and quantified by high-performance liquid chromatography/electrospray ionization-mass spectrometry. Method detection levels were 10 ng/L for all analytes. Analyte recoveries from 27 reagent-water samples spiked at 50 and 100 ng/L averaged 73% with an average standard deviation of 20%. This variability reflects multiple instruments, operators, and the use of automated and manual sample preparation. Spiked environmental water samples had similar recoveries, although for some analytes, the sample matrix enhanced response by as much as 200%. This matrix enhancement was sample and compound dependent. Concentrations of analytes in unspiked, duplicate, environmental samples were typically within 25% of each other. From May to August, 1998, 196 surface- and ground-water samples, collected throughout the Midwestern United States, and more than 150 quality-assurance/quality-control samples were analyzed. Five analytes were detected in more than 24% of all environmental samples. In surface-water samples, the three most frequently detected analytes were imazethapyr (71%), flumetsulam (63%), and nicosulfuron (52%). Average concentrations of these three herbicides ranged from 11 to 92 ng/L. Six other analytes were measured in 2 to 24% of samples.

Environmental Chemistry Oral Session—Paul Gates, U.S. Geological Survey, National Water Quality Laboratory, Box 25046 Federal Center, MS 407, Denver, CO 80225-0046, phone 303-236-3958, fax 303-236-3499, pmgates@usgs.gov

18. *CONTINUING EFFORTS TO REMOVE MTBE FROM A DRINKING WATER RESERVOIR.* M.W. Tikkanen, and R.G. Sykes, East Bay Municipal Utility District, 375 11th Street, Oakland, CA 94607

East Bay Municipal Utility District (EBMUD) provides drinking water to 1.2 million people in 20 cities and 15 unincorporated communities in the California East Bay area. EBMUD has three reservoirs in the East Bay area and in the Sierra Nevada foothills that are drinking water sources upon which recreational motorized activity is permitted. Since 1997, monitoring on these reservoirs has indicated a direct correlation between this activity and the occurrence of the gasoline additive methyl tertiary butyl ether (MTBE) in these reservoirs. In 1998 all District owned and concessionaire owned 2-stroke marine engines that were used on these reservoirs were replaced with 4-stroke marine engines. Monitoring results have shown a particularly dramatic decrease in the concentration of MTBE in the San Pablo reservoir. Results from these occurrence studies will be presented. Other actions taken by EBMUD to eliminate gasoline contamination of these reservoirs will be detailed. The recent California regulation establishing a secondary drinking water standard based on taste and odor will also be discussed.

Environmental Chemistry Oral Session—Maria Tikkanen, MS 606, East Bay Municipal Utility District, 375 Eleventh Street, Oakland, CA 94607, (510) 287-1561, fax (510) 287- 0663, mtikkane@ebmud.com

19. ***DEVELOPMENT OF A SPARGING TECHNIQUE FOR ANALYSIS OF CHLORINATED HYDROCARBONS IN INDUSTRIAL WASTEWATER USING ATR-FTIR SPECTROSCOPY.*** Fiona Regan and Ambrose Hayden, Department of Applied Science, Limerick Institute of Technology, Moylish Park, Limerick, Ireland. E-mail: fiona.regan@lit.ie; Peter McLouglin, Department of Chemical and Life Sciences, Waterford Institute of Technology, Cork Road, Waterford, Ireland.

Chlorinated hydrocarbons are extremely stable industrial compounds. Many have been used as solvents and cleaning agents for various industrial processes and in the production of refrigerants. Some of the compounds have been linked to cancers and birth defects. Both chloroform and carbon tetrachloride have been detected in trace quantities in drinking water in Europe and the U.S. as a result of the chlorination step in water sanitation. Increasing concern about these chlorinated hydrocarbons in air and water has led to developments of new techniques for their analysis Mid-infrared optical techniques are powerful and well established analytical methods for monitoring and identifying chemical species. This work investigates the influence of a selective polymer cladding surrounding an internal reflection element in detecting harmful chlorinated hydrocarbons in aqueous samples using the attenuated total reflection - Fourier Transform infrared (ATR-FTIR) spectroscopy. These chlorinated hydrocarbons of interest are often difficult to quantify as they absorb strongly in the mid-infrared (MIR) or fingerprint region of the spectrum. Also aqueous samples can prove difficult to analyse due to strongly absorbing hydroxyl bonds. These problems are alleviated using a polymer coating on the internal reflection element. A zinc selenide (ZnSe) crystal is coated with poly (isobutylene). This polymer serves to enrich the analytes of interest while eliminating interfering species in the sample. Aqueous solutions however, have proven to present problems with polymer swelling, thereby greatly decreasing polymer life-time. This has been overcome by using an air sparging technique for sample delivery, which prevents contact of the polymer film with water. An important advantage of this technique it that it prevents any interference from characteristic water bands which interfere with quantitation.

The technique has been applied to the analysis of residual solvents in pharmaceutical preparations and analysis of industrial wastewater samples. Detection limits in the low ppm region have been achieved for a range of chlorinated solvents, notably, trichloroethylene, tetrachloroethylene, monochlorobenzene, dichlorobenzene and chloroform.

Environmental Chemistry Oral Session—R. Krska, K. Taga, R. Kellner, Appl. Spectrosc., (1993) 47, 1484. ; F. Regan, B. D. MacCraith, J. E. Walsh, K. O'Dwyer, J. G. Vos and M. Meaney, Vibrat. Spectrosc., (1997) 14, 239.

20. ***ELEMENTAL ANALYSIS OF AMBIENT WATER USING A MAGNETIC SECTOR ICP-MS.*** Rob Henry, VG Elemental, 1812 Mapleton Avenue, Boulder, CO 80304, USA; Dagmar Koller, VG Elemental, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, England.

Ambient waters found in lakes, rivers and streams are hopefully very clean. Ambient waters are monitored in the USA to establish a database for following trends in potential pollution or remediation activities. In order to establish a good database it is necessary to have accurate ëbaselineí data for an extensive range of elements, which, depending on the sampling site may occur over a wide range of concentrations from low ng/L to high mg/L levels. Currently several analytical techniques are required to exactly define the water characteristics of matrix and ultratrace elements. The VG Axiom, Magnetic Sector ICP-MS, is capable of rapidly collecting data at optimum resolution for each analyte in a single analysis cycle for almost all routinely reported elements. Its extremely wide dynamic range (109) and excellent detection capability (< ng/L for most elements) meet the criteria for successful ambient water analysis. A Magnetic Sector ICP-MS used in high resolution mode eliminates these interferences and has favorable signal:noise characteristics even at high resolution. Ambient water analysis using High Resolution ICP-MS also allows the analyst to report accurate data for ëdifficultí elements such as the halogens, sodium, silicon, potassium, phosphorus and sulfur. In addition ëtraceí elements such as lead, silver, cadmium, antimony, arsenic, selenium and mercury can be analyzed accurately at the levels existing in these waters. A protocol was developed to demonstrate the effectiveness of using High Resolution ICP-MS to meet the Data Quality Objectives of the water industry and a range of samples and standards analyzed to demonstrate the analytical performance.

Environmental Chemistry Oral Session—Rob Henry, VG Elemental, 1812 Mapleton Avenue, Boulder, CO 80304, (303) 939-9012, fax: (303) 939-9017, RHenry1812@aol.com

21. ***MULTI-CLASS PESTICIDE RESIDUE ANALYSIS BY SOLID-PHASE EXTRACTION AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY/ELECTROSPRAY IONIZATION-MASS SPECTROMETRY.*** Stephen L. Werner, Bruce D. Anderson, Laura J. Coffey, Mark R. Burkhardt, and Edward T. Furlong, National Water Quality Laboratory, U.S. Geological Survey, Denver, CO 80225

As part of the U.S. Geological Surveyís National Water-Quality Assessment Program, we developed a multiclass pesticide method using high-performance liquid chromatography (HPLC) separation and electrospray ionizationñmass spectrometry for compound-specific detection and quantitation. The 64 pesticides chosen include carbamate insecticides, triazine herbicides and their degradation products, and phenoxyacetic acids. These pesticides were polar and labile, making HPLC the best method for separation. Electrospray ionization was the preferred identification and quantitation method because it provided the greatest sensitivity and selectivity compared to optical methods. Pesticides were isolated from 1-liter water samples using a styrene-divinyl benzene sorbent. A strong anion exchange (SAX) cartridge was used in tandem with the styrene-divinyl benzene cartridge for on-line removal of humic substances and other chemical interferences. The isolated herbicides were concentrated to 500 microliters to improve detection. Reverse-phase HPLC analysis was performed using a 2-mm x 150-mm (millimeter) C-18 reversed-phase column. For most pesticides, detection, confirmation, and quantitation are achieved using electrospray mass spectrometry in either postitive or negative mode. Fragmentation conditions in the electrospray source were controlled so that three characteristic positive ions were produced for each compound. Selected-ion monitoring was used to maximize sensitivi-

ty. For those pesticides that do not exhibit satisfactory mass spectral response, in-line photodiode-array detection is used. All 64 pesticides were separated in less than 65 minutes using a formate-modified, water-acetonitrile gradient. Initial tests indicate that the 64 pesticides can be detected at individual concentrations as low as 10 to 50 nanograms per liter. Method recovery efficiencies of greater than 70 percent were determined for most pesticides.

Environmental Chemistry Oral Session—Stephen L. Werner, National Water Quality Laboratory, U.S. Geological Survey, Denver, CO 80225

22. *PHOTOOXIDATION OF ORGANIC CHEMICALS USING SEMICONDUCTOR NANOCLUSTERS.* J.P. Wilcoxon, Organization 1152, Sandia National Labs, Albuquerque, NM 87185-1421

Contamination of water by aromatic and chlorinated aromatic chemicals is a widespread problem both in the DOE complex and industry in general. Because of the vast volumes of water involved any viable solution will require use of very inexpensive (i.e. free) energy resources. Semiconductor materials like TiO2 are known to be capable of room temperature photocatalytic oxidation of many organics to CO2 and dilute mineral acids (e.g. HCl). However, many technical problems still must be overcome to use these bulk powders are catalysts, chief being their inefficient absorbance of solar light at sea level (~3%). We have been developing and testing novel nanosize semiconductor particles as visible light photocatalysts. In addition to their large specific surface areas, nanoclusters often have unusual surface morphologies and bonding arrangements which can make them effective catalysts. As an example of photocatalysis we discuss the photo-oxidation of organic pollutants using such nanoclusters as MoS2 and SnO2. We have demonstrated that we can vary the redox potentials of these small semiconductors by adjusting their size and studies of the photooxidation of organic molecules have revealed that the rate of oxidation increases with increasing bandgap (i.e. more positive valence band and more negative conduction band potentials). Moreover, when combined with TiO2 as a support material we have sucessfully oxidized phenol using only visible light (>450 nm) and d=8 nm MoS2 with an absorbance onset of ~700 nm. Because these photocatalysis reactions can be performed with the nanoclusters fully dispersed and stable in solution, liquid chromatography can be used to determine both the intermediate reaction products and the state of the nanocluster during the reaction. We have demonstrated that the MoS2 nanoclusters remain unchanged during the photooxidation and that they have better efficiency for PCP photo oxidation than the best TiO2 photocatalysts available, even using only visible >400 nm light.

Environmental Chemistry Oral Session—J.P. Wilcoxon, Organization 1152, Sandia National Labs, Albuquerque, NM 87185-1421

23. *INVITED SPEAKER IN ENVIRONMENTAL CHEMISTRY—SPECIATION OF ARSENIC IN DIETARY SOURCES.* E. D. Pellizzari, Q. Akinbo, R. Fernando, and J. Raymer, Research Triangle Institute, Analytical and Chemical Sciences Unit, P.O. Box 12194, Research Triangle Park, NC 27709

The contribution of diet sources to arsenic exposure is an important piece of information to consider as reductions in the allowable drinking water concentrations are contemplated. Furthermore, the toxicity of arsenic species are not equivalent requiring methods to measure its forms. We are investigating the distribution of toxic arsenic species in composite duplicate diet, drinking water, and urine samples from the EPA Region IV National Human Exposure Assessment Survey (NHEXAS) and from the NHEXAS Children's Exposure Study. To accomplish this goal speciation methods were developed or optimized for a quantifying (1) arsenobetaine (AsB), arsenocholine (AsC), monomethyl arsonic acid (MMA), dimethyl arsinic acid (DMA), arsenite [As(III)], and arsenate [As(IV)] in duplicate diets, (2) AsB, MMA, DMA, As(III), and As(IV) in urine, and (3) MMA, DMA, As(III), and As(IV) in drinking water. Using an anion-exchange separation procedure and detection by ICP-MS, baseline resolution of AsB, AsC, As(III), DMA, MMA, and As(IV) was achieved. The chromatographic conditions to achieve this separation consisted of a Hamilton PRP-X100 Anion exchange column and gradient elution with mobile phase A consisting of 5mM $Na_2CO_3/NaHCO_3$ *(aq), pH7:MeOH, 94:6, v/v and Mobile phase B containing 25 mM* $Na_2CO_3/NaHCO_3$ *(aq), pH7:MeOH, 94:6, v/v, at a flow rate of 1 mL min . Measurement of levels as low as 25 pg for each species (on column) was accomplished. Three food extraction methods were evaluated for their ability to isolate As species from duplicate diet samples. The methods were: (1) MeOH-Water-*$CHCl_3$*, (2) MeOH-Water, and (3) Enzymatic digestion in water (Trypsin-*$(NH_4)_2CO_3$*). A mass balance approach was used to evaluate the extraction efficiency for As species from food composites. Lyophilization, extraction of the powder with acetone and sonication with MeOH-Water yielded the best results. The validated methods are being applied to the analysis of NHEXAS samples, estimate the effects of food preparation methods on their levels, including the cooking of foods in water contaminated with arsenic. These data will be used to examine exposure distributions to As species in EPA Region IV. The coupling of an IC with and the method performance for measuring As species in duplicate diet, urine, and drinking water samples will be presented. Supported by American Water Works Association Research Foundation Project No. 560.*

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24. *IS DISSOLVED URANIUM IN THE LITTLE COLORADO RIVER OF NATURAL OR MINING/MILLING ORIGIN: A 234U/238U STUDY.* M.E. Ketterer; D.L. Hudson; and S.C. Szechenyi, Department of Chemistry, Northern Arizona University, Flagstaff, AZ 86011-5698

Uranium in surface waters is largely present as a result of natural weathering processes, but in specific localized settings the dissolved uranium may be dominated by inputs from mining/milling sources. Throughout the Colorado Plateau region, a large number of potential *point release uranium sources are present, and effective approaches are needed for quantitatively establishing the impact of anthropogenic (mining/milling) vs. natural (background) contributions. The Little Colorado River, which flows through east-central Arizona before joining the Colorado River in the Grand Canyon, constitutes a watershed which is potentially impacted by both of these types of U sources. The issue of whether a specific tailings storage site or mine dump is impacting natural waters is often addressed by comparing local vs. "background" U concentrations, or by looking for elevations in pathfinder elements such as V, Se, and Mo. An additional method of addressing this question is based upon 234U/238U activity measurements. 234U and 238U typically exhibit disequilibrium in surface waters; most often a a slight excess of 234U is present in aqueous phases as a result of a recoil and selective dissolution processes. In contrast, most mining/milling point sources contain U with 234U and 238U present in secular equilibrium, and therefore 234U/238U activity ratios may be used to apportion and distinguish between these sources. We utilize inductively coupled plasma mass spectrometry (ICPMS) as an alternative to radiochemical procedures for obtaining rapid, high-throughput 234U/238U activity ratio measurements in surface waters. Findings regarding sources of dissolved uranium in the Little Colorado River watershed will be presented.*

Environmental Chemistry Oral Session—Michael E. Ketterer, Department of Chemistry, Box 5698, Northern Arizona University, Flagstaff, AZ 86011-5698, (520) 523-7055, fax (520) 523-8111, michael.ketterer@nau.edu

25. *ADVANTAGES OF DUAL-VIEW OPTICS FOR ICP ANALYSIS OF ENVIRONMENTAL SAMPLES.* R.L. Stux, G. Kunselman, R.W. Foster, G.R. Dulude, and G.N. Coleman, Thermo Jarrell Ash Corp. 27 Forge Parkway, Franklin MA 02038

The primary advantage of the axially-viewed ICP, that of enhanced detection limits, has been demonstrated to improve the productivity of the environmental laboratory by allowing the determination of all elemental species, except for Hg, at the levels required by the USEPA. However, axial viewing introduces interferences not found with conventional radial viewing, which must be overcome in order to take full advantage of the ICP. In addition, axial viewing may also limit the upper linear range of some elements, requiring sample dilution.

Plasma loading effects, which are associated with the cooler tail plume of the plasma, cause a suppression of the analytical signal. This effect can be minimized by a variety of approaches, and then eliminated entirely with the use of an internal standard.

Another interference, commonly called the Easily Ionizable Element (EIE) interference, occurs in the base of the plasma and cannot be eliminated by these means. This interference can cause erroneous results for the alkali elements (such as Na and K), and can only be minimized, but not eliminated, by the addition of an excess of another easily ionized element such as Li or Cs.

For these reasons, the ability of the ICP instrument to perform both axial and radial viewing can be a significant benefit for environmental analysis. The presentation will discuss the design and optimization of an optical interface and provide a comparison of analytical performance to axial-only and radial-only measurements.

Environmental Chemistry Oral Session—R.L. Stux, Thermo Jarrell Ash Corp. 27 Forge Parkway, Franklin MA 02038

26. *AFFINITIES AND CAPACITIES OF METAL ION BINDING TO DATURA INNOXIA UNDER MULTIELEMENT- EXPOSURE CONDITIONS.* Patrick A. Williams and Gary D. Rayson, Department of Chemistry and Biochemistry, New Mexico State University, Box 30001 MSC 3C, Las Cruces, NM 88003.

The application of plant materials to the remediation of contaminated water or soil necessitates the exposure of these materials to numerous metal ions, simultaneously. The present work involves the use of a plant material derived from fragments of cultured cells from the anther of Datura innoxia. To provide the mechanical strength necessary to incorporate this sorbent into a flowing system, it has been immobilized within a polysilicate matrix. Surface area and porosity measurements indicate the cell material to be occluded by the inorganic polymer. In an effort to more closely emulate targeted effluent streams, the material was investigated under conditions of parallel exposure criteria for metal-ions. The effluent of each column of the biosorbent was directly coupled to the inlet of an ICP emission spectrometer capable of monitoring each of 27 elements simultaneously. This configuration enabled the monitoring of species both bound to the sorbent and those released. Through the application of frontal elution chromatographic techniques, relative affinities and site capacities for Ni, Zn, and Cd to the immobilized Datura innoxia biomaterial have been determined. The ramification of these results regarding the use of this plant-based biosorbent will also be discussed.

Environmental Chemistry Oral Session—Gary D. Rayson, New Mexico State University, Box 30001 MSC 3C, Las Cruces, NM 88003, (505) 646-5839, fax: (505) 646-2649, garayson@nmsu.edu

27. *ENVIROGEOCHEMICAL EXPLORATION FOR ANTHROPGENIC URANIUM DISTRUBANCES: A LEAD ISOTOPES APPROACH.* M.E. Ketterer; D.A. Lane; J.A. Jordan; D.L. Hudson; and S.C. Szechenyi, Department of Chemistry, Northern Arizona University, Flagstaff, AZ 86011-5698

Uranium occurs in the Earth's crust and surface water, and is cycled naturally through geochemical processes. Owing to its obvious utility as a raw material for weapons and nuclear fuels, human activities have exacerbated the natural geochemical cycles of uranium in specific localized areas. Radiologic, radiochemical, and isotopic measurements may all be readily used to detect these disturbances and evaluate the sources, transport mechanisms and fate of U and/or daughters in the environment. We are investigating the uses of lead isotope systematics as a means of tracking solid-phase transport of daughter-containing U from mining/mineral processing sites. This approach is based upon the presence of elevated 206Pb/204Pb and 207Pb/204Pb signatures in U-bearing minerals; in contrast, unmineralized crustal materi-

als and materials contaminated with anthropogenic lead contain "common" lead of distinguishable isotopic composition. This methodology is applied to case studies of uranium in river sediments impacted by Ti ore processing discharges, and uranium mining/milling sites of the Colorado Plateau.

Environmental Chemistry Oral Session—Michael E. Ketterer, Department of Chemistry, Box 5698, Northern Arizona University, Flagstaff, AZ 86011-5698, (520) 523-7055, fax (520) 523-8111, michael.ketterer@nau.edu

28. *A UNIVERSAL ICP-OES METHOD FOR ENVIRONMENTAL ANALYSES.* Zoe A. Grosser, Lee Davidowski, John Latino, Douglas Sears, and Randy Hergenreder, The Perkin-Elmer Corp., 50 Danbury Road MS-219, Wilton, CT 06897.

Environmental analyses are performed on a variety of matrices such as drinking water, wastewater, and solid and hazardous waste materials. The metals of interest can vary and the concentrations can range from trace levels to higher. The methods developed by the various environmental programs have differed in the quality control required and only slightly in the analyte list. With the move toward method streamlining and performance-based measurements, it now is possible to consider a universal method that will include a superset of the analytes most often determined.

The concentration range requirements will vary by element and is very different among matrices. For the method to be truly universal it must cover the full concentration range requirements covered by several methods or by different sets of conditions used today. The dual-view capability of an ICP-OES spectrometer can be used to extend the dynamic range for elements expected to exceed the range offered by analyses using either a radial or axial view exclusively.

This paper will explore the utility of a universal method for ICP-OES environmental analysis. The analyte list will be developed and compared with environmental requirements in US and other countries. The linear dynamic range will be evaluated for a dual-view spectrometer and the precision, time for analysis, and interference correction will be demonstrated.

Reference materials and real samples will be used to test the capabilities of the developed method. Low level concentrations in drinking water and wastewater will challenge the method for detection capabilities. Soils and digested waste samples will challenge the spectral overlap correction abilities.

Once the method is fully developed and characterized, the parameters necessary for speeding up the analysis will be evaluated. The sample introduction system, washing parameters, and autosampler set up will be optimized and the general procedures described.

Environmental Chemistry Oral Session—Randy L. Hergenreder, Perkin-Elmer Corp., 761 Main Ave, Norwalk, CT, 06859, phone 800-762-4000, FAX 303-403-1708, e-mail: hergenrl@perkin-elmer.com

29. To be announced

30. J. Peisach, Albert Einstein College of Medicine.

No abstract.

31. *PROBING RADICAL INTERMEDIATES IN ENZYME CATALYSIS.* John McCracken, Vinita Singh and R. Bose Muthukumaran, Michigan State University, Department of Chemistry, East Lansing, MI 48824; Victor L. Davidson and Zenyu Zhu, University of Mississippi Medical Center, Department of Biochemistry, Jackson, MS 39216; Stephen W. Ragsdale and Cristina Furdui, University of Nebraska, Department of Biochemistry, Lincoln, NE 68588

Electron Nuclear Double Resonance (ENDOR) and Electron Spin Echo Envelope Modulation (ESEEM) techniques have been used to determine the detailed electronic structures of paramagnetic species that serve as chemical intermediates in the catalytic cycles of pyruvate:ferredoxin oxidoreductase (PFOR) and methylamine dehydrogenase (MADH). For PFOR, ^{1}H-, ^{2}H- and ^{31}P-ENDOR spectra were critical in establishing the identity of a radical species that appears upon anaerobic addition of substrate to the enzyme. For MADH, ^{14}N-ESEEM experiments provided detailed information on the interaction of substrate-derived nitrogen from methylamine with a unique organic cofactor, tryptophan tryptophyll quinone. For both enzyme systems, hyperfine data derived from these advanced EPR studies will be discussed in light of X-ray crystallographic results to gain a better understanding of the catalytic mechanism. This work was sponsored by NIH grants GM-54065, GM-57323, GM-39451(SWR) and GM-41574(VLD).

EPR Oral Session—John McCracken, Michigan State University, Dept. of Chemistry, East Lansing, MI 48824-1322, phone 517-355-9715(ext. 269), fax 517-353-1793, mccracke@pilot.msu.edu

32. ***LONG-RANGE DISTANCES IN SPIN LABELED NUCLEOSOMES BY EPR.*** Michael K. Bowman, Alexei M. Tyryshkin, Vicki Burnett, Joseph Marx, and David L. Springer, Molecular and Cellular Biology and Macromolecular Structure and Dynamics, Pacific Northwest National Laboratory, WR Wiley Environmental Molecular Sciences Laboratory, P.O. Box 999, Richland, WA 99352-0999

Nucleosome cores are large assemblies of eight proteins with DNA wrapped around it to form the basic packaging unit for the eukaryotic genome and an important component in gene transcription and replication. We have used DEER or pulsed ELDOR methods to measure th distribution of distances between site directed spin labels on the tails of nucleosome proteins. The tails are disordered in x-ray structures. We have converted the DEER decay kinetics into distance profiles to determine the locations of the nucleosome tails in solution. Pacific Northwest National Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Work supported by the DOE Office of Biological and Environmental Research.

EPR Oral Session—Michael K. Bowman, PNNL, K8-98, P.O. Box 999, Richland, WA 99352-0999, (509) 376-3299, fax: (509) 376-2303, Mk_bowman@pnl.gov

33. ***MIMS ENDOR INVESTIGATION OF A SUBSTRATE-BASED RADICAL INTERMEDIATE IN ETHANOLAMINE AMMONIA LYASE,*** Russell LoBrutto, Department of Plant Biology, Arizona State University, Tempe, AZ 85287-1601; Vahe Bandarian and George H. Reed, Institute for Enzyme Research, University of Wisconsin, Madison, WI 53705.

Ethanolamine ammonia lyase (EAL) is an adenosylcobalamin (coenzyme B_{12})-dependent enzyme, which catalyzes the conversion of vicina amino alcohols into ammonia and the corresponding oxo compound. The reaction is believed to be initiated by homolysis of the Co-carbo bond of the cofactor generating cob(II)alamin and the 5′-deoxyadenosyl radical. The radical center is transferred to the substrate via H-atom abstraction. The steady-state of the reaction with S-2-aminopropanol consists of an organic radical, 5′-deoxyadeosine, and cob(II)alamin. The two paramagnetic centers in the active site undergo exchange and dipole-dipole coupling such that the radical signal appears as a doublet. CW EPR measurements reveal that the unpaired electron in the radical is located at C_1 of the substrate–the site of H-atom abstraction. In the present study, Mims ENDOR has been used to follow the fate of the atom that is abstracted from the substrate to produce the radical. The steady-state intermediate was generated with $[1,1\text{-}^2H_2]$ S-2-aminopropanol, and Mims ENDOR spectra were obtained at small magnetic field increments across the breadth of the radical absorption. The ENDOR spectra revealed a prominent ^2H doublet signal, centered about the ^2H Larmor frequency. These nuclear transitions were assigned to the abstracted deuteron. Analysis of the magnetic field dependence of the ENDOR spectrum yielded a hyperfine coupling tensor whose isotropic component had magnitude $|A_0|$ = 0.78 MHz, and whose anisotropy corresponded to a distance of 2.7 Å. The same measurement, applied to a sample with unlabeled substrate but with ^1H replaced by ^2H at $C_{5'}$ of deoxyadenosine, produced an essentially identical ENDOR spectrum. ENDOR was also applied to EAL reacted with $[2\text{-}^2H]$ S-2-aminopropanol. The combination of the CW EPR and Mims ENDOR data has provided insight into the geometry of the propanolamine radical itself, and into the spatial relationship between the radical and the species responsible for the initia hydrogen abstraction.

EPR Oral Session—Russell LoBrutto, Department of Plant Biology, Arizona State University, Tempe, AZ 85287-1601, (602) 965-9037, fax: (602) 965-6899, lobrutto@asu.edu

34. ***MIMS PULSED ENDOR AND ESEEM OF METALLOENZYMES: WHERE HAS BILL MIMS LED US?*** Roman Davydov, Peter E. Doan, Brian M. Hoffman, Victoria Kofman, Hong In Lee, Stoyan Smoukov, Ruitian Song, David L. Tierney, Department of Chemistry, Northwestern University, Evanston IL 60208

The two titled techniques are well known, but results to be presented will show that the true power of the former for obtaining structural information is underappreciated. Advances in the analysis of the latter as applied to Kramers systems will be discussed, along with new results for integer-spin, non-Kramers systems.

EPR Oral Session—Brian M. Hoffman, Department of Chemistry & BMBCB, Northwestern University, 2145 Sheridan Road, Evanston, Il, 60208, (847) 491-3104, fax: (847) 491-7713, bmh@nwu.edu

35. ***DIRECT AND INDIRECT DETECTION OF ECHOES—EXPERIMENTS INSPIRED BY BILL MIMS.*** H. Thomann, Exxon Research.

No abstract.

36. ***A NEW ELECTRON SPIN RESONANCE METHOD TO IDENTIFY TRANSITION METAL ION INCORPORATION INTO MOLECULAR SIEVES.*** A. M. Prakash, University of Houston, Department of Chemistry, University of Houston, Houston, Texas 77204-5641; Larry Kevan, University of Houston, Department of Chemistry, University of Houston, Houston, Texas 77204-5641

A new electron spin resonance (ESR) method to identify incorporation of transition metals into the framework of zeolite molecular sieve is reported. A novel niobium silicate molecular sieve of MFI topology, designated here as NbS-1, is synthesized hydrothermally and characterized by ESR and other physical methods such as x-ray diffraction, thermo-gravimetric analysis, scanning electron microscopy, electron microprobe analysis, surface area measurements, and ^{29}Si MAS NMR, UV-visible, FTIR and Raman spectroscopies. Substitution of niobium into the framework has been established by these various methods. Gamma-irradiation of activated NbS-1 shows two radiation-induced hole centers (V centers) by ESR located on Si-O-Si and Nb-O-Si units of the framework. The latter can be identified through a 10-line *hyperfine structure from ^{93}Nb (I = 9/2, 100% abundance) and provides convincing evidence for the incorporation of Nb into the silica framework. Nb(IV) ions are also formed as a consequence of radiation-induced reduction of Nb(V) associated with isolated tetrahedral NbO_4 units and exhibit an axially symmetric ESR signal with a 10 line hyperfine structure due to ^{93}Nb. Silicalite-1, on the other hand, shows radiation induced hole centers located only on Si-O-Si units.*

EPR Oral Session—Larry Kevan, University of Houston Department of Chemistry, Houston, Texas, 77204-5641, (713) 743-3250, fax: (713) 743-2709, KEVAN@UH.EDU

37. ***PULSED ENDOR AT 95 GHZ: NEW OPPORTUNITIES IN STUDIES OF S=5/2 METAL IONS.*** Daniella Goldfarb, P. Manikandan, Tania Shane, Rannan Carmieli, Aharon J. Gilboa, Dafna Arieli, Weizmann Institute of Science, Rehovot Israel 76100.

The EPR spectrum of S=5/2 systems with a dominating Zeeman interaction but with a significant zero field splitting is significantly better resolved at W-band than at conventional X-band, thus leading to simplified pulsed ENDOR measurements as well. This, combined with the increased sensitivity for size limited samples, enabled the study of single crystals of the Mn(II) containing protein concanavalin A. ^{1}H and ^{2}H ENDOR measurements targeted towards the determination of the coupling with two water molecules and a histidine residue will be presented. The applications are naturally not limited to single crystals, as will be demonstrated on polycrystalline samples of Mn(II) and Fe(III) substituted aluminophosphate molecular sieves. In these systems ^{27}Al and ^{31}P ENDOR is used to provide direct evidence for framework substitution in an ^{27}Al site.

EPR Oral Session—Daniella Goldfarb, Department of Chemical Physics, Rehovot 76100, Israel, 972-8-9342016, fax: 972-8-9344123, cigoldfa@wis.weizmann.ac.il

38. ***EPR AND ENDOR STUDIES ON SYNTHETIC MACROMOLECULE-METAL COMPLEXES.*** G. Jeschke, Max-Planck-Institute for Polymer Research, Postfach 3148, D-55021 Mainz, Germany

Synthetic macromolecule-metal complexes (MMC) offer interesting possibilities for 'structure engineering' on different length scales and have applications as catalysts, ion conductors, selective ion exchange materials, and gas separation membranes. Few methods are suitable for structure determination of solid MMC, as these lack long-range order and feature a distribution of coordination geometries to accomodate the preferences of the polymer chain. The slow progress in structural characterization of MMC has now become a bottleneck for their further development (F. Ciardelli, E. Tsuchida, D. Wöhrle (Eds.), (1996), "Macromolecule-Metal Complexes", Springer, Berlin). An approach using the great variety of existing pulse EPR and ENDOR methods should be able to overcome these problems. Such an endeavor should also benefit from the methodology developed so far for metalloproteins, and should itself contribute to this methodology. As a model sample for testing these propositions we use the copper(II) complex of poly(4-vinylpyridine) (CuPVP) which catalyses the oxidative polymerization of 2,6-dimethyl-phenol to the engineering polymer poly(phenyleneether). Samples with metal contents down to 1 Cu^{2+} per 100 ligands can be studied even with elaborate pulse schemes, while samples with high metal content are accessible by diamagnetic substitution of most of the Cu^{2+} by Zn^{2+}. Our primary aims are the characterization of Cu^{2+} coordination by hyperfine couplings and an assessment of the distribution of the coordination geometry. For the first task, we use mainly 2D spectra that correlate nuclear frequencies to EPR resonance fields. This approach has been shown to provide not only information on hyperfine tensor principal values, but also on the relative orientation between the hyperfine and g tensor for nitroxide radicals at W band (Jeschke, G. and Spiess, H.W. (1998), Chem. Phys. Lett. 293, 9). At X-band, pulse ENDOR is the method of choice for obtaining such spectra. It is shown that selective ^{1}H and ^{14}N ENDOR-correlated EPR spectra of CuPVP can be obtained with satisfactory signal-to-noise ratio. These spectra exhibit relatively sharp features event at high metal content where broad distributions of the coordination geometry are expected. Possible reasons for this finding are discussed. The geometry distribution itself can best be inferred from g strain, which is quantified by simultaneous fitting of X-band and W-band spectra of CuPVP. We find that electron spin echo detection provides high-field EPR spectra of better quality for this kind of samples than cw EPR.

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39. ***^{1}H, ^{15}N, ^{2}D HYSCORE SPECTROSCOPY OF METAL ION COMPLEXES IN DISORDERED SYSTEMS.*** Andreas Pöppl, Winfried Böhlmann, Rolf Böttcher, Universität Leipzig, Fakultät für Physik und Geowissen-schaften, Linnéstr. 5, D-04103 Leipzig, GERMANY; Lars Ihlo, and Reinhard Kirmse, Universität Leipzig, Fakultät für Chemie und Mineralogie, Talstr. 35, D-04103 Leipzig, GERMANY

The superior spectral resolution of the two-dimensional (2D) HYSCORE experiment provides the possibility to determine small nuclear quadrupole (nq) splittings and second order shifts in the hyperfine (hf) coupling of ligand nuclei even in spectra of disordered systems. Therefore, the overall coordination geometry of metal ion complexes can be investigated by orientation selective HYSCORE spectroscopy in a very detailed manner even in disordered materials. Two different applications of this 2D ESEEM experiment are presented. Second order hf coupling effects are used in ^{15}N HYSCORE to study isotropic and anisotropic hf interactions of nitrogen ligand nuclei in the fourth coordination sphere of the paramagnetic ion in $(n\text{-}Bu_4N)_2$ $[Cu(II)/Ni(II)(S_2C_2(C^{15}N)_2)_2]$ and $(n\text{-}Bu_4N)_2[Au(II)/Ni(II)(S_2C_2(C^{15}N)_2)_2]$ complexes. The coor-dination geometry of encapsulated $[Cu(py)_4]$ and $[Cu(pic)_4]$ complexes in molecular sieve materi-als is investigated by ^{1}H and ^{2}D HYSCORE experiments. These investigations rely on the analysis of deuterium nq interaction which gives information about the C-D bond directions in the ligand molecules.

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40. ***A CW AND PULSE EPR AND ENDOR INVESTIGATION OF OXYGENATED Co(II) CORRIN COMPLEXES.*** Sabine Van Doorslaer and Arthur Schweiger, ETH Zurich, Laboratory of Physical Chemistry, Zurich, CH-8092, Switzerland

Heptamethyl cobyrinate perchlorate [Cob(II)ester]ClO₄ (1) is structurally comparable to vitamin B_{12r} *in the base-off form, but is known to be more stable in solution and in the solid state and much less readily oxidized in air than vitamin* B_{12r} *itself (Murakami et al., Bull. Chem. Soc. Jpn., 1983, 56, 3642). The reversible oxygenation behavior of complex 1 in different solvents is investigated using CW EPR at X-band and compared with that of vitamin* B_{12r} *and Co(II) porphyrin complexes. Furthermore, the influence of the addition of a nitrogen base to the solutions is investigated. In order to determine the electronic structure of the oxygenated complexes, different pulse EPR and ENDOR methods are applied. The g and* A^{Co} *matrix and their principal axes are determined using a combination of CW EPR at X- and Q-band and* ^{59}*Co Davies-ENDOR at Q-band. From the HYSCORE (Hyperfine Sublevel Correlation) spectra measured at X-band, the interactions with the corrin nitrogen nuclei and the nitrogen of the axial base can be deduced. Comparisons are made with the electronic structure of other oxygenated Co(II) complexes and the relevance of 1 as a model for vitamin* B_{12r} *is discussed.*

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41. ***EPR INVESTIGATIONS OF COPPER-EXCHANGED ZEOLITES.*** Patrick J. Carl and Sarah C. Larsen, Chemistry Department, University of Iowa, Iowa City, IA 52242

Copper-exchanged zeolites are active catalysts for the direct decomposition of nitrogen oxides, such as NO_x *and* N_2O*. The location and coordination of copper ions in the zeolite is crucial to understanding the role of copper in the catalytic process. Electron paramagnetic resonance (EPR) spectroscopy was utilized to probe changes in the local environment of the* Cu^{+2} *centers in copper-exchanged zeolites (Beta, ZSM-5, mordenite and Y). Hydrated samples of Cu-ZSM-5 and Cu-Beta exhibited EPR spectra consistent with EPR signals previously assigned to* Cu^{+2} *in distorted octahedral coordination. EPR spectra of dehydrated Cu-Beta and Cu-ZSM-5 showed the presence of coordination environments that were similar to EPR signals previously assigned to* Cu^{+2} *in distorted square pyramidal and distorted square planar environments. The empirical model of Peisach and Blumberg (Peisach, J.; Blumberg, W. E. Arch. Biochem. Biophys. 1974, 165, 691.) that correlates* $g_\parallel$ *and* $A_\parallel$ *for a series of tetragonal copper model compounds was applied to the copper-exchanged zeolites. The model provides insight into the coordination environment of* Cu^{+2} *in copper-exchanged zeolites and links a number of past EPR studies on different copper-exchanged zeolites. This model also provides an explanation for the observed trends in EPR parameters related to the charge at the copper center. In addition, the effect of Si/Al ratio and copper loading on the EPR parameters for a series of copper-exchanged mordenite, ZSM-5 and Y samples was examined. The EPR spectra of dehydrated Cu-ZSM-5 and dehydrated Cu-Beta recorded at 673 K showed an increase in* $g_\parallel$ *and a decrease in* $A_\parallel$ *when compared to the EPR spectra recorded at room temperature. These changes in spectral parameters are attributed to minor changes in the electronic environment of the copper(II) species.*

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42. ***POSSIBLE SPIN-FRACTON RELAXATION IN THE POLYMER RESIN P4VP DOPED WITH KRAMERS IONS*** Co^{2+}***,*** Nd^{3+}***,*** Yb^{3+}***.*** Jacques Pescia, Laboratoire de Magnétisme et d'éléctronique quantique, 31077 Toulouse Cedex 04, France; Sushil K. Misra, Physics Department, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, Quebec, Canada H3G 1M8; Marat Zaripov, Laboratoire de Magnétisme et d'éléctronique quantique, 31077 Toulouse Cedex 04, France

The temperature dependency of the relaxation rate (T_1^{-1}) *in three poly-4-vinylpyridine (P4VP) resin samples possessing fractal structure was investigated over the 4.2-20 K range. The samples were doped with 2.0%, 0.8%, and 0.5% weight concentrations, respectively, of* $CoCl_2$*,* $NdCl_3$*,* $YbCl_3$*, consisting of Kramers ions* Co^{2+}*,* Yb^{3+}*, and* Nd^{3+}*, characterized by strong spin-orbit coupling. Presence of spin-fracton relaxation was confirmed by (i) the fractal structure of the sample matrix;*[1] *(ii) non-exponential recovery shown by NMR data;*[1] *(iii) the* $T^{4.16}$ *dependency of the relaxation rate in the 12.3 - 19 K temperature range;*[2,3] *(iv) the localization temperature of about 11.8 K, as estimated using Ioffe-Regel criterion;*[4] *and (v) good agreement between the above temperature dependency and that expected theoretically for spin-fracton relaxation with a fracton dimensionally = d = 1.22 for the Raman process involving two-fracton inelastic scattering characterized by high localization.*[2,3,5] *To our knowledge, this is the first-ever confirmation of spin-fracton relaxation by EPR.*

1. *C. Chachaty, J. P. Korb, J.R.C. Van Der Marel, W. Bras and P. Quinn, Phys. Rev. B44, 4778 (1991).*
2. *S. Alexander, O. Entin-Wholman and R. Orbach, Phys. Rev. B B32, 6447 (1985).*
3. *S. Alexander, O. Entin-Wholman and R. Orbach, Phys. Rev. B B33, 3935 (1986).*
4. *A. L. Ioffe and A.R. Regel, Prog. Semicond. 4, 237 (1960).*
5. *S. Alexander, O. Entin-Wholman and R. Orbach, Phys. Rev. B B35, 1166 (1987).*

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43. *POTENTIAL MEDICAL (CLINICAL!!) APPLICATIONS OF EPR (ESR): OVERVIEW AND PERSPECTIVES.* Harold M. Swartz, EPR Center for the Study of Viable Systems, Department of Radiology, Dartmouth Medical School, Hanover, NH 03755

While there are ample reasons for the development and use of in vivo EPR techniques for strictly experimental applications, there are also some very attractive potential clinical applications. In this symposium the rationale, status and future prospects for clinical applications will be summarized. The area with the most obvious immediate and effective clinical use appears to be oximetry, where EPR almost uniquely can make repeated accurate measures of pO2 which can provide clinicians with information that can impact directly on diagnosis and therapy, especially for Oncology and Peripheral Vascular Disease. A closely related area of potential widespread applications is the use of EPR to measure nitric oxide. Another area of potential extensive early applications is in pharmacology where the unique capabilities of in vivo EPR to detect and characterize free radicals may be applied immediately to measure free radical intermediates from drugs and oxidative process. This unique capability, combined with the sensitivity of EPR spectra to the immediate environment (e.g. pH, motion, charge) has already resulted in some very productive applications and these are likely to expand substantially in the near future. There are some challenging obstacles to clinical and experimental uses of EPR. These are especially the non-resonant loss of the microwave in tissues and the presence of physiological motions. Another challenging area is the development of stable paramagnetic materials that can be used safely and effectively in human subjects. There is a reasonable basis to conclude that the challenges will be overcome and in vivo EPR will emerge as an effective experimental AND clinical tool early in the next millennium! Supported by NIH RR11602.

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44. *EPR IN CANCER: PHYSIOLOGY, DIAGNOSIS, AND RESPONSE TO TREATMENT.* Howard J. Halpern, University of Chicago, Chicago, IL 60637

Novel in vivo EPR techniques promise means by which to characterize living tissue and aid in the diagnosis of malignancy. Recent studies have shown increases in a Fe-NO based EPR triplet signal in malignant cells and tissues. Nitric oxide images may allow correlation with tumor angiogenesis. The well known increase in NMR transverse relaxation times in tumor tissues seen in MRI is recapitulated in EPR measurements of malignant animal tissue. Oxygenation status of tumors is a crucial determinant of its response to radiation and certain chemotherapies. The oxygen effect from classical radiation biology demonstrates a factor of three increase in radiation dose necessary to inactivate mammalian cells and normal/malignant tissue if it is hypoxic or poorly oxygenated. Clinical data demonstrates reduction in radiation curability in hypoxic tumors. EPR measurements with particulates in rodent models has characterized the timing of oxygenation of a tumor after a dose of radiation. Delivery of a subsequent fraction of radiation based on this timing information appears to improve radiation effect. EPR oxygen images of tumors can map tumor oxygenation and allow the placement of dose hot spots in areas of hypoxia. In vivo EPR and EPR imaging promises a new window through which we can guide the administration of cancer therapy.

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45. *FREE RADICAL INTERMEDIATES OF DRUGS.* L. J. Berliner, Laboratory of In-Vivo Electron Spin Resonance Spectroscopy,Departments of Chemistry and Medical Biochemistry,The Ohio State University, Columbus, Ohio , USA 43210; H. Fujii, Tokyo Metropolitan Institute of Medical Science, Tokyo 113-8613, Japan

Several drugs have been found to result in relatively stable radical intermediates during their adsorption and metabolism, particularly in the live. One example is nifedipine, [3,5-pyridinedicarboxylic acid, 1,4-dihydro-2,6-dimethyl-4-(2-nitrophenyl)- dimethyl ester], is a calcium channel blocker that has been widely used as a prescription drug for patients with hypertension. Previous studies with intensive irradiation showed that conversion to the nitroso analog and further radical adducts with the solvent can occur. We found that under mild illumination (ie. ordinary light for 24 hrs) nifedipine is completely converted to its nitroso analog without further photochemical degradation. We have found evidence for free radical generation in mice after intramuscular or intraperitoneal injection of illuminated nifedipine as monitored by in vivo L-band electron paramagnetic resonance (EPR) spectrometry. Stable nitroxyl-like radicals were detected in mice 15 min after injection. This was also confirmed by ex-vivo measurements on excised muscle and liver tissue. The nature of these radicals was confirmed by comparing the reaction of the nitroso group of illuminated nifedipine with polyunsaturated fatty acids. Surprisingly, identical radicals were detected from excised liver doped with non-illuminated nifedipine, indicating that pure nifedipine can be enzymatically converted in vivo to its nitroso analog without the requirement for illumination. These results are potentially related to observations that patients taking long term dihydropyridine-type calcium channel blockers have a 60% increased risk of heart attack. The related blockers, nisoldipine, nimodipine and nicardipine are currently under intense study, but appear to be similar in some aspects of their radical chemistry, while differing in other properties,

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46. *PHARMACEUTICAL APPLICATIONS OF IN VIVO EPR.* B. Gallez, Laboratory of Biomedical Magnetic Resonance, Université Catholique de Louvain, Brussels, Belgium; Karsten Mäder, Department of Pharmaceutical Sciences, Freie Universität of Berlin, Germany.

The development of spectrometers working at low frequencies with improved resonators now permits the routine use of non invasive EPR spectroscopy. The capabilities of EPR spectra to reflect microenvironmental conditions, combined with the use of paramagnetic materials as selective non-toxic labels, has led to increasingly widespread and productive applications of the technique to complex problems involving pharmaceutical sciences. Some of the specially promising applications in which EPR appear to provide valuable information will be illustrated including monitoring pharmacokinetics of drugs, characterization of drug releasing systems, and measurement of the effect of drugs modifying oxygen, pH, or NO level of tissues. Possible clinical relevant applications will be discussed.

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47. *STABLE NITROXIDE FREE RADICALS AS ANTIOXIDANTS, RADIO-PROTECTORS, AND IMAGING AGENTS.* James B. Mitchell and Murali C. Krishna, John A. Cook, and Angelo Russo, Radiation Biology Branch, Division of Clinical Sciences, National Cancer Institute, Bethesda, MD 20892; Periannan Kuppusamy, Division of Cardiology, Johns Hopkins University, Baltimore, MD.

Oxidative stress is implicated in the pathogenesis of a variety of human diseases, as well as evoking fundamental genetic responses. The final common pathway in the mechanism of action of ionizing radiation, many chemotherapeutic agents, and immunologic regulation is through oxidizing radical species. Stable nitroxide free radicals have been employed to probe various biophysical and biochemical processes involving oxidative stress. We have demonstrated that nitroxides at non-toxic concentrations are effective as in vitro and in vivo antioxidants when oxidation is induced by superoxide, hydrogen peroxide, organic hydroperoxides, ionizing radiation, or specific DNA-damaging anticancer agents. The protection of oxidative damage in biological systems (both in vitro and in vivo) by non-toxic levels of nitroxides has several plausible chemical explanations: 1) SOD-mimicking action; 2) oxidation of reduced metals that have potential to generate site specific .OH radicals; 3) termination of free radical chain reactions induced by alkyl, alkoxyl, alkylperoxyl radical species, and detoxifying drug-derived radicals; and 4) detoxification of hypervalent toxic metal species such as ferryl and cupryl ions. Examples of the protection of nitroxides against oxidative stress at the cellular and animal level, proposed chemical mechanisms underlying the protective action(s), and the potential use of nitroxides in clinical settings will be presented. Additionally, the application and feasibility of nitroxides and other paramagnetic probes for in vivo Electron Paramagnetic Resonance imaging to study probe uptake, oxygen concentration in tissues, and tissue redox reactivity will be discussed.

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48. *IN VIVO EPR - INSTRUMENTAL CHALLENGES AND POTENTIAL SOLUTIONS.* Tadeusz Walczak, EPR Center for the Study of Viable Systems, Department of Radiology, Dartmouth Medical School, Hanover, NH 03755

Low frequency (300-1300 MHz) EPR spectroscopy requires that several instrumental and practical problems be solved before it attains its full potential as a powerful and versatile method to be used in vivo. The challenges include: • Generally low signal to noise ratio resulting from high nonresonant absorption of RF/microwave radiation by living tissues; • Maximum depth of signal detection is limited to about 10 mm when surface-coil-type resonators are used at 1 GHz; going to lower frequencies can increase this but then there is a decrease in sensitivity;

• Motion of the experimental subjects causes time-dependent changes in matching of the high frequency bridge and may result in distortion, or even complete loss of the signal; • Lineshape distortion also can be caused by phase delay of high frequency magnetic field in conductive materials such as animal tissues; • In CW systems, the applicable amplitude of magnetic field modulation can be limited by the appearance of microphonic effects. In this presentation key solutions and approaches developed in our laboratory for CW, reflection, and transmission systems will be summarized. Additionally, the present status and the possible benefits resulting from the use of newly available approaches such as longitudinally detected (LODESR) and multiquantum (MQ) ESR will be discussed. Supported by NIH RR11602.

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49. *ROCKY MOUNTAIN CONFERENCE PLENARY LECTURE.* M. Bonner Denton, University of Arizona

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50. ***ANALYSIS OF ADRENOLUTIN AND ADRENOCHROME: OXIDATIVE METABOLITES OF CATECHOLAMINES USING HPLC, SPECTROFLUOROMETRY AND ELECTRON PARAMAGNETIC RESONANCE ANALYTICAL TECHNIQUES.*** Steven I. Baskin,
George S. Behonick, and Carmen M. Arroyo, U.S. Army Medical Research Institute of Chemical Defense, Aberdeen Proving Ground, Maryland, 21010-5400; (410) 436-4454; Robert J. Schafer Oak Ridge Institute of Science and Education Research.

The acute hemodynamic effects of organophosphate (OP) intoxication include positive chronotropic and inotropic changes and increases in intraventricular pressure and coronary blood flow. Several mechanisms have been proposed to explain the cardiotoxicity of elevated catecholamine (CA) concentrations; however, it may be the oxidative metabolites, rather than the parent CAs per se, that initiate cardiotoxicity. The chromatographic profile of adrenochrome and adrenolutin in an isocratic, reverse phase HPLC method using UV/VIS and EC detection is described in this study.

The adrenochrome aqueous standard showed a retention time of 1.9 minutes. Using a flow rate of 0.6 mL/min and a UV/VIS detector set at a wavelength of 490 nm several chromatographic peaks were detected following injection of the aqueous adrenolutin standard indicative of different species. A similar multiple peak chromatographic profile was observed with electrochemical (EC) detection. We hypothesized that the complexity of the observed chromatogram, i.e., multiple intermediate species of the adrenolutin, is due to the continued autoxidation of adrenolutin with the generation of a carbon-centered radical at C-2 position. This will interact with oxygen to give an intermediate peroxy radical, which is eventually transformed to 5,6-dihydroxy-1-methyl-2, 3-indoledione. The production of these proposed carbon- and oxygen-centered radicals in the autoxidation of adrenolutin was confirmed by spin trapping experiments using a-phenyl N-tert-butyl nitrone (PBN) as the spin trap agent. When adrenolutin is dissolved in water at neutral pH in the presence of PBN, two different EPR spectra of PBN adducts were obtained. One observed PBN adduct has hyperfine coupling constants (hfsc's) of $a_N = 1.54$ *mT,* $a^{\beta}_H = 0.40$ *mT and* $a^{\gamma}H = 0.13$ *mT ; the other observed PBN adduct has the following hfsc's:* $a_N = 1.50$ *mT and* $a^{\beta}_H = 0.33$ *mT. The detection of these reactive intermediates during the continued autoxidation of adrenolutin may account for the biochemical toxicity of catecholamine metabolism. In addition, methods are described to investigate the oxidative metabolism(s) of epinephrine, which may allow for the characterization of the cardiotoxicity observed after organophosphate (OP) intoxication.*

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51. ***REFOCUSED PRIMARY ESE: A ZERO DEAD TIME DETECTION OF THE ELECTRON SPIN ECHO ENVELOPE MODULATION.*** Andrei V. Astashkin, John H. Enemark, Andrew Pacheco, Arnold M. Raitsimring, University of Arizona, Department of Chemistry, Tucson, AZ 85721.

We report here on the implementation of a new two-dimensional spin echo technique, refocused primary ESEEM (RP ESEEM), its theory and application to model systems and systems of biological interest. It was demonstrated that this technique is virtually free of dead time along one of the time coordinates. It is also shown that the ESEEM obtained by integration of the 2D time domain RP ESEEM data over one of the time coordinates shows the intensity of the sum combination (ν_o) *harmonics* $\propto k^2$ *for* $k << 1$ *and* $\propto k$ *for* $k \sim 1$ *(k is a usual notation for the modulation amplitude factor). This feature of the RP ESEEM allows one to substantially suppress the intensity of the* ν_o *lines of distant matrix protons compared with the standard primary ESEEM, leaving the intensity of the strongly coupled protons practically unchanged. In an experimental application, a virtually zero dead time and suppression of* ν_o *lines of distant protons provided by RP ESEEM in tandem with the low-frequency (C/S band) operations has allowed us to significantly increase the ESEEM amplitude due to strongly coupled protons and to directly detect for the first time the strongly coupled proton with distributed hfi parameters in sulfite oxidase. Application of this technique to a variety of systems is also demonstrated. The financial support of NSF DBI-9604939 is acknowledged.*

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52. ***MULTIFREQUENCY ESEEM OF THE FERRIHEME CENTERS IN PROTEINS.*** Andrei V. Astashkin, Arnold M. Raitsimring, F. Ann Walker, University of Arizona, Department of Chemistry, Tucson, AZ 85721.

The histamine complex of nitrophorine 1 (NP1-Hm) has been studied by pulsed EPR (two-and four-pulse ESEEM) at X-band and S-band. It is found that the proton sum combination feature in X-band ESEEM (8.706GHz) is well resolved at the low-field g-value (g_z) *but is unresolved at high-field g-value* (g_x)*. Decreasing the operational frequency to S-band (3.065GHz) allowed us to obtain well-resolved ESEEM spectra at* g_x *position. As a result, for the first time, both selective orientations* (g_x *and* g_z) *could be exploited for a system with large g-separation to produce a single crystal-like result from a glassy EPR spectrum. This allowed us to minimize the number of the numerical simulations and obtain unequivocal result concerning the orientation of the imidazole-type ligands in NP1-Hm. The results suggest that His-59 is more important in determining the orientation of* g_x *than is the histamine ligand. Similar technique has been applied to study the coordination of histidine to the ferriheme center in housefly cytochrome* b_5*. The features and optimization of multifrequency operations are discussed. The financial support of NSF BIR-9224431 and DBI-9604939, and NIH DK 31038 and HL 54826 is acknowledged.*

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53. *MULTI-FREQUENCY ELECTRON SPIN ECHO ENVELOPE MODULATION (ESEEM) SPECTROSCOPIC STUDIES OF CYTOCHROME C.* Nikolai I. Avdievich and Jack Peisach, Department of Physiology & Biophysics, Albert Einstein College of Medicine of Yeshiva University, Bronx, NY 10461

Nuclear hyperfine and quadrupole coupling parameters for ^{14}N of the proximal histidine in low spin ferric heme complexes have been determined by ESEEM.[1,2,3] *In contrast, measurements of nuclear quadrupole interaction parameters for pyrrole ^{14}N of the porphyrin have presented difficulties.*[3] *Because of larger values of isotropic ^{14}N hyperfine interaction constants (a_{iso} ~ 4 - 5 MHz) one is unable to reach exact cancellation conditions at frequencies typically available to ESEEM spectrometers (9 GHz). For this reason, pyrrole nitrogens produce very shallow modulations. The current study attempts to overcome this problem using excitation frequencies at ku band (12 - 18 GHz) to obtain well-resolved spectral lines arising from the nuclear quadrupole transitions. Magnetic field dependence of double quantum transition lines near and away from the exact cancellation conditions allow us to estimate ^{14}N hyperfine interaction parameters.*

1. *Peisach, Mims and Davis, J. Biol. Chem., 1979, 254, 12379.*
2. *Magliozzo and Peisach, Biochemistry, 1992, 31, 189.*
3. *Magliozzo and Peisach, Biochemistry, 1993, 32, 8446.*

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54. *EPR PROBEHEADS FOR FAST SAMPLE SPINNING AT VARIABLE ANGLES.* C. Bauer, M. Hubrich, D. Hessinger, G. Jeschke, and H. W. Spiess, Max-Planck-Institute for Polymer Research, Postfach 3148, D-55021 Mainz, Germany

Sample reorientation on the time scale of a pulse EPR experiment can be used to characterize the orientation dependence of interactions in powder samples (Sierra G.A. and Schweiger A. (1997), Rev. Sci. Instrum. 68, 1316) and to average anisotropic contributions, so that isotropic spectra can be obtained by the MAS EPR experiment (Hubrich M., Bauer C., and Spiess H.W. (1997), Chem. Phys. Lett. 273, 259). While for transition metal complexes spinning speeds of a few hundert Hz are sufficient for the first task, MAS EPR and reorientation experiments on organic radicals require sample spinning speeds of more than 10 kHz. Since excitation bandwidth is also critical, fast spinning must be combined with at least moderate loaded Q values. Further design criteria are the possibility to perform both right-angle and magic-angle spinning, and the optional fitting of an ENDOR coil. EPR probeheads for fast sample spinning have been designed based on commercial NMR 4 mm and 2.5 mm O.D. rotor technology (Bruker) for maximum spinning speeds of 17 and 30 kHz, respectively. A sapphire dielectric resonator is fitted to the stator in the former case. Minimum $\pi/2$ pulse lengths during sample spinning are about twice as long as with a commercial pulse EPR probehead under otherwise identical conditions. With Q_L= 300 at 20 kHz spinning speed and 220 K and with a filling factor as high as for a conventional dielectric resonator, this setup can even be used for detecting cw EPR signals during spinning for strong samples. The resonator axis is situated in the magnetic field plane, so that the spinning angle can be adjusted by turning the probe head. An ENDOR coil inside the sapphire ring leads to only a slight deterioration of the Q_L value. For experiments where optimum EPR performance is crucial, the ENDOR resonator can be easily substituted by the original one. Stable sample spinning can be achieved over several hours at temperatures down to 200 K. A higher spinning speed up to 30 kHz is achieved at the expense of lower sample volume. Furthermore, the dimensions of the 2.5 mm rotor system are not as well adapted to the requirements of an X-band resonator as those of the 4 mm system, so that typical $\pi/2$ pulse lengths are longer. For these reasons the 4 mm design is superior for longitudinal relaxation times T_1> 10 ms, i.e., for the majority of organic radicals and defect centers. Experimental examples are given for both magic-angle and right-angle spinning.

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55. *W-BAND PULSE PROBEHEAD CONSTRUCTION - THE QUEST FOR MINIMUM LOSS AND MAXIMUM Q_L.* C. Bauer, G. Jeschke, and H. W. Spiess, Max-Planck-Institute for Polymer Research, Postfach 3148, D-55021 Mainz, Germany

High-frequency pulse EPR suffers from limited available excitation power. For instance, W-band spectrometer configurations with high sensitivity and the stability required for routine use feature $\pi/2$ pulse lengths of at least 50 ns, with more typical values in application work of at least 100 ns. Excitation bandwidths are thus by a factor of 10 smaller than in X-band pulse EPR, while spectral widths are larger by up to a factor of 10. Furthermore, in a number of experiments, effective dead times depend on pulse lengths, so that the advantage of high time resolution inherent in high-frequency EPR may be lost. The microwave field strength at the sample position for given incident power at the input is therefore one of the most important design criteria for a high-frequency EPR probehead. Maximizing the microwave field strength requires minimization of power losses and maximization of Q_L and the conversion factor of the resonator. Each of these goals may conflict with other design criteria as convenient sample access and/or sample preparation, provision of additional fields for ENDOR experiments or field modulation, optical access, and good thermal isolation for low-temperature experiments. Given the cost of a high-frequency spectrometer, it makes sense, however, to have a set of probeheads that are optimized for different experimental situations. In this contribution we present a W-band probehead design in which optimum microwave performance is the overriding design criterion. A TE_{011} cavity was machined into a brass block, polished, and chemically plated with gold. Tuning and sample positioning pistons were made in a similar way, and coupling was done by a sliding mechanism operation in a slit of the waveguide as in the Berlin design (Prisner T.F., Rohrer M., and Möbius, K. (1994), Appl. Magn. Reson. 7, 167). The cavity features Q_L= 6000. The relatively large brass block minimizes microphonics. Waveguides and especially the parts for changing the direction of the microwave were carefully selected for minimum power loss. Under otherwise identical conditions, a *probehead with our design outperforms the commercial probehead for the same spectrometer with respect to both sensitivity and flip angle in pulse experiments. Extremely helpful discussions with T. Prisner and M. Rohrer are gratefully acknowledged.*

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56. ***AN X-BAND EPR STUDY ON ASCORBYL FREE RADICALS GENERATED IN RAT HEARTS IN THE PRESENCE OF DIFFERENT TYPES OF ROS SCAVENGERS.*** A.M.Bobst, J.W.Lee, E.V.Bobst, University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221; Y.-G.Wang, M.Ashraf, University of Cincinnati, Department of Pathology, Cincinnati, OH 45267

The objective of this study was to investigate the effect of ROS scavengers on functional recovery and ascorbyl free radical (AFR) formation in isolated ischemic rat hearts. EPR spectroscopy at x-band was used to monitor AFR release in coronary perfusate during the first two minutes of reperfusion as a function of different ROS scavengers. Relative to ischemic controls the administration of the $^1O_2$ *scavengers 2,2,6,6-tetramethyl-4-piperidone HCl (4-oxo-TEMP), carnosine (ß-alanyl-L-histidine) or a combination of the two significantly improved functional recovery as measured by LVDP. While no AFR signal was detected in coronary perfusate collected during preischemic perfusion with and without* $^1O_2$ *scavengers, the AFR background signal due to ischemia was significantly increased with the* $^1O_2$ *and* $^{\cdot}O_2^-$ *scavengers. No such increase was observed with the hydroxyl radical (*$^{\bullet}OH$*) scavenger mannitol. Besides the AFR increase with the* $^1O_2$ *and* $^{\cdot}O_2^-$ *scavengers the functional recovery was only significantly improved with the* $^1O_2$ *scavengers. In contrast to previous AFR studies done by others we found that an increased AFR formation is not necessarily only reflecting increased oxidative stress but can also report improved functional recovery. A scheme outlining possible reactions between ascorbate, ROS and ROS scavengers will be presented to explain the observed AFR formation changes and together with the hemodynamic data we conclude that* $^1O_2$ *may be a major ROS involved in reperfusion injury with* $^{\bullet}OH$ *playing little to no role in this event (supported in part by NIH grant HL23597).*

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57. ***MOLECULAR DYNAMICS SIMULATIONS OF LOCAL SPIN-LABEL MOTIONS AND HIGH-FIELD EPR SPECTRA.*** Rajesh Satyamurti, Nga Nguyen, and David E. Budil, Department of Chemistry, Northeastern University, Boston MA 02115.

Molecular dynamics calculations are applied to simulate the high-field EPR spectra of nitroxides in large, spin-labeled biopolymers including proteins and DNA. The orientational distribution derived from the calculated trajectories of the nitroxide are used to determine the local orienting potential of the macromolecular surface. When the potential is expressed as an expansion in spherical harmonic functions, it may be input directly into an EPR lineshape calculation based on a steady-state Smoluchowksi diffusion equation, without the need to calculate long-time single-body trajectories from the potential. Trajectories of several ns have been calculated for large labeled protein molecules and DNA using the Quanta/Charmm program. In order to reduce computation times for large spin-labeled proteins, a "stochastic boundary" method was utilized. The predictions of such calculations are best evaluated using high-frequency (> 150 GHz) EPR. At such frequencies, the large-scale dynamics of the macromolecule are essentially "frozen out", so that the spectra reflect primarily the details of the local probe motion. Examples are given for a selection of proteins and DNA molecules.

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58. ***LARGE MOLECULAR WEIGHT NITROXIDE CONJUGATES AS RADIOPROTECTORS AND/OR ANTIOXIDANTS.*** Alasdair J. Carmichael, Matthew M. Hamilton, Yashesh N. Vaishnav and Thomas M. Seed. Armed Forces Radiobiology Research Institute, Bethesda, MD 20889-5603. U.S.A.

Nitroxides have been shown to have antioxidant and radioprotective properties. However, widespread nitroxide use has been limited due to their toxicity and solubility problems. In order to address these problems this work describes the conjugating of nitroxides (spin labeling) to larger water-soluble molecules (peptides and proteins) to make them more soluble and less toxic. The antioxidant/radioprotectant efficiency would then depend on the ratio, [N]:[P], of nitroxide to peptide (and/or protein) and should increase as this ratio increases making the toxicity lower on a mole to mole basis when compared to the parent nitroxide compound. Serum Albumin (SA) was labeled at various [N]:[P] ratios ranging from 0-4 using the reagent succinimidyl 2,2,5,5-tetramethyl-3-pyrroline-1-oxyl-3-carboxylate (TMPOC). This reagent specifically reacts with amine groups. The antioxidant/radioprotective mechanisms of nitroxides involve the reaction with and elimination of harmful reactive oxygen species (ROS). Since one of these mechanisms involves the reaction with superoxide ($O_2^{\cdot -}$*) in an SOD-like manner, this work describes the reaction of SA containing various [N]:[P] ratios with* $O_2^{\cdot -}$ *in a mildly reducing environment to prevent the return of the hydroxylamine to the nitroxide. The results show that the eficiency of eliminating* $O_2^{\cdot -}$ *from the solution increases as the [N]:[P] ratio increases when compared on a mole to mole basis with the TMPOC. In vitro toxicity studies and radioprotective ability of these SA-nitroxide conjugates are being investigated in cell cultures. The goal is to determine if their ROS quenching efficiency follows the [N]:[P] ratio in aqueous solutions, therefore, establishing a quenching efficiency order correlated to toxicity for nitroxide antioxidants/radioprotectors.*

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59. ***EPR SPIN LABELING MEASUREMENTS OF NUCLEAR, CHEMICAL AND BIOLOGICAL AGENT-INDUCED ALTERATIONS OF THE INSULIN RECEPTOR IN RED BLOOD CELL MEMBRANES: A POSSIBLE BIOLOGICAL MARKER FOR DOSE ASSESSMENT.*** F. C. Music, T. L. Hadfield, J. A. Centeno, L. Steel-Goodwin, R. E. Sweeney, W. F. Blakely, P. G. S. Prasanna, R. C. Sine, C. M. Arroyo, and A. J. Carmichael, Arned Forces Institute of Pathology and Armed Forces Radiobiology Research Institute, Bethesda, MD.

We used electron paramagnetic resonance (EPR) spin labeling to measure alterations induced by nuclear, chemical or biological (NBC) agents in the membrane-bound insulin receptor proteins of human red blood cells (RBCs). Cells from healthy donors were exposed in vitro to gamma-radiation (^{60}Co, nuclear), sulfur mustard (HD, chemical) or a bacterial polysaccharide substance (biological). The protein hormone insulin was conjugated to the nitroxide reagent succinimidyl 2,2,5,5-tetramethyl-3-pyrroline-1-oxyl-3-carboxylate (TMPOC) to make the spin-labeled ligand for the insulin receptor. Experimental aliquots of the RBCs were exposed to various doses of the NBC agents and then allowed to react at a specific time point after exposure with the spin-labeled insulin before measuring EPR spectra. All data points were normalized to the cell density of the experimental sample. Panel-A shows the EPR dose response to gamma-radiation for 5 independent replicates measured 20 days after exposure. The relevant spectral parameter tended to increase between 0.5-Gy and 5.0-Gy, and then reversed to a decreasing trend at 10-Gy and 20-Gy. Panel-B shows a steady decline in the relative EPR response across the range of HD concentrations tested. Measurements were taken 24-48 hours post-exposure to HD. Exposure for 2 h to the bacterial polysaccharide yielded a completely random EPR response to the concentrations tested and no clear trend could be ascertained (Panel-C). In summary, the EPR/spin labeling analytical technique for measuring alterations in RBC insulin receptors may be a useful alternative for assessing exposure doses in NBC casualties. These results and the limitations of EPR/spin labeling will be discussed in the context of a possible biomarker for NBC exposure assessment.

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60. ***A STABLE LITHIUM-CONTAINING ALUMINUM CENTRE IN CRYSTALLINE QUARTZ.*** Rodney F. C. Claridge, Nick. S. Lees, W. Craig Tennant, Charles J. Walsby, Chemistry Department, University of Canterbury, Christchurch, New Zealand; John A. Weil, Chemistry Department, University of Saskatchewan, Saskatoon, SK, S7N5C9, Canada.

When an Al^{3+} ion replaces a Si^{4+} ion during hydrothermal growth of a quartz crystal, a monovalent positive ion, M+, is usually incorporated nearby to maintain charge balance. Lattice size restricts the compensator ion M^+ to usually be H^+, Li^+ or Na^+. X-irradiation creates hole centres, with the hole trapped at an oxygen ion bonded to the Al^{3+} ion. Such centres are designated $[AlO_4/M]^+$. Annealing to above 150 K generally allows the no- longer-required compensating ion to diffuse away, to compensate some remote electron centre. In this paper, we present data for a newly discovered lithium-containing centre in which the Li^+ ion remains in the vicinity of the aluminum hole centre even at 300 K. The unstable centre $[AlO_4/Li]^+$ also is present. Single-crystal rotational EPR data have been obtained at X-band and 15 K. The resulting spin-hamiltonian parameters as well as molecular-orbital calculations have been used to determine the structure of the new centre, including the position of the lithium ion.

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61. ***INVESTIGATION OF DANGLING BOND CONTENT IN PULSED LASER DEPOSITED AMORPHOUS SILICON CARBIDE THIN FILMS BY ELECTRON SPIN RESONANCE.*** T. Christidis, M. Tabbal and S. Isber, American University of Beirut, Department of Physics, Beirut, Lebanon; M.A. El-Khakani and M. Chaker, INRS-Energie et Matériaux, Varennes, Qc, Canada J3X 1S2.

We report on the Electron Spin Resonance (ESR) analysis of amorphous silicon carbide (a-SiC) thin films deposited by means of the Pulsed Laser Deposition (PLD) technique at temperatures ranging from 25 to 650 °C onto Si (100) substrates. The measured g-value indicates that the detected ESR is, due at a large extent, to C- dangling bonds rather than to Si- dangling bonds. As deposition temperature is increased from 25 to 650°C, the ESR signal decreases by a factor of about 1.5, thus indicating a decrease in dangling bonds content of the films. Such variations are correlated with the increase in Si-C bond density as measured by Fourier Tranform Infra-Red (FTIR) Spectroscopy[1] as well as the improved optical transmission of the a-SiC films obtained at higher temperature.[2] Useful information about the microstructure of the films can also be obtained from the line shape analysis of the ESR signal. Indeed, it was found that, for all samples, the ESR line was found to be Lorentzian with a line width (measured at from 25 °C) that increases from about 0.38 to 0.5 mT as deposition temperature is increased. Such behavior of the ESR line width corresponds to the Gaussian-to-Lorentzian transition of the Si-C IR absorption band that indicates the onset of some long-range order in the films deposited at temperature above 600 °C.[1] Finally, the power saturation behavior of the ESR signal of the films will also be presented and compared to the saturation behavior of Plasma Enhanced Chemical Vapor Deposited (PECVD) hydrogenated a-SiC:H films. The role of hydrogen incorporation in PECVD a-SiC:H films will be discussed. Supported by U.R.B. (A.U.B.).

1. *El Khakani et al., J. Appl. Phys., 1997, 82, 4310.*
2. *El Khakani et al., Proc. SPIE, 1995, 2403, 153.*

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62. ***SPIN-TRAPPING STUDIES OF THE REACTION OF OZONE WITH ALKENES, PHENOLIC, AND SULFUR COMPOUNDS IN SOLUTION.*** Daniel F. Church, Radical Technologies, 12525 N. Oak Hills Pkwy, Baton Rouge, LA 70810; Michelle McAdams, Chemistry Department , Louisiana State University, Baton Rouge, LA 70803; Gilbert Cuadra, Chemistry Department, Louisiana State University, Baton Rouge, LA 70803.

Although there is extensive evidence that the reaction of ozone with a variety of organic molecules results in the formation of free radical intermediates, the presence of these species has been difficult to confirm. Spin trapping has been used to identify apparent radical intermediates in reactions of ozone with alkenes, phenolic compounds, and sulfides in solvents ranging from non-polar organic to water. With α-phenyl-N-tert-butyl nitrone (PBN) as spin trap, organic radicals derived from alkene substrates are observed in the whole range of solvents. PBN alone reacts with ozone to give benzoyl-tert-butyl nitroxide (PBNOx). The mechanism is presumed to involve initial 1,3-dipolar addition of ozone to the nitrone, followed by decomposition to PBNOx via the oxazidiridine-N-oxide. The results with 5,5-dimethyl-2-pyrrolidine-N-oxide (DMPO) in experiments with phenolic compounds or sulfides are less clear-cut. The only species observed is the hydroxyl adduct, both in the absence and in the presence of substrate. However, even low concentrations of the substrate markedly enhance the concentration of the adduct, while higher concentrations suppress it. This behavior appears to be consistent with these strongly electron donating substrates acting to promote the decomposition of ozone via one-electron transfer to hydroxyl radical and oxygen at low concentrations. At higher concentrations, the phenolic compounds and sulfides are superior traps for hydroxyl radical. In the absence of substrate, it has been proposed that the hydroxyl adduct arises from the reaction of ozone with water. However, this process appears to be too slow to compete with the reaction of ozone with DMPO. It is proposed that DMPO (which is more oxidizable than PBN) acts as an electron donor to promote the decomposition of ozone to oxygen and hydroxyl.

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63. ***CHARACTERIZATION OF CHAR MICROPARTICLES BY MEANS OF ADVANCED MAGNETIC RESONANCE TECHNIQUES.*** Boris M. Odintsov, University of Illinois, Illinois EPR Research Center, Urbana, IL 61801, USA; V. A. Atsarkin, Institute of Radioengineering and Electronics, Russian Academy of Science, Moscow 103907, Russia; R. L. Belford, University of Illinois, Illinois EPR Research Center and Chemistry Department, Urbana, IL 61801, USA; Paul J. Ceroke, University of Illinois , Urbana, IL 61801; V. N. Demidov, Institute of Radioengineering and Electronics, Russian Academy of Science, Moscow 103907, Russia; Z. Sh. Idiyatullin; A. N. Temnikov, State Technological University, Moscow, Russia; R. Sh. Vartapetian, Institute of Physical Chemistry, Russian Academy of Science, Moscow 103907, Russia; R. B. Clarkson, University of Illinois, Illinois EPR Research Center and Veterinary Medicine, Urbana, IL 61801, USA.

This work reports an approach to characterize microparticulate chars based on the correlation between porous structure parameters, determined by classical adsorption data, with information obtained by advanced magnetic resonance and other techniques. The methodological foundation has been developed over the last years in our laboratories. Along with water vapor adsorption isotherms and CHN analysis, we used a set of advanced magnetic resonance and other techniques including low and high frequency DNP (dynamic nuclear polarization), NMR, pulsed and cw EPR, pulsed-field-gradient spin-echo NMR spectroscopy and relaxometry, X-ray scattering at small and large angles, SQUID magnetometry, and several independent methods to measure the electron spin-lattice relaxation times on the surface. Such a multimodal approach gives us new opportunities to study the basic chemical-physical aspects of solid-liquid interactions in porous media and opens an avenue to inferring correlations between microcrystal structure, porosity, surface chemistry, and adsorption properties of carbonaceous materials. The approach is applied to a new class of oxygen-sensitive paramagnetic carbon particles recently synthesized at the Illinois EPR Research Center. Supported in part by grants from NATO (HTECH. LG 972264), Fogarty International Foundation (1RO3 TW00998-01), NIH (RBC; GM51630, GM42208), and the U.S. Department of Energy (DE FG22-96 PC 96205); used facilities of the Illinois EPR Research Center (NIH P41-RR01811), an NIH Resource Center.

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64. ***A TWO-DIMENSIONAL ESR STUDY OF AGGREGATION OF GRAMICIDIN IN MEMBRANES.*** Richard H. Crepeau, Mingtao Ge, and Jack H. Freed, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301

Recent advances in the instrumentation of 2D-FT-ESR have greatly enhanced the applicability of ESR to the study of protein-lipid interactions. This is demonstrated by 2D-ELDOR experiments on model membranes containing the peptide: gramicidin A (GA). The improved bridge operating at 17.3 GHz has led to dead-times, τ_d as short as 25 ns. and nearly an order-of-magnitude signal-to-noise increase. This enables one to observe signals from both the bulk and boundary lipids. 2D-ELDOR overcomes the ambiguity and limited resolution of ESR spectra from membrane vesicles, and enables the clear separation of signals from the boundary and bulk lipids due to their very different T_2's and cross-peak evolution as a function of mixing time. GA aggregates in DPPC dispersions when the GA/DPPC molar ratio is greater than 1:15. This ultimately results in boundary lipids appearing in a new phase, a hexagonal (H_{II}) phase, which coexists with the bulk lipid phase. Thus, GA destabilizes the bilayer structure. We show how the 2D-ELDOR experiments relate to our recent model wherein the combined effects of partial hydration of the lipid headgroup by the GA and of the hydrophobic mismatch between GA and DPPC molecules leads to a dynamic bending of the end of the acyl chain, which then leads to dissociation of the GA channel, followed by GA aggregation, and finally H_{II} phase formation, as GA is added.

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65. ***HYSCORE STUDIES OF NO SYNTHASE AND MODEL COMPOUNDS.*** D. C. Gilbert, D. C. Doetschman,[a] S. Dikanov,[a,b] [a]Binghamton University, Department of Chemistry, Binghamton, NY 13902-6000, [b]Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia; D. J Stuehr, L. Huang, The Cleveland Clinic Research Institute, Cleveland, OH 44195; J. A. Smieja,Gonzaga University, Department of Chemistry, Spokane, WA 99258.

Nitric oxide(NO), now known to be of immense biological significance, is synthesized from oxidation of L-arginine(L-Arg) at the heme iron site of NO synthase(NOS). ESEEM spectroscopy is a potentially important tool for spin labeled enzyme pocket structure determination. We examined the HYSCORE spectra of NO labeled NOS with L-Arg and hydroxyarginine(HO-Arg) substrates in light of similar HYSCORE studies of NO-tetraphenylporphyrinato-Fe(II)-pyridine(NO-FeTPP-Pyr). NO-(^{15}N←FeTPP)-Pyr HYSCORE yields ^{15}N dipolar couplings of 0.51MHz<|T/h|<0.82MHz, corresponding to a point dipole model with the electron spin located 0.175±0.010nm from the porphyrin ring center and 0.112±0.009nm above its mean plane. The point spin projects the mean plane 38.4°±0.9° from the nearest pyrrole N, agreeing with a 38.6° NO bond projection in a comparable compound(W. R. Scheidt, A. C. Brinegar, E. B. Ferro and J. F. Kirnerk, J. Amer. Chem. Soc. 99, 7315 (1977)). NO-(^{14}N←FeTPP)-Pyr HYSCORE gives pyrrole ^{14}N quadrupole frequencies of 0.3005±0.0057, 1.2665±0.0051 and 1.5693±0.0075MHz and gives reasonable agreement with nuclear sublevel m_I=+1/2,-1/2 sublevel cross-correlation peaks predicted from a, T values scaled from ^{15}N values. The assignment indicates that only one of the pyrrole ^{14}N achieves cancellation conditions giving appreciable HYSCORE correlation peaks. The HO-Arg-NO-NOS spectrum has qualitatively the same features as NO-(^{14}N←FeTPP)-Pyr with pronounced quadrupole frequencies 0.405±0.021 and 1.610±0.006MHz, whereas no cross correlation peaks are found in L-Arg-NO-NOS. The possibility that a different NO orientation exists in L-Arg-NO-NOS that could remove all pyrrole ^{14}N cancellation conditions will be explored.

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66. ***MAGNETIC RESONANCE STUDIES OF PHENALENYL-ALKALI CATION COMPLEXES IN SOLIDS AND SOLUTIONS.*** D. W. Dwyer,[a] D. C. Gilbert,[a,b] M. F. Ciraolo,[a] D. P. Cheswick,[a] [a]SUNY at Brockport, Department of Chemistry, Brockport, NY 14420-2971; D. C. Doetschman,[b] [b]Binghamton University, Department of Chemistry, Binghamton, NY 13902-6000.

Previous electron spin phase memory time measurements versus temperature indicated indirectly that a weak covalent interaction between phenalenyl(PNL) and faujasite zeolite alkali cations influenced the molecular motion of PNL in the zeolite cage(D.C. Doetschman, D. W. Dwyer, J. D. Fox, C. K. Frederick, S. Scull, G. D. Thomas, S. G. Utterback and J. Wei, Chemical Physics, 185, 343 (1994)). The present work provides ^{7}Li-NMR and CW-EPR spectroscopic evidence for such an interaction between the π system of phenalenyl and Li^+ or Na^+ in solution. In rigorously dried methanol solutions this interaction results in the formation of a complex between phenalenyl and Li^+ or Na^+, which is in equilibrium with solvated cation and phenalenyl. The analysis of ^{7}Li-NMR data for this equilibrium in the Li+ solutions at 320K yields an equilibrium constant of 29±4M^{-1}. Analysis of the CW-EPR data for the Na^+ solutions in methanol at 295K produces an isotropic Na hyperfine frequency for the phenalenyl-Na+ complex of 4.2±0.1 MHz. HYSCORE measurements of PNL in Li-Y-zeolite yields the Li-PNL hyperfine coupling constant. The substantial isotropic part of the Li coupling indicates that 7–15% of the PNL spin may be transferred in the zeolite environment. The analysis of the anisotropic part of the Li-PNL coupling and attempts to observe PNL coupling with other alkali cations in the zeolite will be discussed.

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67. ***COMPETITIVE BINDING OF WATER ANALOGS TO THE OEC IN PHOTOSYSTEM II PROBED BY THREE-PULSE ESEEM.*** Marc Evanchik, Keri Clemens, and R. David Britt, Department of Chemistry, University of California Davis, Davis CA 94596

Competitive binding of substrate water analogs to the Oxygen Evolving Complex (OEC) of Photosystem II (PSII) has been examined by the pulsed EPR technique of ESEEM. Three pulse ESEEM was performed on the multiline EPR signal of a PSII membrane preparation treated with sufficient ammonia and methanol to completely saturate the available binding site(s) for these substrates. PSII membranes simultaneously treated with the water analogs ammonia and methanol display light minus dark ESEEM spectra modulated solely by methanol protons (deuterons). However, upon sample annealing, three sharp electric quadrupole features due to an I=1 ^{14}N nucleus grow in, with no decrease in the deuteron coupling. This suggests that each water analog is binding at separate sites, independently of each other.

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68. ***ESR AND SPIN TRAPPING STUDY OF THE FLUORESCENT DYE, 2'7'—DICHLOROFLUORESCEIN AND ITS IMPLICATIONS FOR OXIDATIVE STRESS MEASUREMENTS.*** Yang C. Fann, ITSS/NIEHS, P.O. Box 12233, Research Triangle Park, NC 27709; Emanuela Marchesi, Cristina Rota, Colin Chignell and Ronald P. Mason, Laboratory of Pharmacology and Chemistry, NIEHS, P.O. Box 12233, Research Triangle Park, NC 27709.

The fluorescent dye, 2',7'-dichlorofluorescein (DCF), has been used extensively to monitor oxidative activity in cells. In the presence of reducing reagent DCF can undergo one-electron reduction during the visible radiation (λ>300nm) under the anaerobic condition to form a semiquinone-type radical that can be directly detected by ESR. The spin trapping study of DCF using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) with reduced glutathione or NADH under the visible light demonstrated the formation of the superoxide dismutate-sensitive

DMPO/O_2^- adduct. In addition, the oxygen consumption measurements showed oxygen is consumed in a light-dependent process. The semiquinone-type radical of DCF when formed under aerobic condition is immediately oxidized by O_2 to form superoxide and regenerate the dye. The one-electron oxidation of DCF by horseradish peroxidase and H_2O_2 forms a phenoxyl radical which oxidize various substrates such as GSH, NADH and ascorbic acid. These results indicated that DCF must be used with caution especially when used to demonstrate superoxide formation in cells under oxidative stress.

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69. ***HIGH-FREQUENCY EPR SPECTROSCOPY OF BIRADICAL TOAC AND MTS SPIN-LABELED PEPTIDES: ANALYSIS OF DIPOLAR AND EXCHANGE INTERACTIONS.*** C. T. Farrar and R.G. Griffin, Massachusetts Institute of Technology, Francis Bitter Magnet Lab, Cambridge, MA 02139; J. McNulty and G. Millhauser, University of California, Department of Chemistry, Santa Cruz, CA 95064; W. Xiao and Y.-K. Shin, University of California, Department of Chemistry, Berkeley, CA 94720.

The technique of site-directed electron spin labeling has become a powerful tool for studying protein structure and dynamics by EPR spectroscopy. In particular, EPR techniques for measuring long-range interspin distances in biradical spin labeled systems have recently been developed that allow protein structure and dynamics to be studied in great detail. Here we examine the advantages of using high frequency EPR (HF-EPR) to extract both distance and orientation information from biradical systems. The use of two different electron spin labels has been investigated: methanthiosulfonate spin labels (MTSSL) were incorporated into an alanine-based a-helical polypeptide at different selective sites and TOAC nitroxide amino acids were incorporated into a 3_{10}-helical hexameric peptide sequence at different selective sites. The HF-EPR spectra demonstrate splittings and linewidth broadening arising from exchange and dipolar couplings between the two nitroxide spin labels. Simulations of the experimental data are employed to extract the biradical distance separations and relative orientations of the spin labels. The spectral simulations indicate that the HF-EPR spectral features are very sensitive to the relative orientation of the two nitroxide spin labels. This complicates the analysis of the MTSSL biradical peptides where a distribution of orientations is obtained due to the mobility of the tethered nitroxide spin label. In contrast, the more rigid TOAC spin label is more amenable to the extraction of orientation information.

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70. ***HIGH-FREQUENCY PULSED EPR AND ENDOR STUDIES OF THE HYDROGEN BONDING ENVIRONMENT OF THE Y_Z TYROSYL RADICAL OF PHOTOSYSTEM II.*** C. T. Farrar and R.G. Griffin, Massachusetts Institute of Technology, Francis Bitter Magnet Lab, Cambridge, MA 02139; D.A. Force and B.A. Diner, Central Research and Development Department, Experimental Station, E.I. DuPont de Nemours & Co., Wilmington, DE 19880; K.A. Campbell, J.M. Peloquin, and R.D. Britt, University of California, Department of Chemistry, Davis, CA 95616.

The high-frequency (139.5 GHz) Echo Detected-EPR (ED-EPR) spectrum of the Y_Z tyrosyl radical of photosystem II in Mn depleted, D2-Y160F mutant samples displays a rhombic powder pattern with principal g values of g_X=2.00760, g_Y=2.00450, and g_Z=2.00230. The value of g_X is consistent with a hydrogen bonded tyrosyl radical. The broad width of the g_X turning point indicates a disorder in the hydrogen bonding environment, as was previously observed at 245 GHz by Un et al. (Biochem., 1996, 35, 679-684). However, in contrast to the 245 GHz CW-EPR spectrum of Y_Z, which observed no structure on the g_X orientation, a splitting or asymmetry is resolved on g_X in the 139.5 GHz ED-EPR spectrum. The observed splitting is attributed to either different hydrogen bonding environments for Y_Z radicals in these Mn depleted samples (in which some radicals retain two hydrogen bonds and others only one) or from resolved electron-nuclear hyperfine couplings. High-frequency pulsed ENDOR experiments are being performed to elucidate the origin of the structure on g_X. Density functional molecular orbital calculations of model systems have been performed to aid in the interpretation of the electron g shifts and the quantitation of the hydrogen bond strength(s).

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71. ***λ/4 ANTENNA COUPLING TO A DIELECTRIC RESONATOR: TIME RESOLVED NUMERICAL ELECTROMAGNETIC FIELD CALCULATIONS.*** Jürg Keller[a], Jörg Forrera, Arthur Schweigera, Rolf Schuhmannb, Thomas Weiland[b], [a]Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule,8092 Zürich, Switzerland., [b]Institut für Hochfrequenztechnik, Technische HochschuleDarmstadt,6100 Darmstadt, Germany.

A λ/4 antenna fixed to a 50 Ω coaxial cable that couples mw energy to and from a high-Q Dielectric Resonator (DR) is investigated by means of time resolved three-dimensional numerical computations. These computations investigate the electromagnetic field propagation between the λ/4 antenna that strongly overcouples the DR oscillating at 9.7 GHz. The propagation of the electromagnetic field is shown in five π/6 increments of a single oscillation (sine function). These time resolved field plots present a new design tool for a better understanding and handling of this λ/4 coupling antenna and give information about the resonator area with maximum field homogeneity.

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72. ***PHARMACOLOGICAL MODIFICATIONS OF THE PARTIAL PRESSURE OF OXYGEN IN MURINE TUMORS: EVALUATION USING IN VIVO EPR OXIMETRY.*** B. Gallez, B. Jordan, C. Baudelet, P.-D. Misson. Laboratory of Biomedical Magnetic Resonance, Université Catholique de Louvain, Brussels, Belgium.

We used EPR oximetry to quantify the pO_2 *in a transplantable mouse liver tumor model (TLT) possessing a low* pO_2 *after administration of 34 different compounds: angiotensin-converting enzyme inhibitors (n=3), calcium antagonists (n=5), alpha antagonists (n=5), potassium channel openers (n=3), beta-blockers (n=4), NO donors (n=4), and peripheric vasoactive agents (n=10). These drugs are routinely used in human for their vasoactive effect, i.e. in the treatment of hypertension or other blood circulation diseases such as Raynaud syndrome or intermittent claudication. The doses of the vasoactive compounds administered to mice were previously shown to be effective in changing hemodynamics (i.e. arterial pressure) in rodents. Results were compared after breathing of pure oxygen or carbogen. Initial control levels* pO_2 *were observed from the center of TLT tumors and were measured at 0 to 3 mm Hg. The* pO_2 *reached after injection as well as the time course of increasing* pO_2 *was quite variable from one tumor to another. The tumor* pO_2 *dramatically increased after the administration of several vasodilators, while other compounds did not lead to any significant change in the tumor* pO_2*.*

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73. ***DIRECT AMPLIFICATION LOW FREQUENCY CW EPR SPECTROMETER.*** Valeri E. Galtsev, Eugene D. Barth, Benjamin B. Williams, and Howard J. Halpern, Department of Radiation and Cellular Oncology, University of Chicago, Chicago, IL, 60637

A low frequency (190 MHz) continuous wave (cw) EPR spectrometer is described based on direct amplification signal processing. The Stanford Research Systems (Sunnyvale, CA) model SR844 lock-in amplifier capable of synchronous demodulation at frequencies up to 200 MHz was used to amplify directly and demodulate the carrier frequency. No field modulation was used in the direct amplification mode. Therefore, experimental spectra represent EPR absorption profiles. Spectra obtained in the direct amplification mode for diphenylpicrylhydrazyl powder, and for narrow line argon equilibrated phthalocianine monolithium powder, and evacuated acqueous solution of trimethylaryl radical were compared with that measured in the conventional field modulated mode. The signal-to-noise ratio was three times worse for the direct amplification mode in comparison with the conventional field modulated mode. This demonstrates the feasability of direct amplification of EPR spectroscopy technique allowing to measure absorption profiles using digital signal processor based synchronous demodulation of the RF power at frequencies less than 200 Mhz. Supported by NIH grant CA69538.

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74. ***IMPROVEMENT OF EPR SENSITIVITY BY USE OF A FERROELECTRIC RESONATOR—TE_{011} STRUCTURE.*** Ilia.N.Geifman, Iryna S.Golovina, Institute of Physics of Semiconductors of NASU, pr.Nauki 45, 252028 Kiev, Ukraine.

We propose a new geometry of the ferroelectric resonator (FR) placed into the center of a standard cavity (TE_{011}*). When we use the FR, the magnetic microwave field on a sample is increased considerably, resulting in signal intensity enhancement. The design structure was tested on continuous wave (CW) experiments at X band within a temperature interval of 77-400 K. Several forms of the FR made from potassium tantalate (*$KTaO_3$*), with dimensions presented in the table, were examined. d represents the diameter of the cylindrical bore, h defines its depth, D is the outer diameter of the FR, L defines its height, A and B are the width and length respectively of a rectangular FR. A cylindrical sample of the soot carbon was inserted inside of the bore to obtain G, the signal-to-noise ratio in the FR-*TE_{011} *structure and in the cavity alone at equal incident power and equal field modulation amplitude. ν is the resonant frequency of the FR-*TE_{011} *structure. Thanks to the unique feature of* $KTaO_3$ *its dielectric losses are decreased as its dielectric susceptibility is increased. Significant sensitivity enhancement can be obtained at low temperatures by optimizing the FR dimensions. Preliminary estimates indicate an increase of nearly 70 times in signal intensity when the spherical-shaped FR is used.*

Characteristics of FR and FR-TE011 structure

No.	*d(mm)*	*D(mm)*	*h(mm)*	*L(mm)*	*A(mm)*	*B(mm)*	*n (GHz)*	*T (K)*	*G*
1	1.9	3.1	2.0	2.0	-	-	9.180	250	5
							9.22	392	4.6
2	1.9	3.2	3.8	4.9	-	-	9.210	365	4.8
3	1.9	-	2.0	3.4	2.8	2.6	9.152	331	16
4	0.9	-	1.4	1.4	1.8	1.8	9.143	165	28.5
5	0.9	-	1.5	3.1	1.5	1.5	9.129	120	35
							9.250	215	37

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75. ***COMPUTER SIMULATION OF RANDOMLY ORIENTED EPR SPECTRA EMPLOYING HOMOTROPY.*** Mark P. Griffin, Centre for Magnetic Resonance, University of Queensland,4072, Brisbane, Australia; Kevin E. Gates, Department of Mathematics, University of Queensland, 4072, Brisbane, Australia; Graeme R. Hanson, Centre for Magnetic Resonance, University of Queensland, 4072, Brisbane, Australia; Chris Noble, Centre for Magnetic Resonance, University of Queensland, 4072, Brisbane, Australia; Kevin Burrage, Centre for Magnetic, Resonance, University of Queensland, 4072, Brisbane, Australia

Traditional methods for the computer simulation of randomly oriented EPR spectra use matrix diagonalisation to evaluate the eigenvalues and eigenvectors of the Spin Hamiltonian matrix. One approach, the eigenfield method[1] *considers each orientation in the angular grid independently. The magnetic field range is divided into a number of intervals, and Matrix diagonalisation performed in each interval. Second order perturbation is then used to locate the resonant field positions. Unfortunately, matrix diagonalisation is a time-consuming process (each diagonalisation requires 8 to 10* n^3 *operations, where n is the size of the Spin Hamiltonian matrix) and is not feasible to simulate EPR spectra from complex spin systems. An alternative approach is Homotopy which traces the eigenvalues and eigenvectors from one Hamiltonian to another (which is adjacent with respect to magnetic field and angle). This results in reduced computational times (each iteration requires 2/3* n^3 *operations)*[2]*. A variation of our Homotopy approach has been developed which uses some concepts of the traditional eigenfield method. Each orientation over the angular grid was considered independently, and the field range at each orientation was divided into a small number of intervals. An iteration of Homotopy was performed once in each interval to determine the eigenvalues. The behaviour of each eigenvalue with respect to field was observed, and rough estimates were produced for each resonant field position. Refinement of the resonant field positions was performed using additional Homotopy iterations. Results of this method suggest that the simulation time of this approach may be less than half that of the eigenfield approach. Both Homotopy implementations include the ability to trace looping transitions and perform the simulations in frequency space. A discussion of the improvements to the homotopy method and a selection of representative examples will be presented.*

1. *Belford et al., J. Magn. Reson., 1973, 11, 251.*
2. *Gates et al., J. Magn. Reson., 1998, 135, 104.*

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76. ***FLOW VELOCITY-SWEEP METHOD TO FOLLOW SUBMILLISECOND REACTION KINETICS OF CHEMICALLY EVOLVING FREE RADICAL SYSTEMS.*** Vladimir M. Grigoryants, Andrei V. Veselov, and Charles P. Scholes, SUNY at Albany, Department of Chemistry, Albany, NY 12222.

We have modified our former dielectric resonator (DR)-based stopped-flow system [Sienkiewicz et al. (1994) Rev. Sci. Instrum. 65, 68] to provide a smaller dead volume and to accommodate a new miniature quartz capillary containing a micro (0.55 mm diameter) platinum-ball mixer. As a function of the resultant delivery time (dead time) between mixing of reactants and their delivery to the active volume of the DR, the signal EPR intensity was followed under condition of continuous flow. The flow velocity was varied in a pre-programmed manner. The timing scale was calibrated and tests of mixing efficiency were performed by following the rapid destruction of 2 mM TEMPO (2,2,6,6-Tetramethylpiperidine-N-oxyl) spin probe by 30 mM sodium dithionite reductant, where probe destruction is linear in time and occurs in milliseconds. Delivery times in the 0.14 to 2.5 ms range were thus calibrated. Based on empirically measured delivery times and programmed flow rates, the dead volume between mixer and the midpoint of the EPR active zone was ~ 0.45 μL, and this dead volume was within 8 % of the dead volume estimated from geometry. Mixing became inefficient and incomplete at slow flow velocities corresponding to delivery times > 2.5 ms. However, our device can be used in standard stopped-flow mode to obtain kinetics for times longer than ~2 ms under initial flow conditions that are efficient. Our fundamental biochemical question is whether protein folding starts with a global burst of fast, submillisecond compacting and collapse. Previous stopped-flow work with limited time resolution, including our own DR-based stopped-flow work on iso-1-cytochrome c spin-labeled at its naturally occurring Cys-102 [Qu et al. (1997) Biochemistry 36, 2884], has shown that an early unresolved majority of protein refolding, called the "burst", occurs. The rapid refolding "burst" kinetics and immobilization of spin label in yeast iso-1-cytochrome c were probed here with an order of magnitude better time resolution than previously. The refolding was followed at room temperature after mixing dilute pH 5.0 buffer with cytochrome unfolded in 0.8 M guanidinium hydrochloride. From the rapid-mix flow technique reported here, we found that a fast component comprising ~35 % of the kinetic refolding was complete within 0.5 ms and was fitted with an exponential time constant of 0.12 ms. This new rapid-mix flow technology is intended to provide a comparative study of submillisecond protein folding at numerous natural and mutated cysteine labeling sites throughout the protein. (This work supported by NSF Grant MCB-9817598 and ACS-PRF Grant 34132-AC4.)

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77. ***MULTI-PHOTON RESONANCES IN PULSE EPR.*** Igor Gromov* and Arthur Schweiger, Physical Chemistry Laboratory, ETH Zentrum, Zurich, Switzerland, CH-8092. *On leave from MRS Lab., Kazan State University, Kazan, Russia, 420008

The use of multi-photon resonances in two-level systems involving odd numbers of photons has been demonstrated in continuous-wave EPR [1] and pulse NMR [2] spectroscopy. Two-photon resonance has been used to monitor of transient nutations in an electron spin system [3]. In the present work, for the first time odd multi-photon resonances have been observed in pulse EPR. Experimental results demonstrate the detection of three- and five-photon resonances. Possible applications of the multi-photon transitions for resolution improvement of EPR spectra and for coherent Raman beat detection are investigated.

1. *P. Sczaniecki, J. Hyde, J. Chem. Phys. 94, 5907 (1991).*

2. Y. Zur, M. Levitt and S. Vega, J. Chem. Phys. 78, 5293 (1983).
3. R. Boscaino, F. Gelardi and G. Messina, Phys. Rev. B, 33, 3076 (1986).

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78. ***INFORMATION CONTENT IN RADIOFREQUENCY EPR SPECTRAL-SPATIAL IMAGES OF TUMORS IN LIVING MICE.*** B. Williams, G.V.R. Chandramouli, E.D. Barth, V. Galtsev, and H.J.Halpern, U. Chicago, Chicago, IL 60637

Radiofrequency EPR images of tumors in a living mouse with narrow single line spin probes obtained from Nycomed Innovations provide a spectral map of living tissue. Within each pixel, a spectrum can be established. Presently available spectral spatial images of tumors and phantoms will be presented with in plane voxel size of 0.3 mm × 0.3 mm × 15 mm (1.35 ml). These voxels likely represent spatial over-sampling of the image, although, from phantom measurements by no more than a linear factor of two (in plane). From within each of these voxels, spectra are obtained with good signal to noise. Similar S/N should be available from 0.6×0.6×4 mm voxels. These are capable of defining the width of the spectral line to within 1%, giving equivalent oxygen partial pressure quantitation to 1 torr or better. The imaging process itself involves various trade offs between spectral and spatial sampling frequencies. Spatial sampling can affect the apparent spectral linewidth. We investigate these effects in order to understand how the process of image formation blurrs spectral information as well as spatial information. These aspects of image formation need to be understood either to correct the image or to understand the conditions under which the image should be obtained to derive information with a specified resolution. Oxygen maps will be presented and related to other modalities.

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79. ***SYNTHESIS AND RADIOPROTECTION OF NOVEL POLY(ETHYLENE GLYCOL) CONJUGATE OF PBN.*** Matthew M. Hamilton, Yashesh N. Vaishnav, Alasdair J. Carmichael, and Thomas M. Seed, Armed Forces Radiobiology Research Institute (AFRRI), Bethesda, MD 20889-5603; Robert F. Brady and Barry J. Spargo, Naval Research Laboratory (NRL), Washington, DC 20375-5348

The nitrone spin trap, α-phenyl-N-tert.-butylnitrone (PBN), has been extensively investigated as an antioxidant and protective agent against free radical damage. However, its insolubility in water and toxicity to cells has limited its utility. The present study describes the synthesis of the novel derivative of PBN, p-hydroxy -α-phenyl-N-tert.-butylnitrone (HPBN), and covalent linking to poly(ethylene glycol) (PEG-HPBN) in order to increase the nitrone's in- vivo efficacy by increasing its solubility and decreasing its toxicity. The trapping efficiency of the polymeric nitrone for radicals generated in- situ with γ-irradiation (^{60}Co) will be compared to HPBN, PBN, α-(4-pyridyl-1-oxide)-N-tert.-butylnitrone (POBN), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), and 3,3,5,5-tetramethyl-1-pyrroline-N-oxide (M4PO). The efficiency of each compound will be correlated to its toxicity in cells in order to determine relative radioprotective strength for each nitrone spin trap.

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80. ***REFINEMENT OF THE EPR PARAMETERS FOR THE HIGH SPIN FE(III) CENTER IN A SWEET POTATO PURPLE ACID PHOSPHATASE - THE INFLUENCE OF STRAIN BROADENING.*** Graeme R. Hanson, Christopher J. Noble, Clare L. Boutchard, Gary Schenk, Susan E. Hamilton, John De Jersey, Centre for Magnetic Resonance and Department of Biochemistry, University of Queensland, St Lucia, Queensland, 4072, Australia.

We have recently purified a purple acid phosphatase from sweet potatoes (SPPAP) and metal ion analyses, EPR and magnetic susceptibility studies indicate the presence of a strongly antiferromagnetically coupled binuclear Fe(III-μ-O-Mn(II) centre.[1] The continuous wave EPR spectra of SPPAP reveal high spin Fe(III) and Cu(II) resonances, the former arising from small proportions of Fe-apo and Fe-Zn centres also present in the purified enzyme. Computer simulation, with XSophe[2] of the resonances arising from high spin Fe(III) with a second order fine structure spin Hamiltonian ($H = g\beta B.S + S.D.S$) reveals the presence of two components. A D- and E-strain linewidth model based on the derivative of the resonant field position with respect to D and E was used to account for the large linewidths. Most of the features were reproduced with the parameters (g=2, D=1.2 cm^{-1}, λ=E/D=0.1925 and a relatively small distribution of D and λ (σ_x=σ_y=σ_z=0.005, σD=0.05 cm^{-1}, $\sigma\lambda$=0.05). While the value of λ was constrained by the resonant field positions, the magnitude of D was unable to be determined accurately. The g_{eff}=4.3 feature may arise arise from either a rhombically distorted Fe(III) ion with λ=1/3 or from a species with reduced rhombicity (λ <1/3) and a large distribution in λ values (g=2, D=1.2 cm^{-1}, λ=E/D=0.27, σ_x=σ_y=σ_z=0.002, D=0.01 cm^{-1}, $\sigma\lambda$=0.1). Further refinement of the lineshape model in XSophe is underway to account for the intensities of the resonances in the experimental spectrum.

1. G. Schenk, L.E. Carrington, J. De Jersey, S. E. Hamilton, C. L. Boutchard, C. J. Noble, G. R. Hanson, K. S. Murry, B. Moubarake, Submitted.

2. M. Griffin, A. Muys, C. J. Noble, D. Wang, C. Eldershaw, K. E. Gates, K. Burrage, G. R. Hanson, Mol. Phys. Rep., in press 1999.

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81. ***ENHANCEMENT OF SIGNAL INTENSITY FOR SAMPLES WITH SLOW ELECTRON SPIN RELAXATION BY OUT-OF-PHASE DETECTION.*** James R. Harbridge, George Rinard, Sandra S. Eaton, and Gareth R. Eaton, University of Denver, Denver, CO 80208

Enhanced EPR signals have been detected 90∞ out of phase with respect to the magnetic field modulation. These signals have been obtained at powers that are much higher than the power at which the maximum signal can be obtained with in-phase detection. The power at which these signals are detected and the degree of enhancement depend upon the relaxation times of the sample. Samples that have long electron spin relaxation times have been shown to produce minimally-distorted out-of-phase signals up to 9 times as large as the in-phase signal. Samples with very short relaxation times show no out-of-phase signals. Samples studied include irradiated vitreous SiO2, Fremy's salt, and various irradiated organic solids.

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82. ***NOVEL SPIN REAGENTS FOR IN VIVO ESR: ACYL-PROTECTED HYDROXYLAMINES.*** Osamu Itoh, Hidekatsu Yokoyama, Masaaki Aoyama, Heitaro Obara, Hiroaki Ohya†, Hitoshi Kamada, Institute for Life Support Technology, Yamagata Technopolis Foundation, 2-2-1 Matsuei, Yamagata, 990-2473, Japan

Novel spin reagents, acyl-protected hydroxylamines, have been synthesized for the detection of reactive oxygen species (ROS) formed in intracellular space, and tried to apply to in vivo ESR measurement of biological systems. It is expected that their acyl sites are deprotected by enzymatic hydrolysis in cells to give hydroxylamines, which are converted into nitroxide radicals by ROS generated inside or outside the cells.We prepared 1-Acetoxy-3-carbamoyl-2,2,5,5-tetramethylpyrrolidine [ACP], 1-Propionyloxy-3-carbamoyl-2,2,5,5-tetramethylpyrrolidine [PCP], 1-Butyryloxy-3-carbamoyl-2,2,5,5-tetramethylpyrrolidine [BuCP], 1-Benzoyloxy-3-carbamoyl-2,2,5,5-tetramethylpyrrolidine [BeCP] in good yields. It has been tried to examine whether their utilization is possible in known cell systems. We have confirmed that acyl-protected hydroxylamines are deprotected to hydroxylamines by enzymatic hydrolysis and the hydroxylamines thus formed are oxidized to corresponding nitroxide radicals by neutrophil superoxide generation system. We have also investigated that acyl-protected hydroxylamines become the imaging reagent, and succeeded in obtaining a characteristic image of rat head with L-band ESR-CT. Conventional in vivo ESR studies only measure distribution and metabolism of radical compounds after their administration, but this study measures the transformation of non-radicals into radicals after in vivo administration. This is the first application observing the distribution of oxidative species in brain of rat more directly than usual spin probe methods.

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83. ***DRESSED ELECTRON SPIN RESONANCE.*** G. Jeschke, Max-Planck-Institute for Polymer Research, Postfach 3148, D-55021 Mainz, Germany

In the presence of resonant irradiation, spins are quantized by the eletromagnetic rather than the static field. The spins can then be considered to be 'dressed' by the electromagnetic field using a term coined by Cohen-Tannoudji for the analogous situation in optics. Transitions of dressed spins can be driven by secondary irradiation parallel with the static field, as has already been pointed out and demonstrated experimentally by Redfield in his first paper on NMR (Redfield, A.G. (1955), Phys. Rev. 98, 1787). No applications of this phenomenon have been developed so far in either NMR or EPR spectroscopy, although the physical situation is certainly interesting. Dressed spins can be prepared with high-field polarization but their states evolve in an effective low field. In addition, the two irradiation fields correlate perpendicular orientations without the requirement for turning the sample. We have demonstrated recently that dressed electron spin transitions can be detected with commercial pulse ENDOR equipment by changing the orientation of the r.f. coil with respect to the static field (Jeschke, G. (1999), Chem. Phys. Lett. 301, 524). Broadband excitation by short r.f. pulses covers the whole range of typical dressed spin resonance (i.e., bare spin nutation) frequencies from about 1 to 20 MHz, so that two-dimensional correlation experiments can be performed easily. In the present contribution we discuss the possible applications of dressed electron spin resonance to disordered systems. The method has advantages for the measurement of broad distributions of nutation frequencies as they arise in this case. It is discussed which information can be obtained from the dependence of such distributions on m.w. field strength and EPR obserever position. The correlation between bare spin nutation frequencies of different transitions and between bare spin and dressed spin nutation frequencies are analysed as a means for resolution enhancement.

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84. *W-BAND FT-EPR AND PULSED ENDOR STUDIES WITH THE BRUKER ELEXSYS E680 SPECTROMETER.* Andreas Kamlowski, Peter Höfer, Dieter Schmalbein, BRUKER Analytik GmbH, EPR Division, 76287 Rheinstetten, Germany

The main advantage of high-frequency/high-field EPR at for example 94 GHz (W-band) is the increased spectral resolution as compared to X-band frequencies. In addition, the higher absolute sensitivity and the accessibility of transitions for samples with large zero field splittings are other advantages. On the other hand, pulse EPR has been well established at X-band, giving access to information not achievable with CW-EPR. The free induction decay (FID) and the electron spin echo experiment following a single or at least two microwave pulse(s) represent the simplest pulse EPR experiments. Obviously, combination of high-frequency EPR and pulse EPR techniques will then lead to unique information. W-band FID pulse EPR experiments on N@C60 will be shown. The comparison to W-band CW-EPR clearly demonstrates the superiority of the pulse experiment with regard to the multiplex advantage and the respective signal-to-noise ratios. Pulse length and shot repetition time of the phase-cycled FID experiment were optimized according to the Ernst angle with small effective flip angles (about 10°) and repetition times ca. 3 times smaller than the T1 time (see also ref. 1 for details). Secondly, pulsed ENDOR experiments will be shown obtained with a newly developed pulsed ENDOR W-band probehead. The rf circuit is tuned for 1H and broad-band for the other nuclei. RF π pulses of below 10 μs are achieved with a 200 W amplifier. Representative examples for both Davies and Mims type pulsed ENDOR experiments for ^{1}H, ^{14}N, ^{13}C, ^{2}D, ^{11}B nuclei are presented.

1. *D. Schmalbein et al., Appl. Magn. Res., 1999, in press.*

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85. *PULSED EPR STUDIES OF 3-DIMENSIONAL STRUCTURE OF ELECTRON TRANSFER COMPONENTS IN PHOTOSYSTEM II.* Asako Kawamori, Hideyuki Hara, Takahiko Yoshii, Kwansei Gakuin Univ., Faculty of Science, Nishinomiya, 662-8501 Japan, and Andrei V. Astashkin, Univ. of Arizona, Department of Chemistry, Tucson, Arizona 85721 USA

The distances between radical pairs and their angles relative to the membrane normal in Photosytem II particles have been determined by ESEEM of laser induced spin polarized radicals [1] and ELDOR of trapped radical pairs, donor and acceptors [2]. The ESEEM results of the membrane oriented PS II particles show that the distance between P680 and Q_A and its angle to be 27.4 Å and 21°, respectively. The "2+1" pulse sequence ESE has shown that those between Q_A and Y_D were 38 Å and 13°, respectively. Based on another data of the distance 29 Å between Y_D and Y_Z and the symmetric arrangement around P680, the distance from P680 to Y_D or Y_Z and its angle were derived to be 20 Å and 43° respectively. 3-dimensional arrangement of most of electron transfer components can be derived by pulsed EPR studies, when X-ray analysis is not available. The limitation of distance determination by pulsed EPR is discussed by a spin de-localization over the radical molecule in the reaction center.

1. *Hara et al., Biochim. Biophys. Acta 1997, 1322, 77.*
2. *Astashkin et al., J. Chem. Phys. 1998, 108, 3805.*

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86. *SPIN-TRAPPING STUDIES OF RADICAL INTERMEDIATES IN AZOESTER HYDROLYSIS: IN SEARCH OF NEW DNA-CLEAVING COMPOUNDS.* Veeraraghavan Srinivasan, Russell Hopson, Stephen V. Kolaczkowski, and David E. Budil, Department of Chemistry, Northeastern University, Boston, MA 02115

Natural enediyne anticancer antibiotics have attracted tremendous interest in the past decade. The difficulty in synthesizing the strained enediyne moiety in these structurally complex natural products has motivated a search for simpler molecules that can mimic the radical chemistry of these compounds. We have sought to identify molecules that can produce 1,4-benzenoid diradicals, which are known to induce DNA cleavage in the natural products. Phenyl-, pyridyl- and pyrimidyl-azoesters have been synthesized, and spin trapping of the hydrolysis intermediates by 2,4,6 tri-t-butylnitrosobenzene has allowed the identification of sp2 carbon radicals. A 1,4-bisazoester has been synthesized, and our studies provide strong chemical evidence for the existence of a 1,4-diradical intermediate. Spin-trapping has also identified an sp2- radical formed by hydrolysis of the 6-azoester substituted 10-methoxy-13H benzo[6,7]indolo[3,2-c]quinoline, a known DNA triple helix intercalator [C.H. Nguyen et al., J. Amer. Chem. Soc., 120:2501 (1998)]. Efforts are under way to achieve sequence-specific radical cleavage of DNA by incorporating the intercalating azoester into a triple helix formed between a target duplex and a short oligonucleotide complement strand.

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87. *220 GHz EPR STUDIES OF TRIPLET STATES IN THE BACTERIAL PHOTOSYNTHETIC REACTION CENTER.* Stephen V. Kolaczkowski, Ronghui Zeng, and David E. Budil, Department of Chemistry, Northeastern University, Boston MA 02115

At high magnetic fields, the yield of triplet state formed by radical pair intersystem crossing in the primary radical pair of photosynthetic reaction centers (RCs) is known to be strongly orientation-dependent. The effect is due to the orientation dependence of the g-factor difference between the primary donor (P^+) and acceptor (BPh^-) radicals, which dominates the rate of intersystem crossing at high fields. Boxer and co-workers [S.G. Boxer, C.E.D. Chidsey, and M.G. Roelofs, Proc. Natl. Acad. Sci. (USA)., 79:4632 (1982)] first demonstrated this *effect by measuring the linear dichroism of the triplet state bleaching at 870 nm relative to the applied field direction. Here it is shown that the yield anisotropy can be fully determined by observing the EPR spectrum of the triplet product at high magnetic field and frequency (220 GHz). Using the known orientations of the triplet zero-field tensor axes and the principal g-axes of P^+, the triplet high-field intensity pattern can be analyzed to determine the principal g-axes of both BPh^- and the triplet state itself. This type of analysis can be applied to either the primary donor triplet state, or that of the carotenoid pigment in carotenoid-containing RC's.*

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88. *EFFECT OF SOLVENT ON RELAXATION AND STRUCTURE OF MANGANESE(II) CENTERS BY MULTIFREQUENCY EPR AND CW ENDOR.* Rachel I. Konda, Yao-Min Xia, R. B. Clarkson and R. L. Belford, Illinois EPR Research Center, University of Illinois, 506 S. Matthews, Urbana, IL 61801.

For a free symmetrical S-state ion like Mn^{2+} in solution, the zero field splitting is determined by the organization of solvent molecules around the metal ion. A combination of approaches was used to study the effect of solvent composition on Mn(II) relaxation. First, the linewidth of $MnSO_4$ in a variety of mixed solvents was measured at three different frequencies (35GHz, 48GHz and 95GHz). The zero field splitting contribution to the spin Hamiltonian should decrease with increasing frequency. These studies showed that for solvents substantially larger than water (e.g. glycerol), linewidth increased as a function of viscosity but for smaller solvents such as methanol, the relationship between linewidth and solvent viscosity was not linear. For the methanol/water system, the linewidth did not monotonicaally increase with mole fraction of methanol but rather went through a maximum. The linewidth measurements for representative complexed Mn(II) showed the same maximum at intermediate solvent composition that was seen in the free Mn. Thus in the second half of these experiments the X-band CW ENDOR of MnSO4 in water:methanol solutions was examined to gather information on the structure of the inner solvation sphere. Supported by NIH P41 RR01811 and RO1 GM42208 and PHS Grant Number 5 T32 CA 09067. Resources provided by Illinois EPR Research Center, an an NIH-funded Resource Center.

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89. *330-670 GHZ EPR STUDIES OF CANTHAXANTHIN RADICAL CATION STABILIZED ON A SILICA-ALUMINA SURFACE.* T. A. Konovalova, University of Alabama, Department of Chemistry, Tuscaloosa, AL 35487; J. Krzystek, National High Magnetic Field Laboratory, Tallahassee, FL 32310; P. J. Bratt, University of Florida, Gainesville, FL 32611; J. Van Tol, National High Magnetic Field Laboratory, Tallahassee, FL 32310; L.-C. Brunel, National High Magnetic Field Laboratory, Tallahassee, FL 32310; L. D. Kispert, University of Alabama, Department of Chemistry, Tuscaloosa, AL 35487

We report the first example of well-resolved 330-670 GHz EPR spectra of a carotenoid radical cation. At 9-250 GHz the carotenoid radical cation cannot be distinguished from other C-H π-radicals observed in powder and frozen glasses, since its g tensor cannot be resolved at these frequencies. The 330 GHz and higher frequency EPR spectra were resolved into two principal components of the g tensor. Spectral simulation indicated this to be the result of g-anisotropy where $g_{\parallel} = 2.0032$ and $g_{\perp} = 2.0023$. This type of g tensor is consistent with the theory for polyacene π-radical cations, which states that the g tensor becomes cylindrically symmetric with increasing chain length. This also demonstrates that the symmetrical unresolved EPR line at 9 GHz is due to a carotenoid π-radical cation with electron density distributed throughout the whole chain as predicted by RHF-INDO/SP molecular orbital calculations. The lack of temperature dependence of the EPR linewidths over the range of 5-80 K suggests rapid rotation of methyl groups even at 5 K that averages out the proton couplings from three oriented b-protons. The present work shows that the 330-670 GHz EPR measurements are sufficient to resolve the individual g tensors components and distinguish carotenoid radical cations from other C-H containing radicals, which have different symmetry. Supported by the Division of Chemical Sciences, the U.S. Department of Energy, DE-FG02-86ER13465 (Tuscaloosa).

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90. *MEASUREMENT OF INTRA- AND INTERMOLECULAR DISTANCES.* Albert H. Beth, Vanderbilt University, Nashville, TN 37232-0615.

Spectroscopic methods are rapidly emerging as important tools for measuring intra- and inter-molecular distances in a wide range of macromolecular systems of contemporary interest. The distance constraints obtained are being used to determine structural features and dynamics of structural transitions in many systems which are not amenable to study using other structural techniques. Determination of the structures of proteins and nucleic acids is a central theme of modern biomedical research and the rapid advances which are being made are leading to establishment of structure-dynamics-function relationships for many important proteins, nucleic acids, and their complexes. Two methods, fluorescence resonance energy transfer (FRET) and EPR are emerging as methods of choice for determining interresidue distances and in some cases, the relative orientations of molecular probes. Both techniques have unique capabilities for modern structural studies and they share many common features. The capabilities of each of these methods will be discussed in light of recent advances in site-directed labeling of proteins and nucleic acids with a wide range of exogenous molecular probes. The challenges which remain for each of these methods to gain more wide-spread use as central tools in modern structural studies will be addressed. Supported by NIH HL34737.

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91. ***SIMULATION OF THE EPR SPECTRA OF DIPOLAR COUPLED NITROXIDES.*** Eric J. Hustedt, Department of Molecular Physiology and Biophysics, 727 Light Hall, Vanderbilt University, Nashville, TN 37232.

Both the interspin distance and the relative orientation of two dipolar coupled, immobilized nitroxides can be precisely determined by simulaton of the CW-EPR when the nitroxides adopt a unique, static geometry [E. J. Hustedt et al., Biophys. J. 74, 1861-1877 (1997)]. Direct spectral simulation also has the potential to produce the most accurate distance and relative orientation information from dipolar coupled nitroxides where the spin labels are not immobilized or do not adopt a single orientation with respect to each other. Models are being developed for the explicit simulation of EPR spectra in these cases. These models are being tested on data obtained from doubly labeled 4K peptides and doubly labeled mutants of T4 lysozyme.

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92. ***DISTANCE MEASUREMENTS IN PROTEINS AND RNA USING SPIN LABELING EPR.*** Yeon-Kyun Shin, Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720

Recent developments of spin labeling EPR make it possible to quantitatively determine distances between pairs of nitroxide spin labels attached to biological macromolecules. This EPR distance measurement strategy, in combination with the site-directed spin labeling for proteins, has been successfully applied to many important biological systems including the synaptic SNARE complex, the aspartate chemotaxis receptor, bacteriorhodopsin, and the maltose binding protein. In particular, a high resolution structure of the SNARE complex has been modeled based on a set of EPR measured long-range distances. The authenticity of this structure has been verified by the later published crystallographic structure. For aspartate chemotaxis receptors the mechanism of transmembrane signal transduction has been fully characterized. These exciting new results on various protein systems will be presented. Additionally, a new site-specific labeling strategy for RNA has been developed in my laboratory for EPR studies. This new RNA spin labeling strategy as well as its application to some interesting RNA systems will be also presented.

93. ***IDENTIFICATION OF PROTEIN FOLDING PATTERNS USING SITE-DIRECTED SPIN LABELING.*** Hassane S. Mchaourab, Biophysics Research Institute, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, WI 53226

Measurement of the distance between two nitroxide spin labels, site-specifically introduced into a protein sequence, can provide the spatial constraints necessary to determine the protein tertiary and quaternary structures. While the theoretical approaches for the analysis and interpretation of the interaction between two nitroxides have been developed, the use of the resulting geometric information in the context of molecular structure determination is in its early stages. Significant issues concerning the selection and number of nitroxide pairs, how to account for the effect of side chain flexibility, and how to transform internitroxide distances into spatial constraints between the corresponding a-carbons are being addressed. One approach is to design the sets of nitroxide pairs with the purpose of identifying the presence of known supersecondary structure and folding patterns. Underlying this approach is the general principle of protein structure that α-helices and β-strands tend to pack in a limited number of motifs, each characterized by a unique set of spatial proximities. Thus the nitroxide pairs can be designed such that the expected differences in the pattern of proximities are larger than the uncertainty associated with the flexibility of the nitroxide side chain. The feasibility of this approach was demonstrated in T4 lysozyme, a protein of known X-ray structure. Patterns of internitroxide proximities were sufficient to characterize the pairwise packing of helices as defined by the angle between their axes. In αA-crystallin, a protein of unknown structure, systematic application of this strategy allows the identification of the folding pattern of the conserved domain. Two β-sheets, one consisting of four strands and the other consisting of three strands, pack face to face forming a β-sandwich with a topology reminiscent of the immunoglobulin fold.

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94. ***DISTANCES BETWEEN COFACTORS AND COFACTOR POSITIONS IN PHOTOSYNTHETIC REACTION CENTERS FROM PULSED EPR.*** S.G. Zech, W. Lubitz, R. Bittl, Technische Universität Berlin, Max-Volmer-Institut (PC 14), Straße des 17. Juni 135, 10623 Berlin, Germany

Light-induced radical pairs (RPs) are short-lived intermediates occurring in the course of electron transfer reactions. Information on the structural arrangement of the electron transfer components in protein-cofactor complexes can be deduced from these RP states using time-resolved EPR methods. The dipolar electron-electron spin coupling is directely accessible in pulsed EPR experiments on spin-polarized RP states and can be used to precisely determine the distance between the cofactors involved. For bacterial photosynthetic reaction centers (bRCs), the distance between the primary electron donor, P_{865}, and the quinone electron acceptor, Q_A, in the electronic ground state is known from X-ray crystallography and can be compared with the distance in the charge-separated RP state. Functional differences in recombination kinetics between bRCs frozen either in the dark or under illumination have been observed previously in optical spectroscopy[1]. Pulsed EPR experiments on such samples allow to determine whether the altered kinetics is the result of a change in cofactor distance.[2] Pulsed EPR has also been applied to Photosystems I and II, where the position of the quinone acceptors is not known from electron density maps obtained either by X-ray crystallography3 or electron cryo-microscopy.[4] For PS II cofactor distances for two different functional states have been resolved in the sequence of the light-induced electron transfer reactions.[5] Full advantage of the determination of the dipolar electron-

electron spin interaction can be taken in experiments on oriented samples, e.g. single crystals. With such samples, three-dimensional information on the direction of the axis connecting donor and acceptor molecule can be obtained. Our results on single crystals of PS I allowed the assignment of the electron acceptor A_1 (a phylloquinone molecule) in the structural model of PS I.[6] Supported by DFG (SFB 312, TP A4 and Bi464/7-1).

1. *Kleinfeld et al., Biochemistry, 1984, 23, 5780.*
2. *Zech et al.,Appl. Magn. Reson., 1997, 13, 517.*
3. *Schubert et al., J. Mol. Biol., 1997, 272, 741.*
4. *Rhee et al., Nature, 1998, 396, 283.*
5. *Zech et al., FEBS, 1999, 442, 79.*
6. *Bittl et al., Biochemistry, 1997, 36, 12001.*

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95. *PROGRESS IN MULTIPLE-QUANTUM ESR SPECTROSCOPY: POWERFUL TOOL FOR DISTANCE MEASUREMENTS.*

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Multiple Quantum Coherence, while well-known in NMR, has only been reported for special cases for ESR. In a recent work, Saxena and Freed reported on the use of "forbidden" coherence pathways in order to generate double quantum coherence (DQC) from a doubly-labeled nitroxide. DQC can be isolated from other coherences by an appropriate phase-cycling technique, and it carries the dipolar information in its modulation pattern, that can be translated into the distance between radicals. We report here on the observation of DQC, generated by allowed coherence pathways, which produce signals 10 to 100 times greater than those for forbidden pathways, and are thus comparable in amplitude to standard single quantum signals. We demonstrate the use of DQC techniques for distance measurements with examples of organic biradicals including nitroxides and bilabeled peptides and proteins. Several pulse sequences were utilized for the different distance measurements. They include a 6-pulse zero-dead time technique that is largely immune to ESEEM effects, a 5-pulse technique, which is less sensitive to T_2 than other pulsed ESR distance measurement techniques, thereby making it appropriate for larger distances, and a 4-pulse technique intended for field-swept DQC spectral mapping. The theory of DQC ESR distance measurements, that we developed for biradicals and spatially disordered systems, is described and is illustrated by extensive experiments. We discuss the progress made in instrumentation for DQ distance measurements, its future development, and we compare it with other ESR methods.

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96. *INTERRADICAL DISTANCES IN DIRADICALS AND IN IONIC CLUSTERS OF IONOMERS FROM DOUBLE ELECTRON ELECTRON RESONANCE.*

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The determination of distances between functional groups is of great interest in biophysics and materials science. In a recent communication[1] reporting four-pulse double electron electron resonance (DEER) experiments on a series of TEMPO diradicals, we showed that end-to-end distances up to at least 2.8 nm can faithfully be determined in this way. Our extension of the DEER-experiment is designed for measuring the dipole-dipole interaction between two radicals without deadtime artifacts. This allows us to study broad distance distributions, which occur in amorphous polymers. As a specific example we report DEER measurements on ionically end-capped homo- and diblock copolymers. There, the ionic end groups play a crucial role in determining the self-organization of these systems to form different macromolecular architectures and structural materials[2]. Structure and dynamics of ionic clusters formed by chain endgroups can easily be probed by TEMPO spin probes with ionic groups. Dipolar spectra are obtained from which the cluster-sizes can be obtained. The diameters of the clusters in the different systems vary between 2.0 and 2.5 nm, typical inter-cluster distances are found to be around 5 nm, in agreement with the findings of small angle x-ray scattering.

1. *Martin et al., Angew. Chem. Int. Ed., 1998, 37, 2834.*
2. *Schaedler et al., Macromol., 1998, 31, 4828.*

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97. *ORIENTATION OF THE TETRANUCLEAR MANGANESE CLUSTER AND TYROSINE-Z IN THE OXYGEN EVOLVING COMPLEX OF PHOTOSYSTEM II: AN EPR STUDY OF THE $S_2Y_Z^{\bullet}$ STATE IN ORIENTED ACETATE-INHIBITED PHOTOSYSTEM II.*

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Inhibitory treatment by acetate, followed by illumination and rapid freezing, is known to trap the $S_2Y_Z^{\bullet}$ state of the O_2-evolving complex (OEC) in photosystem II (PS II). An EPR spectrum of this state exhibits broad split signals due to the interaction of the tyrosyl radical, $Y_Z^{\bullet}$, with the $S = 1/2$ S_2 state of the Mn4 cluster. We present a novel approach to analyze $S_2Y_Z^{\bullet}$ spectra of one-dimensionally (1-D) oriented *acetate-inhibited PS II membranes to determine the magnitude and relative orientation of the $S_2Y_Z^{\bullet}$ dipolar vector within the membrane. Although there exists a vast body of EPR data on isolated spins in oriented membrane sheets, the present study is the first of its kind on dipolar coupled electron spin pairs in such systems. We demonstrate the feasibility of the technique and establish a rigorous treatment to account for the disorder present in partially-oriented 1-D membrane preparations. We find that i) the point dipole-distance between $Y_Z^{\bullet}$ and the Mn4 cluster is 7.9 ± 0.1 Å, ii) the angle between the interspin vector and the thylakoid membrane normal is 70°, iii) the g_z-axis of the Mn4 axis is 70° away from the membrane normal and 35° away from the interspin vector, and iv) the exchange interaction between the two spins is -275×10^{4} cm^{-1}, which is antiferromagnetic. Due to the sensitivity of EPR lineshapes of oriented spin-coupled pairs to the interspin distance, the present study imposes a tighter constraint on the Y_Z-Mn_4 point-dipole distance than obtained from randomly oriented samples. The geometric constraints obtained from the 1-D oriented sample are combined with published models of the structure of Mn-depleted PS II to propose a location of the Mn_4 cluster. A structure in which Y_Z is hydrogen-bonded to a manganese-bound hydroxide ligand is consistent with available data and favors maximal orbital overlap between the two redox center that would facilitate direct electron- and proton-transfer steps. Supported by NIH grants GM32715, GM36442 (Yale) and GM21156 (Denver).*

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98. *EPR STUDY OF THE MOLECULAR AND ELECTRONIC STRUCTURE OF THE $Q_A^{-}\cdot Q_B^{-}\cdot$ STATE OF THE PHOTOSYNTHETIC REACTION CENTER IN RB. SPHAEROIDES R26 AT 35 AND 94 GHZ.* Rafael Calvo, FBCB & INTEC (CONICET-UNL), Santa Fe, Argentina; Wulf Hofbauer; F. Lendzian; W. Lubitz, Max-Volmer Inst., Tech. Univ., Berlin, Germany; M.L. Paddock, E.C. Abresch, R.A. Isaacson, M.Y. Okamura & G. Feher, Phys. Dept., UCSD, La Jolla, CA 92093.

EPR spectra of biradicals may be analyzed in terms of exchange and dipolar interactions. Exchange interactions are related to the chemical path connecting the two spins. Dipolar interactions depend on the relative positions of the radicals in the biradical (i.e, molecular structure). We studied the quinone biradical $Q_A^{-\bullet}Q_B^{-\bullet}$ in photosynthetic reaction centers of Rb. sphaeroides R26. EPR spectra were measured at different frequencies (9.6, 35 and 94 GHz) and temperatures between 1.5 and 80 K, in frozen solution samples containing deuterated quinone and solvent. (Calvo et al, Biophys. J., 1999, 76, A392) The proposed spin Hamiltonian was fitted to the data using the simulated annealing method.(Kirkpatrick et al., Science, 1983, 220, 671) Agreement between the observed and simulated spectra is very good, including the temperature dependence. Magnetic and geometric (structural) parameters were evaluated. The two quinone planes are nearly parallel with a 17.1 ±0.2 Å separation. These geometric results are compared to the Q_A $Q_B^{-\bullet}$ x-ray (light) structure (Stowell et al, Science, 1997, 276, 812). For the magnetic exchange interaction a comparision will be made with the tunneling matrix element of electron transfer theory (Marcus and Sutin, BBA, 1985, 811, 265).

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99. *NEW LOOK INTO THE CHEMISTRY OF STABLE NITROXIDE RADICALS.* Leonid Volodarsky 1640 Ocean Ave. #6N, Brooklyn, NY, 11230

The chemistry of stable nitroxide radicals (SNR) derived from piperidine, pyrrolidine, imidazoline, etc. is rapidly growing due to their academic and practical applications. The SNR in general, being suitably functionalized, undergo a variety of reactions without affecting the radical center. This property of SNR together with their easy registration by EPR spectroscopy makes this class of organic compounds to be ideal reporter molecules, particularly those of biological interest. This spin labeling technique has already become an indispensable tool in diagnostic and mechanistic investigations of biological systems. The development of synthetic chemistry have led to new applications of SNR as was shown by the use of them as pH-sensitive spin labels, in NMR and EPR tomography etc. The development of the SNR chemistry in combination with the chemistry of coordination compounds created new molecules with special electrophysical properties, such as ferromagnetism without conductivity. There is growing interest to an industrial application of SNR as inhibitors and free radical scavengers, which prevent or reduce undesirable polymerization of olefin monomers while they are produced, shipped or stored, instead of very dangerous dinitrophenols, which accumulate in surrounding area without or with very slow decomposition. On the other hand, the development of nitroxide mediated "living" free radical polymerization of olefins provides an effective method of controlling of the polydispersity and molecular weight of growing polymer chains. The interest to this process emerged from understanding that control of macromolecular architectures and molecular weight can lead to new polymers with improved and new mechanical and physical properties. New applications and physicochemical properties of the SNR will be considered in the context of choice of appropriate radical structures, convenient precursors and strategy for their synthesis.

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100. *SITE-DIRECTED SPIN LABELING OF THE MYOSIN REGULATORY LIGHT CHAIN: COORDINATION OF EPR SPECTROSCOPY AND COMPUTER MODELING.* Leslie E.W. LaConte, Michael Enz, Wendy Smith, Will Meland, and David D. Thomas Department of Biochemistry, Molecular Biology, and Biophysics; University of Minnesota Medical School; Minneapolis, MN 55445

Previous work has indicated that the light-chain domain of the muscle protein myosin undergoes at least a 36° rotation upon muscle activation as detected by electron paramagnetic resonance spectroscopy of intact, spin-labeled muscle fibers. These studies were done by label-

ing the myosin regulatory light-chain (RLC) on a single cysteine at position 108 with the spin label FDNASL. EPR spectra of muscle fibers oriented parallel to the magnetic field are primarily sensitive to the axial orientation of the spin label; other information about how the spin label is bound to the protein is unknown. We have recently had success using computer modeling to predict the spin label's exact orientation on the RLC. To do this, we have used the Discover 3.0 module within the modeling package InsightII (Molecular Simulations, Inc.) to perform molecular dynamics on the spin label bound to the RLC. Simulated data agrees remarkably well with values obtained experimentally. We are also able to calculate the spin label's order parameter from the simulations. The ability to predict the order parameter of a spin label bound to a site in a protein could greatly aid in designing labeling sites by mutagenesis. The predictive capabilities of these computer modeling techniques have been tested by modeling FDNASL at sites throughout the RLC (virtual mutagenesis) in conjuction with experimental mutagenesis. Experimental order parameter values consistently agree well with simulated values. Computer modeling thus promises to be invaluable both by providing information about currently labeled sites as well as guiding the selection of future labeling sites.

101. *PARAMAGNETIC DEFECTS AND OXIDE LEAKAGE CURRENTS.* Patrick. M. Lenahan, Jeremy Mele, and Michael Fattu, The Pennsylvania State University, University Park, PA 16802; Robert K. Lowry and Dustin Woodbury, Harris Semiconductor, Palm Bay, FL 32905

Recent theoretical work indicates that E′ centers, unpaired electrons on silicon back-bonded to three oxygens, may be responsible for leakage currents in very thin SiO_2 films of metal oxide silicon (MOS) integrated circuitry. (A.Yokozawa, A.Oshiyama, Y.Miyamoto, and S.Kumashiro, IEEE International Electron Devices Meeting Proceedings, 703, 1997) These centers are often positively charged; the presence of any positive charge in the oxide would of itself increase oxide leakage currents by changing the tunneling barrier encountered by electrons. Recently however, it has been found that neutral E¢ centers can be generated by exposing thin oxide films to extended periods of vacuum ultraviolet light. (J.F.Conley, Jr., P.M.Lenahan, H.L.Evans, R.K.Lowry, and T.J.Morthorst, J.Appl.Phys. 76, 2872, 1994) Using ultraviolet light to generate neutral E¢ centers we find a monotonic, several order of magnitude, increase in oxide leakage currents with increasing E′ density.

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102. *NOTRE DAME RADIATION CHEMISTRY DATA CENTER, 1999 STATUS REPORT: THE NDRL/NIST SOLUTION KINETICS DATABASE, VERSION 3.* Keith P. Madden, Radiation Chemistry Data Center, Notre Dame Radiation Laboratory, 105B Radiation Research Building, University of Notre Dame, Notre Dame, IN 46556-0579 U.S.A.

The Radiation Chemistry Data Center of the Notre Dame Radiation Laboratory is a chemical information resource supported by the United States Department of Energy. The primary function of RCDC is the collection, compilation, evaluation, and dissemination of quantitative information on radiation chemical systems, focusing on transient reactive intermediates. As part of the Center's dissemination function, we have released version 3.0 of the NDRL/NIST Solution Kinetics Database, in association with the National Institute for Standards and Technology. This database includes critically-evaluated chemical kinetic data for free radical processes involving primary radicals from water radiolysis, inorganic radicals and carbon-centered in aqueous solution. The kinetic properties of organic peroxyl radicals in various solvents are also covered. The database contains 23,900 rate determinations, from 14,000 reactions with 11,600 chemical species as reactants or products. The database software is an MS-DOS application, and runs on personal computers using Intel, or equivalent processors.

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103. *SPIN DYNAMICS STUDY IN DOPED POLYANILINE BY CW AND PULSED EPR.* C. J. Magon, R. R. de Souza, A. J. Costa-Filho, E. A. Vidoto, R. M. Faria, O. R. Nascimento, Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 SP Brazil

Continuous-wave (cw) and pulsed electron paramagnetic resonance (pulsed EPR) techniques were used to investigate the spin dynamics in poly(o-methoxyaniline) (POMA), a polyaniline derivative, doped with trifluoroacetic acid (TFA). Strongly and slightly doped samples were studied via the paramagnetic relaxation processes of the polaron spin at the X-band microwave region. Electron spin-echo (ESE) techniques were used to measure the spin-lattice (T_1) and spin-spin (T_2) relaxation times in the temperature range of 4-100 K. Cw linewidth were measured up to 250 K. At low temperatures, the cw lineshape is broadened due to dipole-dipole and hyperfine interaction. This reflects on the appearance of a structure on the cw spectrum below 7 K and in the electron spin-echo envelope modulation (ESEEM) pattern, clearly visible up to 100 K. Under some special conditions was possible to resolve the cw hyperfine splitting at temperatures around 12 K. The narrowing of the line, observed with increasing temperature, is more effective in the strongly doped sample. Spin-lattice relaxation times are almost three orders of magnitude shorter for the strongly doped sample, while spin-spin relaxation rates are almost temperature-independent. The temperature dependence of $1/T_1$, below 25 K, follows the Orbach process, $1/T_1 \propto e^{-\Delta/T}$, with Δ in the range of 15-18 K. To explain the experimental results we consider a picture of the doped POMA structure in which conductive islands (clusters) are formed in the insulating matrix. Experimental data agree with a description in which isolated polarons (in the insulating matrix) can cross-relax, via magnetic dipole-dipole interaction, to polarons belonging to neighboring clusters, which are able to relax more rapidly to the lattice. Supported by the Brazilian sponsoring agencies FAPESP, CNPq, CAPES and FINEP.

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104. *SOLID STATE AND AQUEOUS SOLUTION CHEMISTRY OF PARENT AND HETEROATOM-CONTAINING SYMMETRIC AND ASYMMETRIC BIS(ACETYLACETONATE) OXOVANADIUM(IV) DERIVATIVES.*

Kirk Cryer, Mohammad Mahroof-Tahir, Sean S. Amin, Boyan Zhang, Sujit K. Mondal, Ahmad Raza Khan, Luqin Yang Oren P. Anderson, Susie M. Miller, and Debbie C. Crans, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872, USA

Bis(acetylacetonate)oxovanadium(IV) and new derivatives with substituted acac ligands were studied in aqueous solutions to elucidate structure and stability. Recent studies have shown that two derivatives of VO(R-acac)$_2$ (where R=H and CH$_2$CH$_3$) have significant insulin-mimetic activity [1] as they both are equal or better than VO(malto)$_2$ (malto=3-hydroxy-2-methyl-4-pyrone), a derivative of which is currently in Phase I clinical trials. The solid-state structure of the VO(R-acac)$_2$ complexes (R=CH$_3$ and CH$_2$CH$_3$) and VO(CH$_3$COCHCON(CH$_3$)$_2$)$_2$ were determined by X-ray diffraction and compared to VO(acac)$_2$ and related complexes. In the latter amide ligand complex both oxygen atoms chelate to the vanadium atom and the asymmetry caused by the amide group is reflected in the C—C bond lengths. Room temperature EPR spectroscopy was utilized to determine the composition of mixtures resulting upon dissolution of these and other related complexes in aqueous solution. Oxidation of the species was quantified and isomeric species were observed and their solution structures were proposed. Studies by UV-vis spectroscopy were carried out to confirm the observations made by EPR spectroscopy. Differences in stabilities of the vanadium species were explored as the acac ligand was modified. The effect of speciation with respect to insulin-mimetic properties of these compounds will be discussed.

1. *Reul, Benedicte A. et. al., British J. Pharm., 1999, 126, 467.*

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105. *W-BAND ENDOR SPECTRAL ANALYSIS OF THE MANGANESE-BINDING SITE OF CONCANAVALIN A: FROZEN SOLUTION AND SINGLE CRYSTAL SPECTRA.*

Palanichamy Manikandan, Tania Shane, Raanan Carmieli, A. Joseph Kalb (Gilboa), Daniella Goldfarb, The Weizmann Institute of Science, Rehovot, Israel 76100

Unambiguous assignments and determination of the hyperfine tensors of ligand nuclei in many paramagnetic metalloproteins has become feasible due to recent advances in high field/frequency EPR/ENDOR spectroscopic techniques[1]. Ultra-high resolution low temperature X-ray diffraction[2] and neutron diffraction[3] studies leave a large degree of uncertainty in the hydrogen positions of the two coordinated waters in the Mn(II)-binding site of concanavalin A. This uncertainty can be resolved by W-band ^{1}H ENDOR measurements of a frozen solution of the protein at 4.4 K that reveal four inequivalent protons from two coordinated water molecules and two equivalent protons from the imidazole part of the coordinated histidine. The exchangeable and non-exchangeable protons were differentiated on the basis of ^{1}H and ^{2}H ENDOR spectra of a frozen solution of the protein after exhaustive exchange in D$_2$O. From the axially symmetric powder ENDOR pattern of the frozen solution, the distances between the Mn(II) center and nearby protons were determined. Theoretical simulations of these ENDOR spectra will be presented. Part of the single crystal ENDOR results of the protein with and without deuterium exchange will also be discussed.

1. *Coremans et al, J. Am. Chem. Soc., 1996, 118, 12141.*
2. *Deacon et al, J. Chem. Soc., Faraday Trans., 1997, 93, 4305.*
3. *Habash et al. J. Chem. Soc., Faraday Trans., 1997, 93, 4313.*

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106. *DETECTION OF A PAKE FUNCTION IN THE BROADENING OF TWO NITROXIDE SPIN LABELS COUPLED THROUGH DIPOLAR INTERACTION.*

N. Menhart, L. Cherry, L .W.-M. Fung; Loyola University of Chicago, Department Chemistry, Chicago IL 60626

The use of the Fourier deconvolution technique (Rabenstein and Shin, PNAS 92:8239 '95) to determine the interlabel distances in double label site-directed spin labeling studies is predicated on a theoretical foundation that describes the interacting diradical spectrum as a convolution of the monoradical spectrum by some broadening function. However, the theoretically expected form of this broadening, a Pake function, has not been previously observed. As well as being theoretically unsettling, this has necessitated various approximations in calculating the interlabel distance. Various explanations to account for this failure have been advanced, chiefly concerning conformational isomerization of the scaffolding to which the spin labels are attached. However, a consideration of the algorithms utilized to perform this calculations leads to the conclusion that at least part of this failure may be ascribed to the necessarily discrete and finite data sets involved. However, we show that, at least in some cases, moving into the conjugate Fourier domain allows for recognition of the underlying Pake function. This treatment accounts for a number of fine structure features in this Fourier conjugate broadening function spectrum. The form of this conjugate broadening function also has a number of ramifications for the treatment of real samples, in particular with methods used to compensate for monoradical contamination. This contamination is a serious problem with biological samples since labeling methods are not perfectly efficient; simpler methods that do not account for this contamination may seriously underestimate the coupling strength (and so overestimate the distance). We have derived equations describing the Fourier conjugate of the Pake function, and show that this form may be experimentally observed. Monoradical and diradical components in this conjugate representation are distinct, and features ascribable solely to the diradical coupling (and so distance) may be readily observed experimentally. This results in a more accurate determination of the inter-electron distance. Furthermore, it is also theoretically predicted that the coupling should in many cases have a substantial rhombic component (E>0). This rhombicity has various experimentally observed effects on the broadening function and its conjugate.

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107. ***SINGLE-CRYSTAL EPR STUDIES OF CR(III), FE(III), MN(II), AND NI(II) AT 250 GHZ.*** Sushil K. Misra, Serguei I. Andronenko, Physics Department, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, Quebec, Canada, H3G 1M8; Keith A. Earle, Jack H. Freed, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301

We report the first EPR single crystal rotation studies at far-infrared frequencies (250GHz) of several transition metal ions. At such a high frequency, the spectra are all in the high field limit, which leads to considerable simplification of the spectra and aids in their interpretation. Single crystal EPR spectra of the following ions: Cr(III) in Zinc Maleate Tetrahydrate (0.2%), Fe(III) in $CaYAlO_4$*(2%), Mn(II) in* ZnV_2O_7 *(0.2%) and Ni(II) in* Ni_2CdC_{16} $12H_2O$ *were recorded at 270K at an external field (*B_0*) of up to 9.2T. The values of the spin Hamiltonian parameters were found from a simultaneous fit to all of the observed EPR line positions recorded at various orientations of each crystal with respect to* B_0*. Estimates of zero-field splitting D are as follows: 15GHz for Cr(II), 30GHz for Fe(III), 4.93 GHz for Mn(II), and 7GHz (site I), 31 GHz (site II) for Ni(II). The goniometer used to perform the single crystal rotations was based on quasioptical design techniques and is an integral part of a special Fabry-Pérot resonator. The linewidths can be as large as hundreds of Gauss, which required a rigidly mounted modulation coil as close as possible to the sample. To extend this technique to single-crystal studies of proteins containing metal ions, issues that need to be addressed are: small sample size and optimization of signal-to-noise for widely varying samples.*

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108. ***EPR STUDIES OF DOMAIN FORMATION IN THE PLASMA MEMBRANES OF LISTERIA MONOCYTOGENES.*** Reef (Philip D., II) Morse, Brian J. Wilkinson, and Scott Jones, Departments of Chemistry and Biological Sciences, Illinois State University, Normal, IL 61790-4160.

Listeria monocytogenes is a bacterium that is the cause of listeriosis, a disease that encompasses meningoencephalitis, meningitis, and stillbirths and neonatal sepsis from infection of pregnant women. L. monocytogenes has the ability, unusual among pathogens of warm-blooded animals, to grow at temperatures as low as 0°C. Refrigeration enriches L. monocytogenes in foods, whereas the growth of most other foodborne pathogens is inhibited. Previous results have indicated that cold growing strains of L. monocytogenes have high concentrations of branched-chain fatty acids, but do not maintain membrane fluidity by either homeoviscous adaptation[1] *or protein synthesis*[2]*. It is the goal of this research to determine if lipid domain formation occurs in the cell membrane of L. monocytogenes in response to changes in growth temperature. A nitroxide probe that will probe the deep regions of the lipid bilayer, 7-doxyl tetradecane (7N14) will be used. The collision frequency of 7N14 will be measured by the width of the central line as a function of concentration of 7N14 in both plasma membranes of various cold-tolerant and cold-inhibited strains of L. monocytogenes and DPPC/DPPG liposomes. We suspect that domain formation may account for the immobile phase seen in EPR spectra of L. monocytogenes membranes at low temperatures (0-10° C) and may explain the ability of L. monocytogenes to grow at these temperatures before changes occur in fatty acid composition.*

1. *Edgecomb, M. EPR Comparison of Membrane Fluidity of Wild-Type and Cold-Sensitive Strains of Listeria Monocytogenes. Master's Thesis, 1998.*
2. *Bayles, D. O., Annous, B. A., Wilkinson, B.J. Applied and Environmental Microbiology. 62, 1996, 1116-1119.*

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109. ***PARTITIONING AND MOTION OF HYDROCARBON SPIN LABELS IN LARGE UNILAMELLAR VESICLES OF DIPALMITOYLPHOSPHATIDYLCHOLINE/-DIPALMITOYLPHOSPHATIDYLGLYCEROL.*** Reef (Philip D., II) Morse, Joel Ruggaber, and Shawn Hitchcock, Department of Chemistry, Illinois State University, Normal, IL 61790-4160

A class of straight-chain hydrocarbon-based oxazolidine nitroxides has been developed to more fully exploit the possibilities created by the ability to obtain spectral line widths directly from CW EPR spectra. The nomenclature for these nitroxides is based on the hydrocarbon chain length and position of the oxazolidine on the chain ñ for example, 2-doxyl decane would be called 2N10. We present data on partitioning, motional analysis, and location in the phospholipid bilayer for the following nitroxides: 2N6, 2N8, 2N10, 3N10, 4N10, 5N10, 2N12, 2N14, and 7N14. Our data has been obtained in large unilamellar vesicles composed of 80% dipalmitoylphosphatidylcholine, 20% dipalmitoylphosphatidlyglycerol prepared by extrusion through 0.2 μ Nucleopore filters. Our findings indicate that, as expected, longer chain length nitroxides partition more favorably into the lipid bilayer and that their motion can be easily simulated by appropriate deconvolution software (EWVoigt Scientific Software Services). However, the motion of the nitroxides in the DPPC/DPPG liposomes does not show a smooth increase in motion as the oxazolidine moves down the chain of the XN10 series. We will be presenting detailed analyses of the motion and distribution of these probes in the lipid bilayer.

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110. *AN EPR STUDY OF THE PHASE TRANSITION BEHAVIOR OF BINARY MIXTURES OF NON-MESOMORPHIC SOLUTES IN MESOMORPHIC SOLVENTS.* M. A. Morsy; G. A. Oweimreen; and J. S. Hwang, King Fahd University of Petroleum and Minerals, Department of Chemistry, Dhahran 31261, Saudi Arabia.

Accurate isotropic-to-nematic transition temperatures (T_{IN}) have been obtained for 'pure' liquid crystals and liquid crystals doped with impurities using a novel and fast EPR approach[1,2] In this approach the temperatures for the onset and completion of the phase transition are pinpointed using the doublet for a spin probe across the nematic-isotropic two-phase region alongside a broad spectrum that does not give a doublet at each reported temperature. This paper reports on the phase transition behavior of 'pure' n-pentyl (5CB), n-hexyl (6CB), n-heptyl (7CB), and n-octyl (8CB) cyanobiphenyl liquid crystals and mixtures of each of the solutes n-nonane and 3,3-diethylpentane in each one of them using PD-Tempone as a spin probe. The results were used to obtain β_N and β_I, the moduli of the slopes of the coexistence lines (which are virtually linear) on, respectively, the nematic and isotropic sides of the two-phase region in the reduced nematic-to-isotropic transition temperature (T) versus solute mole fraction (x_2) diagrams.These values are of considerable practical importance, since small amounts of solutes of similar structures are often added to nematogenic mixtures used in liquid crystal displays (LCD's) to adjust their viscosity and electrical conductivity characteristics. Additionally very accurate β_N and β_I values are needed to test various theories of solution.[3,4] The β_N and β_I values obtained from this study are compared to ones obtained for the same systems using visual[4,5] and density[6,7] studies. Since n-nonane and 3,3-diethylpentane are non-polar with identical molar masses this study sheds light on the effect of solute structure on the nematic-to-isotropic phase transition.*

[1]Oweimreen, Morsy, and Hwang, Mol. Cryst. Liq. Cryst., 1995, 265, 197; [2]Oweimreen, Morsy, and Hwang, Appl. Magn. Reson., 1995, 9, 61; [3]Dowell and Martire, J. Chem. Phys., 1978, 68, 1094; 4Oweimreen and Martire, J. Chem. Phys., 1980, 72, 2500; [5]Ghodbane and Martire, J. Chem. Phys., 1987, 91, 6410; [6]Oweimreen and Hassan, Mol. Cryst. Liq. Cryst., 1983, 100, 357; [7]Oweimreen et al., Mol. Cryst. Liq. Cryst., 1986, 138, 327.

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111. *THE ELECTRONIC STRUCTURE OF HYDROXYETHYLTHIAMIN PYROPHOSPHATE RADICAL - A CATALYTIC INTERMEDIATE OF PYRUVATE:FERREDOXIN OXIDOREDUCTASE.* Rajendra Bose Muthukumaran, and John McCracken, Department of Chemistry, Michigan State University, East Lansing, MI 48824; Christina Furdui, and Stephen W. Ragsdale, Department of Biochemistry, University of Nebraska, Lincoln, NE 68588.

Enzyme bound radicals generated by the addition of pyruvate to Pyruvate:Ferredoxin Oxidoreductase (PFOR) were freeze trapped and investigated by continuous wave electron-nuclear double resonance (CW-ENDOR) and electron spin echo envelope modulation (ESEEM) spectroscopy. Isotopic substitution of substrate pyruvate and the thiamin pyrophosphate (TPP) co-factor of the enzyme have been used along with ENDOR and ESEEM spectroscopy to measure ^{31}P, ^{1}H, ^{2}H, ^{14}N, ^{15}N and ^{13}C couplings. The measured hyperfine couplings have been used to determine an electronic structure of this chemical intermediate that is consistent with the hydroxyethylthiamin pyrophosphate (HE-TPP) radical proposed by Menon and Ragsdale (Biochemistry, 1997, 36, 8484-94) as an intermediate in PFOR-catalyzed pyruvate oxidation. Support by NIH GM-54065 (JM) and NIH GM-39451(SWR).

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112. *STUDY OF CYTOCHROME-C AND MEMBRANES BY CW-EPR OF IRON HEME.* M. R. Zucchi, I. L. Nantes*, A. Faljoni-Alário*, O. R. Nascimento. Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 SP Brazil, *Centro Interdisciplinar de Investigação Bioquímica, Universidade de Mogi das Cruzes, Mogi das Cruzes, SP, Brazil, *Departamento de Bioquímica, I. Q., USP, São Paulo, SP, Brazil

Recently, cytochrome c was identified as a proteinaceus factor that can induce apoptosis rapidly in mitochondria free extracts[1]. The authors related the cytochrome c induced apoptosis via activation of protease, with the role played by the holoenzyme. The heme requirement to enable cytochrome c in the apoptosis activation is related with its peroxidatic activity. In its native form, the hexacoordination of the heme iron is provided by a histidine nitrogen and a methionine sulfur, as the fifth and sixth ligand, respectively. Cytochrome c has been known to bind strongly to anionic phopholipid membranes[2]. A dynamic conformational equilibrium is established between a low-spin six-coordinated heme iron and a high-spin five-coordinated heme iron in cytochrome c. This process is controlled by the electrostatic interaction between the positively charged lysine residues in the protein surface and the negatively charged phopholipid headgroups in the membrane surface[3]. Cytochrome c acts in the mitochondrial electron-transfer chain as an intermediary between the b-c1 complex and cytochrome c oxidase. It is probable that the lipid induced conformational changes in cytochrome c, described above, may have relevant functional implications on the efficiency of the electron transfer. In this work we used CW-EPR techniques to follow the changes in the resonance line of the iron heme, induced by the protein-membrane interaction. The lipid components of the inner mitochondrial membrane used in this study are: phosphatidylcholine (PC), phosphatidylethanolamine (PE), cardiolipin (CL). Others artificial membranes as dicetylphosphate (DCP) and dimyristoylphosphatidyglicerol (DMPG) were also used for comparison with literature[4]. Lipids were prepared from stock solution in cloroform or methanol, then dried films were prepared under evaporation in vacuum. The unilamellar vesicles were obtained suspending the lipids in hepes buffer (10mM) and sonicated properly. Cytochrome c (SIGMA Co) were diluted in hepes buffer pH 7.4 (10mM). The EPR spectra are consistent with three different spin states and symmetry of iron heme: a high spin state (S=5/2) with axial symmetry, a different low spin state with rhombic symmetry and a high spin state with rhombic symmetry (g=4.3). This shows evidences for the strong *interaction of cytochrome c with the negative charged membrane. Authors are grateful to the financial support from Brazilian agencies FAPESP, CNPq and FINEP.*

1. *Kluck, R.M, et al (1997) Science, 275, 1132-1136. Yang, J., et al (1997) Science, 275, 1129-1131.*
2. *Kimelberg, H.K. and Lee C.P J. (1970) Membr. Biol. 2, 252-262.*
3. *Pinheiro, T.J.T. and Watts A. Biochemistry (1994) 33, 2459-2467*
4. *Snel, M.M.E., Kruijff, B. and Marsh, D. Biochemistry (1994) 33, 7146-7156*

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113. *DIPOLAR RELAXATION IN A MANY-BODY SYSTEM OF ELECTRON SPINS: FROM MOTIONAL NARROWING TO THE RIGID LIMIT.* Alexander A. Nevzorov and Jack H. Freed, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853.

A system of N interacting identical spins of 1/2, which are allowed to diffuse relative to each other, is considered. By using a symmetry-adapted basis operator set, the equation for the overall density matrix is decoupled into systems of equations for time-resolved isochromat components. Generalized cumulant expansion is used to take full advantage of the statistical independence of the spatial motions of spins. The symmetry of the problem allows one to obtain compact expressions containing two counter-rotating spin isochromats. The free-induction decay and solid-echo signals are considered. The spin isochromats are described by an appropriate stochastic Liouville equation. It allows one to recover in a unified way both Anderson's result for statistical broadening in a rigid lattice, and the Torrey-Bloembergen expression for motional narrowing, as corrected by Hwang and Freed. The line shape expression in the thermodynamic limit, i.e. for a very large number of particles and a large volume, is obtained. It is found that the many-body dipolar line shapes are very close to Lorentzians over the entire motional range studied, with the line widths proportional to the spin concentration, as predicted earlier for the limiting cases. Linewidths plotted versus the translational diffusion coefficient clearly show the solid-state limit, the motional-narrowing limit, and the intermediate region. It is found that in the intermediate region, interactions between the nearby spins become more solid-like; whereas there is still an appreciable motional narrowing caused by the distant spins.

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114. *LOW-NOISE AMPLIFIERS AND OTHER MEANS TO IMPROVE PERFORMANCE OF CW AND PULSED HIGH-FIELD EPR SPECTROMETERS.* Mark J. Nilges; A. I. Smirnov; R. B. Clarkson; R. L. Belford; Illinois EPR Research Center, University of Illinois at Urbana-Champaign, Urbana, IL 61801

The use of a low-noise microwave preamplifier can significantly improve the noise figure of the receiver of both CW and pulsed EPR spectrometers. With the advent of millimeter-wave low-noise amplifiers based upon HEMT (High Electron Mobility Transistors) MMIC (Monolithic Microwave Integrated Circuits) technology, receiver noise figures below 5 dB at 95 GHz (W-band) can be obtained. This makes a homodyne bridge at W-band a highly desirable alternative to a heterodyne bridge. We will show that dramatic improvement in signal-to-noise can be obtained for both CW and pulsed W-band spectrometers. For CW spectrometers, this increase is most noticeable when low modulation frequencies are used. Normally, the improvement in signal-to-noise for CW mode is limited to lower microwave powers by FM noise from the source (in our case a free-running Gunn oscillator). We will show that this can be overcome by using a low-phase noise source, specifically, a cavity stabilized oscillator (CSO). Methods to electrically/mechanically tune the CSO will be presented. This work was supported by NIH (P41-RR01811) and DOE (DE FG22-96 PC 96205). It used the resources of the Illinois EPR Research Center, funded by NIH as a P41 Resource Center.

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115. *COMPUTER SIMULATION OF PULSED ELECTRON PARAMAGNETIC RESONANCE SPECTRA FOR A GENERALISED SPIN HAMILTONIAN AND ARBITRARY PULSE SEQUENCE.* Christopher J. Noble, Graeme R. Hanson, Kevin E. Gates, Kevin Burrage, Centre for Magnetic Resonance, Level 2 Gehrmann Laboratories, University of Queensland, St Lucia, Queensland, 4072, Australia.

A general program for the computer simulation of pulsed electron paramagnetic resonance spectra is currently being developed as an extension to XSophe computer software suite[1]*. The existing features of the XSophe simulation package for cw EPR spectra, including the ability to handle a general spin system and the use of an efficient partition scheme for the calculation of powder spectra, will be maintained for the pulsed EPR simulations. The program will be completely general so that an arbitrary pulse sequence can be simulated but an emphasis will be placed on developing efficient techniques for the simulation of the common two and three pulse ESEEM experiments and HYSCORE. The time domain spectra are simulated by calculating the evolution of the density matrix* $\sigma(t)$ *during the pulse sequence with the Liouville von Neuman equation* $d\sigma(t)/dt = -I[H(t),\sigma(t)]$ *where H(t) is the appropriate Hamiltonian in each of the time intervals. The computation time for the numerical integration of the Liouville von Neuman equation is reduced by a number of techniques so that complex multidimensional spectra can be calculated in a convenient time. These methods include, transformation to the rotating frame or interaction representation, the* *calculation of average Hamiltonians during microwave pulses and the reduction of Hamiltonian dimension when selective pulses are used. The theoretical basis for these calculations will be presented with representative examples of spectra and simulations.*

1. M. Griffin, A. Muys, C.J. Noble, D. Wang, C. Eldershaw, K.E. Gates, K. Burrage, G.R. Hanson, Mol. Phys. Rep., in press 1999.

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116. *MOLECULAR DIFFUSION AND OXYGEN RESPONSE IN AQUEOUS CHAR SUSPENSIONS.* Boris M. Odintsov, University of Illinois, Illinois EPR Research Center, Urbana, IL 61801, USA and Russian Academy of Science, Institute of Radioengineering and Electronics, Moscow 103907; R. L. Belford, University of Illinois, Illinois EPR Research Center and Chemistry Department, Urbana, IL 61801; Paul J. Ceroke, University of Illinois , Urbana, IL 61801; Z. Sh. Idiyatullin; A. N. Temnikov; State Technological University, Moscow, Russia; R. B. Clarkson, University of Illinois, Illinois EPR Research Center and Veterinary Medicine, Urbana, IL 61801.

Correlation is found between changes with time in the 1H NMR spectra of water molecules and oxygen response detected by changes in the EPR linewidths in aqueous suspensions of several newly synthesized oxygen-sensitive chars. NMR data clearly demonstrate changes in water structure near the active carbon surface and the formation of specific hydrophilic centers, which are supposed to be connected with the filling of char microporous structure. Porous structure swelling with water leads to decreased oxygen response of the chars. A model of primary adsorption sites and specific interaction of water with porous carbon surfaces is developed. Several views on the mechanism of water filling of the adsorption porous structure are suggested, in which hydrogen bonds between the sorbed molecules and hydrophilic centers at the surface play a dominant role. The efficiency of oxygen response in porous materials crucially depends on filling of micropores by water molecules at the carbon adsorbent surface. Supported in part by grants from NATO (HTECH. LG 972264), Fogarty International Foundation (1RO3 TW00998-01), NIH (RBC; GM51630, GM42208), and the U.S. Department of Energy (DE FG22-96 PC 96205); used facilities of the Illinois EPR Research Center (NIH P41-RR01811), an NIH Resource Center.

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117. *USING SPIN LABELS TO PROBE THE SURFACES OF COLLOIDAL GOLD NANOPARTICLES.* Agnes E. Ostafin, Hirokazu Miyoshi, Olga Makarova, and James R. Norris, Jr.; †Department of Chemistry, University of Chicago, 5735 S. Ellis Avenue, Chicago, IL 60637.

The nitroxide spin label 4-AminoTEMPO (4-AT) was used to study the negatively-charged surface of Au nanoparticles and in Au core/SiO_2 shell particles. Following addition of spin label to the Au nanoparticles at pH 7.0, the observed nitroxide EPR signal is reduced, and the remaining signal undergoes pH dependent lineshape and linewidth changes. A new EPR signal with linewidth about 30 mGauss is observed. Severe broadening of only the 4-AT EPR signal, is observed when a 2-4 nm SiO_2 shell is grown around the Au nanoparticles. The narrow signal dissappears when the Au core is dissolved. An increased resolution of superhyperfine structure in 4-AT coated Au particles compared with homogeneous aqueous solution, suggests a reduced frequency of Heisenberg spin exchange collisions with molecular oxygen for 4-AT at the negatively charged nanoparticle surface.

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118. *LABEL PROPERTIES EXPLAIN DIFFERENCES IN LOCAL ENVIRONMENTS SENSED BY SPECTROSCOPIC LABELS DURING PROTEIN-PROTEIN INTERACTION.* Rikard Owenius[1], Maria Österlund[2], Mikael Lindgren[1], Magdalena Svensson[2], Per-Ola Freskgård[3], Ole H. Olsen[3], Egon Persson[3], Uno Carlsson[2]. [1]IFM-Chemical Physics and [2]IFM-Chemistry, Linköping University, SE-581 83 Linköping, Sweden; [3]Tissue Factor/Factor VII Research, Novo Nordisk Park, DK-2760 Måløv, Denmark.

Specific protein-protein interactions are an important aspect of the functional activity of a variety of different proteins. As a model system for such an interaction we used the extracellular part of tissue factor (sTF) and the plasma protein factor VIIa (FVIIa), two proteins involved in the initiation of blood coagulation. The interaction between sTF and FVIIa was monitored using site-directed labeling with two spin labels and two fluorescent labels attached to an engineered cysteine in sTF. Furthermore, the properties of the labels, such as size, polarity, and flexibility, were determined, information that was used in the interpretation of the experimental spectra. We found that the labels have quite different properties, and also obtained rather different EPR and fluorescence spectra from them. These results indicate that the properties of the labels have a major influence on their preferred location within the sTF:FVIIa interface, a suggestion which was supported by molecular modeling calculations of the labeled receptor-ligand system. To obtain more details of the local dynamic structure surrounding the spin labels line-shape simulations of the EPR spectra were also performed. These could be improved by using g values and hyperfine splitting constants obtained from experiments with spin labels in solvents similar to the environments they are exposed to when attached to a protein. An understanding of the influence of label properties adds more details to the description of the local environment a spectroscopic label experiences during protein-protein interaction and is especially helpful when using several spin and fluorescent labels.

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119. ***EPR OF DISORDERED SYSTEMS.*** John R. Pilbrow, and Simon C. Drew, Department of Physics, Monash University, Clayton, Victoria, Australia 3168

Computer simulation of the EPR spectra in disordered systems such as glasses is being undertaken using a model based on distributions of spin Hamiltonian parameters . This is in contrast to most reported work on the EPR of glasses which is based on distributions of spin Hamiltonian parameters for relatively high symmetry spin Hamiltonians. In the model it is assumed that spin probes occupy sites with no point symmetry [C_1*]. This implies that the orientations of all of the interactions in the spin-Hamiltonian are random variables in addition to the randomness, within limits, of the spin Hamiltonian parameters themselves. Some early simulations using the Eigenfields method to generate resonance fields and intensities will be reported for transition metal ion probes in ordinary glasses. As a link to disorder suspected in crystals and molecules, nutation experiments on a* Ti^{3+} *in Cesium Titanium Alum , a classic Jahn-Teller system, aimed initially at determining small values of* $g_{\perp}$*, in fact yielded* $g_{\parallel}$*-* $g_{\perp}$ *contour maps showing distribution of local disorder at spin probe sites. If such effects are not limited to Jahn-Teller systems, it is hoped that a connection between local disorder can be related to residual linewidths in all kinds of crystals.*

120. ***NITRIC OXIDE ADSORPTION COMPLEXES IN ZEOLITES: AN ESR AND PULSED-ENDOR STUDY.*** Andreas Pöppl, Thomas. Rudolf, and Dieter Michel, Universität Leipzig, Fakultät für Physik und Geowissenschaften, Linnéstr. 5, D-04103 Leipzig, GERMANY

On the basis of its unique spectroscopic and chemical properties Nitric Oxide is a suitable probe molecule for the study of Lewis acid sites such as cations or aluminum defect centers (true Lewis sites) in molecular sieve materials. ESR and Pulsed-ENDOR spectroscopy have been employed to characterize the structure and dynamics of NO molecules coordinated to monovalent cations and aluminum defect centers in zeolites A and ZSM-5. The results reveal a bent structure of the formed adsorption complexes at low temperatures. Pulsed-ENDOR techniques give access to the bond distance between the NO molecule and the cations. At higher temperatures motional effects within the adsorption complex as well as the desorption of the NO probe molecules are analyzed by X and Q band EPR spectroscopy.

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121. ***PULSED ELECTRON-ELECTRON DOUBLE RESONANCE OF PARAMAGNETIC CENTERS WITH LARGE G-VALUE SEPARATION.*** Andrei V. Astashkin, John H. Enemark, Valeriy V. Kozlyuk, John McMaster, Arnold M. Raitsimring, University of Arizona, Department of Chemistry, Tucson, AZ 85721.

The coupled Mo(V) - low spin Fe(III) systems in sulfite oxidase (SO) are characterized by a large separation in g-values (g_z*~*^{3}*,* g_x*~*$^{1.5}$ *for Fe(III) and g~*^{2} *for Mo(V)). We are investigating the use of pulsed ELDOR to obtain single crystal-like information including distance and mutual orientation of the paramagnetic centers in the Fe(III) g-frame for such systems. We have employed C and S m.w. bands and a set of simple one loop/one gap resonators that have two or three natural modes with the frequency differences of 400-600 MHz. These modes were used interchangingly for pumping and observation. Low operational frequencies allowed us to increase the ELDOR effect by compressing the Mo(V) EPR spectrum. In addition, toggling between the pumping and observation channels allowed us to observe six different positions, including two canonical orientations, in the Fe(III) EPR spectrum while pumping Mo(V), in one experiment. The first pulsed ELDOR results for a covalently linked oxo-Mo(V) - low spin Fe(III) porphyrin system, serving as an analogue of SO, are presented. The ELDOR experiments utilizing small frequency separations (up to 100 MHz) in pumping/observation, which can be used for radical-labelled coupled systems, are also discussed. The financial support of NSF BIR-9224431 and DBI-9604939 is acknowledged.*

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1222. ***OPTIMIZATION OF THE ESEEM ACQUISITION USING HIGH-SPEED DIGITIZING TECHNIQUE.*** Andrei V. Astashkin, Arnold M. Raitsimring, University of Arizona, Department of Chemistry, Tucson, AZ 85721.

We discuss here two interrelated problems of ESEEM: the reasons for the loss of ESE signal amplitude in pulse sequences utilizing a π *pulse to toggle between* α *and* β *manifolds (e.g., HYSCORE), and optimization of the ESEEM acquisition in terms of achieving greater S/N ratio and correct modulation amplitudes. In particular, it is shown by direct simulations and experiments at various operational frequencies that the loss of the four-pulse signal, leaving aside the trivialities related to the incomplete magnetization inversion by the* π *pulse and instantaneous diffusion, is significantly contributed by electron-nuclear interactions. The problem of removing the unwanted signals is solved by processing an entire spin echo envelope acquired using fast digitizing boards (resolution 2 ns, analog bandwidth >200MHz) instead of a standard boxcar. We also demonstrate how processing of the entire ESE signal improves the modulation amplitudes in standard ìhardî-pulse techniques as well in pulse-adjustable sequences.*

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123. ***THE INFLUENCE OF Al_2O_3 CODOPANT ON PHASE AND SPIN-LATTICE RELAXATION OF Nd^{3+} IONS INCORPORATED IN VITREOUS SILICA.*** Sergei Orlinskii and Rafail Rakhmatullin, MRS Laboratory, Kazan State University, Kremlevskay, 18, Kazan, Russia; Sabyasachi Sen, Corning Inc., Corning, NY.

Silica and silicate glasses doped with rare earth ions at a concentration level of a few thousands of ppm are well known for their use in lasers and fiber optic amplifiers. The major drawback in the performance of these materials results from concentration quenching of the fluorescence due to clustering of the rare earth ions in the glass structure. Addition of codopants such as Al_2O_3 to the glass has been found to result in breaking up of these clusters and to create a homogeneous spatial distribution of the rare earth ions. However, the characteristic length scale of the spatial distribution of rare earth ions is not well known. The purpose of our study is to obtain information about the spatial distribution of Nd^{3+} dopant ions in SiO_2 glasses with and without Al_2O_3 as a codopant using the electron spin echo (ESE) technique. This technique relies on the fact that phase and spin-lattice relaxation times of paramagnetic centers are sensitive to their spatial distribution in a solid. Experiments are carried out using a home-built ESE spectrometer operating at a frequency of 9.4 GHz at temperatures ranging between 1.6 K and 4.2 K. For Nd^{3+} centers the phase relaxation times are measured with a two-pulse echo sequence and the spin-lattice relaxation times are measured with a saturation-echo sequence. The analysis of phase relaxation times of Nd^{3+} ions clearly indicates that the average Nd-Nd distances in SiO_2 glass increases on codoping with Al_2O_3. Moreover, the electron spin echo envelope modulation for Nd^{3+} is only observed when the SiO_2 glass is codoped with Al_2O_3 indicating a close proximity of ^{27}Al nuclei and Nd^{3+} ions in the glass structure. These results provide evidences in favor of the formation of Nd-O-Al complexes in the glass as a possible mechanism of breaking up of Nd clusters.

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124. ***A THREE DIMENSIONAL ELECTRON SPIN DENSITY EQUATION FOR ALKENE CATION RADICALS GENERATED BY GAMMA-IRRADIATION AND OTHER OXIDATION METHODS.*** Shawn Shih, Department of Chemical Engineering, Yuan-Ze University, Nei-Li, Taiwan 32026 R.O.C.

Theories of both isotropic and anisotropic proton hyperfine interactions in π - electron systems were developed in the early sixties. They are approximated by the magnetic dipole interactions between each proton and an electron spin magnetization that is distributed in 2s and 2p Slater atomic orbitals center on carbon atoms. We have extended these theories to the cation radicals, which are very important in biochemistry as well as in petroleum catalysis. A three dimensional electron spin density equation was developed to handle some Jahn-Teller vibronic molecules. The new electron spin density equation related the observed proton hyperfine splittings to the non-planar structures of the open-chain alkene cation radicals generated by various oxidation methods. The spin densities and the conformational calculations are also in agreement with more elaborated Molecular Orbital calculations.

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125. ***MOVEMENT OF ISP EXTRINSIC DOMAIN IN THE BC_1 COMPLEX MONITORED BY SDSL EPR.*** M. Guergova; R. Kuras; A. R. Crofts, University of Illinois at Urbana-Champaign, Departments of Biophysics and Microbiology, Urbana, IL 61801; Alex I. Smirnov, University of Illinois at Urbana-Champaign, College of Medicine and Illinois EPR Research Center, Urbana, IL 61801

The ubihydroquinone: cytochrome c oxidoreductase (bc_1 complex) is the central enzyme in respiratory chains of mitochondria and bacteria, photosynthetic chains of bacteria, and oxygenic photosynthesis of cyanobacteria and green plants. Although complete structures for chicken and bovine complexes are now available, the function of bc_1 complex on a molecular level is not completely understood. It is believed that the extrinsic C-terminal domain (head) of the iron sulfur protein (ISP) is mobile and moves between reaction interfaces during catalysis. We have constructed several bc_1 mutants with the cysteines independently introduced into cyt b and also a set of double mutants with the cysteines engineered into both cyt c and ISP. By labeling these cysteines with methanethiosulfonate spin label, we were able to measure distances in the spin pairs from dipolar broadening of CW EPR spectra from bc_1 solutions. Low temperature W-band (95 GHz) EPR spectra from the spin pairs show anisotropic broadening, indicating that partial ordering of the spins is preserved. This work used the resources of the Illinois EPR Research Center Supported by the NIH (P-41 RR01811).

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126. ***PROBING LOCAL EVENTS OF PROTEIN FOLDING BY SDSL EPR.*** Alex I. Smirnov, S.-W. Norby, R. B. Clarkson, R. L. Belford. Illinois EPR Research Center and Departments of Chemistry, Medical Information Science, and Veterinary Medicine, University of Illinois at Urbana-Champaign, Urbana, IL 61801

Understanding protein folding is central to many areas of biophysical chemistry, biotechnology, and medicine. Site-directed spin-labeling EPR is a promising tool to approach this problem because the data that it yields provides structural and dynamics information that is very local in nature. When carried out at high frequencies (ca. >90 GHz, HF-EPR), SDSL EPR folding experiments become even more attractive. Time resolution and sensitivity to motion are increased, optimal sample volume is dropped to ca. 100 nanoliters, and improved angular reso-

lution helps in distance measurements in spin label pairs. To explore the prospects of HF-EPR studies of protein folding with SDSL, we have carried out equilibrium denaturing studies with a one-domain protein, recombinant human growth hormone (rhGH), and compared the results with the CD data. We have also constructed cysteine mutants of a two-domain protein - phosphoglycerate kinase (PGK) to study the sequence of folding/unfolding events. This work used the resources of the Illinois EPR Research Center, an NIH-supported Resource Center (P-41 RR01811).

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127. *MAGNETIC FIELD ORIENTED CRYSTALLIZATION OF CuTPP.* Witold K. Subczynski[1,2], William E. Antholine[1], Marta Pasenkiewicz-Gierula[2], and James S. Hyde[1]. [1]Medical College of Wisconsin, Milwaukee, WI USA; [2]Jagiellonian University, Krakow, Poland.

During slow evaporation of chloroform from a saturated copper(II) tetraphenylporphine (CuTPP) solution placed in a magnetic field, CuTPP crystals are formed on the capillary walls with planes of CuTPP molecules oriented parallel to the magnetic field. Without the magnetic field, crystals are oriented randomly. The degree of crystal orientation depends on the strength of the field, reaching a maximum value at about 1000 G. The orientation was monitored using EPR spectroscopy at X-band and Q-band. The presence or absence of components in the g-parallel and g-perpendicular regions as the capillary was rotated indicated the orientation of CuTPP molecules. Microcrystals of CuTPP are also oriented in viscous solutions. The presence of the magnetic field increases the rate of CuTPP crystallization when chloroform is evaporated from a paraffin oil-chloroform mixture, or when a solution of CuTPP in paraffin oil is cooled.

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128. *MOLECULAR ORGANIZATION AND DYNAMICS OF DIMYRISTOYLPHOSPHATIDYL-CHOLINE BILAYERS CONTAINING CHARGED AND UNCHARGED FORMS OF A TRANSMEMBRANE α-HELICAL PEPTIDE.* Witold K. Subczynski[1,2], James S. Hyde[1], and Akihiro Kusumi[3]. [1]Medical College of Wisconsin, Milwaukee, WI 53226 USA; [2]Jagiellonian University, Krakow, Poland; [3]Nagoya University, Nagoya, Japan.

Previously, we investigated how transmembrane a-helical peptides Ac-$K_2L_{24}K_2$-amide (L_{24}) (with a smooth hydrophobic surface) and Ac-$K_2(LA)_1{}^2K_2$-amide ($(LA)_{12}$) (with a rough hydrophobic surface) affect the molecular organization and dynamics of POPC membranes. All measurements were performed at pH 7.0 where sidegroups of lysines on both ends of the peptides are charged. We have extended our investigations to DMPC, which also allows us to study the effect of these peptides on the main phase transition. We focused on the effect of pH on $(LA)_{12}$-DMPC interaction. At low pH (<8.0) with 10 mol% $(LA)_{12}$, the membrane phase transition was strongly broadened and shifted to lower temperatures. At high pH (>9.0) the effect of 10 mol% $(LA)_{12}$ was significantly weaker and is comparable to that of 3–4 mol% $(LA)_{12}$ at low pH. This effect could be a result of aggregation of the neutral form of the peptide at high pH, resulting in a decrease in the effective $(LA)_{12}$ concentration in the membrane. The effect of the neutral form of $(LA)_{12}$ could be weaker without aggregation. A comparison of the effect of $(LA)_{12}$ on other membrane properties at pH 7.0 and pH 9.5 indicates that the second explanation is true. At both pH levels, conventional EPR spectra detect the existence of a single homogeneous environment. $(LA)_{12}$ increases the rotational correlation time of 16-PC similarly at pH values in the range of 7.0–10.2. The increase in the hydrophobicity of the membrane interior caused by $(LA)_{12}$ is practically independent of pH. However, the effect of 10 mol% $(LA)_{12}$ on the order parameter is lower at pH 9.5 and is comparable to that of ~4 mol% $(LA)_{12}$ at pH 7.0.

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129. *CAN FIELD MODULATION INFLUENCE SPIN EXCHANGE IN WOOD CHARS?* Oleg Y.Grinberg, Harold M. Swartz, EPR Center for the Study of Viable Systems, Department of Radiology, Dartmouth Medical School, Hanover, NH 03755

While EPR studies of coals and chars have been carried out for more than 30 years, many key aspects remain unresolved. Interest in these materials has increased recently because of their potential use for EPR oximetry in vivo. We have found that the EPR spectra of most chars in both gas and water environments can be simulated as being composed of two (broad and narrow) Lorentzian lines, (EWVoigt program, Scientific software). In the absence of oxygen the ratios of the line widths (broad to narrow) are almost the same in both gaseous and aqueous environments. When oxygen is present both components broaden in both environments, but the broadening is less in water. Recently we observed a difference in the effects magnetic field modulation on the oxygen-induced line width broadening of the broad and narrow lines. Surprisingly, the normalized broadening (LW/LW0) from the normalized modulation amplitude (Hm/LW0) for the broad line was more sensitive to the amplitude of modulation than for the narrow line. This unexpected observation could be explained by assuming an interaction of the unpaired electrons with the modulation field. An increase of the magnetic field then might decrease the time of spin collisions, which determines spin-spin exchange. If this is the case, then we are observing an influence of the magnetic modulation field on spin exchange in the chars.Supported by NIH RR11602 and NIH GM51630.

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130. ***PARAMAGNETIC DEFECTS IN OXYGEN-DEFICIENT TiO_2/RUTILE.*** Alexei M. Tyryshkin[1], Michael K. Bowman, Michael A. Henderson, and Glen C. Dunham, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352, [1]Institute of Chemical Kinetics and Combustion, Novosibirsk, 630090, Russia.

Interstitial and substitutional Ti(III) and other transitional metal ions are produced in crystalline and powdered TiO_2 by a number of chemical and photolytic reactions. Heating of rutile crystals in argon produces oxygen-deficient crystals with over 20 different paramagnetic defects. We have characterized several defects including novel paired Ti(III) centers located 2 and 3 unit cells apart along the c axis of crystal. We have used ESEEM to obtain hyperfine and nuclear quadrupole tensors of the Ti(III) nuclei. The paired Ti(III) species with S=1 and the isolated monomers with S=1/2 have been identified and are tentatively assigned to extended defects. We have used X-band EPR imaging to show that the centers are distributed non-uniformly in the crystal and have lowest concentration near the surface. The centers can be divided for the most part into 2 groups, those present in crystals heated to 1100°C and less and those in crystals heated above 1100°C. Characterization of these species in single crystals allows those species to be identified in powders on the basis of their characteristic g-tensors and zero field splittings. Pacific Northwest National Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. This research was also supported by Associated Western Universities, Inc. Northwest Division (AWU NW) under Grant DE-FG06-89ER-75522 or DE-FG06-92RL-12451 with the U.S. Department of Energy and by the U.S. Department of Energy EMSP program.

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131. ***Q-BAND ENDOR OF THE BINUCLEAR HEME-COPPER CENTER IN CYTOCHROME BO_3 FROM ESCHERICHIA COLI.*** Andrei V. Veselov, Charles P. Scholes, SUNY at Albany, Department of Chemistry, Albany, NY 12222; Jeffrey O. Osborne, Robert B. Gennis, University of Illinois, Department of Biochemistry, Urbana, IL 61801.

Cytochrome bo_3 ubiquinol oxidase from Escherichia coli belongs to the heme-copper superfamily of respiratory oxidases that couple aerobic oxygen consumption to proton pumping. This superfamily has a conserved high-spin heme (heme o_3)-copper (Cu_B) binuclear center where dioxygen reduction occurs. Although the crystal structure of the related cytochrome c oxidase is known, there is still uncertainty over the structure within the unique binuclear center and uncertainty over changes that occur there as oxygen reduction occurs. Strong antiferromagnetic coupling between ferric heme and cupric copper of the binuclear site eliminates EPR signals under the oxidizing "resting" conditions used to prepare bo_3 oxidase. Partial reduction eliminates the antiferromagnetic coupling so that a high spin ferric o_3 heme or a cupric Cu_B can then be observed by EPR or ENDOR. Q-band (34 GHz) ENDOR was used for this study because ENDOR at higher frequencies removes spectral overlap of nitrogen and 17O features with proton features. Findings from high-spin ferric heme o_3 were as follows: 1) Heme nitrogen frequencies occurred approximately where they occur from aquometmyoglobin although pre-reduction of the enzyme followed by oxygen-induced turnover led to sharper heme nitrogen features. 2) The proximal histidine nitrogen couplings are at a lower frequency than in aquometmyoglobin. 3) In contrast to aquometmyoglobin, strongly coupled proton features and ^{17}O ENDOR signals from exchangeable water were not detected. The implication for the ferric o_3 heme is that its 6th ligand, if any, is neither exchangeable aquo, hydroxy, nor HOx. Non-exchangeable proton features with couplings comparable to those of the water ligand of aquometmyoglobin were also not observed; the implication is that heme does not have a sequestered, non-exchangeable HOx ligand. Findings from Cu_B were as follows: 1) Strongly coupled, exchangeable deuterons from the Cu_B center were detected and assigned as deuterated forms of an HOx ligand of the Cu_B, and corresponding exchangeable proton features of the Cu_B center were also detected. 2) Non-exchangeable histidine proton features were detected in deuterated solvent over a wide range of g-values so that angle-selected information about orientation of imidazole planes was thereby obtained. 3) Strongly coupled nitrogens of the histidine were observed in 10-25 MHz region, and there is preliminary evidence that their couplings are altered by prior turnover of the enzyme. Work is in progress to determine the overall effect of turnover on ligand hyperfine structure at the Cu_B center and to determine if ^{17}O of water can exchange into the liganding sphere of Cu_B. (This work supported by NIH Grant GM 35103.)

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132. ***Q-BAND ENDOR STUDY OF THE UBISEMIQUINONE CENTER IN CYTOCHROME bo_3 FROM ESCHERICIA COLI.*** Andrei V. Veselov, Charles P. Scholes, SUNY at Albany, Department of Chemistry, Albany, NY 12222; Jeffrey O. Osborne, Robert B. Gennis, University of Illinois, Department of Biochemistry, Urbana, IL 61801.

Cytochrome bo_3 ubiquinol oxidase from Escherichia coli is a member of the heme-copper superfamily of respiratory oxidases that couple aerobic oxygen consumption to proton pumping. Many of these oxidases are cytochrome c oxidases that use ferrocytochrome c as their source of reducing electrons. However, reduced ubiquinol is the source of electrons for bo_3 oxidase which contains a site where ubiquinone is strongly bound and stabilized in its paramagnetic semiquinone form. With partial reduction of the protein, a characteristic large ubisemiquinone EPR signal was produced whose g-values, as resolved at Q-band, resembled those of the well-studied ubisemiquinones in photosynthetic reaction centers [Feher et al. (1972) BBA 244, 222]. Q-band proton ENDOR was observed at liquid helium temperatures under dispersion rapid passage conditions. Large proton hyperfine couplings of 11-12 MHz were observed and assigned to the β-protons of the ubiquinone isoprenoid group from their similarity to the analogous β-proton couplings observed from photosynthetic reactions centers [Feher (1998) Photosynthesis Research 55, 30-31]. ENDOR features of exchangeable deuterium having a coupling of 0.7 MHz and the apparent corresponding ENDOR features of exchangeable protons having a coupling of ~4 MHz were observed; these exchangeable deuteriums and protons are undoubtedly in *the hydrogen bond(s) that couple the oxygen(s) of the ubisemiquinone to the protein. At 77° K faster electron spin relaxation and the angle selection from g-anisotropy lead to better resolution of small proton hyperfine couplings, and to characterize better the specific perturbations that define the ubisemiquinone binding site in bo$_3$ oxidase, Q-band ENDOR work is in progress at 77° K. (This work supported by NIH Grant GM 35103.)*

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133. ***SITE-DIRECTED SPIN-LABELING OF THE CATALYTIC SITES AND OF SUBUNIT B YIELDS INSIGHT INTO THE STRUCTURE OF F_0F_1-ATP SYNTHASE OF ESCHERICHIA COLI.*** Michael Kersten§, Christian Motz§ , Gerhard Kraft§, Derek T. McLachlin#, Stanley D. Dunn#, John G. Wise§* and Pia D. Vogel§* §Fachbereich Chemie/Abteilung Biochemie, Universität Kaiserslautern, 67663 Kaiserslautern, Germany; #Department of Biochemistry, University of Western Ontario, London, Ontario, N6A 5C1, Canada

FoF$_1$-ATP synthase catalyzes the synthesis of ATP from ADP and inorganic phosphate by using a proton gradient across energy coupling membranes. The E. coli ATP-synthase consists of a membrane integral proton channel called Fo composed of 3 different subunits with the stoichiometry ab2c$_{10-12}$ and an hydrophilic F1-part ($\alpha_3\beta_3\gamma\delta$e). In this paper we describe approaches using site-directed spin-labeling to investigate the influence of nucleotides and of subunit b on the catalytic binding sites of F$_1$-ATPase, as well as to investigate structural interactions of subunit b with F1. In our first approach, $^{\beta}$-Tyr 331 of the catalytic site of F$_1$ that was previously mutated to a cysteine was modified with a spin label. The modified enzyme enabled us to study the effects of different nucleotides and protein subunits on the conformation of the catalytic binding sites. The ESR spectra of the spin-labeled F$_1$ clearly show a change in the conformation of the nucleotide binding sites upon addition of nucleotides, clearly indicating a "Binding Change" to happen. Using the same $^{\beta}$-331 spin-labeled F$_1$ and a truncated form of the

b-subunit of Fo (b$_{sol}$), we investigated effects of the binding of bsol on the catalytic sites. The binding of bsol to spin-labeled, nucleotide-depleted F1 drastically changes the ESR-signal , indicating strong effects on the open conformation of the catalytic binding sites, possibly by increasing the population of binding sites in this conformational state. Similar effects of b$_{sol}$ on the catalytic sites were observed in the presence of AMPPNP, ADP or ATP. In our second approach, site-directed spin-labeling was used with a number of different cysteine-mutants of bsol in attempts at mapping the structural interactions of b$_{sol}$ with F$_1$. From the results of experiments using iodo acetamido piperidine spin label reacted with unique cysteines at various positions along the sequence of b$_{sol}$, we have been able to investigate the areas of interaction of b with F$_1$ and with subunit delta within F$_1$, as well as to obtain further information of the structure of the b-dimer itself.

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134. ***POLARONS AND BIPOLARONS IN CONDUCTING POLYMERS OBSERVED FROM THE WIDTH OF THE ESR LINE.*** M.S. Sercheli, C. Rettori , Universidade Estadual de Campinas, Instituto de Física, Campinas, S.P., Brazil, CEP 13083-970; L. Walmsley, Universidade Estadual Paulista, Departamento de Física, Rio Claro, S.P., Brazil, CEP 13500-970 , A.A. Correa, L.O.S. Bulhões and E.C. Pereira, Universidade Federal de São Carlos, Departamento de Química, São Carlos, S.P., Brazil, CEP 13565-970.

In conducting polymers like polythiophene and derivatives, it is known that light doping give rise to the spin ½ charged defects, polarons. The spinless double charged defects, bipolarons, are formed upon heavy doping. In this work we show that from the width of the ESR line it is possible to observe the presence of polarons in pressed pellets of ClO_4^- doped poly(3-methylthiophene) synthesized at 25°C (S25), and of bipolarons in samples synthesized at 5°C (S5). For both kind of samples two ESR lines are observed corresponding to more localized and more delocalized states. For the less doped S25 samples the more delocalized state line is broad due to the dipolar interaction between polarons. Instead, for the more doped S5 samples the more delocalized state line is narrow because the formation of bipolarons cause an effective decrease of the polarons concentration. This conclusion is also supported by measurements of microwave conductivity. The ESR line asymmetry ratio (A/B) shows that the S5 samples have a conductivity four times higher than that of S25 .Also, the total number of spins at room temperature in S5 is more than one order of magnitude smaller than in S25. Supported by Fundação de Amparo à Pesquisa do Estado de São Paulo, Conselho Nacional de Desenvolvimento Científico e Tecnológico and Padct 3, Brazil.

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135. ***ASYMMETRICAL PENETRATION OF MICROWAVE IN A CONDUCTING MEDIA AND DETERMINATION OF THE MICROWAVE CONDUCTIVITY FOR VERY THIN SAMPLES*** A.C. Seridonio and L. Walmsley, Departamento de Física, Universidade Estadual Paulista, Rio Claro, S.P., Brazil, CEP 13500-970.

Dyson's theory[1] has been used in the limit $d \leq \delta$ (d being the thickness of the sample and δ the skin depth of the microwave field) to obtain the microwave conductivity from the asymmetry (A/B) ratio of the ESR absorbed power derivative[2] . In this work we calculate the ESR absorbed power derivative using Kaplan's approach[3] and show that this asymmetry in the A/B ratio can be enhanced if asymmetrical penetration of microwave is used. Therefore, the determination of the microwave conductivity from the ESR asymmetry ratio can be performed for thinner samples. Experimentally, asymmetrical penetration can be obtained if one of the sample's face is recovered with a thin gold or platinum layer. The determination of the microwave conductivity in conducting polymers films is among the possible applications of this *method. Supported by Fundação de Amparo à Pesquisa do Estado de São Paulo e Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil.*

1. *Dyson, Phys. Rev., 1955, 98, 349.*
2. *Pawlicka et al, 1994, J. Magnetic Reson. A, 108, 62.*
3. *Kaplan, 1959, 115, 575.*

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136. *Q-BAND EPR AND ENDOR STUDIES OF CU^{2+} ION BINDING TO DENDRIMER MOLECULES.*

Tomasz J. Wasowicz, Mingqi Zhao, Richard M. Crooks, Victoria J. DeRose, Texas A&M University, Chemistry Department, College Station, TX 77842-3012

Dendrimers are outstanding candidates for use as hosts and supports for a range of different catalytic species because of their regular structure and chemical versatility. A dendrimer has three anatomical elements: a core, repetitive branch units and terminal functional groups. As a consequence of their three-dimensional structure dendrimers are able to act as hosts for certain types of ions and molecules. By changing the amount of branch units (number of generations) it is possible to tune the dendrimer as host for various needs.

In our research we are inversigating the binding of Cu^{2+} ions to two types of G-4 PAMAM dendrimers which are about 45Å in diameter, one terminated with -OH groups and the other terminated with -NH$_2$ groups on the external surface. The Cu^{2+}-G4 complex may serve as a substrate for generation of small metallic nanoclusters or as membrane gates on surfaces of electrodes. Using X- and Q-band EPR and Q-band ENDOR spectroscopies and computer molecular modelling of the dendrimer molecule we have determined a model for the coordination environment of the Cu^{2+} inside the dendrimer. ENDOR results are compared to spectra for other copper complexes (NH$_3$, imidazole, pyridine, polyallylamine and H$_2$O) which served as reference model systems.

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137. *A 1-HYDROGEN 2-LITHIUM CENTRE AND MULTIPLE-HYDROGEN CENTRES IN CRYSTALLINE QUARTZ.*

Rodney F. C. Claridge, Nick. S. Lees, W. Craig Tennant, Charles J. Walsby, Chemistry Department, University of Canterbury, Christchurch, New Zealand; John A. Weil, Chemistry Department, University of Saskatchewan, Saskatoon, SK, S7N5C9, Canada.

We have observed a new silicon-vacancy centre in alpha-quartz, which contains 1 H$^+$ and 2 Li$^+$ ions. The previously discovered multi-H (no Li) centres are also present. Single-crystal rotational EPR data have been obtained at X-band and 100 K. All these centres appear to arise on x-irradiation when an electron hole is trapped on an oxygen atom associated with a Si^{4+} vacancy. The vacancy site may be occupied by charge-compensating H$^+$ and/or Li$^+$ ions, the composition depending on the conditions of hydrothermal crystal growth. Detailed analysis of the spin-hamiltonian (g and hyperfine) parameters will be given, and structural implications discussed.

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138. *MINIMIZATION OF DATA ACQUISITION TIMES FOR 3D SPECTRAL-SPATIAL IMAGING OF LIVING MOUSE TUMORS.*

Benjamin B. Williams, Eugene D. Barth, Valeri Galtsev, Howard J. Halpern, University of Chicago, Department of Radiation Oncology, Chicago, IL, 60637

*Maintaining adequate signal to noise while minimizing the time to acquire a set of 3D spectral-spatial data is crucial for mouse tumor oxygen concentration measurement. In order to avoid image artifacts and accurately measure spatial and spectral features a large amount of data must be acquired with an adequate signal to noise ratio. Data acquistition times are limited by the 45 minute half life of the spin label and the maximum duration of anesthesia. In order to decrease the acquisition time without sacrificing signal to noise we have exploited the symmetry of the Nycomed spin label and dynamically adjusted the modulation amplitude and number of scans collected per projection depending on its sweep width. For a 3D image reconstructed from 512 projections (16*32) maintaining signal to noise through data averaging alone would require over 5 million scans per image. Dynamic increase of the modulation amplitude with the projection sweep width reduces the total number of scans by a factor of 340. By exploiting spectral symmetry this can further be reduced by a factor of 2. A further reduction in the number of scans for the high gradient spatial projections causes a loss in signal to noise, but results in another factor of 10 and aquisition times of 90 minutes with 128 points per projection and a dwell time of 30 ms. After baseline correction and scaling to account for spin label elimination 3D filtered backprojection is used to reconstruct the spectral spatial image.*

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139. ***SPIN DYNAMIC OF THE PHOTOEXCITED TRIPLET STATE OF PENTACENE AT LOW FIELD AND LEVEL ANTICROSSING REGION.*** Tran-Chin Yang, David J.Sloop, S. I. Weissman and Tien-Sung Lin, Washington University, Department of Chemistry, St. Louis, MO 63130.

Zero-field splitting parameters D and E of photoexcited triplet state of pentacene(h_{14},d_{14}) doped in p-terphenyl and benzoic acid crystals are accurately measured by FID signals . The observed intensities depend on the state population, decay rate and spin-lattice relaxation. The effect of the hyperfine parameters to the signals are studied in detail in the low field region. In the ultra-fast field sweeping experiments (10^9 G/sec) , we found the level crossing is an avoided one, and the passage through the crossing reaches non-adiabatic. Theoretical simulations were performed using Landau-Zener theory, time-dependent Schrödinger equation and density matrix formalism.

EPR Poster Session—Tran-Chin Yang, Washington University, Department of Chemistry, St.Louis, MO

140. ***EPR INVESTIGATION OF THE INTERACTION OF TRAPPED EXCITED METASTABLE HE ATOMS WITH SOLID RARE-GAS MATRICES.*** Rem A. Zhitnikov, A.F.Ioffe Physico-Technical Institute, St. Petersburg, 194021 Russia; Yurij A.Dmitriev, A.F.Ioffe Physico-Technical Institute,St. Petersburg, 194021 Russia

Using EPR unstable paramagnetic centres of 10^2 - 10^4 s lifetime are found and investigated which form in Ne, Ar and Kr cryocrystals being condensed from the gas phase and trapping excited metastable He atoms from the helium gas discharge. It is established that these unstable paramagnetic centres are the local metastable $np^5(n+1)s^3P_2$ atomic-type excited states in Ne, Ar and Kr cryocrystals. The mechanisms are elucidated of formation of such local paramagnetic centres.The effect of formation in a neon cryocrystal of atomic-type $2p^53s\ ^3P_2$ centers obtained as a result of He gas discharge products being trapped in a neon matrix condensing from the gas phase[1] is interpreted as a new phenomenon: quasi-resonance transfer of excitation energy from the metastable He 2^3S_1 atom matrix-isolated in a growing neon cryocrystal to the exciton energy band of the neon crystal followed by the exciton self-trapping into the $2p^53p$ state and subsequent decay, ending in the $2p^53s\,^3P_2$ paramagnetic state recorded by EPR in our experiment. A temperature study showed that the rate constant λ of the process of excitation energy transfer from the He 2^3S_1 atom to the neon cryocrystal exciton band follows the Arrhenius-like law $\lambda = \lambda_0 exp(-E/kT)$, the "activation energy" E of the process turns out to be 0.0010(5) eV. Local metastable paramagnetic excited states are found in Ar and Kr cryocrystals when He gas-discharge products are tapped in the growing cryocrystals.[2] These states are detected by EPR and are interpreted as being local metastable excited $np^5(n+1)s\ ^3P_2$ atomic-type states in Ar and Kr cryocrystals. The study showed that the yield of the $^3P_2$ excitations in the above process decreases with increasing temperature. Analysis of the results allows the following explanation of the observed effect to be given. Metastable excited He atoms from the He gas discharge are matrix-isolated in the growing Ar or Kr cryocrystals and transfer their excitation energy to the cryocrystal to form, in the process of internal ionization, a Rg^+ ion and a free electron in the conduction band, whereupon the fast (of 10^{-12} s) self-trapping reaction of a hole follows: $Rg^+ + Rg \rightarrow Rg^+_2$. Thereafter either the dissociative recombination reaction

$Rg^+_2 + e \rightarrow Rg_2^{**} \rightarrow Rg + Rg^*\ (^3P_2)$ or recombination $Rg^+_2 + e \rightarrow Rg + Rg$ to produce diamagnetic ground-state atoms could take place.[2,3] The former is likely at lower temperatures, and the latter at higher temperatures when the vibrational relaxation rate of the Rg^+ molecular ion increases and the mobility of free electrons in the conduction band decreases. This is the reason for the observed temperature dependence.

1. *Zhitnikov and Dmitriev, J. Phys.: Condens. Matter,1994 , 6, 2727.*
2. *Zhitnikov and Dmitriev, J. Phys.: Condens. Matter, 1995, 7, 2819.*
3. *Zhitnikov and Dmitriev, Appl. Magn. Reson., 1995, 8 , 457.*

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141. ***INTERSPIN DISTANCES IN MYOGLOBIN VARIANTS DETERMINED BY PULSED EPR.*** Yi Zhou, Bruce Bowler, Sandra S. Eaton, and Gareth R. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado 80208.

Nitroxyl spin labels were attached to the cysteines of sperm whale metmyoglobin variants. The spin-lattice relaxation times for the nitroxyl, high-spin heme, and low-spin heme, in the absence of spin-spin interaction, were measured as a function of temperature by saturation recovery, inversion recovery, and the temperature-dependent contributions to CW linewidths. Analysis of the data indicated that the dominant contributions were: nitroxyl radical, Raman process; low-spin heme, Raman process plus thermally-activated process; and high-spin heme, two Orbach processes. The effect of the heme iron on the relaxation for the nitroxyl spin label was modeled to determine the iron-nitroxyl interspin distance. Computer simulations of the spin-labeled protein structure also were used to evaluate the interspin distances for comparison with the EPR experiments

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142. ***A MULTIFREQUENCY ESR APPROACH TO STUDY THE COMPLEX DYNAMICS OF BIOMOLECULES.*** Zhichun Liang and Jack H. Freed, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301.

Ever since the advent of nitroxide spin-labeling, it has been clear that ESR studies of spin-labeled macromolecules could provide insight into their complex dynamics. Recent developments of site directed spin-labeling of proteins and of modern ESR methods with enhanced sensitivity to reorientational dynamics may be expected to improve the ability to unravel the complex dynamic modes. We examine how a multi-

frequency approach using high and low (or standard) ESR frequencies can provide such a decomposition to recover (i) the overall tumbling of the protein, (ii) the side chain fluctuations, and (iii) the motion of the spin labels about their tether. The primary virtues of this approach, as compared to e.g. NMR, relate to the favorable time scale of ESR, which leads to dramatic lineshape changes due to the motions, that cannot be simply analyzed by a perturbational approach, (e.g. Redfield theory), and are particularly sensitive to the details of the dynamics. In addition, ESR at higher (lower) frequencies is more sensitive to the faster (slower) dynamics, greatly helping one to decompose the effects of the different dynamic modes. Also, we show how the use of the slowly relaxing local structure model is able to encompass these modes. This approach will be illustrated with recent 250 and 9 GHz experimental examples of spin-labeled T4-Lysozyme and of spin-labeled DNA nucleosides.

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143. *220 GHz EPR STUDIES OF SPIN-LABELED DNA.* David E. Budil, Stephen V. Kolaczkowski, Department of Chemistry, Northeastern University, Boston MA 02115; Alexander Perry‡, Chanakura Varaprasad‡, and Francis Johnson‡, Dept. of Pharmacological Sciences, 607 Graduate Chemistry Building State University of New York at Stonybrook, Stonybrook, NY 11794; and Phyllis R. Strauss, Department of Biology, Northeastern University, Boston MA 02115.

The dynamics of a newly synthesized cytidine spin-label and spin-labeled single- and double-stranded DNA oligomers have been observed by high-field (220 GHz) EPR. Good quality, single-scan spectra may be obtained in aqueous solution at ambient temperature using nanomolar amounts of spin-label. The excellent orientation resolution at 220 GHz allows independent measurement of the rotational rates around all three molecular axes from the slow-motional EPR spectra. The motion of the monomer spin-label could be fitted using a model of fully anisotropic rotation (FAR) over the entire temperature range studied. In the spin-labeled oligomers the high-field spectra revealed the presence of microscopic ordering with macroscopic disorder and suggest that the probe's immediate environment is rather heterogeneous and non-polar. These preliminary studies illustrate the significant amount of new dynamic information that is available about local base motions in DNA from high-field spin-label studies, and demonstrate the utility of multifrequency studies for accurately discriminating the effects of local vs. global motions in labeled macromolecules.

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144. *SUCCESSFUL OBSERVATION OF ALLOWED EPR TRANSITIONS IN HIGH SPIN (S=2) IRON(II): HFEPR OF A REDUCED RUBREDOXIN MODEL.* J. Krzystek, National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310; M. J. Knapp, D. N. Hendrickson, Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, CA 92093; L-C. Brunel, National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310.

Ferrous ion (Fe^{2+}) plays an important role in electron-transfer enzymes and other biomolecules of significant interest. Although paramagnetic in its high spin (S = 2) form, its large zero-field splitting has made it notoriously difficult to observe by conventional EPR except for low-intensity forbidden transitions in certain environments (Petasis, D. T.; Hendrich, M. P., J. Magn. Reson. 1999, 136, 200-206 and references therein). In mononuclear iron proteins such as rubredoxin, the reduced (Fe^{2+}) form is 'EPR silent.' We have succeeded in detecting complete EPR spectra including most allowed transitions in [Fe(SPh)4]$^{2-}$, a model for the reduced form of rubredoxin, by applying electromagnetic frequencies in the 90 – 440 GHz, and magnetic fields in the 0 – 14 T range. The zero-field splitting parameters obtained by simulating the powder spectra (D = + 5.84, E = + 1.42 cm^{-1}) are compared to zero-field FIR data on the same compound (Champion, P. M.; Sievers, A. J., J. Chem. Phys. 1977, 66, 1819-1825) and found in very good agreement. Together with the g-values inaccessible in the FIR experiment ($g_x = g_y = 2.08$, $g_z = 2.00$) they serve as a basis for electronic structure considerations which are extended from the model compound to rubredoxin itself.

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145. *INFLUENCES OF THE MICROWAVE COUPLING ELEMENTS ON OVERCOUPLED PULSE EPR RESONATOR.* Jörg Forrer, Jürg Keller, Arthur Schweiger, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule,8092 Zürich, Switzerland; Rolf Schuhmann, Thomas Weiland, Institut für Hochfrequenztechnik, Technische HochschuleDarmstadt,6100 Darmstadt, Germany.

Adjustments of the microwave (mw) coupling between the transmission line and the EPR resonator are mainly used to set bandwidth, dead time and sensitivity (signal to noise ratio) of the pulse EPR spectrometer. This technique leads not only to a trade-off between these parameters, but also influences the B_1-field homogeneity in the resonator structure and the EPR experiments that depend on it. Rigorous time resolved three-dimensional computations with the software package MAFIA (Solution of Maxwell's equation by Finite Integration Algorithm) for the Dielectric and Bridged Loop Gap Resonator are shown. The pictures lead to a better understanding of the coupling elements (iris, antenna and loop) and their influences on the electromagnetic field distribution in the resonators. The calculations are done at s- and x-band frequencies and include all dielectrics and the mw transmission lines. Calculated B_1-field strengths are compared with electron nutation measurements.

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146. ***USE OF AN ENDOR PROBEHEAD FOR LONGITUDINAL DETECTION OF AMPLITUDE MODULATED EPR.*** Josef Granwehr and Arthur Schweiger, ETH Zurich, Laboratory of Physical Chemistry, CH8092 Zurich, Switzerland

To increase the sensitivity of longitudinally-detected amplitude modulated (AM) EPR spectra (1-3), we focused on the optimization of the filling factor, the quality factor Q of the detection circuit and the use of modulation frequencies ν_{AM} of the microwave amplitude as high as possible. The most straightforward solution was to use a Bruker X-band pulse ENDOR probehead rotated by 90°. The coils were integrated into a resonance circuit which was matched to 50 Ω using a voltage follower. The experiments were performed on a Bruker X-band pulse spectrometer complemented by a CW solid state microwave amplifier, an arbitrary waveform generator to generate the amplitude modulation, and an RF lock-in amplifier for detection. With this setup we could record EPR spectra of metal complexes in powders and in single crystals at room temperature with a surprisingly good sensitivity. The work has been supported by the Swiss National Science Foundation.

1. *Hyde et al., J. Chem. Soc. Faraday Trans. 1, 1989, 85, 3901*
2. *Pescia, Ann. Phys., 1965, 10, 389*
3. *Colligiani et al., Appl. Magn. Reson., 1992, 3, 107*

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147. ***THE CHEMISTRY OF MOLECULES ENCAPSULATED IN NANOBUBBLES AS PROBED BY CW-EPR AND CW-TREPR.*** Martin Jäger, Olga Makarova, Agnes E. Ostafin, and James R. Norris, Jr. The University of Chicago, Department of Chemistry (Searle), 5735 S.Ellis Ave., Chicago, IL 60637; Dan Meisel, Radiation Laboratory, University of Notre Dame, IN 46556.

EPR spectroscopy, in both the steady state and the time-resolved mode, provides a powerful tool to probe molecules within confined areas[1]*. In this respect, nanobubbles are a unique micro-cage for the encapsulation of molecules. Modifying the surface properties of colloidal gold and adding amino-alkoxy-silane spacer, a porous silica shell of determined thickness grows on addition of active silica*[2]*. The gold core can be easily dissolved by cyanide bleaching. Molecules with specific features can be introduced into the cavity. One strategy requires that the compounds be bound to the gold surface, the shell is hence condensed around them*[3]*. Alternatively, the molecules diffuse via pores into the bubble after removal of the core particles, shown in the figure below. The first method is however limited to compounds having functional groups with affinity to gold, the latter allows a greater variety of molecules to enter the nanobubble. EPR and TREPR shall be applied to investigate the properties and chemistry of encapsulated organic molecules such as benzoquinone and benzophenone. Since the porosity of the shell determines the accessibility to the trapped compound, diffusion dependent processes can be controlled. Prolonged radical lifetimes as well as finite spin spin interactions are expected due to the confinement, which can be observed in CIDEP*[4]

1. *G. Closs, M. D. E. Forbes, and J. R. Norris, Jr. J. Phys. Chem., 1987, 91, 3592.*
2. *L. M. Liz-Marzan, M. Giersig, and P. Mulvaney. Langmuir, 1996, 12, 4329.*
3. *O. Makarova, J. Lantz, S. Schlett, J. R. Norris, Jr., and D. Meisel. J. Phys. Chem., 1999, accepted.*
4. *J. B. Pedersen, C. E. M. Hansen, H. Parbo, and L. T. Muus. J. Chem. Phys., 1975, 63, 2398.*

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148. ***PULSED EPR OF THE PENTACENE PHOTOEXCITED TRIPLET AT LOW AND ZERO FIELD WITH FAST MAGNETIC FIELD SWITCHING.*** T. Tran Chin Yang, David J. Sloop, S. I. Weissman, and Tien-Sung Lin, Washington University Department of Chemistry, St. Louis, MO 63130.

We report the observation of the free induction decay (FID) signals of the Tx-Tz and Ty-Tz zero field transitions at 1.34 and 1.44 GHz of the triplet state of pentacene h_{14} and d_{14} in p-terphenyl and benzoic acid crystals at room temperature following photoexcitiation with a pulsed N_2 laser. Additional FID measurements which include pulsed magnetic fields have allowed measurement of low field EPR line splittings. Pulsed fields large enough to cause rapid passage through an avoided triplet crossing result in FID signals that yield useful new spin dynamics information. Some FID signals show clear evidence of the transfer of spin polarization from the photoexcited triplet to the surrounding protons.

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149. ***PHOTOCHEMICAL REACTION: APPLICATION OF LIQUID CHROMATOGRAPHIC POST-COLUMN PHOTOLYSIS TO THE ENHANCED CONDUCTIVITY DETECTION OF FOUR FENICOLS.*** Steve A. Gonzales, Allen P. Pfenning, JosÈ E. Roybal And Sherri B. Turnipseed, Food and Drug Administration, Denver Federal Center, Animal Drugs Research Center, P.O. Box 25087, Denver, CO 80225-0087

A liquid chromatographic system with post-column photochemical derivatization for the conductivity detection of four Fenicols and an internal standard is described. The first of these broad-spectrum antibiotics, Chloramphenicol, was developed around 1950 and the last one being approved in late 1996. Most HPLC methods designed to analyze these drugs use the universal UV detector. The separations and responses of Chloramphenicol (CAP), Thiamphenicol (TAP), Florfenicol (FF), Florfenicol Amine (FFA), the major metabolite of Florfenicol, *are presented. The use of the conductivity detector helps to reduce the level of sample matrix interferences and provide the specificity used in pesticide residue analysis. Incorporation of a Tracor Photoconductivity Detector provides a direct analytical scheme for the multidrug residue screening of various samples. Evaluation of a variety of reverse phase columns, mobile phases and photoconductivity reaction parameters are discussed.*

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150. *ADVANCES IN COMBUSTION TOTAL ORGANIC CARBON ANALYSIS.* Don Harrington, Ken OíNeal, Brian T. Wallace, and Maria Theresa Lee-Alvarez, Tekmar-Dohrmann, 7143 E. Kemper Road, Cincinnati OH 45249;

TOC analysis has been an integral part of evaluating water quality in industrial and environmental laboratories. TOC is determined as a measure of organic contamination for quality control and for wastewater monitoring in the chemical, pharmaceutical, food and beverage and other industries. Analysis of carbon is also essential for drinking water, groundwater, soils and wastewater compliance monitoring. Current advances in technology have paved a way for a reliable and high analytical performance system for doing TOC analysis. It is based on combustion method where carbon in the sample is converted to CO_2 and the CO_2 produced is detected by Non-Dispersive Infrared. Techniques for performing TOC measurements of different types of challenging samples such as wastewater, particulates, and salt water, among others, with great precision will be presented. Analytical figures of merit such as reproducibility, dynamic range, limit of detection, and minimal carry-over will be discussed.

General Poster Session—Brian T. Wallace, Tekmar-Dohrmann, 7143 E Kemper Road, Cincinnati OH 45249, (513) 247-7068, fax: (513) 247-7050, briwal@tekmar.com

151. *CLEANING VALIDATION BY TOTAL ORGANIC CARBON ANALYSIS: INSTRUMENTAL TECHNOLOGY CONSIDERATIONS.* Don Harrington, Ken OíNeal, and Brian Wallace, Tekmar -Dohrmann, 7143 E. Kemper Road, Cincinnati OH 45249;

The analytical strategy developed to assess the amount of organic residues left on pharmaceutical manufacturing equipment surfaces from product or cleaning agent carryover is known as cleaning validation. Current trends in pharmaceutical manufacturing have seen increasing demand for rapid sample analysis time along with low detection limits for Total Organic Carbon (TOC) analysis in cleaning validation. Through improved technology, U/V persulfate TOC analysis today provides the sensitivity for ppb analysis with quick and precise sample analysis. However, even with technology improvements, there are some pitfalls. Some of these areas include high TOC ìhotî samples, blank variability, and recoveries on clean-in-place (CIP) compounds. Steps to eliminate as many pitfalls as possible for TOC analysis along with hints on deciding which TOC method is best for your process will be discussed.

General Poster Session—Brian Wallace, *Tekmar-Dohrmann, 7143 E Kemper Road, Cincinnati OH 45249,* (513) 247-7068, fax: (513) 247-7050, briwal@tekmar.com

152. *DETECTION OF CHROMIUM AND CHROMIUM PICOLINATE IN DIETARY SUPPLEMENTS AND HERBAL PRODUCTS BY FLAME AAS AND BY LC-UV.* Jeffrey A. Hurlbut and Kevin S. Ewing, Chemistry Department, Metropolitan State College of Denver, P. O. Box 173362, Denver, CO 80217; Susan B. Clark, Doug W. Rowe, and Sherri Turnipseed, Food and Drug Administration, Denver Federal Center, P.O. Box 25087, Denver, CO 80217

Chromium is an essential dietary element which possibly influences lipid and carbohydrate metabolism. Many herbal and dietary supplement companies claim that large doses of chromium as chromium picolinate cause weight reduction, increased muscle mass, more efficient carbohydrate metabolism, increased energy, reduction of cholesterol levels, etc. The accepted daily dose of chromium is 50 - 200 ug, and the chromium picolinate dietary pills contain from 50 to 400 ug of chromium per tablet. A literature search revealed that there has been little work done on analysis of chromium picolinate or chromium in these tablets; so, the object of this work was to develop two different methods of analysis: flame AAS for chromium analysis and LC-UV for chromium picolinate analysis. The flame AAS method consists of sonicating the tablets in enough water to bring the chromium level between 1 and 10 ug/mL, adding sodium sulfate as a masking agent, filtering, measuring the absorbance at 357.9 nm, and calculation ofÒ Ò the chromium content from a calibration curve. The LC-UV method consists of sonicatinng of the tablets in enough water to bring the chromium picolinate concentration between 0.1 and 100 ug/mL, 0.4 filtration, injection of 20 uL into a C18 reverse phase column, separation using a 1:1 MeOH:Water mobile phase, detection at 266 nm, and calculation from a calibration curve. Chromium picolinate is not available commercially, and the synthesis as well as the MS and NMR are reported. Results of the two assay methods of analysis are reported.

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153. ***THE DEVELOPMENT OF AN IN-LINE NEAR INFRARED SYSTEM FOR TESTING FAT AND PROTEIN IN MILK AND RELATED PRODUCTS.*** Avril O'Sullivan, APT Group, Food Engineering Department, University College Cork, Ireland; Desmond Brennan, National Microelectronics Research Centre, Cork, Ireland; Dr. Barry O'Connor, APT Group, Department of Food Engineering, University College Cork; ACS Group, National Microelectronics Research Centre, Cork, Ireland.

Traditionally laboratories have depended upon a wide range of analytical techniques to measure the levels of food components such as fat and protein. A number of rapid and instrument methods have been gradually introduced to increase product output and product quality. These have many advantages over traditional techniques. The use of instruments based on Near Infrared Spectroscopy as an accurate and rapid alternative to traditional chemical techniques is becoming widely accepted. The NIR region that this project is concentrating on stretches from 800-1100nm. In recent years Near Infrared Spectroscopy (NIRS) has gained popularity for many reasons including its ease of operation, minimal sample preparation and the ability to analyse material which contains significant amounts of water. Since this project began spectra have been taken from an ultrafiltration unit in the process hall at University College Cork. Typical products used are whole milk, skimmilk and reconstituted whey powder. The in-line flow cell is connected to the spectrometer via a fibre optic connection and via a serial analogue line to the computer where the data is exported to an excel sheet. A cut-off filter removing light below 740nm reduces the effect of stray light from lower orders on the diffraction grating of the spectrometer. The ability of an instrument to detect changes in fat and protein concentrations at a desired sensitivity is dependent on signal to noise ratio and the optical pathlength used in the system. In parallel with the sensor development the effect of pH, temperature and conductivity on NIR measurements will be investigated and an algorithm will be developed to compensate for interference between these variables. These algorithms will be used to deconvolute spectral information acquired by the instrument. The aim is to produce a low cost in-line system for use in industry.

General Poster Session—Ms. Avril OíSullivan, APT Group, Department of Food Engineering, University College Cork, Ireland, (021)-903436, fax: (021) 903091, avril.osullivan@ucc.ie

154. ***DETERMINATION OF RESIDUES OF AZAMETHIPHOS IN SALMON TISSUE BY LC/FLUORESCENCE.*** Allen P. Pfenning, JosÈ E. Roybal, Sherri B. Turnipseed, Steve A. Gonzales, and Jeffrey A. Hurlbut, U.S. Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Denver, CO 80225-0087

A liquid chromatographic (LC) method with fluorescence detection (FLD) is described for determining residues of the pesticide azamethiphos (AZA) in salmon tissue. The sample is extracted with ethyl acetate, centrifuged, dehydrated with anhydrous sodium sulfate, evaporated, reconstituted in water and defatted with hexane; the aqueous phase is passed through a C_{18} Solid Phase Extraction (SPE) column. The SPE column is eluted with methanol, the eluate evaporated to dryness, and taken up in 10% acetonitrile (ACN) in water. The analyte is determined by LC/FLD, employing a C_{18} column, ACN:H_2O (32:68) mobile phase and 230 nm excitation, 345 nm emission wavelengths. Composited salmon tissues were fortified with AZA at 5, 10, 21, 42 and 83 ng/g, or ppb (the target level, X = 10 ng/g). Overall recoveries were 86%, with between day variability of 5.3%. The method detection limit (MDL) was calculated as 1.2 ppb AZA based on a 5 g sample. The LOQ as determined empirically by this method is the lower limit of the standard curve, approximately 5 ppb.

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155. ***A METHOD FOR THE DETERMINATION OF FOUR FLUOROQUINOLONES IN MILK BY LIQUID CHROMATOGRAPHY.*** José E. Roybal, Allen P. Pfenning, Sherri B. Turnipseed, Calvin C. Walker and Jeffrey A. Hurlbut, U.S. Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087

A liquid chromatographic (LC) method with fluorescence detection is presented for the analysis of 4 fluoroquinolones, Enrofloxacin (ENRO), Ciprofloxacin (CIPRO), Sarafloxacin (SARA) and Difloxacin (DIFLX) in milk. The procedure consists of extraction of milk with acidified ethanol, isolation and retention on a cation exchange SPE column, elution with basic methanol and LC analysis with fluorescence detection. LC analysis is performed by isocratic elution utilizing Acetonitrile/2%Acetic Acid (15+85) mobile phase and a Inertsil Phenyl column with fluorescence detection at excitation and emission wavelengths of 278 and 450nm, respectively. A target level of 10ppb for each of the 4 fluoroquinolones has been established for this method. Average recovery from fortified raw milk samples (5-100ppb each) based on a 5-point standard curve calculation was 70-90% with relative standard deviation of <15%.

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156. ***FATTY ACID PROFILING OF HERBAL AND BIOLOGICAL MATRICES.*** John B. Atwater, Paul F. Smith, Hauser, Inc., 5555 Airport Blvd., Boulder, CO 80301

Fatty acids are physiologically important as (1) components of phospholipids and glycolipids, (2) lipophilic modifiers of proteins, (3) fuel molecules stored as triglycerides, and (4) hormones and intercellular messengers. Increased interest has been directed towards characterizing fatty acid active components in herbal and biological matrices. This characterization can consist of not only the fatty acid profile in terms of carbon number, but also the speciation of the fatty acid component, in terms of whether the fatty acid is in its free acid form, methylated, or covalently bound.

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157. ***RESIDUAL SOLVENT IDENTIFICATION LIMITS FOR PHARMACEUTICAL PRODUCTS USING A GAS CHROMATOGRAPHY/MASS SELECTIVE DETECTOR (GC/MSD).*** Pauline Chow, Geneva Pharmaceuticals, Inc., 2655 W. Midway Blvd., Broomfield, CO, 80038

Identification of unknown residual solvents in pharmaceutical active ingredients is an important part of the drug approval process. However, it is often difficult to identify every unknown compound detected by different analytical instruments. In this study, various concentrations of Class 1 solvents defined by the Federal Register and International Conference on Harmonisation, and the organic volatile impurities of the U.S. Pharmacopeia were analyzed by a GC/MSD. Identification limits were determined that can be related to an unknown residual solvent concentration based on the active ingredient concentration.

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158. ***DEVELOPMENT OF A SELECTIVE RP-HPLC METHOD FOR THE ANALYSIS OF LEUPROLIDE ACETATE.*** Michele R. Gehring, Steven F. Volker, Atrix Laboratories, Inc., Fort Collins, CO 80525-4417

A highly selective, short run-time RP-HPLC method has been developed for the analysis of Leuprolide acetate for drug content and purity. The method is based on the draft European Pharmacopoeia (EP) monograph for Leuprolide acetate which utilizes a 100 x 4.6 mm C_{18} *3μm particle size column and a acetate which utilizes a moblile phase consisting of 6% n-propanol (NPA)/9% acetonitrile (ACN)/85% 150 mM triethylammonium phosphate (TEAP) adjusted to pH 3.0. Modifications were made to the organicOto-buffer ratio and the pH of the buffer with the intent of shortening the run time of the method while maintaining the chromatographic performance required in the draft EP monograph. Optimal results were obtained with a mobile phase consisting of 17% (50/50 NPA/ACN) /83% 150 mM TEAP (pH 2.0) and a Phenomenex Luna C18(2) 100 x 4.6 mm 3-μm particle size column. Increasing the organic content of the mobile phase shortens the run time from 60 minutes to 30 minutes. Lowering the pH from 3.0 to 2.0 improves resolution of the Leuprolide peak from both the D-His*^{2} *Leuprolide and des-ethylamide degradants.*

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159. ***A NOVEL SYNTHETIC ROUTE TO THE DOPAMINE AUTORECEPTOR ANTAGONIST (+) UH232.*** Zachary S. Jones, Justin G. Schiro, Christopher K. Murray, Scott A. Peterson, John X. Rizzo, Michael P. Scannell, Lalith R. Jayasinghe, Hauser, Inc.

No abstract.

160. ***RAPID IDENTIFICATION OF PHARMACEUTICALS AND METABOLITES BY HPLC/MS/MS.*** Shane Needham, Patrick Jeanville, Mark J. Cole, Central Research Division, Pfizer Inc., Groton, CT 06340

Metabolite identification is now routinely performed with HPLC/MS/MS instruments. In Drug Development, metabolites above the 1% level require definitive identification. The associated HPLC methods usually have run times of over 30 minutes. Conversely, in the Drug Discovery process often only identification of the major metabolic pathway(s) from in vitro systems is required to understand structure metabolism relationships and allow the chemist to synthesize metabolically stable compounds. Since mainly oxidative metabolism occurs with in vitro systems, the major primary metabolic pathway is usually hydroxylation. Rapid identification of the monohydroxylated products is facilitated by the use of rapid chromatographic separations. This rapid HPLC/MS/MS identification procedure can be performed like other high-throughput screening assays where only the parent drug is measured such as drug absorption and drug lability assays.

In this poster we describe the development of rapid separations for the identification of metabolites by HPLC/MS/MS. Since multiple monohydroxylated metabolites are possible for in vitro systems, chromatographic resolution between positional isomers is beneficial for unambiguous determinations. Therefore, various HPLC conditions were investigated to determine the optimum conditions necessary to achieve adequate resolution of isomeric metabolites in a rapid manner. A rapid gradient was used to produce a separation that is generic for most small pharmaceutical compounds. Optimization of the HPLC conditions included choosing an optimum stationary phase, solvent composition, flow rate and temperature of the separation.

Extending the above approach for simultaneous metabolite identification and drug half-life determination is under investigation. This approach can provide qualitative and quantitative Drug Discovery information in one high-throughput assay.

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161. ***COMPARISON STUDY OF DISSOLUTION PROPERTIES FOR METALS IN SOILS UNDER THE VARIOUS EXTRACTING CONDITION.*** Kang-Sup Chung, Byung-In Choi, Sang-Yeon Kim, Duk-Young Song, Kun-Han Kim, Hak-Je Seong, Korea Institute of Geology, Mining and Materials(KIGAM), P.O. Box 111 Yusung, Science Town, Taejon, Korea

Dissolution properties for the metals(As, Cd, Cu, Pb, Zn, Cr, Sb, Ba, Be, Ni, Ag, Hg) in several kinds of soils under the various extracting conditions were studied. For the experiment, 2 types of test samples were prepared. The one was made by spiking several metals to 3 kinds of fresh *soils which were sand, clay, loam and the other was TCLP soil reference sample. The target metals in these prepared samples were investigated under the various extracting conditions such as extracting time, acid concentration, particle size, etc. and also, the comparison study between EPA method TCLP 1311 and the Korean extraction method was performed. The extracts were analyzed by AAS, FI/HG-AAS and ICP-AES and addition, chemical and mineral composition, ignition loss and cation exchange capacity of each soil samples were examined by XRF, XRD and other chemical analysis in order to get the basic information about adsorptivity. As the results, dissolution properties were affected mainly by acid concentration in extracting procedure and mineral composition of soils. On the other hand, extracting time, sort of acids and particle size of soils had a little influence on the dissolution properties. Cd revealed very high dissolving efficiency and As was very low in whole extracting test.*

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162. *AN INVESTIGATION INTO THE DIFFUSION OF CHLORINATED HYDROCARBONS INTO POLYMER FILMS USING ATTENUATED TOTAL REFLECTANCE FOURIER TRANSFORM INFRARED SPECTROSCOPY.* Rhona Howley, Dr. Peter McLoughlin, Waterford Institute of Technology, Cork Road, Waterford, Ireland; Dr. Fiona Regan, Limerick Institute of Technology, Limerick, Ireland.

Chlorinated Hydrocarbons (CHCs) are a class of organic solvent which pose a serious environmental threat1. Research has been carried out on detecting CHCs in aqueous samples using a polymer coated Attenuated Total Reflection (ATR) element2,3. There are few research publications on the application of this technology to gas phase analysis. In this study a polymer coating on an ATR element was used to enrich CHCs in the evanescent wave region. A Polyisobutylene (PIB) coated ATR element is utilised in order to study the diffusion and enrichment of tetrachloroethylene from the gas phase. The system involves a flow cell of volume 3 cm3 and a zinc selenide ATR crystal coated with 2% PIB in Dekalin. This coating procedure resulted in a polymer film of 12.5 (m in thickness. Standards were prepared using Tedlar sampling bags and zero grade air. Calibration curves for TeCE are linear in the concentration range 50 - 300 ppm with regression values greater than 0.99 after 300 seconds diffusion. Limits of detection for TeCE of 26 ppm have been achieved after 300 seconds. An ATR Fickian diffusion model5 has been investigated which depends on such parameters as the thickness of the polymer coating, the depth of penetration of the IR radiation, the refractive indices of the polymer film and the ATR crystal and the equilibrium absorbance of TeCE. As all of the above parameters are quantifiable a diffusion coefficient for TeCE into PIB can be determined by regressing the experimental data with the diffusion model. A diffusion coefficient of 9.15x10-10 cm2/s was obtained. Theoretical integrated absorbance values are calculated based on the given parameters for the system, and the effect of varying these parameters on the diffusion pattern can be illustrated.

1. *B.J. Alloway, D.C. Ayres, Chemical Principals of Environmental Pollution, Chapmann and Hall, 1994.*
2. *P. Heinrich, R. Wyzgol, B. Schrader, A. Hatzilazaru, D. Lubbers, Applied Spectroscopy, 1990, 44, 1641.*
3. *R. Gobel, R. Krska, R. Kellner, R. Seitz, S. Tomellini, Applied Spectroscopy, 1994, 48, 678.*
4. *Hong, Barbari, Sloan, 1998, 36, 337.*

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163. *HIGH RESOLUTION ICP-MS, THE FIRST DECADE (1989-1998).* C.B. Douthitt, Finnigan MAT, 9412 Rocky Branch Drive, Dallas, TX 75243

High resolution ICP-MS was first described in 1989, with the introduction of commercial HR-ICP-MS instruments from VG Elemental[1] and JEOL[2]. These first systems were instrumental chimeras, with an ICP head grafted onto existing organic mass spectrometer bodies. In the five years from 1989-1993, some 40 instruments were delivered worldwide, (8 instruments/year) with an average cost >700k$, and were documented in 20 papers and 10 presentations. The introduction of a purpose-built instrument in 1994 (Finnigan MAT model ELEMENT) stimulated the demand for HR-ICP-MS; in the five years from 1994-1998, 160 instruments were delivered (32 systems/year, a fourfold increase) with an average cost <400k$, and the published work grew to 175 papers (an eightfold increase) and 525 presentations (a fiftyfold increase)

While the introduction of double focusing analyzers was motivated by their high mass resolution capability (to resolve polyatomic interferences), HR-ICP-MS instruments have many other features with tangible analytical benefits. Compared to Q- and TOF-ICP-MS, HR-ICP-MS has higher sensitivity, lower background, higher signal stability, better peak shape, and less mass bias, which lead to superior limits of detection, more precise multi-element and isotopic analyses, and more accurate isotopic and elemental ratios. HR-ICP-MS, no longer restricted to oligoelement limit-of-detection solution analysis, is increasingly being used for multielemental analyses (15% of papers), isotopic analysis (13% of papers), laser ablation of solids (10% of papers), and speciation analysis (10% of papers).

To avoid matrix separation and preconcentration prior to analysis, considerable ingenuity has been put into devising methods to deal with specific interferences, the most recent innovations being cold plasma and collision cells. While each of these methods is useful some of the time, none of them are useful all of the time—high mass resolution is the only general solution to the problem of polyatomic interferences. With high mass resolution, it is possible to unambiguously identify the existence of interferences; together with accurate mass assignment and appropriate software, one can infer the chemical composition of the interferences. The use of high mass resolution does not preclude the use of the various other techniques used to reduce interferences, and it is a singular strength of HR-ICP-MS instruments that high (and variable) mass resolution can be used in conjunction with such methods as hydride generation, desolvation, and cold plasma within a sin-

gle analytical procedure. Tangible accomplishment of HR-ICP-MS include speciation of Al in biological fluids at natural levels, direct analysis of sub-ppt levels of REE in seawater, sub-ppb detection limits in solids, and accurate low level measurements of As, F and P.

HR-ICP-MS, in its first decade, found its way into all of the national chemical metrology laboratories, many nuclear research and production facilities, the geochemistry and chemical oceanography communities, and the semiconductor industry. The combination of high mass resolution and high sensitivity that has allowed analyses that were hitherto impossible combined with the ongoing evolution to smaller, more automated, more powerful, and lower cost systems, leads us to predict that HR-ICP-MS will become a standard analytical tool within the next ten years.

1. *Bradshaw et al., JAAS, 1989, 4, 801*
2. *Morita et al., Anal. Sci, 1989, 5, 609*

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164. ***OPTIMIZED SAMPLE INTRODUCTION FOR HIGH-SENSITIVITY AND HIGH-RESOLUTION ICP-MS.*** D. Weiderin, Elemental Scientific, Omaha, NE 68131-0396

Advances in ICP-MS instrumentation, such as improved sampling interfaces and ion optics, shielded plasma, improved detection systems and high mass spectral resolution, have resulted in instrument sensitivity and specificity that is several orders of magnitude higher than the first commercial ICP-MS instruments. Taking full advantage of current ICP-MS instrument performance requires commensurate improvement in sample introduction system systems, in particular, reduction of instrument blank levels and improved stability. Two new sample introduction systems are investigated for two important analytical tasks: direct analysis of high purity acids and direct analysis of organic solvents. High purity acids (concentrated HF, HNO3, 10 %H2SO4) were introduced into a single collector sector-field ICP-MS (HR-ICP-MS) using a 100 µL/min self-aspirating concentric Teflon PFA nebulizer and Teflon PFA spray chamber. With the PFA introduction system, instrument BEC values were <1 ng/L for common contaminants such as Na, Al, K, Ca, Fe, Cu, and Zn and detection limits were between 0.08 ng/L and 0.4 ng/L. Sensitivity was >1000 cps/ng/L. Organic solvents (2-propanol, nMP, hexane) were directly analyzed by HR-ICP-MS using a self-aspirating 50 µL/min PFA nebulizer, PFA or quartz spray chambers, and O2 addition. The use of the lower flow nebulizer minimizes the amount of O2 that is required to keep the cones free of carbon deposits. No spray chamber cooling was necessary. Method of additions or addition calibration was used for quantification in organic matrices.

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165. ***SEMICONDUCTOR GRADE CHEMICAL ANALYSIS USING HIGH RESOLUTION ICP-MS.*** R. Henry, VG Elemental, 1812 Mapleton Avenue, Boulder, CO 80304, USA; Dagmar Koller, VG Elemental, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, England.

Currently the Semiconductor industry is producing integrated circuits with 250-nm lithography. As the industry approaches the ë100 nm lithography barrierí, close interaction of the semiconductor manufacturers with equipment and materials suppliers is a fundamental prerequisite. Where ppt detection limits met all requirements only a few years ago, ppq and even sub ppq detection limits for anion and cation contaminants are now becoming essential. ICP-MS detection limits vary according to a number of factors including ionization potential, isotopic abundance, isobaric and polyatomic interferences, as well as the analytical blank, all of which need to be considered when analyzing semiconductor reagents. The detection limits offered by current magnetic sector ICP-MS, such as the VG Axiom, are superior to those of conventional ICP-MS systems, particularly in complex matrices such as sulfuric and phosphoric acid. In addition cool plasma technology combined with desolvating sample introduction systems, further extends the analytical capabilities into the sub-ppq range. The analytical capabilities of the VG Axiom will presented for a range of semiconductor reagents, using a variety of plasma conditions and sample introduction systems. The user-selectable resolution characteristics of the VG Axiom enable simultaneous optimization of resolution and transmission to provide the user with the flexibility to analyze each matrix under optimum sampling conditions.

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166. ***AN IMPROVED SAMPLE INTRODUCTION SYSTEM AND OPTIMIZED SCANNING TECHNIQUES FOR PRECISE ISOTOPE RATIO MEASUREMENTS USING SINGLE COLLECTOR SECTOR-FIELD ICP-MS.*** C.B. Douthitt, M. Hamester, W. Kerl, J. Wills, Finnigan MAT, Dallas, TX; Dan Wiederin, Elemental Scientific, Omaha, NE 68131-0396.

The ICP has a number of strengths as an ion source for isotope ratio mass spectrometry, including the ability to ionize a wide range of elements, relatively low interelement matrix effects, easy sample handling, minimal sample preparation requirements, and fast analysis time. However, noise, derived primarily from the ICP ion source and sample introduction system, has limited isotope ratio precision to not much better than 0.1% for conventional single collector ICP-MS instruments. A partial solution to this problem has been the development of multiple collector ICP-MS instruments which achieve higher precision by simultaneously measuring the ion beams from several isotopes. The present work investigates reducing the noise by stabilizing the ion source on a single collector sector-field instrument. Three main sources of noise were identified: processes within the aerosol spray chamber, turbulence at the base of the ICP torch, and turbulence due to air entrainment into the tail of the ICP. A new sample introduction system, in which improved sample aerosol homogeneity reduces pulses *associated with conventional spray chambers, delivered improvements in signal stability by a factor of 5 and, when combined with a new ICP torch design, led to a four- to fivefold improvement in measurement precision for elemental analysis, to about 0.2 % RSD. External precision for isotope ratios of lead (204Pb/206Pb, 207Pb/206Pb, and 208Pb/206Pb,10 μg/L Pb solution) improved to <0.02%, and the agreement with ratios measured using TIMS was better than 0.05%. The external precision of isotope ratio measurements which require high mass resolution (42Ca/44Ca, 57Fe/56Fe, and 65Cu/63Cu) was improved to between 0.04% RSD and 0.1% RSD. Single-collector sector-field ICP-MS, compared to current multicollector ICP-MS instruments, has simpler hardware, minimal (or no) detector cross calibration, the large dynamic range necessary for measurement of large ratios, and optional high mass resolution. The principal limitation, serial as opposed to simultaneous registration of the ion signals, can be partially overcome by a synchronous electric and magnetic field scanning technique which improves the detector duty cycle to >90%. The improvements in ion source stability, the low mass bias, and scan techniques optimized for isotope ratios, allow HR-ICP-MS to provide isotope ratio data which is superior in precision to that from Q-ICP-MS and, in many cases, comparable to that from MC-ICP-MS.*

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167. *THE DETERMINATION OF TRACE METALS IN SEA WATER USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY.* Thomas J. Gluodenis, Jr., Ela Bakowska, and Steve Wilbur, Hewlett-Packard Company, 2850 Centerville Rd, Wilmington, DE 19808

Analysis of trace metals in seawater by ICP-MS presents a number of challenges. These challenges are due to the typically low level (ppt to low ppb) of most trace metals in ambient seawater and the high concentration of matrix elements such as sodium, potassium, calcium, magnesium, and chlorine which can contribute to significant spectroscopic interferences. Without correcting for the possible interferences, the detection limits can become unacceptably high for many analytes. While no single technique is optimal for all analytes and conditions, some strategies for eliminating or reducing interferences are often applied. The use of elemental equations, hydride generation, matrix elimination, method of standard additions, and ShieldTorch techniques are amongst the used strategies. Various techniques for optimizing and automating the analysis of trace metals in seawater will be discussed. The use of ShieldTorch with hot plasma for the analysis of As, Se and Hg by hydride generation/cold vapor ICP-MS will be presented. Results of the analysis of standard reference materials and low-level matrix spikes will be shown.

ICP-MS Oral Session—Ela Bakowska, Hewlett-Packard Company, 2850 Centerville Rd, Wilmington, DE 19808, (302) 633-7317, fax: (302) 633-8916, ela_bakowska@hp.com

168. *EXPANDING ICP-MS APPLICATIONS USING REVOLUTIONARY ION OPTICS IN A QUADRUPLE MASS SPECTROMETER.* 4, VG Elemental, 1812 Mapleton Avenue, Boulder, CO 80304, USA; Jonathan Batey & Martin Liezers, VG Elemental, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, England.

The detection capabilities of quadrupole-based ICP-MS instruments have been limited by their signal-to-background characteristics, as well as by polyatomic interferences inherent in the argon plasma and specific matrix being analyzed. A new ion optic design has resulted in improvements in both signal-to-background and polyatomic interference reduction such that the analytical capabilities of quadrupole-based systems have been substantially improved for both routine and research applications. The ion optics can be used in a high vacuum regime as a normal ion lens to provide high analyte sensitivity and < 0.1 cps background or can be pressurized with a variety of gases to implement collision cell technology which attenuates significantly many of the molecular ions. Analytical data will be presented that demonstrates the performance of the new ion optics.

ICP-MS Oral Session—Rob Henry, VG Elemental, 1812 Mapleton Avenue, Boulder, CO 80304, (303) 939-9012, fax: (303) 939-9017, RHenry1812@aol.com

169. *NEW WAVELENGTHS, NEW OPTICS AND MORE PRECISE CONTROL EXPAND THE APPLICATIONS OF LASER ABLATION ICP-MS.* Rob Henry, VG Elemental, 1812 Mapleton Avenue, Boulder, CO 80304, USA; Fergus Keenan, VG Elemental, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, England.

Originally, Nd:YAG laser ablation systems, operating at 1064nm, linked to ICP-MS were used for multielement analysis of conducting and non-conducting solid samples. Frequency quadrupling the Nd:YAG laser ablation systems to operate at 266nm was a major advance since the higher coupling efficiency allowed analysis of virtually all solids. Spatial resolution of less than 10μm also made the analysis of microscopic samples such as fluid inclusions or individual crystals in mineral thin sections a routine application. Analytical methodologies for analysis of synthetic, mineral and biogenic materials by both quadrupole and high resolution magnetic sector ICP-MS will be presented to illustrate the analytical state of the art. Data will be shown to the advantages of flat beam energy profiles, dynamic autofocus and precise computer control of the sample stage for a range of solid sampling applications.

ICP-MS Oral Session—Rob Henry, VG Elemental, 1812 Mapleton Avenue, Boulder, CO 80304, (303) 939-9012, fax: (303) 939-9017, RHenry1812@aol.com

170. ***METHODS AND PROCEDURES USED IN ASSESSING TRACE METAL CONCENTRATIONS IN VEGETATION FROM AN ARTIFICIAL WETLAND USING ICP-MASS SPECTROMETRY.*** D.B. Peart, H.E. Taylor, T.I. Brinton, D.A. Roth, R.C. Antweiler, U.S. Geological Survey

No abstract.

171. ***DISTRIBUTION AND TRANSPORT OF SELECTED TRACE METALS DETERMINED BY ICP-MS IN THE SACRAMENTO RIVER.*** D.A. Antweiler, H.E. Taylor, U.S. Geological Survey

No abstract.

172. ***EVOLUTION OF ORIENTATION IN MONO- AND MULTILAYER SURFACE FILMS: MICROSCOPIC INTERPRETATIONS OF MACROSCOPIC MEASUREMENTS.*** Garth J. Simpson, Kathy L. Rowlen, Dept. of Chemistry, University of Colorado at Boulder, Boulder, Colorado 80309-0215.

Measurement of molecular orientation at surfaces and interfaces can provide valuable insights into the structure of surface systems, but is often complicated by the small number of molecules present at a geometrically flat surface. A technique developed in our laboratory, angle-resolved photoacoustic spectroscopy (ARPAS), will be described which allows for simple orientation investigations with sub-monolayer detection capabilities. Recent studies include evaluation of the role of surface roughness on orientation measurements by our technique and othersí, and orientation investigations using a total-internal reflection (TIR) flow cell. The new TIR flow cell both provides a measure of surface-selectivity to ARPAS measurements, and allows for combined ARPAS and second-harmonic generation (SHG) orientation measurements without changing the experimental geometry or sample conditions.

Lasers, Materials and Surfaces Oral Session—Garth Simpson, Dept. of Chemistry, University of Colorado, Boulder, Boulder CO, 80309-0215, (303) 492-1210, fax: (303) 492-5894, simpsong@colorado.edu

173. ***ATOMIC LAYER DEPOSITION OF TUNGSTEN USING BINARY REACTION SEQUENCE CHEMISTRY.*** Jason W. Klaus, Stephen J. Ferro, and Steven M. George; Department of Chemistry, University of Colorado, Boulder, CO, USA.

The deposition of ultrathin and conformal films on high aspect ratio structures is important for forming conducting layers in microelectronic devices. Thin films of tungsten (W) were deposited with atomic layer control using sequential surface reactions [1,2]. The tungsten growth was accomplished by separating the binary reaction WF6 + Si2H6 —> W + 2SiHF3 + 2H2 into two half reactions. Successive exposure to WF6 and Si2H6 in an ABAB... binary reaction sequence produced W deposition at substrate temperatures between 425-600 K. The W deposition rate was 2.5 ≈/AB cycle for WF6 and Si2H6 reactant exposures of e" 800 L and 1600 L, respectively. Atomic force micrographs of the deposited films on Si(100) were remarkably flat indicating smooth and conformal deposition. These results represent the first demonstration of atomic layer deposition of conformal single element films using binary reaction sequence chemistry. Similar surface chemical strategies may facilitate the atomic layer growth of other metals besides tungsten.

1. *S.M. George, A.W. Ott and J.W. Klaus, J. Phys. Chem. 100, 13121 (1996).*
2. *J.W. Klaus, A.W. Ott and S.M. George, Surf. Sci. 418, L14 (1998).*

Lasers, Materials and Surfaces Oral Session—Steven M. George, Department of Chemistry, University of Colorado, Campus Box 215, Boulder, CO 80809, (303) 492-3398, fax: (303)492-5894, george@spot.colorado.edu

174. ***SURFACE INTERACTIONS OF CF_2 RADICALS IN HEXAFLUOROPROPYLENE OXIDE PLASMAS.*** Carmen I. Butoi, Colorado State University

No abstract.

175. ***ATOMIC LAYER CONTROLLED GROWTH OF SiO_2 AND Al_2O_3 ON BN PARTICLES USING SEQUENTIAL SURFACE REACTIONS.*** John D. Ferguson, Dept. of Chemistry, A.W. Weimer, Dept. of Chemical Engineering, and S.M. George, Dept. of Chemistry, Univ. of Colorado, Boulder, CO, 80309

BN particles have a high thermal conductivity and are relatively inert. To improve BN particle coupling in polymer composites for thermal management applications, ultrathin coatings can be deposited that do not degrade the BN thermal properties. SiO_2 and Al_2O_3 were grown with atomic layer control using sequential surface reactions of $SiCl_4/H_2O$ [1] and $Al(CH_3)_3/H_2O$ [2], respectively. The sequential surface chemistry was monitored in a vacuum chamber using in situ transmission Fourier transform infrared vibrational spectroscopy. The initial BN particles displayed B-OH and B-NH2 surface species. These groups reacted with $SiCl_4$ or $Al(CH_3)_3$ and converted the surface species to Si-Cl or Al-CH3. The subsequent reaction with H2O converted the surface species to Si-OH or Al-OH. By repeating the sequential surface reactions, SiO_2 and Al_2O_3 bulk vibrational modes increased with number of reaction cycles. Ex situ transmission electron microscopy studies revealed conformal coatings on the BN particles. X-ray photoelectron spectroscopy analysis was also consistent with uniform and conformal deposition. These results illustrate the potential of sequential surface reactions to *deposit conformal and atomic layer controlled coatings on particles.*

1. *J.W. Klaus, A.W. Ott and S.M. George, Appl. Phys. Lett. 70, 1092 (1997).*
2. *A.W. Ott, J.W. Klaus and S.M. George, Thin Solid Films 292, 135 (1997).*

Lasers, Materials and Surfaces Oral Session—John Ferguson, University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO, 80309, (303) 492-6590, fax: (303) 492-5894, John.Ferguson@Colorado.edu

176. *PHOTOSENSITIZATION OF TIN SULFIDE SINGLE CRYSTAL BY SQUARAINE DYES.* Norihiko Takeda and Bruce A. Parkinson, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872

Dye-sensitized electron injection into the conduction band of semiconductors has been studied because of its possible application to light-to-electricity conversion devices and its importance in understanding interfacial electron transfer processes. Dye-sensitized photocurrents are obtained with photoelectrochemical measurements when suitable energetics exist between semiconductors and adsorbed dye molecules. However, there is still uncertainty about this process especially when the dyes are aggregated on the semiconductor surfaces. In this study, quantum yields of electron injection from 1-1 hydroxysquaraine dye to SnS_2 *single crystals were measured and correlated with the local structures of adsorbed dye aggregates on the van der Waals surface of* SnS_2*. Atomic force microscopies (AFM) were used to obtain this goal.*

Lasers, Materials and Surfaces Oral Session—Norihiko Takeda, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872, (970) 491-5993, fax: (970) 491-1801, nori@lamar.colostate.edu

177. *MOLECULAR ORIENTATION AND REORIENTATION IN NANOSCALE REGIONS OF THIN FILM MATERIALS USING NEAR-FIELD SCANNING OPTICAL MICROSCOPY.* Daniel A. Higgins, Erwen Mei, and Xiangmin Liao, Department of Chemistry, Kansas State University, Manhattan, KS 66506)

Near-field scanning optical microscopy (NSOM) is a new form of optical microscopy that provides valuable information on the properties of thin-film mesostructured materials with nanometer-scale spatial resolution. NSOM is being used extensively in our laboratory for characterization of emerging optical display materials. Of particular importance in our research are polymer-dispersed liquid crystal (PDLC) films. Comprised of micron and smaller droplets of nematic liquid crystal encapsulated in a polymer matrix, these materials are electrically switchable between translucent and transparent states. Liquid crystal organization determines their static optical properties while the dynamics of electric-field-induced reorientation govern their switching properties. Both static and dynamic attributes of these materials are controlled by polymer-liquid crystal interfacial interactions, as well as droplet size, shape, and other film morphological details. We are using NSOM to characterize liquid crystal organization and msec-μsec molecular dynamics in these and similar systems. Static images are recorded using standard transmitted light and/or fluorescence NSOM methods. For dynamics studies, we have developed an entirely new method that allows for the study of electric-field-induced molecular reorientation dynamics in highly localized regions. In this method a concentrated electric field is applied using the metal-coated near-field probe. The effects of the electric field on the sample are observed via near-field optical imaging methods. Information on the trajectories through which the molecules reorient is obtained, along with dynamics data. In initial studies, this method has been applied to PDLC films. Dramatic variations in the time scale and extent of molecular reorientation are observed as a function of field strength and position probed. The data are interpreted based on knowledge of the important intermolecular forces active in these materials. Results of these studies will be described in detail; applications of this method to the study of dynamics in other materials will also be discussed.

Lasers, Materials and Surfaces Oral Session—Daniel A. Higgins, Department of Chemistry, Kansas State University, Manhattan, KS 66506)

178. *AN INTEGRATED NSOM/AFM FOR THE STUDY OF NANOPARTICLE OPTICAL PROPERTIES.* Peter C. Andersen, Kathy Rowlen, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309

The study of size dependent optical properties in nanometer scale particles can be facilitated by modern microscopic and spectroscopic techniques. Atomic force microscopy (AFM) and near-field scanning optical microscopy (NSOM) provide complimentary information on surface topography and optical properties. An integrated NSOM/AFM is currently being developed based on light transmission and reflection through the tip of an AFM cantilever. By creating a sub-wavelength aperture at the cantilever tip, the system will have significantly higher optical throughput than conventional NSOM instruments based on tapered optical fibers. The higher throughput will allow experiments to be performed using optically inefficient processes such Raman scattering and low yield photochemical reactions of the surface. The NSOM/AFM will be used to study the relationship between surface enhanced Raman spectroscopy (SERS) and nanoparticle size and shape. Individual silver nanoparticles will be generated by near-field photoreduction of silver salts. The high spatial control of the NSOM/AFM will allow the size and shape of the particles to be varied in a controlled manner. The SERS activity of the resulting particles can then be studied on a individual particle basis.

Lasers, Materials and Surfaces Oral Session—Peter C. Andersen, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309, (303) 492-3631, fax: (303) 492-5894, andersep@colorado.edu

179. ***SCANNING TUNNELING MICROSCOPY INVESTIGATION OF THE ORDERED STRUCTURES OF SQUARAINE DYE MOLECULES ADSORBED ON TWO DIMENSIONAL SUBSTRATES.*** Michele E. Stawasz, Colorado State University, Department of Chemistry, Fort Collins, CO 80523; David L. Sampson, Digital Instruments, 112 Robin Hill Rd., Santa Barbara, CA 93117; Bruce A. Parkinson, Colorado State University, Department of Chemistry, Fort Collins, CO 80523

Squaraine dyes are known to form aggregates in solution and in the solid state and have been investigated for their photoconductive (Law, Chem. Rev., 1993, 93, 449) and dye-sensitization properties (Kamat et al, J. Chem. Soc. Faraday Trans., 1993, 89, 2397). We have found that squaraines form 2D ordered layers when adsorbed onto various two dimensional (2D) substrates from phenyloctane. We investigated the structures of adsorbed phases of a number of symmetric and asymmetric bis(4-dialkylamino-2-hydroxyphenyl) squaraines with scanning tunneling microscopy. Differences in adsorbate stability and molecular packing are observed when the alkyl tail length and symmetry are varied. Squaraines with relatively short tails exhibit a metastable herringbone structure whereas more stable monolayer and multilayer lamellar domains are formed by squaraines with alkyl tails of eight carbons or longer. One resonance structure of a bis(4-dialkylamino-2-hydroxyphenyl)squaraine dye is shown below. The R substituents represent ethyl, butyl, octyl, dodecyl, or stearyl groups.

Lasers, Materials and Surfaces Oral Session—Michele Stawasz, Colorado State University, Department of Chemistry, Fort Collins, CO 80523, (970) 491-5444, fax: (970) 491-1801, mstawasz@lamar.colostate.edu

180. ***THE EFFECT OF THIN WATER FILMS ON FORCE MICROSCOPY MEASUREMENTS.*** Dana Sedin, Kathy Rowlen, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309

The atomic force microscope (AFM) is a powerful tool for probing surface topography, in addition to chemical and mechanical properties of surfaces. To investigate the chemical properties of a sample, force measurements are made between the AFM's "molecular finger," or probe, and the sample. Force measurements can be made in many environmental conditions, which makes the AFM a versatile instrument. However, in ambient conditions most samples are covered by a thin layer of water. When the AFM probe comes into contact with the thin water layer, a capillary bridge forms between the AFM probe and sample. Because of this water layer, it is believed that in ambient conditions a non-surface specific capillary force dominates the adhesive force between the AFM probe and sample. To investigate the capillary force, pull-off-force as a function of relative humidity was monitored on chemically different substrates. Our results suggest that capillary forces are surface specific. The results of our experiments along with possible explanations will be presented.

Lasers, Materials and Surfaces Oral Session—Dana Sedin, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309, (303) 492-3631, fax: (303) 492-5894, sedin@colorado.edu

181. ***SPECTROMETRY FOR THE MASSES: NEW APPROACHES AND NEW APPLICATIONS.*** Richard N. Zare, Ansgar Brock and Nestor Rodriguez, Stanford University, Department of Chemistry, Stanford, CA 94305-5080

Many common ion sources produce continuous streams of ions, such as electron impact, atmospheric ionization, electrospray, etc. Yet the simplest and least expensive form of mass spectrometry is time-of-flight mass spectrometry (TOF-MS). What is the best way it to interface these two when one is continuous whereas the other requires start and stop pulses?

The standard way to operate a time-of-flight mass spectrometer (TOFMS) is to produce an ion packet, accelerate the ions in the packet to the same energy, and let them drift in a field-free region of fixed length where they disperse in time before striking a detector. The detector signal represents directly the time-of-flight distribution of the ions, which is readily converted into a mass spectrum by means of a square root relationship that links flight time and mass for ions of the same energy. If a continuous ion source is to be employed, such as electrospray, this mode of operation results in low ion usage because ions are not measured during the time the ion packet disperses in the field-free region of the instrument. We describe an alternative approach that overcomes this poor duty cycle. A continuous ion beam emerging from the source is accelerated and then modulated by a pseudo-random sequence of ioní and ioffi pulses. The data acquisition period is set to match the period of the modulation sequence, and data are acquired synchronously with the modulation of the ion beam. The modulation sequence is deconvoluted from the data using a fast Hadamard transform algorithm to extract the time-of-flight distribution of the ions. This multiplexing scheme increases the ion usage to approximately 50% and improves the signal-to-noise level considerably over that of conventional TOFMS. Sample mass spectra will be presented illustrating the power of this new type of TOF-MS.

Lasers, Materials and Surfaces Oral Session—Richard N. Zare, Marguerite Blake Wilbur Professor in Natural Science, Stanford University, Department Of Chemistry, Stanford, California 94305-5080, (650) 723-3062, fax: (650) 725-0259, Zare@Stanford.Edu

182. ***USE OF ATOMIC FORCE MICROSCOPY TO STUDY THE GAS-SOLID REACTIONS OF OZONE WITH CARBONACEOUS NANOPARTICLES.*** Amy E. Michel, Kathy L. Rowlen, John W. Birks, University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO 80309-0215

Atomic force microscopy (AFM) is a potentially powerful tool for imaging and characterizing small particles and surface features in the size range from 0.001-1.0 µm. Due to the resolving power of AFM, the reaction between an individual particle and a reactive gas can be monitored as long as the reaction products are gaseous. As the reaction progresses, the size decrease of the particle is monitored. By observing the reaction of gases with solids using AFM, insight may be gained into how particles react in the atmosphere. In particular, the reaction of ozone with soot is of considerable interest because of its potential effect on the concentrations and atmospheric lifetimes of both species.

Ozone in the upper atmosphere protects the Earth from biologically damaging ultraviolet radiation, while soot particles strongly absorb visible radiation and may act as cloud condensation nuclei. Other forms of carbonaceous particles, specifically polycyclic aromatic hydrocarbons (e.g. anthracene and pyrene), buckminsterfullerene (C_{60}), carbon nanotubes and graphite, are related to soot in that they also contain sp2 hybridized carbons. Therefore, it is expected that a systematic study of the ozonation of these soot-like nanoparticles will lead to an improved understanding of the complex mechanism of the ozone reaction with soot particles in the atmosphere. Preliminary experiments for the reactions of ozone with the various carbonaceous particles will be discussed.

Lasers, Materials and Surfaces Oral Session—Amy E. Michel, University of Colorado, Department of Chemistry and Biochemistry, Campus Box 215, Boulder, CO 80309-0215, (303) 492-6535, fax: (303) 492-1149, michelae@ucsub.colorado.edu

183. *INVESTIGATION OF THE DYE-TiO_2 (ANATASE) INTERFACE: DYE COVERAGE AND CRYSTAL FACE EFFECT ON SENSITIZATION EFFICIENCY OF TiO_2 (ANATASE) NATURAL SINGLE CRYSTALS.* Akiko Fillinger, and B.A. Parkinson, Colorado State University, Department of Chemistry, Fort Collins, CO 80523.

The effect of dye coverage and crystal face on the dye sensitization efficiency of TiO_2 (anatase) natural single crystals has been measured. The (101) and (001) faces, as determined by the crystal shapes and Laue back-reflection measurements, were primarily studied. Differences in dye sensitization efficiency between these faces were observed. Several possible explanations for the different sensitization efficiencies for the faces will be discussed. The crystal face effects were also studied using different dyes. These dyes are all ruthenium complexes where the number and type of ligands are varied to investigate the binding to the anatase surface. The adsorption of the dye molecules to anatase surface as investigated with atomic force microscopy will also be reported.

Lasers, Materials and Surfaces Oral Session—Akiko Fillinger, Colorado State University, Department of Chemistry, akko@lamar.colostate.edu

184. *ATOMIC LAYER DEPOSITION OF TUNGSTEN FILMS STUDIED USING AUGER ELECTRON SPECTROSCOPY.* Jeffrey W. Elam, Christine E. Nelson, Steven M. George, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215

We have recently demonstrated the atomic layer deposition of tungsten (W) metal films using self-limiting sequential surface reactions. Tungsten was deposited by alternating exposures of disilane (Si2H6) and tungsten hexafluoride (WF6). In the present study, the nucleation and growth of W on a silica (SiO2) substrate under UHV conditions was monitored with Auger electron spectroscopy. The Auger data showed that approximately 10 sequential exposures are required before W growth is initiated at 573 K using 105 Langmuir Si2H6/WF6 exposures. Following this nucleation period, W deposition proceeds at a growth rate of 2.8 per reaction cycle or ~ 1 W monolayer per Si2H6/WF6 exposure. A quantitative model including electron backscattering effects was developed to explain the Auger signals. Additional Auger experiments have yielded the adsorption kinetics for both Si2H6 and WF6 on the tungsten surface during atomic layer deposition.

Lasers, Materials and Surfaces Oral Session—Jeffrey W. Elam, University of Colorado, Department of Chemistry and , Biochemistry, Boulder, CO 80309-0215, (303) 492-6992, fax (303) , 492-5894, elamj@stripe.colorado.edu

185. *DIRECT EVIDENCE FOR OZONE OXIDATION OF A SELF-ASSEMBLED ALKANETHIOL MONOLAYER DURING EXPOSURE TO UV LIGHT.* Matthew M. Ferris, K. L. Rowlen, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309.

Self-assembled alkanethiol monolayers (SAMs) on noble metal surfaces have shown potential uses in thin film optics, microelectronics and information storage. Many of these uses require selective removal of the alkylthiolate SAM which has been carried out primarily with UV light. The products formed by irradiation with UV light or ozone generated ex situ are qualitatively the same and have been identified as adsorbed sulfonate species. While the mechanism of this oxidation process is unclear, the role of photo-generated ozone has been shown to be significant. Surface enhanced Raman scattering (SERS) is used to confirm the primary role of ozone in the oxidation of 1-decanethiol monolayers on silver surfaces. It is shown that UV wavelengths, in the presence of oxygen and water, are not capable of producing oxidation products when diffusion of photo-generated ozone to the SAM is blocked with a quartz windowed cell. When ozone is then flowed through this cell, the oxidation of the SAM to the sulfonate species is observed by the SERS spectra.

Lasers, Materials and Surfaces Oral Session—Matthew M. Ferris, University of Colorado at Boulder, Department of Chemistry and Biochemistry, Boulder, Colorado 80309, (303) 492-1210, fax: (303) 492-5894, Ferrism@Colorado.edu

186. *SOLIDS, LIQUIDS, AND AEROSOLS FOR ON-LINE MALDI SAMPLE INTRODUCTION.* Kermit K. Murray, Emory University, Department of Chemistry, Atlanta, GA 30322

Matrix assisted laser desorption ionization (MALDI) is entering its second decade as a technique for the analysis of large biomolecules and synthetic polymers. Although the technique is maturing, there is much room for improvement, particularly in the area of sample delivery. A typical MALDI sample preparation involves depositing a solution of matrix and analyte on a sample probe, waiting for solvent evapora-

tion, and insertion of the sample probe into the mass spectrometer. MALDI analysis of liquid separations such as liquid chromatrography or capillary electrophoresis requires fraction collection prior to sample preparation. My research group is developing new methods for on-line MALDI sample introduction that use aerosols, liquid capillaries, and rotating balls to deliver samples into time-of-flight mass spectrometers. Both ultraviolet and infrared lasers are used for desorption and ionization. The liquid capillary method is the most direct: the analyte is pumped into the mass spectrometer in a liquid matrix. We have found that small alcohols and other solvents can be used as the matrix when the OH stretch is irradiated at 2.9 µm. With the aerosol method, the matrix and analyte solution is converted into a spray or single particle stream before entering the mass spectrometer. The rotating ball method is the most complex but is also the most versatile. Here, the matrix and analyte solution is delivered through a capillary to one side of a metal ball rotating slowly in the mass spectrometer ion source. As the ball rotates, the matrix and analyte solution is exposed to vacuum and the solvent evaporates. Ionization occurs by laser desorption from the ball surface. Solid and liquid matrices and UV and IR lasers can be used with the rotating ball inlet. The performance of the three sample introduction configurations and the outlook for on line LC and CE MALDI will be discussed.

Lasers, Materials and Surfaces Oral Session—Kermit K. Murray, Department of Chemistry, Emory University, Atlanta, GA 30322, (404) 727-2254; fax: (404) 727-6586, kmurray@emory.edu

187. ***COUPLED PLASMON-WAVEGUIDE RESONANCE (CPWR) SPECTROSCOPY: A NEW TOOL FOR CHARACTERIZING ANISOTROPIC THIN FILMS, INCLUDING BIOLOGICAL MEMBRANES.*** G. Tollin and Z. Salamon, Department of Biochemistry, University of Arizona, Tucson, AZ 85721.

A variant of surface plasmon resonance (SPR) spectroscopy has been developed that involves a coupling of plasmon resonances in a thin metal film (e.g. silver) and waveguide modes in a thicker dielectric overcoating (e.g. silica)[1]. The latter functions as an optical amplifier, as a mechanical and chemical shield for the metal layer, and as a surface that allows various types of molecular immobilization strategies. Compared with conventional SPR, this new technique (called CPWR spectroscopy) provides a greatly enhanced sensitivity (due to increased evanescent electromagnetic field intensities at the dielectric surface) and spectral resolution (due to greatly decreased resonance linewidths). It also provides the ability to directly measure, using p- and s-polarized excitation, anisotropies in refractive index and optical absorption coefficient in a thin dielectric film deposited onto the surface of the overcoating. We have applied this technology to studies of lipid bilayers self-assembled on the silica surface, of the spontaneous incorporation of integral membrane proteins into these bilayers by detergent dilution methods[2,3] and of ligand binding to these integral proteins[2,3]. By fitting theoretical resonance curves to the experimental data, surface mass density, film thickness, and structural anisotropy of proteolipid films can be evaluated. Examples of several such applications will be described. Supported by NSF MCB-9404702.

1. *Salamon, Macleod and Tollin, Biophys. J. 1997, 73, 2971.*
2. *Salamon, Huang, Cramer and Tollin, Biophys. J. 1998, 75, 1874.*
3. *Salamon, Lindblom and Tollin, Biophys. J., submitted.*

Lasers, Materials and Surfaces Oral Session—Gordon Tollin, University of Arizona, Department of Biochemistry, Tucson, AZ 85721, (520)621-3447, fax (520) 621-9288, HYPERLINK mailto:gtollin@u.arizona.edu , gtollin@u.arizona.edu

188. ***A SINGLE MOLECULE FLUORESCENCE IMAGING TECHNIQUE FOR ULTRA-HIGH THROUGHPUT DNA FRAGMENT SIZE ANALYSIS IN FLOW CYTOMETRY.*** Alan Van Orden, W. Patrick Ambrose, and Richard A. Keller, Chemical Science and Technology Division (CST-1), MS M888, Los Alamos National Laboratory, Los Alamos, NM 87545

Ultrasensitive, laser-based spectroscopy techniques for the detection and characterization of individual molecules are providing many new opportunities in the analytical sciences. For example, our group has developed a technique for DNA fragment size analysis that involves the fluorescence detection of individual DNA fragments as they flow through the focal region of a tightly focused laser beam in a flow cytometry apparatus. Dramatic improvements in the sensitivity and analysis time compared to conventional methods for DNA fragment size analysis have been realized. This talk describes a new development in single molecule DNA fragment sizing that has resulted in more than an order of magnitude improvement in the sample throughput compared to our earlier approach. The technique involves excitation with a planar sheet of laser light and imaging of the fluorescence from single DNA fragments that flow through the laser onto a CCD camera. DNA fragments in the size range of 2 to 200 kilobase pairs can be detected and sized with a detection frequency of several thousand fragments per second in this way. The application of this new technique to rapid, high throughput bacteria fingerprinting will be discussed.

Lasers, Materials and Surfaces Oral Session—Alan Van Orden, Chemical Science and Technology Division (CST-1), MS M888, Los Alamos National Laboratory, Los Alamos, NM 87545, (505)665-2092, fax: (505)665-3024, avo@lanl.gov

189. ***BIOABSORBABLE POLYMER MATERIALS FOR MEDICAL DEVICE AND DRUG DELIVERY APPLICATIONS.*** Newton K. Seitzinger, and Richard L. Dunn, Atrix Laboratories, Inc., Fort Collins, CO 80525

Bioabsorbable polymers dissolved in a biocompatible solvent can be used in a variety of applications for medical devices and drug delivery. The rate of bioabsorption and drug release are affected by the polymer type, molecular weight, and concentration, along with the solvent used. Analytical challenges include characterization of the polymer solution and the active drug in the solution, stability of the drug in the polymer solution, and both in vivo and in vitro release of drug.

Lasers, Materials and Surfaces Oral Session—Newton Seitzinger, Atrix Laboratories, Inc., 2579 Midpoint Dr., Fort Collins, CO 80525, (970) 482-5868, fax: (970) 482-9735, nseitz@atrixlab.com

190. *ADVANCES IN THE DESIGN AND APPLICATIONS OF SENSORS BASED ON LUMINESCENT TRANSITION METAL COMPLEXES..* J. N. Demas, Wenying Xu, and Kristi Kneas. Department of Chemistry, University of Virginia, Charlottesville, VA 22904; B. A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807.

A variety of inorganic complexes show great promise as molecular probes and luminescence-based sensors. The majority of work uses d^6 *systems Ru(II), Re(I), and Os(II) with a-diimine ligands (e.g., 2,2'-bipyridine, 1,10-phenanthroline, and analogues). Central to the rational design of practical systems is an intimate understanding of the interactions between the probe or sensor molecule and the polymer based support or the target. Advances in understanding the interactions of metal complexes and polymeric supports will be discussed using examples from oxygen and pH sensors. As we will show these areas are still in their infancy and that the ultimate goal of a totally rational design of probes, luminescence enhancers, and polymer-supported sensors is as yet an imperfectly realized goal.*

Luminescence Oral Session—J. N. Demas, Department of Chemistry, University of Virginia, Charlottesville, VA 22904, (804) 924-3343, fax: (804) 924-3710, jnd@virginia.edu

191. *OPTICAL DIAGNOSTIC TECHNIQUES FOR CHARACTERIZING VORTEX-FLAME INTERACTIONS.* James R. Gord, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433-7103; Gregory J. Fiechtner, Keith D. Grinstead, Jr. and Campbell D. Carter, Innovative Scientific Solutions, Inc. 2766 Indian-Riple Road, Dayton, OH 45440-363; Paul-Henri Renard and Juan Carlos Rolon, Laboratoire d'Énergétique Moléculaire et Macroscopique, Combustion, École Centrale Paris, Grande Voie des Vignes, 92295 Châtenay-Malabry Cedex, France

A thorough understanding of turbulent reacting flows is essential to the continued development of practical combustion systems. Unfortunately, these studies represent a tremendous research challenge due to the inherent complexity of such flows. In an effort to reduce the complexity of these systems while capturing the essential features that define the physics and chemistry of turbulent reacting flows, we have been studying the interaction of a vortex with a flame. The experimental apparatus includes a piston-cylinder device configured to provide a precisely controlled toroidal vortex or starting jet. The generated vortex interacts with a nonpremixed hydrogen-air, methane-air flame supported in a counterflow burner. The counterflow configuration permits precise control of the flame and the associated strain field accomplishing numerical modeling of vortex-flame interactions. Two-color particle-image velocimetry (PIV) and acetone-vapor planar laser-induced fluorescence (PLIF) have been employed to characterize the vortex and to describe the underlying counterflow velocity field. Other laser-based flow-visualization techniques have been exploited to explore vortex-flame interactions in the counterflow burner. In particular, flame extinction during these interactions has been studied through the use of OH PLIF, and temperature fields have been imaged through the use of planar Rayleigh scattering techniques.

Luminescence Oral Session—James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, OH 45433-7103, (937) 255-7431, fax: (937) 656-4570, gordjr@pr.wpafb.af.mil

192. *THE USE OF LUMINESCENT SPECIES FOR PRESSURE MEASUREMENTS.* Patricia B. Coleman, Ford Motor Company, PO Box 2053, Mail Drop 3083/SRL, Dearborn, MI 48121-2053

For the past four years, work has been underway to find the most sensitive oxygen sensor for near ambient pressure measurements. As part of this endeavor numerous polymers have been synthesized and tested as possible binders and several different luminescent species have been investigated. A controlled environment chamber was designed and built for evaluating the sensors. The environment in the chamber, which fits into the fluorescence spectrometer sample compartment, is totally under computer control. The temperature can be held constant or varied during a test run, and the oxygen concentration can be varied either by changing the mixture of oxygen and nitrogen or by using pressure and vacuum to simulate the particular testing condition. From this effort a detailed protocol has developed for testing pressure sensor materials. This talk will discuss the testing protocol and compare lab results to actual tests.

Luminescence Oral Session—Patricia B. Coleman, Ford Motor Company, PO Box 2053, Mail Drop 3083/SRL, Dearborn, MI 48121-2053, (313) 322-0567, fax: (313) 621-0646, pcoleman@ford.com

193. *CAPTURING GAS TURBINE SPARK IGNITION THROUGH ULTRAFAST IMAGING.* Keith D. Grinstead Jr. and Gregory J. Fiechtner, Innovative Scientific Solutions, Inc., 2766 Indian-Riple Road, Dayton, OH 45440-3638; James R. Gord and Charles Tyler, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433-7103; Michael Cochran and John R. Frus, Unison Industries, 7575 Baymeadows Way, Jacksonville, FL 32256

Spark-ignition systems play a critical role in the performance of essentially all gas turbine engines. These devices are responsible for initiating the combustion process that sustains engine operation. Demanding applications such as cold start and high-altitude relight require continued enhancement of ignition systems. To characterize advanced ignition systems, we have developed a number of laser-based diagnostic techniques configured for ultra fast imaging of key spark parameters including emission, density, temperature and species concentrations. These camera and high-repetition-rate laser sources, including modelocked TI sapphire oscillators and regenerative amplifiers. Spontaneous-emission measurements as well as laser-based schlieren and interferometry have been applied to the study of a novel Unison spark igniter. This particular igniter features a multiple-spark "plume" mode of operation that show great promise for improved cold-start and high-altitude-relight capability over igniters currently in use throughout military and commercial fleets. Details of the imaging instrumentation, particularly the CCD camera and laser sources, are presented.

Luminescence Oral Session—Keith D. Grinstead Jr., Innovative Scientific Solutions, Inc., 2766 Indian-Riple Road, Dayton, OH 45440-3638, (937) 255-6980, fax: (937) 255-3139, grin@ward.appl.wpafb.af.mil

194. *STUDYING THE SOLVENT-DEPENDENT SPECTROSCOPY OF IR-125 THROUGH ASYNCHRONOUS OPTICAL SAMPLING.* Christopher E. Bunker, Idaho National Engineering and Environmental Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2208; James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, OH 45433-7103; Keith D. Grinstead Jr. and Gregory J. Fiechtner, Innovative Scientific Solutions, Inc., 2766 Indian-Riple Road, Dayton, OH 45440-3638;

Solvents often have profound effects on the spectroscopic characteristics of luminescent solutes. Many steady-state and time-resolved studies have been accomplished to explore these solvent dependencies and enhance our understanding of solvent dynamical effects on chemical reactivity. Typically these time-resolved data are acquired using ultrafast-laser-based techniques, including time-correlated single-photon counting and pump-probe spectroscopy. While the pump-probe configuration delivers exceptional temporal and spatial resolution, it suffers from some significant limitations when practiced in a traditional delay-line-based geometry. Time-resolved data acquired with a slow-scanning delay line are subject to baseband noise, and any deviation from perfect delay-line alignment and beam collimation produces erroneous pump-probe signals arising from walk off and blooming effects. Asynchronous Optical Sampling (ASOPS) offers solutions to these limitations. The pump-probe delay is realized in the form of a repetitive phase walk out between two modelocked lasers operating at slightly different pulse-repetition rates. ASOPS and its application to studying the solvent-dependent spectroscopy of IR-125 (Indocyanine Green) are discussed in this presentation.

Luminescence Oral Session—James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, OH 45433-7103, (937) 255-7431, fax: (937) 656-4570, gordjr@pr.wpafb.af.mil

195. *OPTICAL DETERMINATION OF ADDITIVES IN AVIATION FUEL.* Donald K. Phelps, Christopher E. Bunker, James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, OH 45433-7103;

The presence of additives in aviation fuel can present problems in certain situations. Oftentimes it is not desirable to mix additized fuel to that without additives or to place it in storage not designed to accommodate those additives. In order to discriminate between such fuels, one must detect either the additive in fuel or a chemical marker mixed with the additive. Test results for three different chemical-marker systems are presented. The additive package of interest contains a surfactant. The ability of surfactants to solubilize water in fuel allows the additive to be detected directly by mixing the fuel with concentrated dye-water solutions. Test results are presented for two water soluble dyes: one is detected by fluorescence, the other by absorbance.

Luminescence Oral Session—Donald K. Phelps, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, OH 45433-7103, (937) 255-7405, fax: (937) 656-1125, Donald.Phelps@wpafb.af.mil

196. *FLUORESCENCE INVESTIGATION OF PYRENE, TETROLS, AND TETROLS WITH DNA IN METHANOL: WATER SOLVENTS.* Robert J. Hurtubise, , Department of Chemistry, University of Wyoming, Laramie, WY, 82071; Paul B. Steinbach, Department of Chemistry, Stephen F. Austin State University, Nacogdoches, TX 75962

Pyrene is frequently used as a polarity probe to determine the polarity of microenvironments. In this study, the fluorescence properties of pyrene, four tetrol isomers (I-1,I-2, II-1, and II-1), and the tetrols with DNA present were investigated in several methanol (MeOH):water solutions. Tetrols are the hydrolysis products of benzo[a]pyrene DNA adducts, and they are important in cancer research. The fluorescence intensity ratios of the first to the third vibronic bands (R value) in the fluorescence emission spectra were compared for the systems studied. Unique insights were obtained about the interactions of the stereoisomeric tetrols in the MeOH:water solvents with and without DNA present. Plots of R values versus the mole fraction of methanol for pyrene and the four tetrols showed that the plots were very different for the tetrols compared to pyrene. The data for pyrene indicated that preferential solvation was occurring for pyrene near a MeOH mole fraction of 0.16. The plots for I-2 and II-2 gave plateau regions from zero to 0.23-mole fraction of MeOH. However, the plots of R values versus mole fraction of MeOH for I-1 and II-1 gave essentially linear relationships. The R values for the four tetrols as a function of the mole fraction of MeOH showed that the tetrol solvation properties were different compared to pyrene. Of considerable interest were the differences that emerged by comparing the R-value plots for I-1 and II-2, as a set, to the R-value plots for I-2 and II-2 as a set. Tetrol I-1 and II-1 have their hydroxyl groups in the 9 and 10 positions on opposite sides of the hydroaromatic rings in the tetrols. Tetrol I-2 and II-2 have their hydroxyl groups on the same side of the hydroaromatic rings in the 9 and 10 positions. By comparing the plots of R values versus mole fraction of methanol for the two sets of tetrols, it was obvious that the shapes of the plots were quite different for the two sets of compounds. Also, R values in MeOH:water solutions were obtained for the four tetrols in 5.0 mg/mL of DNA. The R values versus mole fraction of MeOH for the four tetrols with DNA were quite different compared to the corresponding tetrol without DNA. The results implied that DNA was undergoing structural changes as the amount of methanol decreased. In general, the methods developed permitted a new way to study structural features of isomers with small stereochemical differences. Also, the approach provided an effective means for the investigation of tetrols in the presence of DNA.

Luminescence Oral Session—Robert J. Hurtubise, University of Wyoming, Department of Chemistry, Laramie, WY 82071,(307) 766-6241, fax: (307) 766-2807, hurtubis@uwyo.edu

197. *ROOM-TEMPERATURE PHOSPHORESCENCE QUENCHING TO STUDY OXYGEN DIFFUSION THROUGH ORAL BIOFILMS.* J.A. Ekhoff, K.L. Rowlen, Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215

Biofilms are known to be at least 500 times more resistant to antimicrobials that are their planktonic counterparts, although the reason for this is now well understood. Our present study is focused on determining the diffusion rate of oxygen through a biofilm. The results will *provide information on the aerobic and anaerobic regions of the biofilms, as well as illustrate a model for the diffusion of other small molecules including antibiotics. Experiments are based on the room-temperature phosphorescence quenching of A1(III)-ferron chelates immobilized on strongly basic anion exchange resin beads dispersed in a silicon rubber matrix. (Liu et al. Anal. Chem. 1994, 66, 836-840). To investigate the activity of oral biofilms, streptococcus mutans was chosen as the model bacteria. These biofilms are grown on the surface of the silicone matrix containing the sensing beads. The oxygen quenching data was quantified using Stern-Volmer analysis.*

Luminescence Oral Session—RJ.A. Ekhoff, Campus Box 215, University of Colorado, Boulder, CO 80309-0215,(303) 492-1210, fax: (303) 492-5894, ekhoff@ucsub.colorado.edu

198. *SOLID-MATRIX LUMINESCENCE OF HETEROCYCLIC AROMATIC AMINES IN GLUCOSE GLASSES PREPARED FROM A GLUCOSE MELT.* Shaun D. Mendonsa, Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071

Heterocyclic aromatic amines (HAA) are a class of mutagenic/carcinogenic substances found in cooked meat, fish, and other environmental samples. HAA are formed at ng/g levels during the heating process and are the pyrolysis products of amino acids and proteins. All of the known HAA test positive in the Ames/Salmonella microsome mediated mutagenicity test. Many of them are known to induce tumors in the liver, lung, breast, small and large intestines, and other sites. All this suggests that these compounds appear to be ubiquitous environmental pollutants and their daily exposure to humans is a cause for concern. 2-Amino-1-methyl-6-phenylimidazo[4,5-b]pyridine (PhIP) is an example of an HAA. Room temperature phosphorescence (RTP) and room temperature fluorescence (RTF) of trace organic compounds has been readily obtained in glucose glasses prepared from crystalline glucose. For the first time, a glucose melt was used to prepare the glasses. The glasses prepared with the glucose melt showed several advantages over glasses prepared with crystalline glucose. Since the glucose melt is more soluble in methanol than is crystalline glucose, glasses could be prepared with pure methanol instead of a methanol-water mixture. This eliminated the use of water which is a known phosphorescence quencher. Using pure methanol also resulted in shorter drying times for the glasses. The glasses prepared with the glucose melt were more rigid than crystalline glucose glasses, and this resulted in a two to three-fold increase in the RTP signals of some of the analytes studied leading to lower limits of detection. RTP and RTF spectra for several HAA were obtained in glasses prepared with the glucose melt and crystalline glucose, and their spectra were compared. With the exception of PhIP, very little has been published about the luminescence properties of HAA. PhIP was used primarily as a model compound and was studied in detail. Analytical figures of merit were obtained for PhIP in glucose glasses prepared from both crystalline glucose and a glucose melt. A heavy-atom salt, NaI, was also added to the glasses and a significant enhancement in the RTP signal of PhIP was observed.

Luminescence Oral Session—Shaun D. Mendonsa, Department of Chemistry, University of Wyoming, Laramie, WY 82071, (307)766-4844, fax: (307) 766-2807, shaunm@uwyo.edu

199. *SOLID-MATRIX LUMINESCENCE OF HYDROXYL AROMATIC METABOLITES ON WHATMAN 1PS PAPER.* Barry W. Smith and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071.

Solid-matrix luminescence methods were developed for human biomonitoring that employ room-temperature fluorescence (RTF) and phosphorescence (RTP) for the detection and identification of 1-hydroxypyrene, tetrol I-1, 3-hydroxyphenanthrene, and 9-hydroxyphenanthrene and various mixtures of some of these compounds. Due to similarities in the hydroxy-phenanthrenes, they could not be distinguished from each other, and consequently they were not investigated in detail. To identify the different metabolites that were in high-performance liquid chromatography fractions from human urine samples, two methods were developed to obtain optimal luminescence signals. Each compound of interest was adsorbed on Whatman 1PS paper with thallium nitrate as a heavy-atom salt under neutral and basic conditions. A microwave oven was implemented in this study rather than a convection oven, which was used in previous studies. This shortened the sample drying time and kept down the production of oxides of thallium, which diminished the heavy-atom effect. At larger concentrations of the metabolites in the mixtures (upper pg to lower ng range), RTF and RTP were used in combination to identify the metabolites. Once very low levels of luminescence were reached (lower pg range), RTP was the only method that could be utilized, due to the noise level in the RTF signals. The limits of detection were in the femtomole range with RTP for each metabolite.

Luminescence Oral Session—Barry W. Smith, Department of Chemistry, University of Wyoming, Laramie, WY 82071, phone 307-766-4844, fax 307-766-2807, drwho@uwyo.edu

200. *LUMINESCENCE-BASED OXYGEN SENSORS: FLUORESCENCE MICROSCOPY AS A PROBE OF SENSOR HETEROGENEITY.* Kristi A. Kneas, J. N. Demas, Department of Chemistry, University of Virginia, Charlottesville, VA 22901; Ammasi Periasamy, Department of Biology, Advanced Cellular Imaging Facility, University of Virginia, Charlottesville, VA 22901; B. A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807

Luminescence-based sensors, especially those utilizing platinum-group complexes, are of significant and growing practical importance. Sensors employing ruthenium(II) complexes as the luminophore are now commercially available for measuring oxygen in blood and as pressure sensitive paints for wind tunnel studies. The detailed role of the polymer support in controlling photophysical behavior, however, is still poorly understood. Polymeric sensor heterogeneity has a tremendous effect on luminescence, quenching, and photochemistry, and important unresolved details include the number and types of sites occupied by the sensor molecules, the local environment, the quenching processes, and the correlation of these properties to different sensor supports. We will show that fluorescence microscopy has been an invaluable tool as we have begun to address such issues. We have observed microheterogeneous regions within luminescence-based oxygen *sensor films which exhibit enhanced luminescence intensity but poorer quenching relative to the bulk response. By performing pixel-by-pixel statistical analyses, we have been able to correlate microscopic film characteristics to the sensor response observed macroscopically. Based on these and other observations, we will make suggestions regarding the source of nonlinear Stern-Volmer plots and nonexponential luminescence decays, which are features of most all sensor systems; and we will make recommendations for a more rational approach toward sensor fabrication.*

Luminescence Oral Session—Kristi A. Kneas, Department of Chemistry, McCormick Road, University of Virginia, Charlottesville, VA 22904, (804) 924-3688, fax (804) 924-3710, Kak4w@virginia.edu

201. *SPECTROSCOPIC STUDIES OF PHOTO AND THERMAL STABILITIES OF VARIOUS EVA ENCAPSULANTS FOR PHOTOVOLTAIC APPLICATIONS.* S.H. Glick and F. J. Pern. Engineering and Reliability Division, National Center for Photovoltaics, National Renewable Energy Laboratory, 1617 Cole Blvd., M/S 3214, Golden, CO 80401. (303)-384-6615.

Field irradiance results in uniform yellow-to-brown discoloration of commercially formulated ethylene vinyl acetate (EVA) encapsulants for photovoltaic modules. In contrast, simulated accelerated exposure testing (AET) at irradiance of ~7.5 or ~9.0 UV suns and respective black panel temperatures (BPT) of 85°C and 145°C produced nonuniform browning in laminated EVA. Samples heated in an oven at 85°C, however, displayed insignificant browning. To investigate the photo-thermal effects on pottant degradations and browning pattern under UV exposure, we are conducting experiments with various EVA formulations laminated between a borosilicate glass plate and a substrate of the same glass plate or polymer film. Present results from fluorescence and color index measurements show increased emission intensity and yellowness index for the samples of EVA formulations that contain UV absorbers and are exposed under ~9.0 UV suns at a BPT of ~65°C for 400 h. Although no discoloration is visible yet, the degradation of EVAs of commercial formulations under these AET conditions is faster than that for EVA heated in an oven at 85°C. In comparison, samples heated in an oven at 125°C exhibit some faint yellow-brown color within 100 h. The increase in the fluorescence emission intensity is attributed to photochemical decomposition of UV absorbers, which are used in some of EVA formulations and are intended to provide protection from UV-induced photodegradation. More detailed results and discussion will be presented in the meeting. This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-98-GO10337.

Luminescence Oral Session—Stephen Glick, NREL, 1617 Cole Blvd., M/S 3214, Golden, CO 80401-3393, phone 303 384-6650, fax 303-384-6490, stephen_glick@nrel

202. *MULTI-DIMENSIONAL FLUORESCENCE FOR THE INVESTIGATION OF DIETARY HABITS OF FREE-RANGING HERBIVORES.* Gary D. Rayson and Timothy L. Danielson, New Mexico State University, Box 30001 MSC 3C, Las Cruces, NM 88003; Dean M. Anderson, R. Estell, E. L. Fredrickson, K. M. Havstad, USDA Jornada Experimental Range, Box 30001 MSC 3JER, Las Cruces, NM 88003.

The determination of the dietary intake of domestic livestock is necessary for their effective management. This becomes more difficult when the animals are allowed to feed on native flora in open rangeland. Efforts in the past to provide information regarding a particular animalís dietary habits have used either highly invasive techniques or methods that are time and labor intensive and very subjective. The objective of the present study is to develop instrumentation to enable the interrogation of sample extracts using multi-dimensional fluorescence measurements for objective, rapid determination of plants eaten by a specific animal. Initial work has concentrated on the acquisition and post-processing of the excitation/emission wavelength fluorescence matrices for each of six plant species typically eaten by free-ranging sheep in the desert southwestern United States. Results of these investigations will be presented with a description of the instrumentation used. The utility of alternate dimensions, including lifetimes and extracting solvent polarity, will be discussed.

Luminescence Oral Session—Gary D. Rayson, New Mexico State University, Box 30001 MSC 3C, Las Cruces, NM 88003, (505) 646-5839, fax: (505) 646-2649, garayson@nmsu.edu

203. *SAMPLE PREPARATION REQUIREMENTS FOR HIGH-THROUGHPUT AND HIGH-SENSITIVITY HPLC-MS.* Ronald E. Majors, Hewlett-Packard, 2850 Centerville Road, Wilmington, DE 19808.

Sample preparation is still considered to be a major bottleneck in many analytical laboratories. Indeed, in the areas of high-throughput screening, combinatorial chemistry and QA/QC where fast HPLC analysis is often the norm, sample preparation can become the rate-limiting step. The same can be said for the needs of modern HPLC-MS and HPLC-MS/MS where the need for high sample throughput and high sensitivity analysis have created new demands on sample preparation. In some cases, the need for speed has compromised the requirement for proper sample cleanup and has led to the sample preparation techniques that merely keep major contaminants from reaching the MS ionization source. The MS system is expected to provide the analytical resolution. On the other hand, new sample preparation devices such as the 96- and 384-well solid-phase extraction plates, convenient column-switching systems, and automated liquid handling systems have come onto the market that can often meet the demands of high throughput interfacing. This talk will focus on some of the newer manual and automated sample preparation devices and techniques that provide high-speed method development capability and high-throughput analysis.

For high sensitivity requirements, newer extraction technologies such as supercritical fluid-, accelerated solvent-, and microwave-assisted-extraction have given improved tools to the analyst to provide cleaner samples without the need for copious amounts of organic solvent and *with much faster turnaround. Even old technologies such as Soxhlet extraction and liquid-liquid extraction have improved versions that can provide faster and cleaner samples. Some of these newer sample preparation techniques will be explored and compared.*

Finally, the future of analytical measurements with the rapidly moving area of miniaturization and ìlab-on-a-chipî technology will have a profound effect on sample preparation and analysis. In this lecture, we will speculate on how these future developments may impact sample preparation requirements.

MS, GC/MS, LC/MS/Phamaceutical Analysis Oral Session—Ronald E. Majors, Hewlett-Packard, 2850 Centerville Road, Wilmington, DE 19808, (302) 633-8222, fax: (302) 633-8902, ron_majors@hp.com

204. *A NOVEL APPROACH FOR RAPIDLY DEVELOPING AN EFFICIENT SOLID PHASE EXTRACTION METHOD.* Jianmei Ding, Parnela Ireneta, Uwe Neue, Waters Corporation

Analysis of drugs and metabolites in biological matrices (e.g., plasma, urine, serum, etc.) by liquid chromatography-mass spectrometry (/mass spectrometry) (LC-MS(/MS)) has become a routine task in today's pharmaceutical industry. As a result, there are several critical issues that an analyst must resolve on a daily basis. Before biological samples are introduced to a LC-MS system, it is crucial that they are processed in a manner that isolates the analytes of interest from matrix interferences. Traditional sample preparation methods include protein precipitation, solid phase extraction, liquid-liquid extraction and on-line column switching. The choice of a sample clean-up method influences the speed, the recovery, and the cleanliness of the extract. Correspondingly, the cleanliness of the extracts impacts the mass spectrometric detection with respect to ion suppression, precision of quantitation and detection limits

This study addresses the fundamental issues involved in preparing biological samples for analysis at trace level by mass spectrometry. Extracts from protein precipitation, liquid-liquid extraction, a simple and generic SPE method, and a specific pH and organic modulated SPE (2-D SPE) method [1] were analyzed by MS. Matrix interferences from the different extracts were revealed by full scan mass spectra and the results of the precision of quantitation of the drugs and the metabolites. In addition, recoveries for each method are discussed. We found that the 2-D SPE method results in the best overall performance in terms of speed, percent of recovery and cleanliness of sample preparation.

In order to obtain a 2-D SPE method for any compound rapidly, we have investigated an online 2- D SPE-LC-MS method[2] which not only allows one to develop a 2-D SPE method within 3 hours, but also provides the HPLC separation profile for a drug and its metabolites. Importantly, this method can be readily transferred to a 96-well SPE plate, enabling a large batch of samples to be prepared in parallel. Thus, the combination of on-line SPE-LC-MS with off-line SPE LC-MS methods can provide great benefits to the analysis of compounds generated at both drug discovery and drug development stages of the pharmaceutical research.

1. *Cheng, Y.-F.; Neue, U.D.; Bean, L. J. Chromatogr. 1998, 828, 273.*
2. *Jemal, M.; Xia, Y.Q.; Whigan, D.B. Rapid Commun. Mass Spectrom., 1998,12,1389.*

MS, GC/MS, LC/MS/Phamaceutical Analysis Oral Session—Jlanmej Ding, Waters Corp., 34 Maple St., Milford, MA 01757, (508) 482-3039, fax: (508) 482-3100, jianmei-ding@waters.com

205. *OPTIMIZED STATIONARY PHASES FOR THE ANALYSIS OF BASIC PHARMACEUTICALS BY HPLC/MS.* S.R. Needham, Drug Metabolism Analytical Technology Department, Pfizer Central Research, Groton, CT 06340; P.R. Brown, Chemistry Department, University of Rhode Island, Kingston RI 02881-0801; Dave Bell and K.J. Duff, Restek Analytical Services, Restek Corporation, Bellefonte, PA 16823-8812

Stationary phases, optimized for the analysis of basic drugs by HPLC/ESI/MS were investigated. With these stationary phases analytes still have adequate retention even when used with mobile phases containing high percentages of organic solvent. The use of a high percentage of organic solvent is important in the electrospray ionization process because solutes can be easily desolvated and the MS signal enhanced. In addition, these phases provide better peak shape than the more popular C8 and C18 phases for the analysis of difficult, basic pharmaceuticals. This good peak shape is obtained without the use of ion-pairing or ion-suppressing reagents in the mobile phase, which is known to decrease the MS signal. The separations obtained with these columns were compared to those obtained with typical hydrophobic chain phases such as C8 and C18. The advantages of using the new columns for the HPLC/MS analysis of basic pharmaceuticals will be discussed.

MS, GC/MS, LC/MS/Phamaceutical Analysis Oral Session—Shane Needham, Pfizer Central Research, Bldg. 118/Box 104 , Eastern Point Road, Groton, CT 06340, (860) 441-8550, fax: (860) 715-7547, needhs@pfizer.com

206. *REFLECTIONS ON CHIRALITY; A RAPID AND INTUITIVE METHODS DEVELOPMENT STRATEGY FOR THE SEPARATION OF ENANTIOMERIC COMPOUNDS.* S.J. Brunet, Beckman Coulter, Fullerton, CA 92834

Development of methodology for the separation and quantitation of enantiomers has historically been a difficult and time-consuming process. The traditional chromatographic approach requires the use of specialty columns which suffer from narrow application ranges, poor resolution, limited lifetimes and time consuming methods development strategies. Analysis in solution with capillary electrophoresis, has proven to be a more suitable tool for this purpose as methods development is rapid, more intuitive and yields better resolution. Capillary columns are low cost, with essentially all analyses being performed within a single capillary tube. In this lecture we will describe a rapid *methods development strategy using a combination of native, modified and charged cyclodextrins to optimize the separation of compounds with chiral centers. These methods are robust and sensitive, capable of detecting less than 0.1% distomer contamination.*

MS, GC/MS, LC/MS/Phamaceutical Analysis Oral Session—Sandra J. Brunet, Beckman Coulter, 4300 N. Harbor Blvd., M/S E-28-C, Fullerton, CA 92834, (800) 742-2345, fax: (949) 472-8261, sbrunet@beckman.com

207. *ON-COLUMN REFRACTIVE INDEX DETECTOR FOR FLASH COLUMN CHROMATOGRAPHY.* Sarah G. Westerbuhr, Kathy L. Rowlen, University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO 80309

Flash column chromatography is a simple, commonly used technique for the separation of reaction mixtures. However, the tedious tasks of collecting fractions and analyzing each fraction are commonly required to complete the isolation of mixture components. A universal detector for on-column analysis in flash chromatography that reduces or eliminates the need for post-column analysis will be presented. The detection scheme takes advantage of refractive index changes as analytes move through an illuminated region of the column. The column packing material in flash chromatography is a diffuse scattering medium when the refractive index of the solvent is significantly different than that of the packing material. For an analyte with a refractive index different than the mobile phase, the magnitude and direction of light scattering depends on the degree to which the refractive index mismatch with the packing material is changed. This detection scheme provides a simple, inexpensive means to monitor the end of a flash chromatography column in order to determine the exit time of the species of interest, thus greatly reducing the post-column analysis time.

MS, GC/MS, LC/MS/Phamaceutical Analysis Oral Session—Sarah Westerbuhr, Department of Chemistry and Biochemistry, University of Colorado, Boulder CO 80309, (303) 492-3631, fax: (303) 492-5894, westerbu@colorado.edu

208. *QUANTITATIVE ANALYSIS OF COATING THICKNESS AND ACTIVE INGREDIENTS IN PHARMACEUTICAL TABLETS BY FT-NIR SPECTROSCOPY.* Qian Wang; Steve DeJesus; Basil Desousa; Sameer Londhe, Bruker Optics, Billerica MA 01821 USA

The feasibility of using NIR spectroscopy as a quick and nondestructive method for quality control of coating thickness of pharmaceutical tablets was investigated. Near infrared spectra of a set of pharmaceutical tablets with varying coating thickness were measured with a diffuse reflectance fiber optic probe connected to a Bruker IFS 28/N FT-NIR spectrometer. Challenges encountered in this study included: (1) The similarity of the formulation of core and coating materials, (2) The availability of insufficient calibration samples and (3) The non-linear relationship between NIR spectral intensity and coating thickness. However, a peak at 7184 cm-1, that differentiates the core material from the coating material was identified when NIR spectra are collected at a high resolution (2 cm-1, 0.4 nm at 7184 cm-1) offered by the FT-NIR spectrometer employed. The study shows that coating thickness can be analyzed by polynomial fitting of the peak area of this selective peak, while partial least squares calibration of the same data failed due to the lack of availability of sufficient calibration samples. Due to the typically low absorption coefficient in the short wavelength region (800 to 1400 nm) of NIR spectroscopy, high quality transmittance spectra of pharmaceutical tablets or capsules of approximately 5 mm thickness can been collected within a few seconds with a Bruker IFS 28/N FT-NIR spectrometer. In this second study, Zantac capsules (Glaxo-Wellcome) are used to demonstrate feasibility of analysis of the active ingredient in the core of capsules by NIR transmittance. The capsules were measured in both transmittance and reflectance modes. The active ingredients of the capsules were then analyzed with HPLC. The study shows that the concentration of the active ingredient in the core of the capsules can be determined satisfactorily by transmittance measurements, but not by reflectance measurements due to interference on the part of the relatively thick capsule walls.

MS, GC/MS, LC/MS/Phamaceutical Analysis Oral Session—Sameer Londhe, NIR Applications Scientist, Bruker Optics, Inc., 19 Fortune Dr., Billerica MA 01821, (978)-667-9580 ext.110, fax: (978)-667-1207, SL@bruker.com

209. *FAST LC/MS-TOF ANALYSIS.* Craig M. Whitehouse, Erol Gulcicek, Bruce Andrien and Shida Shen, Analytica of Branford, Inc., 29 Business Park Drive, Branford, CT 06405.

Rapid LC separations allow increased throughput in sample analysis for many applications. As Liquid Chromatography (LC) separation time decreases with LC peak widths reducing to one second or less, performance advantages have been demonstrated using Time-Of-Flight mass spectrometers when compared with conventional scanning or dispersion mass spectrometers (MS) as LC-MS detectors. An Atmospheric Pressure Ion Source orthogonal pulsing Time-Of-Flight mass spectrometer (API-TOF-MS) has been developed with performance that can scale with slow or fast LC separation times without compromising sensitivity, mass accuracy, resolution or quantitative performance. The orthogonal pulsing TOF mass spectrometer includes a multiple vacuum stage ion guide that is operated as a linear trap. The linear ion trap, traps ions from a continuous ion beam delivered into vacuum from an API source before releasing a portion of the trapped ions with synchronized timing into the pulsing region of the Time-Of-Flight mass analyzer. The trapped ions released from the ion guide are subsequently pulsed orthogonally into the flight tube of the TOF mass analyzer. The ion guide ion trapping and release operation, synchronized with the TOF pulsing effectively converts a continuous ion beam into a pulsed ion beam while simultaneously increasing duty cycle and sensitivity. The TOF-MS operates with a pulse rate of up to 20,000 pulses per second and can save over 100 summed mass spectra to disk per second. An analog to digital (A/D) converter, not a time to digital converter, is used to detect ion signal. The A/D converter recorded signal amplitude is proportional to the number of ions impacting the detector per time bin per TOF pulse. Due to the combination of trap and pulse operation with A/D converter detection, the ion signal for a given summed spectra acquired over a fixed time is independent of the number of pulses per spectra. To improve the analytical capability of the LC-TOF-MS detector during fast LC separations, the API-TOF-MS is capable of switching MS experimental conditions or states at a rate of up to 100 times per second with little or no loss of *duty cycle, sensitivity, mass accuracy or resolution. For example, by switching the capillary to skimmer potential for alternating spectra, parent and fragment ion data can be acquired during an LC-MS run. For fast LC peaks eluting in one second, ten parent and ten fragment ion spectra can be acquired under each LC peak by acquiring summed TOF mass spectra at a total rate of 20 spectra per second. In addition, the API source can include multiple Electrospray or Atmospheric Pressure Chemical Ionization probes that allow the simultaneous addition of an internal calibration solution during an LC-MS run without mixing the calibration solution into the LC eluant. Ions formed from multiple sprayers operating simultaneously, mix in the gas phase resulting in acquired mass spectra containing internal standard peaks. In this manner mass measurement accuracy below 10 ppm can be achieved in fast LC-MS analysis. Examples of fast LC-API-TOF-MS analysis will be reported for a range of compound classes with rapid TOF-MS state switching and high mass measurement accuracy.*

MS, GC/MS, LC/MS/Phamaceutical Analysis Oral Session—Craig M. Whitehouse, Analytica of Branford, Inc., 29 Business Park Drive, Branford, CT, 06405, phone (203) 488-8899, fax (203) 488-0416, email craigw@aob.com

210. *LC/MS CONFIRMATION OF ANIMAL DRUG RESIDUES FOR REGULATORY USE.* Sherri B. Turnipseed, Animal Drugs Research Center, Food and Drug Administration (ADRC/FDA), Denver, CO 80225; JosÈ E. Roybal, ADRC/FDA, Denver, CO 80225; Allen P. Pfenning, ADRC/FDA, Denver, CO 80225; Steve A. Gonzales, ADRC/FDA, Denver, CO 80225

Monitoring of foods of animal origin for drug residues is important due to concerns of antibiotic resistance and individual sensitivity to these compounds. LC methods exist to quantitate many of these drugs at residue (low ppb) levels in complex food matrices. For regulatory purposes, unambiguous identification of any suspect residues found in a sample by the determinative (LC) method is critical. Mass spectral analysis is the preferred technique for confirmation of suspect residues due to its inherent specificity and sensitivity. LC/MS is required for the confirmation of many antibiotic residues. Several examples of animal drug confirmation methods developed in our laboratory using a single quadrupole LC/MS instrument will be presented. For example, an electrospray LC/MS procedure has been developed for the confirmation of four fluoroquinolone residues in aquacultured species such as catfish, shrimp and salmon. The residues of ivermectin and related compounds have been confirmed in food matrices including salmon, milk and beef liver using negative ion atmospheric pressure chemical ionization. In addition, a multiresidue electrospray method has been developed to identify several ionophores, including monensin, in a variety of animal feeds. The challenges of developing these multiresidue confirmation methods for complex matrices will be discussed in terms of sample preparation, optimization of LC/MS conditions, and adherence of the resulting data to regulatory requirements.

MS, GC/MS, LC/MS/Phamaceutical Analysis Oral Session—Dr. Sherri B. Turnipseed, Animal Drugs Research Center

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211. *COLUMN SWITCHING APPROACHES IN LC/MS/MS FOR HIGH THROUGHPUT BIOANALYSIS OF PHARMACEUTICALS.* Vince Gao, PE Biosystems, 850 Lincoln Center Dr., Foster City, CA 94404

Today's pharmaceutical industry demands greatly for automated high throughput bioanalysis of drug candidates for pharmacokinetic studies. LC/MS/MS has proved to be a reliable, rapid, robust, sensitive and selective analytical method in support of preclinical and clinical studies. However, the bottleneck for high throughput LC/MS/MS analysis is still the sample preparation process. One of the economic and practical strategies for reducing sample preparation efforts is to use column switching. This presentation will discuss the establishment of flexible, effective and reliable column switching approaches in conjunction with fast gradient liquid chromatography and state-of-the-art triple quadruple mass spectrometers. The theoretical and practical aspects of this approach will be addressed. The application of this approach for the determination of multiple compounds in dog and rat plasma in support of preclinical studies will be demonstrated.

MS, GC/MS, LC/MS/Phamaceutical Analysis Oral Session—

212. *IDENTIFICATION OF AN UNKNOWN DEGRADANT IN A PHARMACEUTICAL DRUG FORMULATION BY LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY (LC/MS).* Pauline Chow and Michael Bray, Geneva Pharmaceuticals, Inc., 2655 W. Midway Blvd., Broomfield, CO, 80038; David Manley, 3M Pharmaceuticals, 3M Center, Building 270-4S-02, St. Paul, MN, 55144-1000

Identification of unknown compounds in drug formulations is an important part of the drug approval process. In this study an unknown was detected in a pharmaceutical drug formulation that was stressed at 40°C and 75% relative humidity (ICH conditions). LC/MS and UV data were used to determine a structure of the unknown. The unknown is a result of the Maillard Reaction which was formed from the interaction of lactose used as an excipient and the active drug ingredient.

MS, GC/MS, LC/MS/Phamaceutical Analysis Oral Session—Pauline Chow, Geneva Pharmaceuticals Inc., 2655 W. Midway Blvd., Broomfield, CO, 80038, phone 303-438-4375, fax 303-438-4600, pauline.chow@gx.novartis.com

213. ***LARGE SCALE QUANTITATIVE ANALYSIS OF PHARMACEUTICALS VIA LC-MS AND LC-MS/MS WITH AN ION TRAP MASS SPECTROMETER.*** Jack Cunnift, Dieter Drexler, Rohan Thakur, Finnigan Corporation, San Jose, CA 95134

Commercially introduced during the early 1980's, ion traps have long been recognized for their MS(n) potential. Very little recognition has been focused on their potential as a quantitative tool. A major reason for this lack of recognition appears to stem from the poor quantitative performance of early ion traps. The first ion traps were equipped with electron impact (EI) sources and coupled to gas chromatographs. With the earliest devices, ionization occurred within the trap and there was no regulation of the number of ions produced/trapped. Another drawback to early traps was the limited dynamic range of the trap. Overfilling the trap resulted in phenomena that became known as "space-charging" problems. The effects of space-charging included poor resolution and mass accuracy along with an increased risk of ion molecule reactions. In the latter half of the 1980's, the regulation of the number of ions trapped via gating became possible and most of the problems associated with "space-charging" were eliminated. Gating also effectively increased the dynamic range of the trap by 5 orders of magnitude by linking "intensity" with the amount of time the gate was open. Ion molecule reactions, however, were still often evident between EI produced ions and water present in the trap.

Fortunately, ions produced within an Atmospheric Pressure Ionization (API) source are relatively stable. Furthermore, any ion-molecule reactions that might occur in the trap will occur under the atmospheric and water saturated source prior to entering the trap. Thus, the inherent problems and challenges of interfacing an EI-source with an ion trap are largely absent with an API-ion trap device. Quadrupole ion traps have several inherent advantages that make them well suited for high-throughput automated quantitation. Unlike linear quadrupole instruments, ion traps do not pay a penalty in sensitivity for operating in full scan MS/MS mode over selective reaction monitoring (SRM). Ion dissociation through resonance excitation provides near universal collision conditions, and the precursor/product ion transitions are quantitative. These advantages allow the user to forgo most of the prework involved in setting up conditions for quantitative analysis, such as choosing analyte and internal standard product ions and optimizing the collision energies and collision cell pressure. Instead, operating in Full-Ssan MS/MS mode under universal collision conditions allow the appropriate SRMís to be determined after data collection with no loss of sensitivity or selectivity. In addition, the resonance excitation and high pressure buffer gas employed in quadrupole ion traps often produce simpler MS/MS spectra compared to those from linear quadrupoles. Quantitative transformation of the precursor ion to relatively few product ions can enhance sensitivity. Along these lines, quantitative results generated via the interfacing of Liquid Chromatography (LC) with several ion traps will be tabulated, summarized and presented. Over 5000 samples and 100 structurally diverse compounds are represented. Particular strengths and weaknesses of the technique will be highlighted.

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214. ***A BENCHTOP TIME-OF-FLIGHT MASS SPECTROMETER FOR ROUTINE ACCURATE MASS LCMS MEASUREMENTS.*** Jeffrey W. Finch, Brian Williamson, Terry Kehoe, PE Biosystems, 500 Old Connecticut Path, Framingham, MA 01701

The coupling of electrospray (ESI) and atmospheric pressure chemical ionization (APCI) with a compact benchtop orthogonal time-of-flight analyzer provides chemists with a powerful new tool for characterizing complex mixtures by LCMS. Resolution of these systems (> 5000 FWHM) is sufficient to provide mass accuracy to within 5 ppm of the theoretical mass, making it possible to obtain elemental composition data. Isotope profiles can also be matched and scored against theoretical isotope patterns of possible elemental compositions, which are within a defined search tolerance of the accurate mass result. Additional structural information can be obtained using in-source CID by switching the nozzle potential ìon-the-flyî during the course of the LC analysis. The purpose of this presentation will be to highlight characteristics of API-TOF for accurate mass LCMS, including a discussion of issues such as ionization source robustness, internal vs. external calibration, detector saturation, and acquisition speed. Several examples of LCMS applications using the API-TOF are presented, including trace impurity analysis, metabolite identification, natural products characterization, peptide mapping, and combinatorial synthesis product characterization.

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215. ***RECENT DEVELOPMENTS IN TOROID CAVITY NMR SPECTROSCOPY, RHEOLOGY AND IMAGING.*** Klaus Woelk, Peter Trautner, University of Bonn, Institute of Physical and Theoretical Chemistry, Wegelerstr. 12, D-53115 Bonn, Germany; Rex E. Gerald II, Robert J. Klingler, Jerome W. Rathke, Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439-4873, USA

During the past several years, toroid cavities have been used as NMR detectors for specialized applications in NMR spectroscopy, rheology, and imaging. The unique cylindrical geometry and the confinement of the radio-frequency magnetic field to within the cavity predestined its simultaneous use as an NMR detector and high-pressure/temperature autoclave for in situ NMR studies. Recent probe designs that have been optimized for different high-pressure applications will be introduced, and spectroscopic results from catalytic hydrogenation and hydroformylation reactions that have also been conducted in supercritical fluids will be presented. In addition, chemical-shift resolved rotating-frame NMR microscopy in toroid cavities enables distance resolution on the micrometer scale and facilitates flow and diffusion measurements of isotropic, anisotropic and even mixed-phase systems. The intrinsic high precision, to which flow and diffusion is determined in toroid cavities, can be enhanced by carefully reviewing the magnetization-grating rotating-frame imaging (MAGROFI) experiment and by comparing the imaging results with numerical solutions of partial differential equations conducted under the consideration of toroid cavity boundary conditions. Recent diffusion measurements and imaging of NMR parameters in polymer electrolytes show only a few applications of this *award-winning toroid cavity imager [1]. Furthermore, a recently developed NMR technique makes it possible to detect and quantitatively determine angular flow around the central conductor of toroid cavity resonators. Investigations that can lead to a new combination of NMR and fluid chromatography as well as the new NMR viscosimeter will be introduced. Supported by U.S. DOE W-31-109-Eng-38 (Argonne) and DFG WO 613/2-2 (Bonn).*

1. R&D 100 Award 1994

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216. *MAGNETIC RESONANCE OUTSIDE THE LABORATORY.* B. H. Sults, A. N. Ganoway, and J.B. Miller, Naval Research Laboratory, Chemistry Division, Code 6122, Washingtor, DC 20375, Michigan Technological University, Physics Department, Houghton, MI 49931

Our work in the use of nuclear quadrupole resonance (NQR) for the detection of explosives "in the field" has led us to consider the implications of performing magnetic resonance experiments in uncontrolled environments. In these real world applications of magnetic resonance, signals must be excited and detected efficiently with a minimum of interference from outside sources. In this talk we will focus on coil designs to minimize external rt interference and strategies for minimizing coil loading by the environment.

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217. *LANDMINE DETECTION BY NUCLEAR QUADRUPOLE RESONANCE.* G.A. Barrall, D. Gregory, R. Matthews, S.A. Vierkötter, Quantum Magnetics, Inc., San Diego, CA 92121; A.D. Hibbs, Information Systems Laboratories, Inc., San Diego, CA 92121

Under DARPA sponsorship, Quantum Magnetics is developing a nuclear quadrupole resonance (NQR) based landmine detection system. The current system uses 14N NQR to detect both RDX and TNT based non-metallic landmines. NQR combines the compound specific detection capability offered by chemical detection techniques with the spatial localization capability and convenience of an induction coil metal detector. In the 20 years since NQR was first applied to mine detection in the U.S., there has been tremendous improvement in the NQR detection sensitivity due to significant progress in hardware design and pulse sequence development. In recent field trials at various military bases, Quantum Magnetics successfully demonstrated the detection capability of a mobile, unshielded system. We will review the progress made by Quantum Magnetics in this area over the last two years, including an overview of the technique, a description of the system hardware, methods for coping with radio frequency interference, and a summary of the results from recent field trials. Supported by DARPA DAAK60-97-C-9221 and USMC N00164-97-C-0004.

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218. *SOME NEW ASPECTS CONCERNING THE ANALYSIS OF LOCAL ORDER AND DISORDER IN SOLIDS CONTAINING QUADRUPOLAR NUCLEI.* Jean-Paul Amoureux, Université des Sciences et Technologies de Lille, Bat P5, 59650 Villeneuve d'Ascq (France); Marek Pruski, Iowa State University, 214 Spedding Hall, Ames, IA, 50011

New methods combining for quadrupolar nuclei the high-resolution aspect of MQMAS and the determination of connectivities are presented. These methods are either qualitative or quantitative. The first case corresponding to CP-MQMAS and HETCOR. These methods will be exemplified and their limitations will also be shown. The second case to MQ-t1-REDOR for long distances, to MQ-t2-REDOR for short distances and to DD-MQMAS for fast semi-quantitative determination. When the sample is amorphous, vitreous or ill-crystallized, it presents a distribution of surroundings. This distribution can be quantified and a distribution map obtained.

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219. *FAST RF AMPLITUDE MODULATION IN MQMAS-NMR SPECTROSCOPY.* Amir Goldbourt, P.K.Madhu, Lucio Frydman and Shimon Vega, Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, ISRAEL and Department of Chemistry (M/C 111), University of Illinois at Chicago, Chicago, IL 60607-7061, USA.

MQMAS-NMR spectroscopy has become a powerful and routine method to obtain high-resolution spectra of quadrupolar nuclei. One of the main problems in the performance of this experiment has been the poor efficiency of the CW pulses in converting triple quantum coherence to observable single quantum coherence. As MQMAS experiment is basically an echo experiment this problem can be related to the quality of the echo that is produced by the CW pulses which in turn affects the conversion profile. In this presentation we investigate various aspects of the formation of echo laying down the conditions for getting a pure echo thereby enhancing the signal intensity and resolution in MQMAS experiments. In this connection we also present a new scheme for MQMAS experiments which employs fast rf amplitude modulated pulses, FAM, that serve as conversion pulse instead of the normal CW pulses. The FAM pulse will be shown to create the ideal conditions for the formation of an echo and give a substantial intensity and resolution enhancement of the signal over the commonly used

MQMAS pulse schemes. Experimental results highlighting the utility of FAM will be presented along with its ability to be used successfully in samples possessing multiple quadrupolar sites with varying interaction strengths of both quadrupolar and chemical shift anisotropy.

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220. ***DETERMINATION OF INTERNUCLEAR DISTANCES FROM SOLID-STATE NMR: DIPOLAR TRANSFORMS AND REGULARIZATION METHODS.*** Frederick G. Vogt, David J. Aurentz, James M. Gibson, and Karl T. Mueller, The Pennsylvania State University, Department of Chemistry, 152 Davey Laboratory, University Park, PA, 16802-6300.

Many NMR experiments have been designed to measure homonuclear or heteronuclear distances, and often generate time-domain dipolar signals that need to be analyzed to extract the relevant dipolar coupling constants. These constants yield internuclear distances directly, and therefore an accurate and easily understandable extraction of these couplings from potentially noisy data is a major concern. Several dipolar signals will be considered in this presentation, including those obtained from the REDOR, MELODRAMA, and SEDOR experiments, as well as a new series form for the C7 and DCP signals. A review and discussion of an existing transform-based method[1] for dipolar signal analysis is presented, along with two new generalized methods for the extraction of coupling constants[2] One of the new methods is a fast procedure based on asymptotic signal forms, while the other is a regularization method specifically formulated to account for experimental noise, and shows significant performance gains over other methods when applied to noisy time-domain REDOR signals. In addition to its noise-handling ability, the second method also has wide application to many other types of dipolar signals currently available in NMR experiments, and is the only method of those discussed that can effectively yield a C7/DCP "transform." Applications of the new methods to various systems are discussed, including scenarios involving three-spin systems. Experimental results on test molecules, such as labeled glycine, are also presented.

1. *K. T. Mueller et. al, Chem. Phys. Lett., 1996, 254, 281.*
2. *F. G. Vogt, D. J. Aurentz and K. T. Mueller, Mol. Phys. 1998, 95, 907.*

NMR Oral Session—Frederick G. Vogt, Department of Chemistry, 152 Davey Laboratory Box 82, Pennsylvania State University, University Park, PA, 16802-6300, 814-863-8674, fgv100@psu.edu

221. ***HOMONUCLEAR DOUBLE-QUANTUM NMR STUDIES OF CONFORMATION AND PACKING IN DISORDERED POLYMERS.*** Hironori Kaji[1,2], Matthew G. Dunbar[1], Douglas J. Harris[1], Jörg Rupp[1], Herbert Zimmermann[3], Klaus Schmidt-Rohr[1], [1] Department of Polymer Science and Engineering, University of Massachusetts, Amherst MA 01003, [2] Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, JAPAN, [3] Max-Planck-Institut für Medizische Forschung, Jahnstrasse 29, D-69120, Heidelberg, Germany

The local packing and backbone conformation in amorphous and paracrystalline polymers are long-standing problems. We present static two-dimensional (2D) homonuclear double-quantum (DQ) NMR investigations of the packing of sp^2- and sp-hybridized sidegroups and the conformation of sp^3 and sp^2 backbone segments in these polymer systems. High-quality DQ spectra even for large chemical-shift anisotropies are obtained with radio-frequency jumps before and after the DQ evolution, enabling off-resonance evolution with all the pulses on-resonance. The relative orientation of two ^{13}COO carbons, separated by 5.7 Angstrom, in the terephthaloyl residue of doubly 13COO-labeled poly(ethylene terephthalate) is characterized; not only trans but also 55(±10)% of cis conformers are found in the glassy state. In atactic poly(vinyl acetate), non-random ^{13}COO-sidegroup packing is observed, with preferred relative orientations attributed tentatively to intramolecular planar packing of sidegroups. The backbone conformation in paracrystalline atactic poly(acrylonitrile) (PAN), investigated in a 15% $^{13}CH_2$-labeled PAN sample is predominantly in a state close to trans. The deviation from exact trans torsion angles are quantified by measurements on a 100% ^{13}CN-labeled and ^{13}CN-^{2}H-labeled PAN sample. The local packing in bisphenol-A-polycarbonate, which is still controversial, is also investigated by the DQ technique. The ability to detect the trans state or parallel segments with high sensitivity is a crucial advantage of the DQ approach over 2D exchange NMR. Supported by NSF DMR-9703916.

NMR Oral Session—Hironori Kaji, Department of Polymer Science and Engineering, University of Massachusetts, Amherst MA 01003, 413-577-2466, fax: 413-545-0082, kaji@mail.pse.umass.edu

222. ***FLUORINE AND CARBON SOLID-STATE NMR FOR THE CHARACTERIZATION OF FLUOROPOLYMERS.*** Ulrich Scheler, Institute for Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

Fluorine-19 is very attractive as a probe nucleus for NMR because of the high receptivity and the large chemical shift range, if the dipolar couplings can be averaged using high-speed MAS (here up to 35 kHz). Additional information about the distances and connectivities can be obtained from two-dimensional spectra, which in the solid state are dominated by the dipolar coupling. While highly resolved spectra are acquired under high-speed MAS in both dimensions, relevant interactions can be reintroduced during the mixing period by rf pulses. The dipolar coupling can be utilized to either generate double quantum coherences or zero quantum coherences (spin exchange) between strongly coupled nuclei. As the dipolar coupling is distance dependent, the rate of exchange or the intensity of the double quantum signals are a measure of the distance. Double quantum spectra exhibit superior resolution because only spins involved in double quantum coherences contribute to the signal, no diagonal signal from non-exchanging nuclei is observed. For fluorine-19 pulse sequences with a large the excitation bandwidth are required. Carbon-13, on the other hand, spectra permit good resolution for protonated and fluorinated parts of *multiphase systems simultaneously. The superior resolution in the fluorine-19 spectra can be utilized for the assignment in the carbon-13 spectra via a HETCOR experiment. In addition dual step cross polarization involving protons, fluorine and carbon can be used to select the interface between protonated and fluorinated parts of the sample. Applications include PTFE and modified PTFE, co an terpolymers thereof, semi-fluorinated block copolymers and a model systems.*

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223. ***THE EFFECT OF SOLUTION PROCESSING ON SOLID-STATE STRUCTURE: MAS NMR STUDY OF POLYANILINE FILM.*** Matthew Espe, Tanya Young, Department of Chemistry, University of Akron, Akron, OH-44325; Dali Yang, Benjamin Mattes, Santa Fe Science and Technology, Santa Fe, NM 87505.

Polyaniline, a conducting organic polymer, currently can be processed into films and fibers, forms important for commercial applications. The solution processing of this polymer involves the use of gel-inhibitors (amines) to enhance the polymer solubility, however, the type and amount of amine used significantly impacts the solid-state properties of the polyaniline samples. With the application of MAS solid-state NMR the impact of the amines has been investigated and we have determined that the amines : 1) are trapped in the polymer matrix, both physically (likely H-bonding) and through a chemical reaction with the quinoidcering of the repeat unit; 2) impact the chain packing and chain dynamics of the polymer; and 3) enhance the chemical reactivity of the polymer. Attack of the amines also causes changes in the electronic structure of the affected repeat units (self-doping, positive charge distribution) and these changes have been monitored with ^{15}N SSNMR. The amount of amine present in the films/fibers has also been determined and the extent of reaction between amine and polymers correlates well with the amine K_b values. In addition, when the fibers are stretched there is an increase in conductivity. The extent of the orientation of the polymer chains upon stretching has been studied by monitoring the ^{13}C chemical shift tensors for the films oriented parallel and perpendicular to the sample rotor.

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224. ***SOLID STATE NMR STUDIES OF ENVIRONMENTAL CATALYSTS.*** Jianjun Wu, Alexander Panov, Russell Larsen, Vicki Grassian and Sarah Larsen, Chemistry Department, University of Iowa, Iowa City, IA 52242

Solid state NMR techniques have been used to investigate environmental catalysts. Zeolite catalysts, such as H-ZSM-5 and Cu-ZSM-5, are active for the thermal SCR (selective catalytic reduction) of NOx with hydrocarbons in the presence of excess oxygen. We have used solid state MAS NMR to investigate the role of potential reaction intermediates, such as acetone and acetone oxime, in the SCR of NOx over H-ZSM-5 and CuZSM-5. The carbon- and/or nitrogen-containing surface species, as well as the products formed under conditions of thermodynamic equilibrium, have been monitored and identified using ^{13}C-^{1}H cross polarization and ^{15}N MAS NMR. When ^{15}NO and unlabeled acetone oxime are reacted on CuZSM-5, the ratio of 14N15NO / ^{15}N^{14}NO is approximately three suggesting that the NO bond of gas phase NO remains intact when it reacts with acetone oxime to form N_2O. In another example of environmental catalysis, the photooxidation of hydrocarbons, such as toluene, with molecular oxygen, on cation-exchanged zeolites has also been studied using solid state NMR. The reactant toluene is strongly adsorbed and immobilized at the cation site in barium-exchanged zeolites. The photooxidation of toluene yields benzaldehyde as the major product. This process exhibits potential as an environmentally benign method for the selective oxidation of hydrocarbons.

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225. ***MULTINUCLEAR SOLID-STATE NMR STUDIES OF TIN COMPOSITE OXIDE ANODE MATERIALS.*** G. R. Goward, L. F. Nazar, and W. P. Power, Department of Chemistry, University of Waterloo, Waterloo, ON, N2L 3G1 CANADA

Significant developments have been made recently in the area of anode materials for lithium ion batteries. In particular, tin composite oxide (TCO) glasses such as Sn1.0Al0.4B0.56P0.4O3.6 have been shown to cycle lithium efficiently and offer several advantages over graphite; the current anode of choice industrially. The mechanism of lithium insertion in this composite glass is not well understood. Efforts have been made to interpret the lithium insertion process on the basis of a reduction of Sn(II) first to metallic tin and further to lithium-tin alloys. The initial reduction, forming tin metal, is assumed to correspond with the ejection of oxygen to form a lithium oxide matrix that is subsequently inert to the electrochemical processes. We have studied this system extensively using ex situ $^{6/7}$Li, ^{119}Sn, ^{27}Al, ^{31}P and ^{11}B solid-state NMR of batteries "sacrificed" at various stages of the electrochemical cycle. Our results point to several intriguing effects at work in these systems. First, the $^{6/7}$Li NMR spectra provide no evidence of a significant lithium Knight shifts that would indicate the formation of a true alloy, but instead show only small shifts (~10 ppm) to higher frequency. Secondly, the $^{6/7}$Li NMR results for the electrodes (upon charge) indicate that oxygen plays a key role in the process. In fact, the lithium-oxide matrix appears to be a fundamental factor in the reversibility of the electrochemical reaction, not simply an inert component of the system. The ^{27}Al NMR spectra indicate that the structure of the "spectator" components of the glassy matrix is reversible as well.

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226. *NONDESTRUCTIVE DETERMINATION OF STRUCTURAL FEATURES BY COUPLED NMR-ACOUSTIC INSPECTION.* S. W. Sinton, J. H. Iwamiya, J. Bellin, E. Olsen, Lockheed Martin Missiles and Space, 3251 Hanover St., Palo Alto, CA 94304.

NMR has been proposed, and in some cases developed, as a method for evaluating material properties in structures such as aircraft and rocket motors. These applications often rely on some relationship between the NMR relaxation rates (of protons, typically) and bulk mechanical properties of interest (such as shear modulus). However, for the long-term environmental aging assessment of some materials the sensitivity of the NMR-mechanical relationship and how well it allows subtle changes to be tracked can be issues. For example, proton spin-spin relaxation rates in elastomers are often correlated with modulus, but the degree of change in T2 is small until significant age-induced decrosslinking occurs. This limits the ability to use NMR inspection data for predictive assessments of product service life. An alternative approach is to use imaging NMR methods to detect vibrations induced within a structure from an externally applied acoustic source. The amplitude and wavelength of the vibrations at points determined by NMR can be used to assess the local viscoelastic response of the structure. Because this approach directly measures a mechanical response it does not rely on any relaxation-material property correlation and therefore is not subject to the uncertainties of such a correlation. The determination of shear modulus by MRI in materials similar to biological tissues has been recently demonstrated (R. Muthupillai, D. J. Lomas, P. J. Rossman, J. F. Greenleaf, A. Manduca and R. L. Ehman, Magnetic resonance elastography by direct visualization of propagating acoustic strain waves, Science, 269, 1854-1857, 1995). It is our goal to develop similar methods that can be applied to large, composite structures. We demonstrate the detection of acoustic vibrations down to the micron level in solid-filled elastomers by NMR using a low-field, non-enclosing magnet. Experiments and numerical simulations are used to elucidate how critical structural properties can be monitored by this NMR-acoustic method.

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227. *COMPARATIVE STUDY OF LI-ION MOBILITY IN SWOLLEN IONOMERS AS MEASURED BY ^{7}Li MAS LINESHAPE, T_{1R}, ^{7}Li DIFFUSION AND CONDUCTIVITY.* A. J. Vega, E. F. McCord, M. Doyle, and M. G. Roelofs, DuPont Central Research and Development, P. O. Box 80356, Wilmington, DE 19880-0356.

Ionomers where all the anions are covalently attached to the polymer backbone have the simplifying property that their electrical conductivity is exclusively determined by the diffusivity of the positive counterions, in contrast to polymeric electrolytes where the conductivity is facilitated by dissolved salts. We demonstrate that it is possible in such a system to establish semiquantitative relationships between (a) the residence time of Li-ions at anionic sites as derived from MAS lineshapes and T1r, (b) the diffusion coefficient describing the migration of Li-ions among anionic sites, as determined by the DOSY NMR technique, and (c) the macroscopically measured conductivity.

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228. *SOLID-STATE NMR INVESTIGATION OF COMPLEXES OF LEAD (II) DIHALIDES WITH ORGANIC LIGANDS.* A. Glatfelter, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716; C. Dybowski, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716; G. Neue, Lehrstuhl fuer Physikalische Chemie, Universitaet Dortmund, Dortmund, Germany; D.L. Perry, Lawrence Berkeley Laboratory, University of California, Berkeley, California, Berkeley, CA 94720; M. Blake, Lawrence Berkeley Laboratory, University of California, Berkeley, California, Berkeley, CA 94720.

Reactions of lead ion with ligands such as 1,10-phenanthroline, 2,2'-bipyridine, and thiourea produce materials, the nature of which has been a topic of study by a variety of structural and spectroscopic techniques. The nature of bonding in these materials can be addressed by NMR spectroscopy through the effects on chemical shifts. Here we report solid-state 207Pb and 13C NMR results for a series of complexes of lead (II) dihalides with organic ligands. The NMR results are interpreted in terms of the effects of ligation and ion interactions on bonding. Work at Lawrence Berkeley Laboratory (DLP and MB) was supported by Contract No. DE-AC03-76F00098 from the U.S. Department of Energy. Work at the University of Delaware (AG, CD, and GN) was supported by Grant No. 33633 of the Petroleum Research Fund of the American Chemical Society.

NMR Oral Session—Alicia Glatfelter, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, phone 302-831-6927, fax 302-831-1490, glatfea@udel.edu

229. *SOLID-STATE ^{25}MG, ^{27}AL AND ^{29}SI NMR INVESTIGATIONS OF MG (II), AL (III) AND SI (IV) CHEMICAL ENVIRONMENTS AND ORDERING IN VARIOUS MONTMORILLONITE CLAY CHEMICALS.* John J. Fitzgerald, Department of Chemistry Biochemisty, South Dakota State University, Brookings, SD 57007; Don Eisenhour, American Colloid Company, Chicago, IL 60004; Herman Lock and Gary E .Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO 80573.

Solid-state NMR spectroscopy has emerged as an important technique to examine unique structural features and reaction chemistry associated with clay minerals. The 2:1 dioctahedral mineral, montmorillonite, represents an unique clay system where knowledge of its surface and hydration chemistry is intimately associated with its structure and geochemistry. The state of hydration and surface chemistry of montmorillonite, including ion exchange and intercalation reactions, are of significance in environmental and materials science. Solid-state ^{27}Al and ^{29}Si MAS NMR measurements of a series of hydrated and dehydrated montmorillonite materials, including several high-quality *commercial montmorillonite materials, several museum specimens and Clay Mineral Depository materials, are reported. These studies provide unique information about the complex structural issues of montmorillonites due to mayor variations in caution substitution of magnesium(II), aluminum(III) and silicon(IV) centers in these highly expandable, layered materials. Interpretation of the* ^{27}*Al and* ^{29}*Si spectra in terms of local 4-coordinate* $Si(OSi)_{4-x}(OAl)_x$ *and 6-coordinate* $Al(OAl)_{6-x}(OM)_x$ *chemical environments (where x = 0 to 6, and M = Mg(II) or Fe(III)/Fe(II) ions) are discussed. Solid-state* ^{27}*Al and* ^{29}*Si MAS NMR measurements, together with chemical and mineralogical analysis, have also provided detailed quantitative information about the degree of cation substitution and potential ordering of Mg(II), Al(III) and Fe(II)/Fe(III) ions in the tetrahedral silicate and octahedral aluminum oxyhydroxide layers of these montmorillonites, This information thus provides a means to understand the structural origins of the local charge contributions of these cations to their overall hydration behavior, ion exchange properties and surface chemistry. These studies suggest new directions for more detailed solid-state NMR investigations of the influences of cation substitution on the surface and reaction chemistry of montmorillonites of relevance to environmental and materials science.*

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230. *NMR OF PARAMAGNETIC LANTHANIDE GLUTARATES.* Joseph R. Sachleben, Campus Chemical Instrument Center, The Ohio State University, 176 W. 19th Ave, Columbus, OH 43210, USA; Anthony Cheetham, Materials Research Laboratory, University of California, Santa Barbara, CA, 93106, USA; GÈrard FÈrey, Institut Lavoisier, UMR CNRS 173, UniversitÈ de Versailles Saint-Quentin-en-Yvelines, 45, Ave. des tats-Unis, 78035 Vesailles cedex, France; Thomas Luxbacher, Institut Lavoisier, UMR CNRS 173, UniversitÈ de Versailles Saint-Quentin-en-Yvelines, 45, Ave. des …tats-Unis, 78035 Vesailles cedex, France; Fabien Serpaggi, Institut Lavoisier, UMR CNRS 173, UniversitÈ de Versailles Saint-Quentin-en-Yvelines, 45, Ave. des tats-Unis, 78035 Vesailles cedex, France.

We have recently synthesized microporous lanthanide glutarates, which are made from chains of lanthanide metal cations held together by the glutarate dianions. Spaces between the glutarate anions form 1-dimensional channels, which are capable of absorbing small molecules. We have performed 1H and 13C Nuclear Magnetic Resonance (NMR) spectroscopy on a series of Ln-glutarates, [Ln(H20)]2[O2C(CH2)3CO2]3 4H20 where Ln is Y, La, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, and Yb. Both 1H and 13C NMR spectra of show a broad series of sidebands extending for 100's of ppm. These broad sideband patterns are due to the paramagnetic shift anisotropy arising from the orientation dependence of the local magnetic field created by the ordered paramagnets in the sample. If the g-tensor of the paramagnetic lanthanide is isotropic, the paramagnetic shift anisotropy is a second rank tensor. If the g-tensor is highly anisotropic, the paramagnetic shift anisotropy is a sum of 0 to 6th rank tensors. In many of our samples, the g-tensor is approximately isotropic and the observed sideband patterns resemble broad chemical shift anisotropies. Computer simulations have shown that by measuring the paramagnetic shift anisotropy, paramagnetic, and the asymmetry parameter, paramagnetic, one can localize the position ofthenucleusintheunitcell.We will attempt to demonstrate this behavior in our samples. We also examine the temperature dependence of the paramagnetic shiftan is otropy and the isotropic paramagnetic shift. These studies provide a good model system for understanding paramagnetic shifts and will allow the development of a more general understanding of these shifts in paramagnetic solids. Understanding these shifts will provide a new tool for probing the structure and dynamics of paramagnetic solids.

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

One- and two-dimensional solid-state 93Nb NMR spectra have been measured at multiple magnetic fields for a series of niobates, including: LiNbO3, NaNbO3, KNbO3, AlNbO4, ScNbO4, InNbO4, Mg2NbO6, Zn2NbO6, Pb2NbO6, and Pb2NbO7. The chemical shift (diso, daniso, and hCS) and quadrupolar (Cq and hQ) parameters, as well as the spin-lattice and spin-spin relaxation times have been determined. The isotropic chemical shift varies from -1000 to -1170 ppm, the absolute anisotropic chemical shift from 100 to 500 ppm, and quadrupolar coupling constants as large as 54 MHz have been measured. From these measurements, 93Nb NMR spectroscopy is found to be sensitive to the local electronic environment of niobium and relationships between the NMR-measured parameters and the local chemical environment have been explored. The utility of nutation and MQMAS techniques for 93Nb has also been examined. While 93Nb nutation spectroscopy has been used to resolve multiple sites and to determine quadrupolar coupling constants, 93Nb MQMAS spectroscopy yields the highest resolution and was used to resolve multiple 93Nb resonances in complex samples.

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232. *ROCKY MOUNTAIN CONFERENCE PLENARY LECTURE*—M. Bonner Denton, University of Arizona

See page 32

233. *MULTIPLE-PULSE SOLID-STATE NMR: SYSTEMATIC DESIGN, MAGNITUDES AND ORIENTATION OF ANISOTROPIC INTERACTION TENSORS.* Nielsen Chr. Nielsen, Instrument Centre for Solid-state NMR Spectroscopy, Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark; Morten Hohwy, University of Aarhus, Department of Chemistry, DK-8000 Aarhus C, Denmark; Mads Bak, University of Aarhus, Department of Chemistry, DK-8000 Aarhus C, Denmark; Jimmy T. Rasmussen, University of Aarhus, Department of Chemistry, DK-8000 Aarhus C, Denmark; Flemming H. Larsen, University of Aarhus, Department of Chemistry, DK-8000 Aarhus C, Denmark; Hans J. Jakobsen, University of Aarhus, Department of Chemistry, DK-8000 Aarhus C, Denmark; Malcolm H. Levitt, Physical Chemistry Division, Stockholm University, S-20691 Stockholm, Sweden; Paul D. Ellis, Environmental Molecular Sciences Laboratory, Pacific Northwest Laboratory, Richland, Washington 99352

By using appropriate combinations of high-order effective Hamiltonian theory[1] and effective numerical simulation procedures[2] it is possible to systematically design multiple-pulse solid-state NMR experiments providing detailed information about magnitudes, orientation, and dynamics of anisotropic interaction tensors while maintaining high resolution, sensitivity, and efficient artifact suppression. The presentation will describe elements of high-order effective Hamiltonian theory, new twists to fast calculation of solid-state NMR spectra, and give some practical examples involving a series of solid-state NMR experiments (variants of HORROR, POST-C7,[3] GATE, MSHOT, FSLG, QCPMG,[4] MQMAS, and MQ-QCPMG-MAS) for selective re- and decoupling of anisotropic interactions and sampling of high-sensitivity second-order spectra of quadrupolar nuclei. The various methods will be illustrated by experiments involving powder and uni-axially oriented samples.

1. *Hohwy and Nielsen, J. Chem. Phys., 1998, 109, 3780.*
2. *Bak, Rasmussen, Nielsen, to be submitted.*
3. *Hohwy et al., J. Chem. Phys., 1998, 108, 2686*
4. *Larsen et al., Mol.Phys., 1998, 95, 1185.*

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234. *MAXIMUM ENTROPY INVERSION OF MQMAS SPECTRA.* T. Charpentier, J. Virlet, Service de Chimie Moléculaire, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France.

The MQMAS spectroscopy has now become a widespread method for obtaining high-resolution NMR spectra of quadrupolar nuclei, especially for crystallized material. Its success is certainly due to its easy implementation through the use of an ordinary MAS probe. For study of amorphous material, this technique is very powerful because, like in DAS, it separates the chemical shift and quadrupolar interaction line distribution in the two-dimensional MQMAS spectrum. Nevertheless, the extraction of the two-dimensional distribution of the quadrupolar interaction correlated to the isotropic chemical shift is a difficult task and special inversion procedures are required[1]. Moreover, the manipulation of multiquantum transitions by RF pulses makes the MQMAS spectroscopy non-quantitative and numerical simulation are necessary for obtaining correct site-populations. Recently, we have proposed a theoretical approach of the MQMAS experiment[2] leading to an efficient and accurate MQMAS simulation program (MQSIM)[3]. In the present study, we describe an inversion procedure based on a Maximum Entropy (MaxEnt) algorithm[4] and on the MQSIM program for reconstructing the underlying distribution of a MQMAS spectrum. The original procedure[4] combines singular-value decomposition (SVD) with the MaxEnt approach. Here, we introduce an extension allowing combination with regularization procedures. The method may be applied to any MQMAS spectrum and provides a convenient way for obtaining information contained in MQMAS spectra. Limitation due to the transfer efficiencies will also be discussed and different pulse sequences will be compared. Experimental examples and applications will be detailed in an another contribution.

1. *J.W. Zwanziger, Solid State NMR, 1994, 3, 219.*
2. *T. Charpentier, C. Fermon, J. Virlet, J. Chem. Phys., 1998, 109, 3116.*
3. *T. Charpentier, J. Virlet, Solid State NMR, 1998, 12, 227.*
4. *R.K. Bryan, Eur. Biophys. J., 1990, 18, 165.*

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235. *STRUCTURAL ANALYSIS OF NEW ALUMINOPHOSPHATE MATERIALS USING HIGH RESOLUTION SOLID-STATE NMR.* Marek Pruski, Ames Laboratory, Iowa State University, Ames, IA, 50011; Alain Bailly, Jean-Paul Amoureux, Laboratoire de Dynamique et Structure des Matériaux Moléculaires, CNRS URA 801 Université de Lille, F-59655 Villeneuve d'Ascq, France; L. Delmotte, Laboratoire de Matériaux Minéraux, CNRS URA 428, Ecole Nationale Supérieure de Chimie de Mulhouse, F-68093 Mulhouse Cedex, France.

The development of new high-resolution methods in NMR inspires subsequent progress in measurements of interactions between the observed nuclei and their neighbors. The development of high-resolution methods for half-integer quadrupolar spins in solids offered no exception. We have applied a number of experimental methods in NMR of ^{19}F, ^{27}Al and ^{31}P, including magic angle spinning (MAS), multiple-quantum (MQ) MAS, MQMAS with cross polarization (CP-MQMAS), rotational echo double resonance (REDOR), MQ-REDOR and heteronuclear correlation spectroscopy (HETCOR) to characterize the structure of a recently synthesized aluminophosphate UiO-7. We will test *the applicability to these techniques in the studies of both short and intermediate range order. In particular, we will scrutinize the process of cross polarization between a group of strongly coupled spin-1/2 nuclei and a half integer quadrupolar spin under the condition of very fast MAS. The effect of dipolar couplings, the spinning speed, the S spin value, the strengths of RF-fields involved and the off-resonance effects on the Hartmann-Hahn matching curve will be studied in the presence of first and second-order quadrupole interaction. The cross polarization processes that involve multiple quantum transitions will be also analyzed.*

NMR Oral Session—Marek Pruski, 230 Spedding Hall, Ames Laboratory, Iowa State University, Ames, IA 50011, (515) 294-2017, fax (515) 294-5233, mpruski@iastate.edu

236. ***A STUDY OF THE CROSS RELAXATION POLARIZATION TRANSFER PATHWAY FROM LASER POLARIZED XENON TO SURFACE SPECIES.*** Ernesto MacNamara, Jay Smith, Charles V. Rice and Daniel Raftery; H.C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393

Polarization transfer from optically polarized ^{129}Xe to surface species has the potential for extending the utility of surface NMR studies. In our version of the experiment, optically polarized ^{129}Xe is introduced into a MAS rotor at approximately 120 K using a flow-through optical pumping apparatus. At this temperature a significant amount of ^{129}Xe is adsorbed onto the sample surface. Mobile ^{129}Xe atoms on the surface transfer their polarization to surface nuclei (^{1}H or ^{13}C in our experiments) via the nuclear Overhauser effect (SPINOE) induced by the large, non-equilibrium ^{129}Xe nuclear spin polarization. We have studied the cross-relaxation transfer pathways and efficiencies in detail for a model 3-spin system (methanol/silica) and will present our results on the competitive avenues for polarization transfer.

NMR Oral Session—Daniel Raftery, H.C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393, raftery@chem.purdue.edu

237. Jeffrey A. Reimer

No abstract.

238. ***R. W. VAUGHAN PLENARY LECTURE: "SCATTERING AND MAGNETIC RESONANCE SPECTROSCOPY"***—Professor Hans W. Spiess, Max-Planck-Institut for Polymer Research, P.O. Box 31 48, D-55028 Mainz, Germany.

Most of our knowledge of the structure of molecules has in the past been provided by x-ray and neutron scattering. Likewise, the most detailed information about the dynamic behavior of matter has been extracted from neutron- and light scattering. These powerful techniques, therefore, represent stimulating challenges for other fields, such as magnetic resonance, to develop alternative methods of comparable strength and versatily. Even more important, such alternatives are desperately needed in order to study disordered or only partially structured materials. The lecture will give an overview of our efforts in the last 20 years to develop multidimensional solid state NMR techniques to study conformation and alignment of macromolecules, their rotational and translational dynamics as well as their phase structure. Particular emphasis will be placed on comparisons of multidimensional NMR and scattering pointing out the almost striking analogies in the physics and the information content of the two approaches. Specific examples from different field of materials science will be given including inorganic and molecular crystals, inorganic and polymeric glasses as well as liquid crystals and supramolecular aggregates.

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239. ***SOLID STATE NMR OF PEPTIDES AND PROTEINS.*** olid State NMR of Peptides and Proteins. Oleg Antzutkin, John Balbach, Francisco Blanco, Yoshitaka Ishii, Carl Michal, David Weliky, and Robert Tycko, Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, Maryland 20892-0520. 1on leave from Luleå University, Luleå, Sweden. 2current address: Department of Chemistry, Michigan State University, East Lansing, Michigan.

Solid state NMR measurements have the unique capability of providing atomic-level structural information about high-molecular-weight biopolymers in noncrystalline solids and disordered membrane-bound systems. This talk will cover recent progress in our laboratory in the development and application of solid state NMR techniques for structural studies of peptides and proteins. Topics will include: ^{13}C magic angle spinning NMR techniques for the determination of peptide backbone conformations at specific isotopically labeled sites (1); the application of these techniques to studies of antibody-bound peptide conformations (2); high-order multiple quantum excitation in solid state ^{13}C NMR (3); application of multiple quantum ^{13}C NMR to fibril-forming peptides; heteronuclear multidimensional solid state NMR techniques for resonance assignments and structure determination in uniformly ^{15}N- and ^{13}C-labeled, oriented peptides and proteins; optical pumping methods for NMR sensitivity enhancement (4).

1. A.E. Bennett, D.P. Weliky, and R. Tycko, "Quantitative conformational measurements in solid state NMR by constant-time homonuclear dipolar recoupling", J. Am. Chem. Soc. 120, 4897-4898 (1998); D.P. Weliky and R. Tycko, "Determination of peptide conformations by two-dimensional magic angle spinning NMR exchange spectroscopy with rotor synchronization", J. Am. Chem. Soc. 118, 8487-8488 (1996).

2. D.P. Weliky, A.E. Bennett, A. Zvi, J. Anglister, P.J. Steinbach, and R. Tycko, "Solid-state NMR evidence for an antibody-

dependent conformation of the V3 loop of HIV-1 gp120", Nature Struct. Biol. 6, 141-145 (1999).

3. O.N. Antzutkin and R. Tycko, "High-order multiple quantum excitation in 13C nuclear magnetic resonance spectroscopy of organic solids", J. Chem. Phys. 110, 2749-2752 (1999).

4. C.A. Michal and R. Tycko, "Nuclear spin polarization transfer with a single radio-frequency field in optically pumped indium phosphide", Phys. Rev. Lett. 81, 3988-3991 (1998); R. Tycko, "Optical pumping in indium phosphide: 31P NMR measurements and potential for signal enhancement in biological solid state NMR", Solid State Nucl. Magn. Reson. 11, 1-9 (1998).

NMR Oral Session—Robert Tycko, National Institutes of Health, Building 5, Room 112, Bethesda, MD 20892-0520, phone 301-402-8272, fax 301-496-0825, tycko@helix.nih.gov

240. ***USE OF THE "b" SINE-CORRELATION TECHNIQUE TO MEASURE WEAK DIPOLAR INTERACTIONS IN ORDERED SOFT CONDENSED MATTER.*** P.T. Callaghan, Massey University; E.T. Samulski, University of North Carolina

No abstract.

241. Huub de Groot

No abstract.

242. ***ASPECTS OF STRUCTURE AND DYNAMICS IN DISORDERED MATERIALS BY SOLID STATE NMR.*** Hellmut Eckert, Joern Schmedt auf der Guenne, Guido Regelski, Sylvia Kaczmarek, Michael Witschas, Institut fuer Physikalische Chemie, Westfaelische Wilhelms-Universitaet Muenster, Schlossplatz 7, D48149 Muenster, Germany

Phenomena of order/disorder are diverse and multi-faceted in solid state materials. They include local structural aspects related to the chemical bond distribution, the distribution of topological parameters, and ordering phenomena on the nanometer length scale (intermediate range order). They also include aspects of local dynamics such as molecular reorientations and ionic motion. Solid state NMR provides powerful techniques for addressing both of these aspects of disorder and for relating them to each other. Direct structural information is often available on the basis of magnetic dipole-dipole coupling constants, which are calculable from internuclear distances. For example, multidimensional zero- and double-quantum (DQ-) MAS-NMR techniques have been utilized to derive connectivity maps based on homonuclear dipole-dipole couplings. This will be illustrated with new applications to the solid state chemistry of crystalline and glassy polyphosphides. Furthermore, plastic crystalline solid solutions formed in these systems demonstrate the simultaneous presence of static and dynamic disordering. The interplay of these phenomena has been studied by means of temperature dependent NMR lineshape and relaxation time measurements.

NMR Oral Session—Yue Wu, Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255, phone: (919)962-0307, fax: (919)962-0480, yuewu@physics.unc.edu

243. ***HIGH RESOLUTION SOLID-STATE NMR : A POWERFUL TOOL FOR DESCRIPTION OF STRUCTURE AND DYNAMICS IN INORGANIC SOLIDS AND LIQUIDS, FROM ROOM TEMPERATURE UP TO VERY HIGH TEMPERATURE.*** Dominique Massiot, Thomas Vosegaard, Pierre Florian; Catherine Bessada; Frank Fayon; Jean-Pierre Coutures; CRMHT – CNRS , 1D ave Recherche Scientifique, 45071 Orléans cedex 2, France

Thanks to recent developments Solid State NMR has become a very powerful tool for investigating the structure of inorganic solid materials (reference crystalline phases, disorder bearing crystalline phases, amorphous or glassy materials) as well as the structure and dynamics of high temperature liquid oxides or fluorides. These progresses arose from both methodological (correlations, multiple quantum excitation, double resonance) and technological improvements (high fields and spinning rates). They improved the ability of solid state NMR to provide resolved isotropic and anisotropic characterization of both dipolar (^{1}H, ^{29}Si, ^{31}P) and quadrupolar nuclei (^{17}O, ^{27}Al, ^{71,69}Ga, ^{139}La...). We shall give examples of recent achievements obtained in our laboratory.

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244. ***INTERMEDIATE RANGE ORDER IN BORON OXIDE GLASS: THE FRACTION OF RINGS FROM ANISOTROPY-CORRELATED TWO-DIMENSIONAL NMR.*** C. G. Joo, U. Werner-Zwanziger, and J. W. Zwanziger, Indiana University, Dept. of Chemistry, 800 E. Kirkwood Ave., Bloomington, IN 47405-7102

A recently developed two-dimensional experiment was applied to determine the intermediate range order in boron oxide glass. The experiment correlates the powder pattern of boron-11 obtained under magic angle spinning with those of neighboring sites, with the coupling induced by off-magic-angle spinning during a mixing period. Because the local structure in this glass consists of trigonal planar boron oxide polyhedra, which serve to define the quadrupole principal axis direction, this experiment in effect measures the dihedral angle distribution of neighboring sites. Thus the ring structure can be estimated, since neighboring sites in rings will be co-planar, while other interme-

diate range structures will not be. By comparing the resulting 2-D spectra to those of crystalline model compounds, we find that some 80% of the boron are in rings in the glass. This is the first direct measure of this quantity in this important bench-mark glass-former.

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245. *^{17}O MQMAS AND DOR NMR STUDIES OF POROUS MATERIALS IN THE HIGH FIELD.* Dieter Freude, Dieter Michel, Ulf-Torsten Pingel, Universität Leipzig, Linnéstraße 5, Leipzig, Germany, 04103; Ago Samoson, Institut of Chemical Physics, Akadeemia tee 23, Tallinn, Estonia, EE0026; Jean-Paul Amoureux, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, France, 59655

Oxygen-17 enriched zeolites Na-ZSM-5, Na-Y, ferrierite, silicalite, Na-A, LSX and the layer silicate Na-Ilerite were studied by MAS, MQMAS, DOR, CP and REDOR NMR in the field of 17.6 T. It has been shown that multiple-quantum and double rotation techniques are complementary tools for getting highly-resolved ^{17}O NMR spectra of solids. SiOSi and SiOAl bonds are studied in zeolites Na-ZSM-5, ferrierite and Na-Y, whereas zeolite Na-A and LSX contain only SiOAl bonds. For hydrated zeolite Na-A, the spectrum was fully resolved into three lines by DOR and 5QMAS. The values of the isotropic chemical shift of the different SiOAl sites in Na-A and Na-LSX are presented as a function of the bond angle.[1] The influence of cations on the isotropic chemical shift was studied in case of the Na-, Cs- and Li-form of LSX. It has been shown that the increase of the basic properties of the zeolite oxygen framework going from the sodium to the cesium form of the zeolite LSX is reflected by a downfield shift of ca. 6 ppm. The ^{17}O 3QMAS spectra of hydrated, dehydrated and octane-loaded zeolite Na-Y show different line shapes due to the effect of adsorbed molecules on the zeolite framework. For the layer silicate Na-Ilerite, a resolution into three lines (SiOH, SiOSi, H_2O) was achieved by MAS NMR in the field of 17.6 T. The assignment of the SiOH line was proven by CP MAS and REDOR NMR. Furthermore, the $^{17}O\{^1H\}$ MQ-t_2-REDOR sequence was successfully applied to Na-Ilerite.

1. *Pingel et al., Chem. Phys. Lett., 1998, 294 (1998) 345.*

NMR Oral Session—Prof. Dr. Dieter Freude, Universität Leipzig/Physik, Linnéstr. 5, 04103 Leipzig, Germany, phone +49 341 97 32 503 Fax +49 341 97 32 549, E-mail freude@physik.uni-leipzig.de

246. *NMR OF QUADRUPOLAR NUCLEI IN SOLIDS: CROSS-POLARIZATION AND ^{17}O MULTIPLE-QUANTUM MAS.* Stephen Wimperis, University of Oxford, Physical and Theoretical Chemistry Laboratory, Oxford OX1 3QZ, United Kingdom

In 1995, Frydman and Harwood published a new two-dimensional NMR technique that they called multiple-quantum magic angle spinning (MQMAS). This experiment allows high-resolution NMR spectra of half-integer quadrupolar nuclei, such as ^{17}O, 23Na and ^{27}Al, to be obtained using conventional MAS NMR hardware. The method is now widely used in the study of minerals, glasses, zeolites and other microporous materials. We are using MQMAS to study the ^{17}O NMR spectra of a variety isotopically-enriched synthetic mantle silicates. By correlating either three- or five-quantum coherence with single-quantum coherence in a two-dimensional experiment under MAS conditions, the technique yields ^{17}O NMR spectra in which the inhomogeneous second-order quadrupolar broadening is refocused and the crystallographically-distinct oxygen species are resolved. In some samples, however, we have been unable to observe all the oxygen species present using MQMAS and additional methods have had to be used, such as cross-polarization from ^{1}H to ^{17}O and comparison with other ^{17}O-labelled synthetic minerals. More generally, we are finding cross-polarization to quadrupolar nuclei to be a useful experimental technique, in relation both to the MQMAS experiment and to other static and MAS NMR studies. Recently, we have demonstrated that it is possible to cross-polarize from ^{1}H directly to the central three-quantum coherence of ^{27}Al in a powered sample under MAS conditions and we have combined this new technique with MQMAS. We have also shown that five-quantum cross-polarization is feasible. We have been investigating the intensities and lineshape distortions in single- and multiple-quantum cross-polarized static and MAS ^{23}Na ($I = 3/2$) and ^{27}Al ($I = 5/2$) spectra and have developed computer simulation programs that aid in the interpretation of these experimental data.

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247. *MULTIPLE QUANTUM MAS NMR EXPERIMENTS ON I=5/2 NUCLEI.* M.E.Smith, R. Dupree and T. Mildner, Department of Physics, University of Warwick, Coventry, UK, CV4 7AL, E.R.H. van Eck School of Physical Sciences, University of Kent, Canterbury, Kent , UK, CT2 7NR and S.C. Kohn, Department of Geology, University of Bristol, Bristol, UK, BS8 1RJ.

The multiple quantum (MQ) MAS NMR experiment has proved to be extremely useful at improving the resolution of spectra from quadrupole nuclei. This paper examines two particular cases of the MQ experiment applied to I=5/2 nuclei. The use of rotationally induced excitation (RIACT)1 of both triple and quintuple quantum coherences is examined. The advantages of rotationally induced excitation are good sensitivity at moderate rf fields and less dependence of the excitation on the size of the quadrupole interaction. A pulse sequence for producing purely absorptive lineshapes from the RIACT scheme is discussed. One of the most exciting applications of MQ MAS NMR is to the study of 17O in aluminosilicates to resolve different framework fragments which significantly overlap in conventional MAS NMR spectra. RIACT allows efficient excitation of sites with quite large quadrupole interactions. In hydrous aluminosilicate gels and glasses 17O observation of OH groups can be problematic under MQ which appears to be related the apparently small quadrupole interaction and rapid relaxation. The optimum conditions for observing the OH groups in hydrous gels and glasses is discussed. This research was partially supported by the EPSRC through grant GR/K74876 and HEFCE is thanked for funding of the high field spectrometer through a JREI grant.

1. G. Wu, D. Rovnyak and R.G. Griffin, *J. Am,. Chem. Soc., 1996, 118, 9326.*

NMR Oral Session—Mark E. Smith, Department of Physics, University of Warwick, Coventry, UK, CV4 7AL, 0044-1203-522380, fax: 0044-1203-692016, M.E.Smith.1@warwick.ac.uk

248. *USING ^{31}P{^{1}H} CROSS POLARIZATION MAS NMR TO PROBE THE SURFACE DISSOLUTION OF PHOSPHATE GLASSES.*

Todd M. Alam and David P. Lang, Sandia National Laboratories, Department of Material Aging and Reliability, Albuquerque, NM 87185-1407.

The dissolution process in alkali phosphate glasses has been probed by using ^{31}P{^{1}H} Cross Polarization (CP) MAS NMR techniques. By utilizing the magnetization of protons that originate directly from the hydration layer involved in the dissolution of the glass, it is possible to filter or select ^{31}P signals that originate from the aged surface. This filtering allows the chemistry of the aged surface to be probe independently from the unaged bulk glass material. The CP dynamics for the different surface phosphate signals are investigated and allow details about the variation in chemistry to be determined. In addition, the ^{31}P{^{1}H} CP can be used as a prefilter for two-dimensional (2D) ^{31}P-^{31}P RFDR exchange experiments enabling the phosphate backbone connectivity directly at the interface between bulk and aged surface to be probed. These results will be discussed in terms of present mechanisms concerning aging in phosphate glasses. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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249. *LYSOZYME DYNAMICS.*

Richard Wittebort, Department of Chemistry, University of Louisville, Louisville, Kentucky. 40292.

Dynamics in proteins are doubly important for NMR spectroscopists. First, they provide us with an interesting phenomena to study and, in turn, they ultimately limit the resolution and/or sensitivity of our experiment. We have used 2H NMR to study backbone dynamics of the slowly exchanging amide sites of fully hydrated, crystalline lysozyme. This experimental approach is distinct from solution NMR studies where both the amplitudes and rates of internal motions are determined from relaxation measurements and separated from macromolecular rotational diffusion. Here,macromolecular rotational diffusion is absent, order parameters are determined from the residual quadrupole coupling and dynamical rates are determined from spin lattice relaxation at three NMR frequencies (38.8, 61.5, and 76.7 MHz). Values of S2 increase from 0.85 at 290°K to 0.94 at 200°K . Below 250°K, relaxation is independent of the NMR frequency indicating that backbone motions are fast compared to the NMR frequencies. Moreover, the correlation times compare well with those determined by molecular dynamics. Two curious features, however, are observed for $T > 250$°K. In contrast to fast motions in simple fluids, relaxation is significantly more efficient at higher temperature and is field dependent (most efficient at the lowest NMR frequency). This indicates the presence of additional motions that are slow compared to the NMR frequencies. Using the values of S2 determined from the residual quadrupole coupling and a model-free relaxation formalism which allows for fast and slow internal motions, we conclude that the slow motions have correlation times in the range of 0.1 to 1.0 μs and are effectively frozen out at 250°K where fast motions of the amide planes with ~15 ps effective correlation times and 9° rms amplitudes dominate relaxation. The fast internal motions increase slightly in amplitude as the temperature rises toward 290°K but the correlation time, as is also observed in solution NMR studies of RNase H, is approximately constant. These findings are consistent with hypotheses of dynamic glass transitions in hydrated proteins arising from temperature-dependent damping of harmonic modes of motion above the transition point.

NMR Oral Session—Richard Wittebort, Department of Chemistry, University of Louisville, Louisville, Kentucky. 40292.

250. *NMR STUDIES OF REARRANGEMENT PATHWAYS IN SOLIDS.*

Zeev Luz, Rehovot 76100, Israel

Molecules in solids are not as rigid as we often tend to believe; They librate, reorient, diffuse and even undergo chemical transformations. Such solid state processes may be strongly affected by the packing forces of the lattice and as a result their rates and detailed mechanistic pathways, may differ from those in the neat liquid or in solutions. A point in case is the bond shift (Cope) rearrangement in the "Cage-like" molecules of bullvalene ($C_{10}H_{10}$) and its derivatives, and the derivatives of the heptaphosphorus anion (P_7^{3-}).

The Cope rearrangement in both compounds was extensively investigated in solution, principally by High-Resolution solution NMR. Somewhat surprisingly it was found that the reactions also proceed in the solid state. We have studied the mechanisms and kinetics of these solid state reactions, using a variety of NMR techniques and a number of magnetic nuclei, including ^{13}C, D, ^{31}P and ^{7}Li. The main techniques used involve, dynamic line broadening in static and spinning samples, magnetization transfer and 2D-Exchange NMR.

Bullvalene and its derivatives, usually crystallize in well-ordered lattices. Consequently, the rearrangement proceeds in concert with a proper reorientation, which ensures the preservation of the crystal order. This results in very special dynamic lineshapes and characteristic cross peaks arrays in the 2D spectra, which uniquely identify the reaction pathways.

The only phosphorus cage compound studied so far by this approach is Li_3P_7, which is an amorphous solid. The three Li^+ ions compensate for the negative charges on the three bridging phosphorus atoms in the cage. Here the reaction pathway is not as well defined; it may or may not involve reorientation and different sites in the lattice may have different pathways. Our attempts to elucidate the rearrangement mechanism in this system, using ^{31}P and ^{7}Li NMR will be described.

NMR Oral Session—Zeev Luz, Rehovot 76100, Israel

251. ***2D NMR INVESTIGATIONS OF BACTERIAL CELLULOSE AND CELLULOSE II.*** Christian Jäger, Stephanie Hesse. Friedrich Schiller University Jena, Institute of Optics and Quantum Electronics, Max Wien Platz 1, D-07743 Jena, Germany; Thomas Heinze, Friedrich Schiller University Jena, Department of Chemistry and Geology, Humboldtstr., D-07743 Jena, Germany; Hans-Peter Schmauder, Forschungszentrum für Medizintechnik und Biotechnologie e.V., D-99947 Bad Langensalza, Germany

The investigation of the supramolecular structure of cellulose and, most importantly, of the hydrogen bonding system is a most difficult task. Results of structural studies of bacterial cellulose and cellulose II will be presented using ^{13}C and ^{1}H NMR.

^{13}C PHORMAT NMR has been used to determine the anisotropy of the ^{13}C chemical shifts for the resolved resonances. The data is compared with theoretical simulations of the structure of cellulose that include the hydrogen systems. Alternatively, the proton system of the bacterial cellulose can been diluted by deuterons to access the hydrogen bonding systems directly by ^{1}H and ^{2}H MAS NMR. First results are presented. Furthermore, ^{13}C enriched cellulose has been prepared to verify and figure out connectivities of the various carbon sites and their resonances for bacterial cellulose and cellulose II using DQ NMR.

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252. ***IDENTIFICATION OF HISTIDYL AND LYSYL RESIDUES AT A POTENTIAL ALLOSTERIC SITE OF RIBULOSE 1,5-BISPHOSPHATE CARBOXYLASE/OXYGENASE.*** Lynda M. McDowell, Washington University, Department of Chemistry, One Brookings Drive, St. Louis, MO 63130-4899; Joe S. Schriner, Kansas State University, Department of Biochemistry, Manhattan, KS 66506-3207 (current address: Procter & Gamble Manufacturing Company, 19th and Kansas Avenue, Kansas City, KS 66110); Karinne Cortes, Kansas State University, Department of Biochemistry, Manhattan, KS 66506-3207; Matthew E. Merritt, Washington University, Department of Chemistry, One Brookings Drive, St. Louis, MO 63130-4899 (current address: Department of Chemistry, University of Washington, Seattle, WA 98195); Jacob Schaefer, Washington University, Department of Chemistry, One Brookings Drive, St. Louis, MO 63130-4899; Delbert D. Mueller, Kansas State University, Department of Biochemistry, Manhattan, KS 66506-3207

Ribulose 1,5-bisphosphate carboxylase/oxygenase (Rubisco), a hexadecamer of 537 kDa comprised of 8 large and 8 small subunits, catalyzes the initial steps in both CO_2 and O_2 fixation during photosynthesis and photorespiration. Before Rubisco can catalyze either reaction, however, it must be activated by CO_2. Activation by CO_2 is strongly enhanced by effectors such as 6-phosphogluconate (6PGA). It is not known how 6PGA exerts its effect, but allosteric site binding is a possible mechanism. Accordingly, we have demonstrated the presence of potential allosteric sites by showing that 6PGA tightly binds comfrey Rubisco ($K_d = 14\ \mu M$) even when the active site is blocked by the exchange inert inhibitor 2-carboxy-D-arabinitol 1,5-bisphosphate(CABP) (J.R. Shriner, et. al., Eur. J. Biochem., submitted). To help locate this site we have used rotational-echo double resonance (REDOR) NMR of 6PGA bound at pH 7.9 to 99%-U-^{15}N- Rubisco complexed with CABP. The lyophilized samples contained either [1-^{13}C]6PGA, unlabeled 6PGA, or no 6PGA. Nitrogen observe phosphorous dephase REDOR spectra of samples without 6PGA provided the REDOR difference spectra arising from active site Lys, His, and Arg residues in the proximity of the CABP phosphorous groups. Additional dephasing of Lys and His residues is observed when 6PGA is bound. This provides strong evidence that one or more Lys and His residues are near the 6PGA phosphate group when it is bound to the putative allosteric site. Carbon observe phosphorous dephase REDOR spectra of samples with [1-^{13}C]6PGA bound, after correction for natural abundance dephasing using samples with unlabeled 6PGA, gave a [1-^{13}C] to 6-P distance in bound 6PGA of 6.4 ± 0.1 Å. Molecular models show the maximum value for this distance is 8.6 Å (Paul Smith, personal communication) which is also the distance found in crystals of sodium 6PGA grown from neutral pH solutions. Molecular graphic investigations utilizing the X-ray structure (I. Andersson, J. Mol. Biol. (1996) 259, 160-174) of the spinach Rubisco-CABP combined with the Lys and His distances derived from solid-state NMR of the comfrey enzyme have identified three promising 6PGA allosteric binding sites.

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253. ***SOLID STATE NMR STUDY OF POLYMORPHISM AND NONCLASSICAL PHASE TRANSFORMATION IN 3MEDNBP.*** Asher Schmidt, Shifra Kababya, Michael Appel, Mark Botoshansky, Soliman, Khatib, and Yoav Eichen., Department of Chemistry and Solid State Institute, Technion, Haifa 32000, Israel

Polymorphism and phase transitions in 2(2,4-dinitrobenzyl)-3-methylpyridine were investigated using C-13 and N-15 solid state NMR, crystallographic, and calorimetric techniques. A simple scheme for complete C-13 and N-15 spectral assignment is presented for two polymorphs with N-15 labeled nitro groups. In this scheme we employ a set of 1-D experiments including - interrupted decoupling, C-13[N-15] REDOR, selective N-15 --> C-13 TEDOR, and a T-jump. The feasibility of the TEDOR experiment from N-15 labels to C-13 nuclei at natural abundance is demonstrated. A precise temperature calibration scheme for the MAS NMR experiments was devised in order to monitor the phase transition as function of fine temperature steps. Temperature gradients across the sample were kept below 1.5 K. The coexistence of two polymorphs over at least 8-9 K around their first order phase transition temperature is observed by C-13 and N-15 CPMAS experiments, and by following the thermally activated tautomerization kinetics in a single crystal. These observations are interpreted in terms of a distribution of mesoscopic domains within the crystal, differing in their local pressure. Presence of dynamic processes on time scales shorter than minutes is excluded by both the NMR measurements, and by the tautomerization kinetics. Experiments to assess the presence of putative slow dynamic processes and their time scale are underway.

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254. ***TESTING THE SURROGATE PROBE STRATEGY USING SOLID-STATE ^{67}ZN NMR.*** Andrew S. Lipton and Paul D. Ellis, Environmental Molecular Sciences Laboratory, Battelle, Pactfic Northwest National Laboratory. PO Box 999 MSIN K8-98, Richland, WA 99352.

In order to understand the function of many metalloproteins and enzymes it is desirable to directly observe the metal in the active site of these systems. However, the native metals often have poor spectroscopic properties (such as low γ, low natural abundance, or large quadrupole broadening) which makes data acquisition difficult or even impossible. The past twenty-five years or so have seen the development of a surrogate probe strategy, involving the substitution of Cd^{+2} for Zn^{+2} and/or Ca^{+2} (and more recently for Fe, Mg, Mn, and Cu sites), in the nuclear magnetic resonance (NMR) investigations of metalloproteins. The excellent NMR spectroscopic properties of the cadmium in substituted proteins have allowed valuable information to be extracted from many systems. The large body of cadmium models have been used to develop rules correlating structure and shielding. Based on the similarities of the metal properties and the retention of some biological activity in substituted systems, it has been assumed that the cadmium reflects the behavior of the native metals. However, this assumption has not been verified experimentally. We have therefore undertaken the task of testing the surrogate probe strategy by investigating the solid state NMR lineshapes of zinc systems. Discussed are the experimental details (i.e. overcoming the sensitivity issues of ^{67}Zn NMR), lineshape simulations and projections for future work.

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255. ***SEGMENTAL DYNAMICS IN DRY AND SWOLLEN ELASTOMERS AS FUNCTION OF CROSS-LINK DENSITY AND FILLER CONTENT STUDIED BY THE NMR DIPOLAR-CORRELATION EFFECT.*** Winfried Kuhn*, Farida Grinberg+, Maciej Garbaczyk#, Stefan Jurga#, Rainer Kimmich+*IIC Innovative Imaging Corp., 66440 Blieskastel, Germany, +Universität Ulm, Sektion Kernresonanzspektroskopie, 89069 Ulm, Germany, #Uniwersytet Im. Adama Mickiewicza w Poznaniu, 61-614 Poznan, Poland

Cross-link density of sulfur cured and carbon black filled natural rubbers is one of the most important structural properties affecting the mechanical, thermal and aging behavior of technical elastomers such as car tires, seals, etc. During the past ten years, it has been shown that chemical and physical cross-linking can be determined by NMR techniques using Hahn spin-echo methods, to study molecular dynamics of rubber networks. To overcome some disadvantages of this technique related to pulse sequence timing and complicated data evaluation problems, we used the dipolar correlation effect (DCE) on the stimulated echo to determine segmental chain dynamics in a series of differently cured natural rubber samples, as used as reference materials in rubber industry. The attenuation curves of the dipolar correlation quotient, that is, the quotient of the stimulated and primary echo amplitudes, were analyzed using analytical expressions. The mean squared fluctuation of the dipolar coupling constant, and correlation times were determined. An important finding of our work is the strong dependence of the cross-link density on the dipolar correlation effect, while the carbon black filler content on the DCE is neglectable. Consequently, magnetic susceptibilty effects on our measurements can be excluded. The results are in good agreement with earlier measurements using not only NMR, but also other techniques such as measurements of swelling behavior and mechanical properties.

256. ***USING $^{31}P\{^{1}H\}$ CROSS POLARIZATION MAS NMR TO PROBE THE SURFACE DISSOLUTION OF PHOSPHATE GLASSES.*** Todd M. Alam and David P. Lang, Sandia National Laboratories, Department of Material Aging and Reliability, Albuquerque, NM 87185-1407.

The dissolution process in alkali phosphate glasses has been probed by using 31P{1H} Cross Polarization (CP) MAS NMR techniques. By utilizing the magnetization of protons that originate directly from the hydration layer involved in the dissolution of the glass, it is possible to filter or select 31P signals that originate from the aged surface. This filtering allows the chemistry of the aged surface to be probe independently from the unaged bulk glass material. The CP dynamics for the different surface phosphate signals are investigated and allow details about the variation in chemistry to be determined. In addition, the 31P{1H} CP can be used as a prefilter for two-dimensional (2D) 31P-31P RFDR exchange experiments enabling the phosphate backbone connectivity directly at the interface between bulk and aged surface to be probed. These results will be discussed in terms of present mechanisms concerning aging in phosphate glasses. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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257. ***LOCATION OF PROTONS IN ANHYDROUS KEGGIN HETEROPOLYACIDS BY USING 1H<->31P REDOR AND MOLECULAR MODELING.*** Alain Bailly, Jean-Francois Paul, Jean-Paul Amoureux, Michel Fournier, Michel Guelton, Université des Sciences et Technologies de Lille, Bat P5, 59650 Villeneuve d'Ascq (France); Subramanian Ganapathy, University of Pune, National Chemical Laboratory, Pune 411 008, India

The catalytic properties of heteropoly compounds have drawn wide attention for many years. Among these very extensively studied compounds are the basic relevant ones belonging to the well-known Keggin structure,especially the acidic form XnM12O40H8-n, with X=Si, P and M=Mo, W. Their acidic and redox properties, well known in solution, are still not understood in the solid state, especially at the catalytic reaction temperatures. At the present time, there are many discrepancies about the acidic sites in Keggin units, especially in the solid *state. The main objective of the present study is to determine the proton locations by a combination of 1H<->31P REDOR and Molecular Modeling. The density functional quantum chemical calculations revealed the most energetically favorable site for the acidic protons. In the case of H3PMo12O40, we can deduce without any ambiguity that the protons are located on the second type of bridging oxygen atoms (dP-H = 0.49 nm). However, in H3PW12O40, REDOR measurements lead to dP-H = 0.57 nm, suggesting that protons are located on the terminal oxygen. These measurements thus provide for the first time a consistent ranking of acid strength for the important class of Keggin solid catalysts.*

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258. *CHARACTERIZATION OF BRONSTED ACID SITES IN ZEOLITES BY MQ-REDOR NMR.* Subramanian Ganapathy, University of Pune, National Chemical Laboratory, Pune 411 008, India; Laurent Delevoye, Alain Bailly, Jean-Paul Amoureux, Université des Sciences et Technologies de Lille, Bat P5, 59650 Villeneuve d'Ascq (France)

Zeolites are porous aluminosilicates extensively used as shape-selective catalysts in petrochemical industry. Proton acid sites are generated when excess negative charges, due to the replacement of SiO4 tetrahedra by the AlO4 tetrahedra in the zeolite framework, are neutralised by protons. The catalytic activity of acid sites depends on the proton affinity at the charged framework location. This, in turn, depends on the exact topographical location of the binding Al sites in a given zeolite structure and further on the structural details of the Si-O(H)-Al environment. We address the question of a very effective acid site characterization by a combination of MQ-MAS and REDOR NMR. By way of 3Q 27Al MAS NMR, we are able to resolve the distinct tetrahedral framework Al environments and by reintroduction of the heteronuclear proton-aluminium dipolar coupling through 27Al-1H REDOR, we provide the first evidence to uniquely identify the proton binding Al sites within the nonequivalent AlT-sites in the zeolite of a given framework topology. experimental demonstration and structural elucidation are provided in the crystalline aluminosilicate, 1H-mordenite.

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259. *RECENT DEVELOPMENTS OF CP MAS BETWEEN QUADRUPOLAR NUCLEI AND SPIN 1/2.* Jean-Paul Amoureux, Alain Bailly, Université des Sciences et Technologies de Lille, Bat P5, 59650 Villeneuve d'Ascq (France); Marek Pruski, Iowa State University, 214 Spedding Hall, Ames, IA, 50011

The process of cross polarization (CP) between a group of strongly coupled spin-1/2 nuclei I and a half integer quadrupolar spin S is analyzed under the condition of very fast MAS. When the second-order quadrupole interaction is neglected, the polarization transfer can be described by a simple formula, which includes the dipolar couplings, the spinning speed, the S spin value, the strengths of RF-fields involved and the off-resonance effects. When second-order quadrupole interactions are introduced, many of the "resonances" in the Hartmann-Hahn matching curve become less efficient. The cross polarization processes that involve multiple quantum transitions are also analyzed and explained. The analysis of interatomic connectivities in solids via CP-MQMAS and HETCOR-MQMAS is discussed.

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260. *CHEMICAL SHIFT TENSORS OF POLYCYCLIC AROMATIC MOLECULES DETERMINED BY MAGIC ANGLE TURNING.* Dewey H. Barich; A. M. Orendt; J. Z. Hu; R. J. Pugmire; D. M. Grant; University of Utah, 315 S. 1400 E. Salt Lake City, UT 84112.

^{13}C Chemical shift tensors for several polycyclic aromatic molecules (azulene, biphenylene, dibenzofuran, carbazole, etc.) have been studied in natural abundance powdered samples with combined cross polarization (CP) and magic angle turning (MAT) techniques. Specifically, the FIREMAT and PHORMAT experiments (with TIGER data processing) were used to determine the tensor principal values. In these experiments, a pseudo-2D data set is collected with an isotropic and an anisotropic dimension. Slices are taken from that data set which contain only those tensors that cannot be resolved in the isotropic dimension. The spectra in each slice are then analyzed to determine the principal values of the tensors. While the FIREMAT method is generally superior to PHORMAT, several cases are presented in which PHORMAT outperforms FIREMAT because of the large linewidths (thus relatively poor resolution) in the spectra. Spectral assignments are based on a variety of methods including literature references, spectral editing experiments, and molecular orbital calculations, the latter of which also provided orientations for the chemical shift tensors in the molecular frame of reference. Due to very long 1H relaxation times (> 1000 s in some cases), most samples were doped with a stable free radical to reduce the 1H T1s. Suported by DOE DE-FG03-94ER14452.

D. W. Alderman, G. McGeorge, J. Z. Hu, R. J. Pugmire, D. M. Grant, Mol. Phys., 1998, 95, 1113-1126.

G. McGeorge, J. Z. Hu, C. L. Mayne, D. W. Alderman, R. J. Pugmire, D. M. Grant, J. Magn. Res., 1997, 129, 134-144.

J. Z. Hu, W. Wang, F. Liu, M. S. Solum, D. W. Alderman, R. J. Pugmire, D. M. Grant, J. Magn. Res. Ser. A, 1995, 113, 210-222.

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261. ***A ^{2}H AND ^{13}C EXPERIMENTAL SOLID-STATE NMR AND THEORETICAL STUDY OF ZEISE'S SALT, $K[PtCL_3(C_2H_4)]\bullet H_2O$.*** Guy M. Bernard; Roderick E. Wasylishen, Department of Chemistry, Dalhousie University, Halifax, NS, Canada B3H 4J3

The carbon chemical shift tensors of a $^{13}C_2$-labeled sample of Zeise's salt have been determined using the dipolar-chemical-shift method. Coordination of ethylene with Pt(II) results in an increase of approximately 50 ppm in the isotropic shielding of the carbon nuclei relative to the corresponding values for the free ligand (Zilm, K.W.; Conlin, R.T.; Grant, D.M.; Michl, J. J. Am. Chem. Soc. 1980, 102, 6672), but the orientations of the carbon chemical shift tensors are not affected significantly. Experimental carbon chemical shift tensors are compared to those calculated using the HF/GIAO method. A solid-state NMR investigation of a ^{2}H-labeled sample of the title compound at 4.7 and 9.4 T reveals very long T_1s, suggesting that the ethylene moiety is rigid in the solid state, contrary to previous suggestions in the literature.

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262. ***STRUCTURE DETERMINATION OF PEPTIDES AND PROTEINS USING SOLID STATE NMR.*** Peter V. Bower; Joanna R. Long; Nathan A. Oyler; Gary P. Drobny, University of Washington, Department of Chemistry, Seattle, WA 98195-1700

We present two new Solid State NMR technique for determining structure in peptides and proteins. We show how the torsional angle ϕ can be determined from a simple homonuclear distance measurement. We demonstrate this for a simple tri-peptide AGG and for a designed 14-mer. We also approach this problem through a Double Quantum experiment that independently determines the two torsional angles (ϕ,ψ). We show for both experiments that the inclusion of quadrupolar effects from the neighboring ^{14}N has no effect on the experimental results.

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263. ***MAGNETIC RESONANCE MICROIMAGING (MRM) OF PETROLEUM COKE.*** Eric B. Brouwer, National Research Council, Institute for Chemical Process and Environmental Technology (ICPET), Ottawa, Canada K1A 0R6; Igor Moudrakovski, National Research Council, Steacie Institute for Molecular Sciences (SIMS), Ottawa, Canada K1A 0R6; Keng H. Chung, Edmonton Research Centre, Syncrude Canada, 9421-17 Avenue, Edmonton, Canada T6H 1H4; Yves Deslandes, National Research Council, ICPET, Ottawa, Canada K1A 0R6; John A. Ripmeester, National Research Council, SIMS, Ottawa, Canada K1A 0R6.

The structure of petroleum coke is fundamental to the understanding of its formation, role and behavior in petroleum upgrading and refining processes. In the past, coke structural studies have focused on diffraction, scanning electron and optical microscopy, porosimetry, vibrational and NMR spectroscopy. We present the first MRM studies of coke, and discuss the impact of MRM in characterizing coke structure, formation and in situ behavior. Void space images obtained of cyclohexane from density-, T_2-relaxation- and diffusion-contrast mechanisms show a significant interconnected interior pore system demonstrating both the permeability of an exterior shell layer of ~100 mm thickness, and suggesting an agglomeration formation mechanism. With spherical coke particles (4.1 mm o.d.) an in-plane resolution of $(20\ \mu m)^2$ is obtained. MRM of both H_2O and CH_4 in coke are presented; these probes show lower resolution due to the decreased sensitivity relative to cyclohexane, but can be useful in exploration of a broader range of diffusion. The cyclohexane MRM images are compared to scanning electron microscopy images. While both techniques show similar structural characteristics, MRM additionally gives dynamic information in the form of diffusion and relaxation features that are related in turn to coke reactivity.

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264. ***EXPERIMENTAL ^{9}Be SOLID-STATE NMR STUDY OF $Be(acac)_2$ AND THEORETICAL STUDIES OF ^{9}Be ELECTRIC FIELD GRADIENT AND CHEMICAL SHIELDING TENSORS. THE FIRST EVIDENCE FOR ANISOTROPIC BERYLLIUM SHIELDING.*** David L. Bryce; Roderick E. Wasylishen, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J3

Beryllium-9 NMR in the solid state remains relatively unexplored, especially for small molecules small for which ab initio calculations of the electric field gradient (EFG) and chemical shielding (CS) tensors are feasible. This is in spite of the small quadrupole moment of ^{9}Be and the 100% natural abundance of this isotope. Recently, a combined solution-state ^{9}Be and ^{13}C NMR T_1 study of bis(acetylacetonato) beryllium(II) ($Be(acac)_2$) has been carried out in order to obtain the ^{9}Be quadrupolar coupling constant, C_Q(Kanakubo, M.; Ikeuchi, H.; SatB, G. P. J. Chem. Soc. Faraday Trans. 1998, 94, 3237). In general, dual spin probe relaxation studies of this type can only yield $[C_Q^2(1+\eta^2/3)]^{1/2}$. In addition, the success of the technique relies on several assumptions including a reliable estimate of the square of the time-averaged value of the ^{13}C-^{1}H dipolar coupling constant. Here we present the results of a ^{9}Be NMR study of solid Be(acac)2. The interpretation of the NMR data is facilitated by the results of X-ray diffraction experiments which indicate two unique sites (Onuma, S.; Shibata, S. Acta Cryst. 1985, C41, 1181). NMR spectra acquired at 4.7 and 9.4 T for MAS and stationary samples were fitted in order to extract C_Q. The analyses also reveal that the Be shielding at both sites is anisotropic. Ab initio calculations (HF/GLAO) on $Be(acac)_2$ are used to propose orientations for the EFG and CS tensors with respect to the molecule. This represents the first characterization of a beryllium CS tensor. To put the Be(acac)2 data in context, calculations of the EFG and CS tensors for a series of compounds spanning the known range of ^{9}Be chemical shifts are also presented.

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265. ***REMOTE ACCESS TO NMR SPECTROMETERS AT THE EMSL DOE USER FACILITY.*** Sarah Burton; Andrew Lipton, PNNL, 902 Battelle Blvd., P.O. Box 999, Richland WA, 99352

The convenience of collaboration with scientists and the use of state-of-the-art instrumentation have been increased by the use of Internet collaboratory software. The Environmental Molecular Sciences Laboratory (EMSL) DOE user facility located in Richland WA, has developed and used software tools which broadcast real-time information from spectrometer and office workstations. Solid-state NMR experiments at the EMSL facility are run at a variety of field strengths, 800, 750, 500, 400 and 300. Very low temperature (>= 4.2K), single crystal and μ-imaging as well as the more routine static, wideline, CRAMPS and CP/MAS experiments are capabilities being utilized on sight. This poster will cover the solid-state capabilities of the facility and function of the different collaboratory tools used to assist remote access of the spectrometers.

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266. ***INVESTIGATION OF LOCAL STRUCTURE ENVIRONMENT IN GLASSES BY ^{17}O, ^{23}Na AND ^{27}Al MQ-MAS NMR.*** F. Angeli, T. Charpentier, P. Faucon, J.-C. Petit, J. Virlet, Service de Chimie Moléculaire, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France.

In order to improve the models describing the vitreous structure, it is essential to characterize the degree of disorder in glasses. In fact, the possibility of studying the glass structure can particularly be achieved from complementary probes like oxygen, sodium and aluminum nuclei. In the present study, we describe a first approach to apply Multiple Quantum Magic-Angle Spinning (MQ-MAS) NMR to amorphous materials using a spectrum-inversion approach for extracting information from the MQ-MAS spectrum. This allows the reconstruction of the underlying two-dimensional distribution of the isotropic chemical shift correlated to the quadrupolar interaction, and this may be correlated to structural local information. Theoretical aspects of the present inversion procedure are presented in another contribution.

Here, the local structure of different silicate glasses has been studied using ^{17}O, ^{23}Na and ^{27}Al 3Q-MAS NMR. These nuclei have allowed the investigation of the short-range and the intermediate-range order in these glasses. The interpretation of the different site distributions is discussed in term of topological disorder, i.e. the distribution of specific geometrical parameters like bond distances and angles. Using semi-empirical relationships established with crystalline silicate compounds1-2, a distribution of Na-O distance and Al-O-Si bond angle have been determined from the extracted distributions of isotropic chemical shift. Inversions of ^{17}O 3Q-MAS NMR lead to the quantification of the several observed sites corresponding to different sort of bridging and non-bridging oxygen atoms. Limitations in the interpretation of the quadrupolar interaction distribution are also discussed.

[1] E. Lippmaa; A. Samoson, M. Mägi, J. Am. Chem. Soc. 1986, 108, 1730.
[2] H. Maekawa, T. Nakao, S. Shimokawa, T. Yokokawa, Phys. Chem. Min. 1997, 24, 53.

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267. ***^{13}C NMR STUDIES OF THE SELECTIVE OXIDATION OF n-BUTANE ON VANADIUM PHOSPHORUS OXIDE CATALYSTS.*** Bin Chen, Eric J. Munson, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455

Selective oxidation is widely applied in industry to add valuable functional groups (e.g. -COOH, -OH, -CHO) to hydrocarbons. The oxidation of n-butane to maleic anhydride on vanadium phosphorus oxide (VPO) catalysts is of general interest because it is the only example of an industrially practiced selective oxidation involving alkane activation. In this study ^{13}C-labelled n-butane and butadiene were used to investigate the mechanism for the selective oxidation of n-butane on VPO catalysts. n-Butane or butadiene was flowed over VPO catalysts that had vanadium oxidation states between 3.6 and 4.9. The catalysts were heated between 330 – 600 ∞C. For VPO in which the average vanadium oxidation state was < 4^{+}, butenes, butadiene and furan were observed, whereas maleic acid was not detected. Significant label exchange between the 1, 4 and 2, 3 carbons of butadiene was observed. If the catalysts contained V^{5+}, a significant amount of maleic acid was formed but intermediate oxidation products were not detected. Moreover, consistent label scrambling was observed for the reaction of n-butane on all the catalysts tested, namely, C1 and C4 of n-butane became C2 and C3 of maleic acid. Label scrambling was not observed for the oxidation of butadiene. These results suggest that there may be two different mechanisms for the reaction. The first and usually dominant mechanism involves the oxidation of butane that does not invoke butadiene as an intermediate. The second mechanism, which supports label scrambling, contains butadiene as an intermediate. These proposed mechanisms reconcile much of the work that has been done on n-butane oxidation on VPO catalysts.

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268. ***NMR STUDIES OF ^{129}Xe DIFFUSION IN ETHYLENE-PROPYLENE COPOLYMERS.*** Naira M. da Silva, Maria Ines B. Tavares, Instituto de Macromoléculas Prof. Eloisa Mano, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brasil; Hanna Gracz, E. O. Stejskal, Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204

Polymers are often modified to improve their properties and expand the range of their application. Properties of semicrystalline polymers like isotactic polypropylene (iPP) can be strongly influenced by copolymerization with ethylene. The mole fraction and of ethylene and the structure of the second phase in the copolymer is expected to have influence on the mechanical properties. We have probed the structure of *two different EP copolymers using NMR measurements on absorbed ^{129}Xe. These experiments yield information on sample morphology via the NMR lineshapes and isotropic chemical shifts and their temperature dependences. Separate xenon lines were observed for gas dissolved in the different regions of the propylene-ethylene copolymers. Some of the spectra were temperature dependent. This allows the characterization of the rate of xenon exchange between the different polymer phases. Xenon pulsed field gradient diffusion measurements provides the necessary additional information to allow the estimation of domain sizes.*

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269. ***NMR SPECTROSCOPY AND SOLID PHASE SYNTHESIS: POLYMER SIGNAL SUPPRESSION VIA ISOTROPIC MIXING IN 1D GEL PHASE ^{1}H NMR*** Michael J.T. Ditty, R.M.E. Mainville and W.P. Power, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada, N2L 3G1; H.N. Hunter, Brantford Chemicals Inc., Brantford, ON, Canada, N3T 5W5.

The simultaneous application of solid-state and high-resolution NMR techniques permits effective in situ analyses of polymer bound species (epitopes). Application of high resolution magic angle spinning (HRMAS) as well as refinement of some standard pulse sequences to the unique aspects of swollen resin gels has allowed us to substantially improve suppression of background polymer signals among weak epitope signals. A non-selective one-dimensional version of the TOCSY[1] experiment is employed with a multiple-pulse isotropic mixing sequences DIPSI-2[2] or FLOPSY-8[3], during the mixing period, which efficiently removes polymer signals while maintaining quantitative integrals of the ^{1}H NMR epitope signals. These sequences are more effective at transferring coherences of different orders over a broader spectral range and longer time periods. This allows for the efficient decay of polymer signals through a combination of coherent and incoherent pathways. In comparison to other methods currently used to suppress polymer signals, such as presaturation, spin echo and multidimensional correlation experiments, this technique does not 1) affect signals that are isochronous with the polymer frequency (ies), 2) generate non-quantitative integrals and 3) require excessive calibration or experiment time.

1. *Braunschweiler, L.; Ernst, R.R. J. Magn. Reson. 1983, 53, 521.*
2. *Shaka, A.J.; Lee, C.J.; Pines, A. J. Magn. Reson. 1988, 77, 274.*
3. *Kadkhodaie, M.; Rivas, O.; Tan, M.; Mohebbi, A.; Shaka, A.J. J. Magn. Reson. 1991, 91, 437.*

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270. ***SOLID-STATE NMR CHARACTERIZATION OF ^{93}NB, ^{19}F SPIN PAIRS IN NIOBIUM FLUORIDES AND OXYFLUORIDES.*** Lin-Shu Du, Robert W. Schurko, Kwang Hun Lim and Clare P. Grey, SUNY at Stony Brook, Department of Chemistry, Stony Brook, NY 11794-3400

A variety of NMR interactions were characterized in niobium fluorides and oxyfluorides, such as direct dipolar coupling, indirect spin-spin coupling, chemical shielding anisotropy and the quadrupolar interaction. The spinning sidebands were separated from the isotropic when the ^{93}Nb MAS NMR spectra were acquired at high spinning speeds (ν_{rot} = 35 kHz). Simulations of these spectra yielded the ^{93}Nb quadrupole coupling constants, C_Q, the asymmetry parameter, η, and the isotropic chemical shifts, δ_{iso}. The ^{93}Nb MAS NMR spectra acquired at lower spinning speeds, where the spinning sidebands are not separated from the centerband, were simulated by using an efficient time propagation algorithm[1] based on Floquet theory[2]. Niobium chemical shielding anisotropy and the relative orientation of the electric field gradient (EFG) and chemical shielding (CS) tensors were determined from the analysis of ^{93}Nb NMR spectra of stationary samples. Distorted multiplets are observed in the ^{19}F MAS NMR spectra, which arise from J-coupling and residual dipolar coupling between the ^{19}F and ^{93}Nb nuclei. Using the known values of C_Q and η obtained from the ^{93}Nb NMR spectra, simulation of the ^{19}F MAS NMR spectra yield the values of $1J$ (^{93}Nb, ^{19}F) and δ_{iso}.(^{19}F), the sign of C_Q, as well as the relative orientation of the EFG tensor and the dipolar vector. Similar methods were used to study a variety of disordered oxyfluorides and the effect of temperature on C_Q in a series of ferroelastic materials was investigated.

1. *M. Eden, Y. K. Lee and M. H. Levitt, J. Magn. Reson. 1996, 120, 56.*
2. *T. Charpentier, C. Fermon and J. Virlet, J. Magn. Reson., 1998, 132, 181.*

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271. ***Se NMR MEASUREMENTS ON EXCEPTIONAL SE-AS GLASSES.*** Birgit Effey, Ohio University, Department of Physics & Astronomy, Athens, OH 45701; J. R. Sachleben, Solid-State NMR Facility, The Ohio State University, Columbus, OH 43210; D. A. Drabold, Ohio University, Department of Physics & Astronomy, Athens, OH 45701; R. L. Cappelletti, Ohio University, Department of Physics & Astronomy, Athens, OH 45701

^{77}Se NMR measurements on two binary, covalent $Se_{(1-x)}As_x$: Nd_2S_3 glass systems display some remarkable T_1 relaxation phenomena. The glasses were doped with approximately 1000 ppm of Nd_2S_3. For x = 0.4 all selenium atoms in the glass network relax at the same rate confirming the fact that the dopant does not influence the network topology. In the As_3Se_2 alloy (x=0.6), two distinguishable selenium sites with different relaxtion rates are observed. This behavior suggests that higher arsenic concentration glasses contain dynamically isolated molecular units within the glass network which may represent departures from network connectivity. We present supporting neutron inelas-

tic scattering data which show sharp modes in the vibrational density of states of As_2Se_2. Furthermore, aiMD calculations and additional evidence are provided to support the idea of dynamically isolated molecular clusters in Se-As glass.

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272. ***PHOSPHORUS CHEMICAL SHIFT TENSORS FOR TETRAMETHYLDIPHOSPHINE DISULFIDE—A ^{31}P SINGLE CRYSTAL NMR, DIPOLAR—CHEMICAL SHIFT NMR AND Ab INITIO STUDY.*** Myrlene Gee, Roderick E. Wasylishen and Klaus Eichele, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J3; James F. Britten, McMaster University, Hamilton, Ontario, Canada, LOS 4M1.

Phosphorus chemical shift tensors have been characterized for tetramethyldiphosphine disulfide (TMPS) by analysis of ^{31}P NMR spectra obtained at 4.7 T for a large single crystal. In addition, ^{31}P CP NMR spectra of stationary powder samples have been acquired and analyzed using the dipolar-chemical shift method. A 2D spin-echo NMR spectrum was also obtained to independently determine the effective dipolar coupling constant. The crystal structure of TMPS (space group C2/m) consists of six molecules per unit cell. In two of the six molecules, the two phosphorus nuclei are related by an inversion centre (site 1), while the remaining four molecules possess mirror planes containing the S-P-P-S bonds (site 2). The differences between the two sites are very subtle, as revealed by a redetermination of the X-ray crystal structure. The phosphorus chemical shift tensors obtained from both single crystal and dipolar-chemical shift NMR are in excellent agreement. For site 1,
δ_{11} = 90.6 ppm, δ_{22} = 74.9 ppm, and δ_{33} = -63.2 ppm. The results for site 2 are very similar. The phosphorus chemical shift tensors for both sites are oriented such that the most shielded components are close to the P-S bond while the least shielded components are perpendicular to the plane containing the S-P-P-S bonds. Ab initio (RHF) calculations for the phosphorus chemical shift tensors of site 1 accurately reproduce the experimental line shape as well as the orientation; however, the calculated isotropic chemical shift is too shielded.

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273 ***APPLICATIONS OF TOROID CAVITY NMR DETECTORS TO METALS, POLYMERS, RADIOACTIVE MATERIALS, AND SUPERCRITICAL FLUIDS.*** Rex E. Gerald II, David E. Fremgen, Luis H. Nuñez, Donald T. Reed, Robert J. Klingler, Jerome W. Rathke, Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439-4873, USA; Klaus Woelk, University of Bonn, Institute of Physical and Theoretical Chemistry, Wegelerstr. 12, D-53115 Bonn, Germany

A nuclear magnetic resonance (NMR) detector in the form of a toroid coil minimizes electromagnetic coupling to external metal surfaces because the field flux is largely contained within the coil. The high degree of flux confinement allows the toroid coil to be used effectively for high pressure/temperature NMR studies in small-diameter pressure vessels[1]. A toroid cavity is a continuous form of the toroid coil. That is, while the toroid coil consists of coil turns that are wound in series, a toroid cavity consists of a canister with a central conductor, such that an infinite number of coil turns appear to be wound in parallel. The toroid coil is a high inductance device similar to a solenoid, while the toroid cavity is a very low inductance device. The inverse-distance dependence of the radiofrequency magnetic field (B_1) in the toroid cavity can be used to record one-dimensional radial concentration profiles of samples placed in the cavity volume. The rotating-frame imaging technique introduced by Hoult in 1979 is the basis for recording these radial images. One-dimensional radial images were reported for a series of radially-disposed capillary tubes and a thin polymer film[2]. A thorough analysis of the B_1 gradient in the toroid cavity was reported and demonstrated very good agreement with experimental results.[3] The application of a single radiofrequency pulse in a toroid cavity detector modulates the alpha and beta nuclear spin states, thus spin-labeling the molecules across the radial dimension. Stochastic and coherent molecular displacements scramble this labeling, and analyses of the data gives diffusion and other transport numbers.[4] The cylindrical geometry and central conductor of the toroid cavity detector make it suitable for in situ NMR studies of electrochemical systems, wherein a static electric field in the radial direction is applied to effect ion transport in the bulk phase and oxidation/reduction reactions at metal interfaces[5]. In this presentation, several applications of the toroid cavity detector will be discussed. NMR investigations of the surface layer of bulk metals was accomplished by incorporating each metal sample into the toroid cavity as the central conductor. NMR spectra of ^{7}Li and ^{57}Fe were recorded for an Al-Li alloy and iron, respectively. The capability of the detector for imaging broad inhomogeneous resonances, such as quadrupole powder patterns in excess of 80 kHz, is demonstrated for ^{7}Li nuclei in a polymer electrolyte system. The application of the toroid cavity for ^{133}Cs analysis in radioactive samples will be discussed. Finally, NMR studies of reverse micelles in supercritical CO_2 demonstrate the unique capabilities of the toroid cavity imager for investigating the evolution of these initially heterogeneous systems. 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.

1. *J. W. Rathke, J. Magn. Reson., 1989, 85, 150.*
2. *K. Woelk, J. W. Rathke, R. J. Klingler, J. Magn. Reson. A, 1993, 105, 113.*
3. *K. Woelk, J. W. Rathke, R. J. Klingler, J. Magn. Reson. A, 1994, 109, 137.*
4. *K. Woelk, R. E. Gerald II, R. J. Klingler, J. W. Rathke, J. Magn. Reson. A, 1996, 121, 74.*
5. *R. E. Gerald, R. J. Klingler, J. W. Rathke, G. Sandí, and K. Woelk, Chapter 9 of Spatially Resolved Magnetic Resonance, Eds., P. Blümler, B. Blümich, R. Botto, and E. Fukushima, Wiley-VCH, New York, pp. 111-119 (1998).*

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274. *DISTRIBUTION OF CRYSTALLINE AND AMORPHOUS POLYMER ELECTROLYTE IN AN ELECTROCHEMICAL CELL.*

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The phase diagrams of many polymer electrolytes indicate regions that are composed of amorphous and crystalline solids. In the polymer electrolyte $LiN(SO_2CF_3)_2$*/PEO the crystalline phase is a helical structure with the stoichiometry* $PEO_3\ LiN(SO_2CF_3)_2$*. This phase does not contribute to ionic conductivity and, therefore, is considered a chemical-phase bystander. Since this crystalline phase can coexist in (metastable) equilibrium with the ionic-conducting amorphous phase, it is desirable to understand what fundamental role it plays in performance characteristics of the polymer electrolyte. For example, how rapidly will the crystalline phase dissolve in response to a change in lithium ion concentration in the amorphous phase brought about by cell polarization? What is the ion mobility in the interfacial phase? Does the ratio of crystalline to amorphous phases change in the regions adjacent to the electrodes due to changes in the chemical potential at the electrode-electrolyte interface? In order to answer these questions it is necessary to record spatial maps of the chemical components that constitute the crystalline and amorphous phases of a polymer electrolyte throughout a charge/discharge cycle in an electrochemical cell. We utilized a device called the near-electrode imager to perform in situ analyses of electrochemical systems, under operating conditions, by nuclear magnetic resonance (NMR) spectroscopy and magnetic resonance imaging (MRI). This NMR device was used in the traditional manner of a conventional NMR probe to record high-resolution and wideline NMR spectra; however, because it is also an imaging device, it has the capability to correlate NMR parameters such as chemical shift (δ) and spin-lattice relaxation (*T_1*) with a spatial dimension, namely the dimension directed radially from the central conductor/electrode. We will present the first radial concentration profiles for the* $^7Li^+$ *cations in the crystalline and amorphous phases of* $LiN(SO_2CF_3)_2$*/PEO in the region adjacent to the working electrode at different stages of cell polarization. An analysis of this data provides insight into the mechanisms for ion transport in an actual concentration gradient in contradistinction to measurements in a series of homogeneous samples of different concentrations. 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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275. *ROTATIONAL SIDEBAND SEPARATION AT HIGH SPINNING SPEEDS: APPLICATIONS TO* ^{207}Pb*,* ^{139}La *AND* ^{93}Nb *NMR.*

James M. Gibson; Frederick G. Vogt; David J. Aurentz; Alan J. Benesi; Karl T. Mueller, 152 Davey Lab, Pennsylvania State University, Department of Chemistry, University Park, PA 16802-6300

The phase-adjusted spinning sidebands (PASS) experiment is a useful technique for simplifying NMR spectra that contain overlapping or complicated spinning sideband manifolds. The sequence separates spinning sidebands by order in a two-dimensional experiment. A sheared projection of the 2-D spectrum effectively yields an "infinite spinning speed" spectrum, with no overlapping sidebands[1]*. The 2-D PASS experiment was designed for slower MAS speeds of 3-5 kHz, which is reasonable for* ^{13}C *spectroscopy. In the case of nuclei such as* ^{207}Pb*, the large chemical shift anisotropy yields too many spinning sidebands to be handled by a typical 2-D PASS experiment. The use of higher spinning speeds leads to a requirement for fewer 2-D rows and a correspondingly shorter experimental time. Therefore, we have designed PASS pulse sequences that occupy several MAS rotor cycles, and are intended for use in high speed situations such as those required by* ^{207}Pb*. The sequences optimize the spacing between RF pulses, and also avoid many problems associated with the spinning speed approaching the RF power. These sequences are demonstrated on numerous test compounds and will be useful in obtaining information about a variety of lead glasses. Another experiment, quadrupolar PASS (QPASS), has also been developed for the analysis of second-order quadrupolar sidebands observed in MAS spectra of quadrupolar nuclei*[2]*. In the case of quadrupoles, the infinite spinning speed spectrum provides a simplified spectrum that still contains measurable quadrupolar parameters. Multiple-rotor-cycle QPASS experiments were designed*[3] *and have been demonstrated on the chemically interesting* ^{139}La *and* ^{93}Nb *nuclei.*

1. *Antzutkin et al., J. Magn. Res., 1995, 115A, 7-19*
2. *Massiot et al., Chem. Phys. Lett., 1997, 272, 295-300*
3. *Aurentz et al., J. Magn. Res., 1999, 138, in press*

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276. *TIN COMPOSITE OXIDE ANODE MATERIALS AS PROBED BY MULTINUCLEAR NMR, DIFFRACTION AND X-RAY ABSORBTION SPECTROSCOPY.*

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Our research on tin- composite-oxide (TCO) electrodes for lithium ion batteries such as $Sn_{1.0}Al_{0.4}B_{0.56}P_{0.4}O_{3.6}$*, patented recently by Fuji, and the parent tin oxide SnO, has provided several new insights into these systems. To investigate these anodes, we have used multinuclear solid state NMR (* $^{6,7}Li$*, 27Al, 31P and 11B), concurrently with X-ray absorption spectroscopy (XAS) at the Sn edge, and X-ray diffraction including analysis of the radial distribution function (RDF) using a direct Fourier transform method. The 6,7Li NMR shows there is no Knight shift at any point during the discharge/charge process, which would correspond to the formation of a true alloy. Instead a small shift to higher frequency is observed, on the order of 10ppm. We attribute this to the formation of nanophase Li-Sn-O clusters, in which both small particle size and intimate contact with the oxide matrix mediate the Knight shift. Most significant among these findings has been the role of oxygen in the cyclablity of the battery. Corroborating this interpretation is the RDF data from both XAS and direct diffrac-*

tion techniques, which show that Sn-O bonds are broken and reformed reversibly during cycling. The roles of the Al, P and B within the tin-composite-oxide glass are also significant. These ions participate reversibly in the electrode processes; contributing to the flexibility oxide matrix. Density of states calculations on the thermodynamically stable lithium-tin will be compared with those obtained on smaller clusters in an attempt to understand the factors governing the observed lithium NMR signals.

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277. *PASSIVE-SHIMMING DESIGNS OF TOROID CAVITY PROBES USING SPECTRAL DISTORTION PARAMETERS.*

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The distortion of the NMR frequency spectrum due to induced magnetic field distortions is dependent upon the geometric distribution of susceptibility mismatches relative to the detection volume of the NMR probe. Often, this spectral distortion can be of the same order of magnitude as the susceptibility mismatch (ppm) and may inhibit the use of some probe geometries in high-resolution NMR studies. One such probe, the toroid cavity detector, has been presented[1] as a probe that is suitable for illustrating and, under certain conditions, verifying an iterative integral equation technique[2] that calculates B_0 field inhomogeneities. The Spectral Dispersion Function (SDF) can then be estimated from volumetric samples of field distortion using a histogram technique. In this study, characterization of the first and second moments of the estimated SDFs (spectral shift and spectral spread, respectively) have been used for evaluating different toroid probe designs. The full width at half-height (FWHH), width at 10% of peak maximum, range of dispersion, and spectral symmetry, were calculated. Field distortions and SDFs were calculated for copper toroid probes filled with liquids of different susceptibilities. Additionally, calculations were done for different dimensions of the inner cavity, outside surfaces, and so-called passive shimming features were varied in order to find toroid probe geometries that gave favorable results for the parameters listed above. Estimated values for spectral spread ranged from 0.1 to 1.0 ppm depending upon the susceptibility of the contents and the proximity and geometry of the susceptibility mismatch boundaries. Values of FWHH ranged from 0.01-0.25 ppm, which corresponded to previously published values in the literature[3]. Spectral features near the baseline were observed to extend over larger ranges, 5.0 ppm or more in some extreme cases. Data was collected on a toroid probe with a sample volume of the same dimensions as a standard 10-mm probe, which were considered in the computations discussed above. Comparisons of computed results to experimental data and to industry-standard specifications on resolution and lineshape for other probes will be presented. 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.

1. *E. Growney et al., The 40th ENC, Orlando, FL, Feb. 28 to Mar 5, 1999*
2. *E. Growney, G. Friedman, and R. Gerald, J. Appl. Phys., 85(8): 1-3, April, 1999.*
3. *K. Woelk, J. Rathke, and R. Klingler, J. Magn. Reson. A 109, 137-146 (1994).*

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278. *SOLID STATE NMR STUDY OF MOLECULAR MOTION IN HEXAKIS(TRIFLUOROMETHYL)BENZENE.*

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The symmetrical molecule, hexakis(trifluoromethyl)benzene, is the perfluoro analogue of hexamethylbenzene, HMB. Unlike HMB, which undergoes both methyl group rotation and rotation about the sixfold molecular axis at room temperature, the fluoro analogue participates in neither motion at room temperature, as shown by ^{19}F T_1 measurements. The molecule undergoes a solid/solid phase transition near 50°C, to a state that appears amorphous by single crystal x- ray diffraction. Transition to the high temperature state is accompanied by the onset of molecular motion which we are investigating by non-spinning, variable temperature ^{13}C NMR. Our NMR, differential scanning calorimetry (DSC) and powder x-ray results will be presented. This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-960R22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

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279. *SOLID-STATE NMR ANALYSIS OF SEMICONDUCTOR CLUSTERS AND THIN FILMS.*

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Semiconductor clusters and thin films have been prepared by ultra-high vacuum techniques. These materials have garnered considerable interest because they generally exhibit novel electronic and optical properties (e.g., enhanced quantum efficiency of luminescence). The production of clusters with well-defined structures and minimal surface contamination, which may profoundly affect the physical properties of these materials, has been a major obstacle in the investigation of these compounds in the past. We have synthesized clusters of GaAs and *alkali metal doped silicates and are studying their structures by solid-state NMR. Essentially, we are looking for size-dependent effects, to see how NMR parameters such as chemical shift, T_1, and T_2 scale with the size of the clusters. In addition, we plan to use NMR to discriminate between groups on the surface and those in the interior of the cluster.*

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280. ***SURFACE AND DEFECT CHARACTERISATION BY ^{27}AL NMR AND PALS OF INTERMEDIATE PHASES FORMED DURING CALCINATION OF GIBBSITE, AL(OH)$_3$, TO CORUNDUM, α-AL$_2$O$_3$.*** Anita J.Hill, Timothy J.Bastow and Steven Celotto, CSIRO Manufacturing Science and Technology, Private Bag 33, South Clayton MDC, Victoria 3169, Australia

The conversion of gibbsite to corundum has been studied in 100°C calcination stages by ^{27}Al NMR, positron annihilation lifetime spectroscopy (PALS), differential thermal analysis (DTA), XRD and gas-sorption surface area measurement (BET). NMR and PALS measurements were performed at ambient laboratory conditions (22°C and 50% relative humidity). The concentration of AlO$_4$ sites that appear when the transition aluminas form has been measured as a function of calcination temperature by ^{27}Al NMR. This data has been correlated with measurements on the same set by PALS, which detects isolated defects, extended defects and surfaces via the three principal positron annihilation lifetimes and associated intensities τ_i, I_i , and XRD. In particular the value of t1, attributed to point defects, exhibits an abrupt decrease after 800°C which mirrors the transformation of the g-alumina phase, in which 1/3 of the tetrahedral sites in the cubic spinel structure are vacant, to the briefly stable penultimate δ-,θ-alumina phases, and then finally to α-alumina (corundum). While the XRD data show an abrupt transition from gibbsite to boehmite (AlOOH), for the 100°C calcination steps used here, NMR detects ~10% AlO$_4$ sites (attributed to χ-alumina) during the formation of boehmite in which there is only AlO$_6$. The presence of χ-alumina is not efficiently detected by XRD in the presence of a dominant concentration of well ordered, crystalline boehmite. The high pressure hydrothermal processes which accompany the gibbsite→boehmite transition cause a sudden increase in specimen surface area which is mirrored in a sharp peak in I_3 at 300°C. A subsequent peak in I_3 at 500 C correlates well with a secondary peak in the surface area data at this temperature, and an abrupt increase in AlO$_4$ content consequent on the formation of g-alumina. The temperature at which a second step appears in the plateau region of the τ_3-T plot corresponds to the calcination temperature beyond which rehydration does not occur on cooling to room temperature. The positronium surface probe (τ_3, I_3) gives a relative measure of the total (internal and external) surface are of the specimen; such data is important when determining optimum support characteristics for catalytic applications.

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281. ***STOCHASTIC WIDELINE NMR SPECTROSCOPY—ADVANTAGES, PROBLEMS AND SOLUTIONS.*** Ole Hirsch, Friedrich Schiller University Jena, Institute for Optics and Quantum Electronics, Division for High Frequency Spectroscopy, Max-Wien-Platz 1, D-07743 Jena, Germany; Frank Weingarten, Rheinisch-Westfälische Technische Hochschule Aachen, Institute of Technical and Macromolecular Chemistry, Worringer Weg 1, D-52076 Aachen, Germany

Noise excitation is an alternative way for measuring wideline NMR spectra of solids.This methode is well known for high resolution liquid state investigations [1]. Only a few groups published experimental results for solid state NMR so far [2], [3] . Stochastic excitation should excellent suitable in wideline spectroscopy due to a number of inherent properties: —Uniform excitation of large spectral regions is easy to perform. —Quantitative spectra of quadrupolar nuclei can be measured [3]. —In contrast to slow passage spectroscopy it keeps the multiplex advantage. —Echo experiments are not necessary to avoid deadtime problems. But stochastic wideline spectroscopy has actually also its own problems: —Because of receiver-recovery times it's not possible to use any small dwelltime.

—The first points of the calculated FID signal may be disturbed. If they are lost, the fourier transform results in a disturbed spectrum .—The finite length of the excitation sequence causes switch-on disturbances. The lecture starts with a short introduction to the principles of Stochastic NMR Spectroscopy. Possibilities and problems are illustrated with measured spectra of different solids. These are for instance static powder spectra of perdeuterated dimethyl sulphone and sodium tripolyphosphate, and the magic angle spinning spectrum of yttrium aluminum garnet. To overcome the named problems, hardware modifications and signal processing methods are presented and discussed [4]. Additionally, a short outlook to future developments will be given. Supported by Ja 552/13-1 (Jena) and Bl 231/21-1 (Aachen) German Research Foundation

[1] B.Blümich in "Progress in Nuclear Magnetic Resonance Spectroscopy", 1987, 19, 331.
[2] G.L. Hoatson and B. Blümich, J. Magn. Reson. 1991, 95, 446.
[3] Ming-Yuan Liao, Benjamin G.M. Chew, David B. Zax Chem. Phys. Letters, 1995, 242, 89.
[4] D.-K. Yang and David B. Zax, J. Magn. Reson., 1998, 135, 267.

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282. *SOLID-STATE ^{25}Mg AND ^{93}Nb NMR STUDIES OF THE FORMATION OF LEAD MAGNESIUM NIOBATE PB(MG$_{1/3}$NB$_{2/3}$)O$_3$.*
J. Huang, S. Prasad, J. Shore and J J. Fitzgerald, Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007, H. Lock and G. B. Maciel, Department of Chemistry, Colorado Stat University, Fort Collins, CO 80523

Solid-state ^{25}Mg and ^{93}Nb MAS NMR investigations of the atomic-level changes occuring in the local Mg(II) and Nb(V) B-site chemical environments in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) perovskite and related lead niobate pyrochlores formed during the solid-state synthesis of PMN are reported. ^{93}Nb MAS NMR spectra of complex PMN powders containing different PMN (perovskite/pyrochlore) phase contents, several lead niobates and a low-Mg content PMN pyrochlore were measured at 9.4 and 14.1 Tesla The ^{93}Nb MAS NMR spectra, chemical shift and quadrupolar parameters, together with XRD measurements, have provided atomic-level information about both the short- and long-range structural changes occurring during the formation of polycrystalline PMN. Additional ^{25}Mg and ^{93}Nb MAS NMR investigations are reported for PMN materials prepared at different reation temperatures by the mixed oxide reaction, and at different MgNb$_2$O$_6$/PbO ratios by the columbite reactoin sequence. These ^{25}Mg and ^{93}Nb NMR results provide unique insights into the pyrochlore → perovskite phase transition that occur during the formation of PMN. These solid-state NMR results, together with XRD and SEM measurements, are being used to develop solid-state structural models for transformations important to the conversion of lead niobates and magnesium niobates into the different local Mg(II) and Nb(V) B-sites formed in the Mg(II)-rich and Nb(v)-rich nanodomain regions for PMN of the perovskite structure.

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283. *SOLID-STATE ^{13}C NMR INVESTIGATION OF RING-FLIPPING DYNAMICS OF BENZYL-ETHER DENDRITIC MACROMOLECULES.* Joseph S. H. Huang and Christopher A. Klug, Stanford University, Department of Chemical Engineering, Stanford, CA 94305

Dendrimers are branched polymers that are highly controlled in architecture. These macromolecules have branch points at each repeat unit so that the number of end groups in each successive layer doubles. Due to the highly controlled nature of the system, their potential applications range from drug-delivery vehicles to low-κ dielectric materials, but their behavior in the solid state is still largely unexplored. We used solid-state ^{13}C NMR to probe the dynamics of the benzyl-ether dendritic system. Investigations of the ^{13}C T_1 relaxation behavior of the dendrimer show that multi-exponential relaxation behavior occur for the carbons associated with the outer rings. Measurements of the ^{13}C $T_{1\rho}$ relaxation also show multi-exponential decay for these same carbons, suggesting cooperative motion in the range of tens of kHz in addition to the hundreds of MHz behavior seen in the T_1 relaxation. Finally, Dipolar Rotational Spin-Echo (DRSE) was used to measure ^{13}C-^{1}H dipolar coupling for protonated carbons of outer rings. From comparisons to simulations, we have determined that the outer rings are undergoing 180° flips. Future work will focus on studying the effects on ring dynamics of blending these materials with linear polymers.

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284. *SOLID-STATE ^{1}H AND ^{29}Si NMR STUDIES OF HYDROGEN-LOADED AND ULTRAVIOLET-IRRADIATED OPTICAL FIBER MATERIALS.* Margaret Hubbard, Erin Gill, and Sarah Gilbert, National Institute of Standards and Technology, Optoelectronics Division, Boulder, CO 80303; Jincheng Xiong, Herman Lock, and Gary E. Maciel, Colorado State University, Department of Chemistry, Fort Collins, CO 80523

Fiber Bragg gratings are wavelength-selective devices which are becoming increasingly important for routing optical signals in a variety of telecommunications systems. Fiber gratings are produced by exposing a single-mode optical fiber with a germanosilicate core to an interference pattern of highly focused ultraviolet light, creating a permanent spatial modulation of the core refractive index along a few centimeters of the fiber. By immersing the fiber in a high-pressure hydrogen atmosphere prior to the uv exposure, the refractive index modulation of the grating may be increased by an order of magnitude from its typical value in an unloaded fiber. However, the exact bonding and structural changes that result from uv exposure, especially in the case of hydrogen-loaded materials, are still not well understood. We have carried out ^{1}H CRAMPS experiments on hydrogen-loaded and uv-irradiated germanosilicate fiber preform materials to identify the hydrogen-related species formed during uv exposure. Three peaks with distinctly different relaxation times (T_1, $T_{1\rho}$, and T_2) can be identified from the ^{1}H CRAMPS spectrum. We also present ^{29}Si spectral data from single-pulse and ^{1}H - ^{29}Si CP/MAS experiments performed on similar materials.

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285. *DEVELOPMENT OF VARIABLE-TEMPERATURE ISOLATED FLOW AND LARGE SAMPLE VOLUME MAS NMR PROBES FOR HETEROGENEOUS CATALYSIS STUDIES.* Lauren E. Kaune, Paul K. Isbester and Eric J. Munson, Department of Chemistry, Smith Hall, University of Minnesota, Minneapolis, Minnesota 55455.

Two limitations of current NMR studies of heterogeneous catalysis are the inability to accurately emulate a typical industrial reactor, and the necessity of using labeled reactants to observe signals on low and medium surface area materials. We are developing an isolated flow VT MAS NMR probe to enable simultaneous observation of events occurring on a surface with characterization of the effluent using an external analytical instrument. Utilizing ceramic bearings and baffles we have achieved isolation of drive, variable-temperature (VT), and flow gas streams at spin rates in excess of 2 kHz and we have reached temperatures greater than 300°C. This high-temperature capability *allows observation of heterogeneous catalysis in situ. Currently we are investigating the reactions of methanol on zeolite catalyst HZSM-5. We have observed methanol (99.5% ^{13}C) convert to dimethyl ether under batch reaction conditions and under continuous flow conditions at 200°C. There is a significant difference in the species observed. Under batch conditions, both methanol and dimethyl ether are observed, but under flow conditions, only dimethyl ether is detected. Currently we are monitoring this process with two-dimensional exchange NMR to gain information about reaction intermediates. In the future we plan to study the conversion of methanol to gasoline (MTG) using this technique and add external analysis via an online GC to obtain information about reaction intermediates. We are also developing a large sample volume MAS system to increase sensitivity of NMR studies of catalysts and materials. Ceramic bearings are used to support the rotor. Preliminary studies suggest that speeds of >2 kHz can be achieved using a sample volume of 30 mL.*

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286 ***SOLID-STATE NMR STUDIES OF TRI-P-TOLYLAMINE/POLYCARBONATE BLENDS.*** Brian Kesling, Eric Hughes, and Terry Gullion, Department of Chemistry, West Virginia University, Morgantown, WV 26506

Tri-p-tolylamine forms a miscible blend with polycarbonate to form a molecularly doped polymer. Tri-p-tolylamine is a charge-transporting molecule and is a member of a class of organic compounds that, when blended with polycarbonate, are important in xerography and other photoconducting technologies. The structural aspects of the blend are not well known because of the amorphous nature of the material. Results of various blends of tri-p-tolylamine and polycarbonate studied by ^{13}C-^{14}N REAPDOR and ^{13}C-^{2}D θ-REDOR are presented. The ^{2}D experiment shows that the amine molecules are in intimate contact with the polymer, but the ^{14}N experiment suggests that the nitrogen is far from the polymer. These results are consistent with a previously proposed model where the tri-p-tolylamine molecules form stacks within the polycarbonate matrix. Supported by NSF CHE-9796188 and the Petroleum Research Fund.

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287. ***^{87}Rb MAS AND MQMAS NMR STUDIES OF HIGH TEMPERATURE PHASE TRANSITIONS IN LiRBSO$_4$.*** Hae Jin Kim, Marek Pruski, Jerzy W. Wiench, Ames Laboratory, Iowa State University, Ames IA 50011; Sung Ho Choh, Department of Physics, Korea University, Seoul 136-701, Korea.

Magic angle spinning (MAS) and multiple-quantum (MQ) MAS spectra of ^{87}Rb were measured between 373 K to 490 K to investigate the phase transition phenomena in crystalline LiRbSO$_4$, which is a high temperature superionic conductor. The temperature dependence of the quadrupole coupling constant, asymmetry parameter and the spin-lattice relaxation time clearly show the discontinuities near the temperatures at which the phase transitions occur. The spin-lattice relaxation in the slowing-down region of the paraelectric-ferroelectric phase transition yields a dielectric polarization. In the disorder-incommensurate phase transition, the phase transition mechanism is due to the direct one-phonon process through the condensation of a soft phonon mode. The ^{87}Rb MQMAS spectra revealed the temperature dependence of the isotropic shift that could not be detected by the MAS technique alone.

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288. ***SOLID-STATE ^{19}F NMR STUDY OF MOLECULAR DYNAMICS OF PFPE LUBRICANT FILMS ON AMORPHOUS CARBON SURFACES.*** Yoojin Kim and Christopher A. Klug, Stanford University, Department of Chemical Engineering, Stanford CA 94305

Perfluropolyether lubricants are used to decrease dynamic friction as well as static friction during head-disk contacts in today's hard disk drives. Increasing growth in storage densities places great demands on the performance of these lubricants. Mobility of molecularly thin Zdol 2000 ($HOH_2CF_2C(OC_2F_4)_p(OCF_2)_qOCF_2CH_2OH$, $p/q = 0.7$, $M_w/M_n = 1.5$, $MW = 2000$) on amorphous carbon was studied via ^{19}F NMR. The spin-spin relaxation time (T_2) decreases and the linewidth increases with decreasing Zdol coverage, while the spin-lattice relaxation time (T_1) is constant as the coverage of Zdol is varied. This indicates that motions of the molecules in the kHz range are restricted but those in the MHz range unaffected as the coverage decreases. To gain further insights (e.g. activation energy) into the mobility of the molecules, variable temperature relaxation measurements were performed as a function of Zdol coverage and polydispersity.

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289. ***A 380 MHZ GYROTRON-BASED DNP SPECTROMETER.*** Kenneth E. Kreischer, Christian T. Farrar, Robert G. Griffin, Richard J. Temkin and Jeffrey R. Vieregg, Plasma Science and Fusion Center and Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139.

We are presently constructing a 380 MHz spectrometer suitable for dynamic nuclear polarization (DNP) studies. This research is motivated by our DNP experiments at 211 MHz in which enhanced magic angle spectra (MAS) of the protein T4 lysozyme were obtained using a 140 GHz gyrotron as the microwave source. In those experiments, we achieved enhancements at 55 K of ~50±15 in 15N spectra which reduces signal *averaging times by ~2500. This dramatic increase in signal strength permits structure/function studies of macromolecules with molecular weights of 105 Da or greater. We are presently extending this technique to higher fields where the resolution and sensitivity will be further improved. The critical factor that has impeded the extension of DNP research to higher frequencies has been the lack of microwave sources with adequate power. We have recently overcome this problem with the successful development of a compact, 250 GHz cw gyrotron that has operated reliably at powers up to 25 watts. This fundamental free-running gyrotron oscillator operates in the TE-031 mode, and utilizes a 12 kV, 50 mA electron beam to generate the microwaves. The gyrotron can run for many hours with a power stability of ±2%, and has shown no signs of degradation. The bandwidth was measured to be 150 kHz FWHM. An internal quasi-optical mode converter converts the TE-031 cavity mode into a Gaussian rf output beam about 1 cm in diameter. A quasi-optical transmission line will be used to efficiently couple this microwave power from the gyrotron into the cavity holding the sample. We are presently completing the 380 MHz spectrometer and will soon initiate DNP studies. This spectrometer will consist of a 125 mm bore, 9.0T NMR magnet with a ±1 T sweepable field, and DNP/MAS probes. We will compare enhancements achieved with both cylindrical and Fabry-Perot sample cavities.*

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290. *SOLID-STATE NMR STUDY OF EXCHANGED ZEOLITES.* Theresa A. Lalain, Karl T. Mueller, The Pennsylvania State University, 152 Davey Lab, University Park, PA 16802; D.E.W. Vaughan, Exxon Research and Engineering Company, Route 22 East, Annandale, N.J. 08801; James R. Fehlner, The Pennsylvania State University, Dunmore, PA 18512.

Zeolites are crystalline aluminosilicates that posses catalytic, ion-exchange and sorption properties. Many zeolites of interest contain a variety of cations (Li^+, Na^+, Cs^+). The ability to identify the cation locations and their interactions with the zeolite framework are of primary importance for many environmental and industrial applications. Solid-state NMR can be used to probe the different framework and cation environments, yielding structural and chemical information related to the absorption and exchange processes. Double-resonance NMR experiments are important in determining the through-bond connectivities or through-space proximities of the cations to the framework atoms. Double-resonance techniques such as transfer of populations via double-resonance (TRAPDOR) and rotational-echo double-resonance (REDOR) are used to provide information concerning the locations of the sorbed cations and their relationship to the aluminosilicate framework. Some of our ongoing studies to be presented include detailed measurements on: lithium and sodium exchanged dehydrated zeolite X; sodium LZ-105 loaded with different chlorododecane and bromododecane molecules, producing differences in catalytic properties in alkene production; cesium exchanged zeolites and FAU-EMT intergrowth materials, opening the possibility of using cesium for identification of the cage sizes within the intergrowth materials.

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291. *USING ^{27}Al, ^{31}P MAS AND ^{31}P/^{27} Al TRAPDOR NMR SPECTROSCOPIES TO STUDY SODIUM ALUMINOPHOSPHATE GLASSES.* David P. Lang and Todd M. Alam, Sandia National Laboratories, Dept. of Material Aging and Reliability, Albuquerque, NM 87185-1407

A series of glasses in the $Na_2O{\bullet}Al_2O_3{\bullet}P_2O_5$ (NAP) system were analyzed using solid state MAS NMR. NAP glasses have potential use in metal-glass seals, and variations in the local structure may provide insight into the different dissolution durabilities and thermal expansion coefficients observed for this series of glasses. Utilizing ^{27}Al and ^{31}P MAS NMR, along with ^{31}P/^{27}Al TRAPDOR experiments, qualitative and quantitative information about the backbone and modifier structure as a function of the mole percentage ^{27}Al and its coordination will be described. The transfer-of-populations-in-double-resonance, TRAPDOR, experiment allows for the detection of the dipolar coupling between, and therefore the proximity of, ^{31}P to ^{27}Al. Using a combined ^{1}H-^{31}P CP ^{31}P/^{27}Al TRAPDOR experiment, dissolution of the surface layer of glasses exposed to hydration can be directly probed, as the coordination of the water molecules to the glass framework, or their depolymerization of it, can be identified. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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292. *SOLID-STATE VANADIUM-51 NMR STUDIES OF DIOXOVANADATE(V) COMPLEXES.* Man-Ho Lee, Kyungpook National University, Department of Industrial Chemistry, Taegu 702-701, Korea; Shigenobu Hayashi, National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

Vanadium is widely recognized as a biologically important element. The interest in vanadium is increasing when it become apparent that vanadium is an endogenous component present in trace amounts in tissue of higher animals, and is essential for growth and development, as well as for the normal growth of mammalian cell in culture.[1] In 1980 a new interest in vanadium emerged when it was found that like insulin, vanadate increases hexose uptake and glucose metabolism in isolated rat adipocytes. Shortly after, vanadate was shown to mimic insulin in inhibiting lipolysis.[2] Recently the insulin-mimic properties of bis(maltolato)oxovanadium(IV) was reported.[3] We studied the structure of vanadate(V) complex by X-ray and NMR spectroscopies.[4,5] In the present study we synthesized several dioxovanadate(V) complexes and measured the chemical shift anisotropies and the quadrupolar coupling interactions from magic-angle-spinning(MAS) spectra of the powder solid samples. In the results the spectra showed large chemical shift anisotropy (-800 ~ -720 ppm vs. $VOCl_3$) and large quadru-

pole coupling constants (7.50 ~ 9.16 MHz) for vanadium atoms in the complexes.
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1. *Chasteen (ed.), "Vanadium in Biological Systems", Kluwer, 1990.*
2. *Degani et al., Biochem., 1981, 20, 5795.*
3. *McNeill et al., J. Med. Chem., 1992, 35, 1489.*
4. *Lee et al., Polyhedron, 1998, 17, 55.*
5. *Hayashi, Magn. Reson. Chem., 1996, 34, 791.*

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293. ***TOWARDS AN EXACT SOLUTION TO THE DIFFICULTIES IN REDOR FOR MULTIPLY COUPLED HETERONUCLEAR SPIN SYSTEMS.*** Oskar Liivak, Cornell University, Dept. of Physics, Ithaca, NY 14853; David B. Zax, Cornell University, Dept. of Chemistry and Chemical Biology, Ithaca, NY 14853.

Through its ability to measure internuclear distances, NMR spectroscopy has become a useful tool in the determination of molecular structure. In the solid state, Rotational Double Resonance (REDOR) has proven to be a very effective method for determining the distance between two dilute, different spin 1/2 nuclei (ie a dilute IS spin system). Unfortunately, a single distance does not uniquely define molecular structure and the spectroscopist would like to address the question of distance determination in a multiply coupled spin systems (ie $IS_1S_2\ldots S_N$ *spin systems). The standard REDOR experiment is not capable of unambiguous distance determination in a multiply coupled spin system. Gullion and Pennington's THETA-REDOR (Chem. Phys. Lett. 290 (1998) 88-93) is a successful approximate solution to these experimental difficulties. We present a methodology that suggests an exact solution to this problem. In addition this methodology is an exact solution for all spin systems of the type* $IS_1S_2\ldots S_N$ *even as N becomes large. Possible experimental hurdles such as the homonuclear dipolar interaction of the* $S_1S_2\ldots S_N$ *spins are explored. In addition, the usefulness of the methodology to other areas of NMR are considered.*

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294. ***ANALYSIS OF THE MULTIPLE QUANTUM CROSS POLARIZATION NMR EXPERIMENT FOR*** $^{19}F/^{23}Na$ ***AND*** $^{1}H/^{27}AL$ ***SPIN SYSTEMS IN SOLIDS.*** Kwang Hun Lim and Clare P. Grey, Department of Chemistry, SUNY Stony Brook, Stony Brook, NY 11794-3400, USA.

We have been investigating multiple quantum cross polarization (MQCP) between spin 1/2 and quadrupolar nuclei ($^{19}F/^{23}Na$*;* $^{1}H/^{27}Al$*), in order to develop more efficient spectral editing technique for MQMAS spectra. MQCP matching profiles as a function of the r.f. field strength of I=1/2 nuclei were obtained at various r.f. field strengths of quadrupolar nuclei and spinning speeds, for* $^{19}F/^{23}Na$ *and* $^{1}H/^{27}Al$ *spin systems. The MQCP matching profiles were very broad in comparison to single quantum CP matching profiles, under both static and MAS conditions. The MQCP NMR lineshape changes were also observed as a function of the r.f. field strength of I=1/2 nuclei. A physical picture is presented in order to understand the MQCP process qualitatively, by considering the orientation dependence of the nutation frequency associated with multiple quantum transition of quadrupolar nuclei. Numerical simulations using GAMMA[1] have also been performed, in order to investigate the molecular orientation dependence of the efficiency of the MQCP experiment.*

1. *S.A. Smith, T.O. Levante, B.H. Meier and R.R. Ernst, J. Magn. Reson., 1994, A106, 75.*

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295. ***EXPERIMENTAL INVESTIGATION OF THE POSSIBLILITIES OPEN BY RECENT SENSITIVITY IMPROVEMENTS OF THE QUADRUPOLAR MQ-MAS EXPERIMENT.*** Thomas Vosegaard, Pierre Florian, Valérie Montouillout, and Dominique Massiot; CNRS-CRMHT, F-45071 Orléans cedex 2, France.

Recently proposed schemes for sensitivity enhancement of the MQ coherence (MQc) excitation and MQc -> 1Qc reconversion in the quadrupolar MQ-MAS experiment,[1] e.g., by amplitude modulated[2,3] or composite[4] pulses are explored experimentally and numerically. We specially investigate the applicability of these improved sensitivity of these experiments to access quadrupoles normally associated with low MQc transfer amplitudes (e.g., ^{71}Ga*). We propose new pulse sequences that enable acquisition of pure-phase 2D spectra using amplitude-modulated conversion pulses.*

1. *Frydman and Harwood, JACS 117, 5367 (1995).*
2. *Kentgens and Verhagen, CPL 300, 435 (1998).*
3. *Madhu, Goldbourt, Frydman, and Vega, 40th ENC, Orlando, FL (1999). Poster MT096.*
4. *Marinelli, Medek, and Frydman, JMR 132, 88 (1998).*

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296. ***DETERMINATION OF INTERNUCLEAR DISTANCES FROM SOLID-STATE NMR: APPLICATIONS OF MONTE CARLO ERROR ANALYSIS TO REDOR DATA.*** Sue M. Mattingly, Fredrick G. Vogt and Karl T. Mueller, The Pennsylvania State University, Department of Chemistry, 152 Davey Laboratory, University Park, PA, 16802-6300; Leonard J. Mueller, University of California at Riverside, Department of Chemistry, Riverside, CA 92521

Numerous techniques have previously been developed in order to extract the dipolar coupling constants from Rotational Echo Double Resonance (REDOR) data. These spectra contain a level of uncertainty due to experimental noise present in the original signal but this error is difficult to estimate since performing multiple experiments is often labor-intensive. We have designed and implemented a computer program which will calculate values of the standard error present in the dipolar coupling constant from a single REDOR experiment. The algorithm is based upon a Monte Carlo (MC) Bootstrap Method[1] in which the NMR data are first characterized by a best-fit curve and the error is estimated by the pooling of multiple simulated data sets to which experimentally-determined noise has been randomly added. The MC error estimation method was applied to experimental REDOR data acquired from a glycine test sample containing 2-^{13}C, ^{15}N di-labeled glycine at 10% by weight in order to determine the dipolar coupling frequency between the C-N pair. The acquired time domain data were also subjected to Tikhonov Regularlization[2] and the REDOR Transform[3] prior to the characterization of uncertainty via MC error analysis. Multiple REDOR experiments were performed and the results of the standard error present in the experimental data were compared with MC error analysis. We also examined the behavior of the error estimates obtained by MC methods as the number of simulated data sets was modified.

1. *L. Mueller, Ph.D. Thesis. California Institute of Technology (1997), p. 89*
2. *F.G. Vogt, D. J. Aurentz and K.T. Mueller, Mol. Phys., 1998, 95, 907.*
3. *K.T. Mueller, T.P. Jarvie, D.J. Aurentz and B.W. Roberts, Chem. Phys. Let., 1996, 254, 281.*

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297. ***IDENTIFICATION OF HISTIDYL AND LYSYL RESIDUES AT A POTENTIAL ALLOSTERIC SITE OF RIBULOSE 1,5-BISPHOSPHATE CARBOXYLASE/OXYGENASE.*** Lynda M. McDowell, Washington University, Department of Chemistry, One Brookings Drive, St. Louis, MO 63130-4899; Joe S. Schriner, Kansas State University, Department of Biochemistry, Manhattan, KS 66506-3207 (current address: Procter & Gamble Manufacturing Company, 19th and Kansas Avenue, Kansas City, KS 66110); Karinne Cortes, Kansas State University, Department of Biochemistry, Manhattan, KS 66506-3207; Matthew E. Merritt, Washington University, Department of Chemistry, One Brookings Drive, St. Louis, MO 63130-4899 (current address: Department of Chemistry, University of Washington, Seattle, WA 98195); Jacob Schaefer, Washington University, Department of Chemistry, One Brookings Drive, St. Louis, MO 63130-4899; Delbert D. Mueller, Kansas State University, Department of Biochemistry, Manhattan, KS 66506-3207

Ribulose 1,5-bisphosphate carboxylase/oxygenase (Rubisco), a hexadecamer of 537 kDa comprised of 8 large and 8 small subunits, catalyzes the initial steps in both CO2 and O2 fixation during photosynthesis and photorespiration. Before Rubisco can catalyze either reaction, however, it must be activated by CO2. Activation by CO2 is strongly enhanced by effectors such as 6-phosphogluconate (6PGA). It is not known how 6PGA exerts its effect, but allosteric site binding is a possible mechanism. Accordingly, we have demonstrated the presence of potential allosteric sites by showing that 6PGA tightly binds comfrey Rubisco (Kd = 14 μM) even when the active site is blocked by the exchange inert inhibitor 2-carboxy-D-arabinitol 1,5-bisphosphate(CABP) (J.R. Shriner, et. al., Eur. J. Biochem., submitted). To help locate this site we have used rotational-echo double resonance (REDOR) NMR of 6PGA bound at pH 7.9 to 99%-U-15N- Rubisco complexed with CABP. The lyophilized samples contained either [1-13C]6PGA, unlabeled 6PGA, or no 6PGA. Nitrogen observe phosphorous dephase REDOR spectra of samples without 6PGA provided the REDOR difference spectra arising from active site Lys, His, and Arg residues in the proximity of the CABP phosphorous groups. Additional dephasing of Lys and His residues is observed when 6PGA is bound. This provides strong evidence that one or more Lys and His residues are near the 6PGA phosphate group when it is bound to the putative allosteric site. Carbon observe phosphorous dephase REDOR spectra of samples with [1-13C]6PGA bound, after correction for natural abundance dephasing using samples with unlabeled 6PGA, gave a [1-13C] to 6-P distance in bound 6PGA of 6.4 ± 0.1 ≈. Molecular models show the maximum value for this distance is 8.6 ≈ (Paul Smith, personal communication) which is also the distance found in crystals of sodium 6PGA grown from neutral pH solutions. Molecular graphic investigations utilizing the X-ray structure (I. Andersson, J. Mol. Biol. (1996) 259, 160-174) of the spinach Rubisco-CABP combined with the Lys and His distances derived from solid-state NMR of the comfrey enzyme have identified three promising 6PGA allosteric binding sites.

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298. ***HETERONUCLEAR 2D LOCAL FIELD NMR SPECTROSCOPY UNDER FAST MAS: PRINCIPLES AND APPLICATIONS TO ORGANIC SOLIDS.*** Dan McElheny, Enrico DeVita and Lucio Frydman; Department of Chemistry (M/C 111), University of Illinois at Chicago, Chicago, Illinois 60607-7061

The acquisition of 2D heteronuclear NMR local field spectra under moderately fast MAS and in the absence of multiple-pulse irradiation is discussed. It is shown both experimentally and with numerical simulations on multispin systems that as sufficiently fast MAS rates are employed (around 10-12 kHz for "real" organic solids), quantitative sideband patterns from directly bonded 13C-1H spin pairs can be obtained even in the absence of 1H-1H multiple-pulse decoupling. The processing of these data can include a renormalization-repetition *procedure applied to just a single rotor echo, which greatly reduces both the acquisition time and the effects of the residual H-H couplings. Local field line shapes obtained in these manner are thus free from scaling factors and can be easily used in the analysis of motional dynamics. Examples of this will be presented for model compounds as well as for synthetic liquid crystalline polymers, where the temperature dependence of the local field anisotropy was used to shed light on the nature of motional dynamics in both the intermediate- and fast-exchange regime. Additional investigations on the possibility of using the simple homonuclear decoupling afforded by this fast MAS procedure towards spectral editing will also discussed.*

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299. *DISTANCE MEASUREMENTS TO THE PHOSPHOSDIESTER BACKBONE OF NUCLEIC ACIDS USING SOLID-STATE NMR.* Matthew E. Merritt*; Gary A. J. Meints*; Snorri Th. Sigurdsson*; Gary P. Drobny*. *University of Washington, Department of Chemistry, Box 351700, Seattle, WA 98195-1700

With the increasing recognition of the importance of the phosphate backbone in nucleic acid structure and function, we became interested in applying solid-state NMR to the study of this region. We have used the rotational-echo double-resonance (REDOR) experiment to measure distances between nuclei within DNA and RNA (Gullion and Schaefer, J. Mag. Res. 1989, 81, 196). In particular, we have measured distances between ^{19}*F-labeled bases and chemically shifted* ^{31}*P backbone positions. As there is no resolution between backbone positions, it was necessary to incorporate a phosphorothioate at the appropriate position to chemically shift the phosphorous from the rest of the backbone background signal (Merritt, et. al. Submitted to JACS). Distance measurements within nucleic acids help to develop an understanding of the overall structure of these molecules.*

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300. *A SOLID-STATE DEUTERIUM NMR STUDY OF DNA METHYLTRANSFERASE BINDING SITES: EFFECTS OF METHYLATION ON BACKBONE AND FURANOSE RING DYNAMICS.* Gary A. J. Meints, University of Washington, Department of Chemistry, Box 351700, Seattle, WA 98195-1700; Karen B. Geahigan, 3M Specialty Materials Division, 3M Chemicals, 3M Center, Building 236-2B-11, St. Paul, MN 55125-1000; Mary E. Hatcher-Skeers, W. M. Keck Science Center, Claremont Colleges, 925 N. Mills Ave, Claremont, CA 91711; Gary P. Drobny, University of Washington, Department of Chemistry, Box 351700, Seattle, WA 98195-1700

Recently, interaction between the enzyme and the DNA backbone was implicated in the base-flipping mechanism of the M. HhaI methyltransferase (O'Gara, et. al. Nature Struct. Biol. 5, Oct. 1998, 872). Therefore it would be interesting to investigate the dynamics of the native DNA to determine what role they might play in the protein binding. In previous solid-state deuterium NMR work, it has been shown that there are unusual, large amplitude dynamics in both the furanose ring and backbone of the cytidine in the binding site of the EcoRI restriction endonuclease, -GAATTC- (Hatcher et. al. J. Am. Chem. Soc. 120, 1998, 9850). Base analog substitution of 5-methylcytosine in the binding site has been shown to inhibit binding and cleavage by the nuclease (Brennan et. al. J. Biol. Chem, 261, 1986, 7270). This substitution has also been shown to slightly alter the dynamics of the furanose ring of the cytidine, but it dramatically perturbs the dynamics of the backbone (Geahigan et. al. To be submitted). We decided to determine if analogous results could be observed in the HhaI system. Large amplitude motion has been observed in the furanose ring of the first cytidine in the HhaI binding site, -GCGC-, by solid-state deuterium NMR. Methylation at the 5 position in the first cytosine of this binding site, which is the target cytosine of the methyltransferase, also inhibits cleavage by the endonuclease (Kessler et. al. Gene, 33, 1985, 1). Our current work investigates the effects of methylation on motion in the cytidine furanose ring and backbone in the HhaI binding site.

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301. *FINITE PULSE WIDTHS AND INFINITE LINEWIDTHS: ECHO SHAPES AND RELATIVE INTENSITIES.* Joel B. Miller, Naval Research Laboratory, Code 6120, Washington, DC 20375-5342

We have been investigating magnetic resonance in very strong magnetic field gradients for materials detection and imaging. Detection of a magnetic resonance signal under such conditions requires the formation of an echo. We wish to select rf pulses to optimize the amplitude and / or spatial localization of the signal, however traditional methods of determining the pulse flip angle cannot be used on resonances of infinite linewidth. Here, I present simulations of echoes formed from resonances with linewidths much greater than the pulse excitation bandwidth, and show that the echo shape and the relative echo intensities in multiple-echo experiments can be used to determine the pulse flip angle. The simulations are compared to data acquired from samples in field gradients >>100 G/cm.

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302. *^{109}Ag NMR STUDIES OF SILVER-EXCHANGED ZEOLITES.* Igor L. Moudrakovski, National Research Council, Steacie Institute for Molecular Sciences (SIMS), Ottawa , Canada K1A 0R6; Christopher I. Ratcliffe, National Research Council, SIMS, Ottawa , Canada K1A 0R6; John A. Ripmeester, National Research Council, SIMS, Ottawa , Canada K1A 0R6.

Silver-exchanged zeolites, particularly AgA, AgY and AgX, are interesting materials for studies concerning the structure, transformation and reactive properties of small metal clusters. Their sensitivity to light and reversible oxidation/reduction properties make them potential candidates for novel optical and electronic materials. Interest in these compounds is also fuelled by the prominent catalytic activity of the silver. ^{109}Ag has a very low resonance frequency, and its sensitivity relative to protons is only10^{4}. Obtaining ^{109}Ag NMR is consequently a rather challenging task even for solutions, and it becomes even more difficult in the solid state. Because silver has a very broad range of chemical shifts (thousands ppm), the chemical shift anisotropy is also expected to be very large. Long spin-lattice relaxation times can also make measurements very difficult. Here we report the first ^{109}Ag NMR spectra of silver-exchanged A, X and Y zeolites. Dehydration of the zeolites in vacuum at different temperatures results in partial reduction of the lattice Ag^+ ions and produces several distinct materials. These transformations are reflected in the ^{109}Ag NMR spectra, and several characteristic signals were detected. Variations in the observed anisotropic signals are believed to be the result of differences in the local environment of silver atoms in the zeolites' framework. Interaction of the silver clusters with small molecules adsorbed in the structure of zeolites has also been observed by NMR. Assignment of the lines in the spectra in relation to composition and the location of the clusters will be discussed.

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303. *QUANTIFICATION OF PHOSPHORUS-CHALCOGEN BONDING PREFERENCES IN TERNARY PHOSPHORUS-SULFUR-SELENIUM GLASSES BY MULTIPLE-PHASE ^{31}P AND HIGH-TEMPERATURE ^{77}Se NMR.* Paul F. Mutolo, University of California at Santa Barbara, Department of Chemistry, Santa Barbara, CA 93106; Hellmut Eckert Institut für Physikalische Chemie, WWU, Münster Germany.

Systematic studies of melt-quenched glasses in the ternary phosphorus-sulfur-selenium system by multiple-phase ^{31}P NMR and variable high-temperature (VT) ^{77}Se NMR have afforded understanding of the structural features in this system. Investigation of the chemical bond distributions of these samples, especially in comparison to the two dissimilar binary systems, P-S and P-Se, has afforded quantitative results regarding phosphorus-chalcogen bonding preferences. Glasses in the P-S system are composed almost exclusively of P_4S_n molecular units, resulting in "zero-dimensional" type glasses also evidenced by low glass-transition temperatures (T_gs) of these samples. In contrast, P-Se glasses are much more polymeric, resulting from the efficient competition between four-coordinate $Se{=}PSe_{3/2}$ and three-coordinate $PSe_{3/2}$ groups. Five series of ternary P-S-Se glasses have been systematically studied by multiple-phase (solid, solution, and molten) ^{31}P NMR. Results reveal the tendency for these samples to phase separate into structures conforming to the bonding patterns of the two binary systems. This phase separation can be effectively explained by the preference for P-S over P-Se bond formation.

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304. *^{207}Pb AND ^{27}AL SOLID STATE NMR STUDIES OF LEAD-EXCHANGED ZEOLITES.* Heiko G. Niessen, Jeffrey A. Reimer, Alexis T. Bell, University of California, Berkeley, Department of Chemical Engineering, Berkeley, CA 94720-1462, USA; C. Dybowski, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716-2522, USA; David R. Corbin, DuPont Company,, Central Research and Development, Experimental Station, Wilmington, DE 19880-0262

The catalytic activity of various types of zeolites is well known and therefore their investigation is the subject of intense research. Zeolites are used in a wide variety of industrially important processes, e.g. cracking of mineral oils, production of higher hydrocarbons, destruction of pollutants, etc. Metals otherwise known to be of minimal catalytic activity, e.g. lead or copper, exhibit rich catalytic chemistries, when exchanged into a well-defined alumino-silicate structure. Through varying the metal and the type of zeolite one is able to influence the reactivity and the catalytic properties in very specific ways. In order to understand the catalytic properties of a zeolite, it is necessary to investigate how the internal structure and the presence of other substances, e.g. water, are influencing the exchanged metal ion. We report here on ^{207}Pb solid state NMR (static sample) and ^{27}Al MAS NMR investigations of the lead-exchanged zeolites RHO, X, Y, and ZSM-5. Even though ^{207}Pb is not a very common nucleus in NMR Spectroscopy, it has been found to be very suitable for our purpose. ^{207}Pb is the heaviest stable nucleus with spin-1/2 and has a quite high natural abundance (30 %); the shift range of ^{207}Pb is very large and shows a very strong sensitivity to the local environment. To get an idea of symmetry of the environment of the lead sites and the possibility of multiple crystallographic sites, the influence of water (H_2O) and D_2O) on the spetroscopical data, e.g. line width of the powder pattern, has been measured by ^{207}Pb NMR. ^{27}Al MAS NMR was used to determine the number lead ions associated with each aluminum atom

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305. ***DYNAMIC NUCLEAR POLARIZATION IN AQUEOUS CHAR SUSPENSIONS AT 9.4 GHz.*** B.M.Odintsov[1,3]; V.A. Atsarkin[3]; R.L.Belford[1,2]; P.J.Ceroke[1]; V.N. Demidov[3]; R.B.Clarkson[1]. [1]Illinois EPR Research Center and [2]Department of Chemistry, 506 S. Mathews, University of Illinois, Urbana, IL 61801; [3]Institute of Radioengineering and Electronics, Russian Academy of Science, Moscow 103907, Russia

The presence of two different phases (solid and liquid) in aqueous char suspensions suggests the possibility of coexistence of different DNP mechanisms, such as the "solid effect" typical for solids and the Overhauser effect, which is known to be characteristic of liquids with dynamical nuclear-electron interactions. The equipment for nuclear-electron DNP effect study in char suspensions at electron frequency 9.4GHz (NMR proton frequency 14MHz) was constructed. A Bruker ER 200 X-band spectrometer with 200 mW klystron and H_{012} *rectangular resonator were used to saturate EPR Zeeman levels of paramagnetic centers in chars. In accord with our previous observations, both positive as well as negative "liquid" Overhauser effects were observed in different samples with the EPR saturation field centered on the EPR line* ($\Delta\omega = 0$)*. At the same time, the experiments demonstrate some traces of a "solid effect" DNP at* ($\omega_S = \omega_I$)*, which is usually observed in solids at low temperatures. The results correlate well with the model of molecular and spin dynamics at solid-liquid interface developed in our previous works. The research was supported in part by grants from NATO (HTECH. LG 972264), Fogarty International Foundation (IRO3 TW00998-01), NIH (RBC; GM51630, GM42208), and the U.S. Department of Energy (DE FG22-96 PC 96205) and used facilities of the Illinois EPR Research Center (NIH P41 -RR01811).*

NMR Poster Session—Prof. R. B. Clarkson, 217-244-1375, clarkson@uinc.edu

306. ***SPIN-LATTICE RELAXATION AND NMR SPECTROSCOPY IN AQUEOUS CHAR SUSPENSIONS.*** B.M.Odintsov[1,4]; R.L.Belford[1,2]; P.J.Ceroke[1]; Z.Sh.Idoyatullin[3]; A.N. Temnikov[3]; R.B.Clarkson[1]. [1]Illinois EPR Research Center and [2]Department of Chemistry, 506 S. Mathews, University of Illinois, Urbana, IL 61801; [3]State Technology University, [4]Institute of Radioengineering and Electronics, Russian Academy of Science, Moscow 103907, Russia

Spin-lattice proton relaxation as well as NMR spectra have been studied in aqueous suspensions of several newly synthesized chars intended as oximetry probes in living tissue. NMR data clearly demonstrate changes in water structure near the active carbon surface. NMR spectra of char suspensions consist of two lines in accordance with two types of water molecules in porous structure and in the reminder of the surface layer. Lines intensities as well as spin-lattice relaxation times are essentially different. The results are quantitatively interpreted in terms of a two-stage molecular exchange model. A porous cage effect leads to slow exchange between molecules inside and outside pores, in contrast to fast molecular exchange at the solid-liquid interface, where a familiar two-site formalism can be applied. NMR methods have been used for evaluation of specific volume and porous size of the micropores. The dependence of the relaxation upon surface properties was analyzed. The research was supported in part by grants from NATO (HTECH. LG 972264), Fogarty International Foundation (IRO3 TW00998-01), NIH (RBC; GM51630, GM42208), and the U.S. Department of Energy (DE FG22-96 PC 96205) and used facilities of the Illinois EPR Research Center (NIHP41-RR01811).

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307. ***SOLID-STATE*** ^{27}***A1 MAS NMR INVESTIGATIONS OF AlON POWDERS AND CERAMICS.*** Tom Offerdahl and John J. Fitzgerald~ Department of Chemist~y and Biochemist~y, Sou~ Dalcota State University, Brookings, SD 57007, Steven 17 Dec7 Department of Chemishy, Colorado School of Mines and Technology, Golden, CO 80027; and Gary E. Macid, Depardnent of Chenıis~y. Colorado State Universi~y, Fort Collins, CO SO523.

AlONs are complex transparent ceramics composed of variable Al_2O_3*/ALN compositions from 27 to 40 mole% ALN. Of me various AlON phases that exist based on microstructural analysis and XRD,* γ*-AlON phase with the spinel structure and composition 35 mole% AlN* ($Al_{23}O_{27}N_5$) *is the most well-characterized material Solid-state* ^{27}*Al NMR investigations of the synthesis and structural characterization of AlON materials are of significance in understanding the chemical bonding and unique structural features of 4- and 6-coordinate aluminum oxynitride sites in these materials, the more complex aluminum/siliconoxynitride sites in SiAlON ceramics and in glass composites such as BaMgSiAlON Solid-state* ^{27}*Al NMR spectroscopy measurements obtained at 9 4 Tesla and 14.1 Tesla and multiple-quantum (MQMAS)* ^{27}*Al NMR investigations at 9.4 Tesla for a range of AlON materials are reported. The* ^{27}*Al NMR spectra of venous AlON materials have numerous resonances, including several assigned to 6-coordinate* AlO_6 *and 4-coordinate* AlO_4 *and* AlN_4 *sites, and three resonances assigned to 4-coordinate* $AlO_{4-x}N_x$ *(where x = 1,2 and 3) oxynitride chemical environments The* ^{27}*Al NMR spectra are influenced by both* ^{27}*Al and* ^{14}*N quadrupolar and* ^{27}*Al-*^{14}*N dipolar interactions that can be useful in understanding the structure and bonding of the various* AlO_xN_y *chemical environments in these materials. While the* ^{27}*Al MAS NMR measurements at 14.1 Tesla provide increased spectral resolution needed to resolve and quantify different types of* ^{27}*Al resonances in AlON materials, the* ^{27}*Al MQMAS NMR measurements allow quantitation of chemical shift and quadrupolar parameters needed to more fully understand these ceramic materials. Interpretation of the relationship between the* ^{27}*Al MAS and MQMAS NMR results for selected AlON materials is also discussed.*

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308. *DETERMINATION OF THE ORIENTATION OF THE GLYCINE-ALPHA CARBON CSA TENSOR IN THE DIPEPTIDE AG.* Nathan A. Oyler, John Stringer, and Gary P. Drobny, Dept. of Chemistry, Univ. of Washington, Seattle WA 98195

DRAWS was used to determine the distance between ^{13}C-(methyl)-Alanyl -^{13}C-(alpha)-Glycine at field strengths of 9.4 and 17.4 tesla. A crystal structure for AG has been determined in the literature, and the distance agrees reasonably well at both field strengths. Double quantum (DQ) DRAWS was used to obtain experimental DQ spectra of the sample at both field strengths. At the lower field, the DQ spectrum looks like a dipolar DQ pattern and, at the higher field the spectrum looks like an eta = 1 chemical shift pattern. In orienting the alpha CSA tensor, the methyl CSA tensor was determined to be very near axially symmetric and was assumed to be oriented along the methyl bond axis. Chi squared plots at each field were generated as a function of dipolar orientation and alpha CSA tensor orientation in order to elucidate the information content in the spectra. In order to confirm our results the orientation of the alpha-N bond was determined in the frame of the alpha carbon.

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309. *COMPARISON ^{13}C CP/MAS NMR AND POWDER X-RAY DIFFRACTION FOR ANALYZING SOLID ORGANIC COMPOUNDS.* Brian E. Padden, Mark T. Zell, Zedong Dong, David J.W. Grant, Eric J. Munson, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455; Steve A. Schroeder, The Monsanto Company, 601 East Kensington Avenue, Mount Prospect, IL 60056.

Polymorphism is the ability of a substance to exist in two or more distinct forms that differ in the conformation and/or arrangement of molecules in the crystal lattice. Polymorphism is particularly relevant to the pharmaceutical and food industries because different polymorphs can have different solubilities, stabilities, and bioavailabilities. Solid-state NMR spectroscopy has emerged as a powerful analytical technique in the characterization of polymorphism in crystalline organic compounds. Solid-state NMR spectroscopy is also useful for distinguishing solvates and studying amorphous forms. We have used ^{13}C CP/MAS NMR to study three known forms of aspartame (L-aspartyl-L-phenylalanine methyl ester) which is widely used as an artificial sweetener. Currently we are studying mixtures of the solid forms of a new sweetener called neotame (N-(3,3-dimethylbutyl)-L-aspartyl-L-phenylalanine methyl ester). We have found that many forms of neotame can be generated by altering the crystallization and drying conditions. Up to seven distinct resonances for the quaternary phenyl carbon are observed among the different forms. Unfortunately the conditions used to generate most of these forms do not result in pure phases. We are investigating the relative merits of using solid-state NMR and powder X-ray diffraction to analyze mixtures of forms of neotame. Powder X-ray diffraction is currently the most common method of determining polymorphism, but is susceptible to particle size and preferred orientation effects, does not reveal site specific information, and is unable to probe amorphous materials. Solid-state NMR spectroscopy is better suited for investigating polymorphic mixtures since it is not as sensitive to particle size effects, does reveal information on the local environment of nuclei, and can be used to study amorphous materials. We are also studying various drug compounds both in bulk and in dosage forms. For instance, we are using solid-state NMR spectroscopy to investigate the different polymorphic forms of bupivacaine (1-butyl-N-[2,6-dimethylphenyl]-2-piperidinecarboxamide hydrochloride) and the drug diluted in a bioresorbable polymer device.

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310. *INVESTIGATIONS OF TITANOSILICATE MATERIALS BY SOLID-STATE ^{29}Si AND ^{47,49}Ti NMR SPECTROSCOPY.* R.L. Peterson and J.J. Fitzgerald, South Dakota State University

Recent developments in the study of titanosilicate framework materials as redox catalysts and ion exchangers have indicated that these materials contain important structural Ti-O-Si linkages, where variations in the coordination number of the titanium (IV) ion may influence their functional properties. Initial solid-state ^{29}SI and ^{47,49}Ti NMR studies of a range of titanocilicates (eg., ETS-10, JDF-L1 and 2:1 and 4:3 Ti/Si ion exchangers) and various model titanium oxides and Ti/Si-containing minerals are reported. Solid-state ^{29}Si MAS NMR studies of titanium silicate materials reveals that incorporation of Ti(IV) into the silicate framework results in a paramagnetic contribution of 5-10ppm to the isotropic chemical shift for each replacement of a Si-O-Si bridging oxygen by an Si-O-Ti bridge. This paramagnetic trend is due to the asymmetric distribution of the p electrons of the silicon nucleus and is more dramatic with the increasing covalent character of the bond. Solid-state ^{47,49}Ti NMR measurements of various model titanates ($CaTiO_3$, $BaTiO_3$, Ba_2TiO_4 and $SrTiO_3$), Ti/Si containing minerals (benitoite, fresnoite, titanite) and ion-exchange materials ($Na_2Ti_2O_3SiO42H_2O$ and $HK_3Ti_4O_4(SiO_4)_34H_2O$) are also reported. The use of ^{49}Ti NMR spectroscopy has shown that the effect of next-nearest neighbor silicon results in a shift toward high field over a range of at least 300 ppm. These ^{29}Si and ^{47,49}Ti NMR studies suggest the potential utility of these approaches to obtain important structural information regarding the Si-O-Ti linkage and to examine the effects that the coordination number and symmetry of the titanium (IV) ion chemical environments have on the catalytic and ion exchange properties of these materials.

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311. *SOLUTION ^{13}C, ^{47,49}Ti AND ^{93}Nb NMR STUDIES OF TITANATE AND NIOBATE ALKOXIDE SOL-GEL PRECURSORS TO ELECTRONIC MATERIALS.* J. Qi, J. Huang and J.J. Fitzgerald, South Dakota State University

The solution chemistry of Ti(IV) and Nb(V) methoxyethoxide and thoxide precursors to electronic materials has been studied by ^{13}*C,* ^{47,49}*Ti and* ^{93}*Nb NMR spectroscopy. Alkoxide solutions (1.25 M to 0.1 M) in ethanol and benzene show the presence of monomeric, dimeric, trimeric and oligomeric species involved in complex equilibria. Variable-temperature* ^{93}*Nb NMR has been used to determine equilibrium constant between themonomeric and dimeric species in* $Nb(OEt)_5$ *ethanol solutions. The* ^{93}*Nb NMR spectra of the* $LiNb(OEt)_6$ *precursor to lithium niobate show the presence of a linear oligomericcomplex, in agreement with single crystal x-ray diffraction structure. A linear structure for* $Mg[Nb(OEt)_6]_2$ *complex in solution is also postulated based on the similar* ^{93}*Nb and* ^{13}*C NMR behavior to that of LiNb(OEt)6 solutions. The* $Pb_3MgNb_2(OEt)_{18}$ *precursor to the ferroelectric material* $Pb(Mg_{1/3}Nb_{2/3})O_3$ *is also proposed to consist of a linear* $Mg[Nb(OEt)_6]_2$ *network that is cross-linked by Pb(II) alkoxide units. Variable temperature* ^{13}*C and* ^{47,49}*Ti NMR spectra show that only monomeric species exists in Ti(OProj)4 benzene solutions, whereas a dimeric species exists in* $Ti(OCH_2CH_2OCH_3)_4$ *benzene solutions.* $PbTi(OCH_2CH_2OCH_3)_6$*, by contrast, is composed of linear Ti(VI) oligomeric alkoxide groups connected to linear Pb(II) alkoxide units by bridging alkoxides. These solution* ^{13}*C,* ^{47,49}*Ti and* ^{93}*Nb NMR studies demonstrate the utility of multinuclear NMR techniques to advance our understanding of the solution chemistry of complex Ti(IV) and Nb(V) alkoxide systems, thsu providing a structural framework for future studies of hydrolysis and condensation reactions important to sol-gel processing.*

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312. *NMR OF PARAMAGNETIC LANTHANIDE GLUTARATES.* Joseph R. Sachleben, Campus Chemical Instrument Center, The Ohio State University, 176 W. 19th Ave, Columbus, OH 43210, USA; Anthony Cheetham, Materials Research Laboratory, University of California, Santa Barbara, CA, 93106, USA; GÈrard FÈrey, Institut Lavoisier, UMR CNRS 173, UniversitÈ de Versailles Saint-Quentin-en-Yvelines, 45, Ave. des …tats-Unis, 78035 Vesailles cedex, France; Thomas Luxbacher, Institut Lavoisier, UMR CNRS 173, UniversitÈ de Versailles Saint-Quentin-en-Yvelines, 45, Ave. des …tats-Unis, 78035 Vesailles cedex, France; Fabien Serpaggi, Institut Lavoisier, UMR CNRS 173, UniversitÈ de Versailles Saint-Quentin-en-Yvelines, 45, Ave. des …tats-Unis, 78035 Vesailles cedex, France.

We have recently synthesized microporous lanthanide glutarates, which are made from chains of lanthanide metal cations held together by the glutarate dianions. Spaces between the glutarate anions form 1-dimensional channels, which are capable of absorbing small molecules. We have performed ^{1}*H and* ^{13}*C Nuclear Magnetic Resonance (NMR) spectroscopy on a series of Ln-glutarates,*
$[Ln(H_2O)]_2[O_2C(CH_2)_3CO_2]_3 \bullet 4H_2O$ *where Ln is Y, La, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, and Yb. Both* ^{1}*H and* ^{13}*C NMR spectra of show a broad series of sidebands extending for 100's of ppm. These broad sideband patterns are due to the paramagnetic shift anisotropy arising from the orientation dependence of the local magnetic field created by the ordered paramagnets in the sample. If the g-tensor of the paramagnetic lanthanide is isotropic, the paramagnetic shift anisotropy is a second rank tensor. If the g-tensor is highly anisotropic, the paramagnetic shift anisotropy is a sum of 0 to 6th rank tensors. In many of our samples, the g-tensor is approximately isotropic and the observed sideband patterns resemble broad chemical shift anisotropies. Computer simulations have shown that by measuring the paramagnetic shift anisotropy,*
$\delta_{paramagnetic}$*, and the asymmetry parameter,* $\eta_{paramagnetic}$*, one can localize the position of the nucleus in the unit cell. We will attempt to demonstrate this behavior in our samples. We also examine the temperature dependence of the paramagnetic shift anistropy and the isotropic paramagnetic shift. These studies provide a good model system for understanding paramagnetic shifts and will allow the development of a more general understanding of these shifts in paramagnetic solids. Understanding these shifts will provide a new tool for probing the structure and dynamics of paramagnetic solids.*

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313. *ANILINE OLIGOMERS AS A MODEL FOR POLYANILINE: A SOLID-STATE NMR STUDY.* P. Michael Schmeida, Matthew Espe, Department of Chemistry, University of Akron, Akron, OH 44325

Most of the studies of polyaniline, a conducting polymer, have focused on the bulk propertiesœof the material and not on the local structure that is controlling these properties. In addition,œin casting films of the polymer the solvent used has a significant impact on properties such asœconductivity. In order to gain a better fundamental understanding of the polymer structure weœare using solid-state NMR to characterize low molecular weight oligomers of aniline. As theœpolymer has a repeat unit consisting of three phenyl rings and one quinoid ring, ^{13}*C MAS NMR has been used to investigate the relative position of the quinoid ring in the monomer unitœand to determine the relative amount of each of the possible isomers when different castingœsolvents are used. Polyaniline is converted into its conducting form by protonation with aœvariety of acids. The affect of acid on oligomer structure, electronic and geometric, will alsoœbe compared with results from the polymer.*

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314. ***EXAMPLES OF SODIUM AND GALLIUM CHEMICAL SHIELDING ANISOTROPY.*** Robert W. Schurko, Clare P. Grey, SUNY at Stony Brook, Department of Chemistry, Stony Brook, NY 11794-3400; Roderick E. Wasylishen, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3; Anthony Bielecki, Bruker Instruments, Inc., Billerica, MA 01821

There are very few cases of sodium chemical shielding anisotropy (CSA) (1,2) and only one instance of gallium chemical shielding anisotropy (3) reported in the literature. In these studies, the chemical shielding (CS) tensors were characterized by single-crystal NMR techniques. Here, we present new examples of sodium and gallium CSA, which are determined from analysis of ^{23}Na, ^{69}Ga *and* ^{71}Ga *NMR spectra of powders acquired at 8.5 T, 9.4 T, 11.4 T and 18.8 T. Sodium-23 and gallium-69/71 nuclear quadrupole coupling constants and asymmetry parameters were determined from analysis of magic-angle spinning (MAS) NMR spectra. Comparison of spectra of stationary samples acquired at different fields allow for the determination of the relative orientations of the CS tensors and electric field gradient (EFG) tensors. Ab initio calculations of sodium CS and EFG tensors were also performed, and found to be in qualitative agreement with experimental results.*

1. *L.C. West, T. Cole and R.W. Vaughan. J. Chem. Phys. 1978, 68, 2710.*
2. *(a) S.F. Sagnowski and J. Ogar. Phys. Stat. Sol. B 1981, 107, K125. (b) S.F. Sagnowski, Z. Sulek, M. Stachura and J. Ogar. Z. Phys. B. Cond. Matt. 1982, 46, 123.*
3. *T. Vosegaard, D. Massiot, N. Gautier and H.J. Jakobsen, Inorg. Chem. 1997, 36, 2446.*

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315. ***CHARACTERISATION OF STRUCTURE AND DYNAMICS IN NANOCRYSTALLINE OXIDES BY SOLID STATE NMR.*** I.J.F. Poplett, M.E. Smith, Department of Physics, University of Warwick, Coventry, UK, CV4 7AL; A.V. Chadwick, and J.H. Strange, School of Physical Sciences, University of Kent, Canterbury, Kent, CT2 7NR, U.K.

Nanocrystalline solids are currently generating intense research interest. Such solids have complex structures that are difficult to characterise by conventional probes. The great potential of ^{17}O *NMR for study nanocrystalline oxides is presented by the spectroscopic observation of surface and bulk, as well as defect sites in nanocrystalline MgO. It is also shown that prior to crystallisation* ZrO_2 *gels are monoclinic in structure right up to the point of crystallisation. Comparison is made to other local structural probes such as Zr EXAFS. A new probe for in situ high temperature (up to 1000°C) observation of* ^{17}O *using optical heating is described. The probe is used to follow dehydroxylation directly and measure relaxation times in sol-gel formation of such oxides.* ^{1}H *and* ^{13}C *MAS NMR are also very informative in showing the loss of organic species, which is intimately linked to the initial crystallisation of these oxides. It is also apparent that significant proton-content remains well above the point of initial crystallisation. This research was supported by the EPSRC through grant GR/K74876.*

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316. ***MULTIPLE QUANTUM MAS NMR EXPERIMENTS ON I=5/2 NUCLEI.*** M.E. Smith, R. Dupree and T. Mildner, Department of Physics, University of Warwick, Coventry, UK, CV4 7AL, E.R.H. van Eck School of Physical Sciences, University of Kent, Canterbury, Kent, UK, CT2 7NR and S.C. Kohn, Department of Geology, University of Bristol, Bristol, UK, BS8 1RJ.

The multiple quantum (MQ) MAS NMR experiment has proved to be extremely useful at improving the resolution of spectra from quadrupole nuclei. This paper examines two particular cases of the MQ experiment applied to 1=5/2 nuclei. The use of rotationally induced excitation (RIACT)[1] of both triple and quintuple quantum coherences is examined. The advantages of rotationally induced excitation are good sensitivity at moderate rf fields and less dependence of the excitation on the size of the quadrupole interaction. A pulse sequence for producing purely absorptive lineshapes from the RIACT scheme is discussed. One of the most exciting applications of MQ MAS NMR is to the study of ^{17}O *in aluminosilicates to resolve different framework fragments which significantly overlap in conventional MAS NMR spectra. RIACT allows efficient excitation of sites with quite large quadrupole interactions. In hydrous aluminosilicate gels and glasses* ^{17}O *observation of OH groups can be problematic under MQ which appears to be related the apparently small quadrupole interaction and rapid relaxation. The optimum conditions for observing the OH groups in hydrous gels and glasses is discussed. This research was partially supported by the EPSRC through grant GR/K74876 and HEFCE is thanked for funding of the high field spectrometer through a JREI grant.*

1. *G. Wu, D. Rovnyak and R.G. Griffin, J. Am,. Chem. Soc., 1996, 118, 9326.*

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317. ***SOLID-STATE NMR INVESTIGATION OF LEACHED LAYERS IN SODIUM-ALUMINOSILICATE GLASSES.*** Natia Tsomaia, James Hamilton, Karl T. Mueller, Penn State University, Department of Chemistry, University Park, PA 16802

Examinations of a number of sodium aluminosilicate glasses (especially in the context of the immobilization of radioactive fission products produced during the recycling of nuclear fuel) show that they effectively cease to dissolve in water after a short time.[1] *This behavior is interpreted as due to altered surface layer formation on the glass, which protects the underlying aluminosilicate structure from further dissolution. However, the structure and composition of any newly formed layers have not been adequately defined for a clear elucidation of* *the surface and sub-surface chemistry. In our studies, glass samples in the family Na_2O - xAl_2O_3 - $(3-x)$ SiO_2 have been exposed to both acidic (pH=2) and basic (pH=9) solutions at 25°C for up to 1000 hours, followed by characterization with solid-state NMR spectroscopy. Depending on the bulk aluminum concentration, these glasses exhibit total dissolution or they form an extensive surface layer.[2] The ^{27}Al MAS spectra of a preliminary series of acid-leached glasses (with bulk compositions corresponding to x = 0.2, 0.4, 0.6) clearly indicate that for all compositions studied the aluminum in the bulk has a tetrahedral coordination (Al(IV)). Other surface-sensitive techniques (such as SIMS depth profiling) show that for these acid-leached glasses all protons are present near to the surface. Therefore $^1H \rightarrow X$ (X= Si, Al) cross-polarization has been successful as a surface-selective NMR technique. ^1H MAS has also been performed on acid-leached samples, and signals indicative of strong hydrogen bonding have been detected. We report on our progress toward complete characterization of the dependence of surface structure and corrosion chemistry on bulk aluminum concentration for a range of sodium aluminosilicate glass compositions (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0). In order to better describe the structures present in the leached layers, transfer of populations in double resonance (TRAPDOR) NMR experiments[3] (combined with $^1H \rightarrow {}^{29}Si$ CP for surface selectivity) are in progress.*

1. *Harvey K.B., Litke C.D.,(1984) J. Am. Ceram. Soc. 67, 553*
2. *Hamilton J.P., Pantano C.G., (1997) J. Non-Crist. Solids 222, 167*
3. *Grey C.P., Vega A.J., (1995) J. Am. Chem. Soc. 117, 8232-8242.*

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318. ***COMPARATIVE STUDY OF Li-ION MOBILITY IN SWOLLEN IONOMERS AS MEASURED BY ^7Li MAS LINESHAPE, $T_{1\rho}$, ^7Li DIFFUSION, AND CONDUCTIVITY.*** A. J. Vega, E. F. McCord, M. Doyle, and M. G. Roelofs, DuPont Central Research and Development, P. O. Box 80356, Wilmington, DE 19880-0356.

Ionomers where all the anions are covalently attached to the polymer backbone have the simplifying property that their electrical conductivity is exclusively determined by the diffusivity of the positive counterions, in contrast to polymeric electrolytes where the conductivity is facilitated by dissolved salts. We demonstrate that it is possible in such a system to establish semiquantitative relationships between (a) the residence time of Li-ions at anionic sites as derived from MAS lineshapes and T1r, (b) the diffusion coefficient describing the migration of Li-ions among anionic sites, as determined by the DOSY NMR technique, and (c) the macroscopically measured conductivity.

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319. ***DYNAMICS OF POLARIZATION TRANSFER IN HIGH SPEED CPMAS EXPERIMENTS.*** Vladimir Ladizhansky, and Shimon Vega, Department of Chemical Physics, the Weizmann Institute of Science, Rehovot, 76100, Israel.

We present a coherent model that describes the S-spin signal enhancement during Hartmann-Hahn matched cross polarization high speed MAS (CPMAS) experiments on small spin systems I_NS with N=1÷10. The enhancement is calculated as a function of the CP contact time. The CPMAS Hamiltonian is written in an interaction representation, which made it possible to substitute the time-dependent heteronuclear and homonuclear interaction terms by effectively time-independent terms. This enables us to extend the dimensionality of the spin systems, that can be treated numerically, from N=6[1] to N=10. Buildup curves of S-spin signals are evaluated and Fourier transformed, resulting in CPMAS spectra. The lineshapes of these spectra are a function of the multi-nuclear CP spin-dynamics and their analyses allow us to extract important structural information, such as heteronuclear ^{13}C-^1H distances. The polarization transfer processes are dependent on the structure of the homonuclear proton network and can be controlled by changing the off-resonance proton frequency during the mixing time. Off-resonance values that match the Lee-Goldburg condition[2] make the CP buildup process of ^{13}C in $^{13}CH_N$ mainly dependent on its nearest neighboring protons. Numerical results are compared with exact CPMAS results, that are obtained from simulations based on Floquet theory. In addition experimental results are shown that can be described by the theory and that show the sensitivity of CPMAS heteronuclear distance measurements.

1. *S. Ray, V. Ladizhansky, and S. Vega, J. Magn. Reson. 135, 427 (1998).*
2. *M. Lee, and W.I. Goldburg, Phys. Rev. A 140, 1261 (1965).*

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320. ***RESIDUAL DIPOLAR COUPLINGS BETWEEN QUADRUPOLAR NUCLEI IN SOLID STATE MQMAS NMR SPECTRA.*** Sungsool Wi and Lucio Frydman; Department of Chemistry (M/C 111), University of Illinois at Chicago, Chicago, IL 60607

The effects of residual dipolar couplings between directly bonded quadrupolar nuclei (S,I > 1/2) on multiple-quantum magic-angle-spinning (MQMAS) NMR were investigated. It is shown that as it happens when spin-1/2 nuclei S are close to quadrupolar I spins (e.g., 13C-14N pairs), the tilting of the latter quantization axis induces non-secular residual dipolar broadenings that are not averaged out by MAS. These are shown to affect as well the MQMAS NMR line shapes of coupled nuclei. Average Hamiltonian theory was employed to derive the residual dipolar coupling interaction, which for heteronuclear systems coincided with the one obtained by Olivieri et al for spin pairs containing S = 1/2 [1]. This effect dictates a resolution limit on the MQMAS experiment, which worsens as the order m1 of the MQ transition increases. For the hitherto unobservable homonuclear case additional off-diagonal terms arise; although an analytical description of the resulting MQMAS multiplet became elusive even for the simplest I=S=3/2 case, a full numerical analysis could be carried out to completion. MQMAS

NMR simulations and experiments that illustrate this effect on a variety of systems containing quadrupolar spin pairs will be presented.

1. A. C. Olivieri, L. Frydman, and L. E. Diaz, J. Magn. Reson. 75, 50 (1987); R. K. Harris and A. C. Olivieri, Progr. NMR Spectrosc. 24, 435 (1992).

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321. ***MEASUREMENTS OF CONNECTIVITIES BETWEEN PO_4 UNITS IN ZINC PHOSPHATE GLASSES.*** Jerzy W. Wiench, Marek Pruski, Ames Laboratory, Iowa State University, Ames, IA, 50011; Brad Tischendorf, Joshua Otaigbe, Department of Materials Science and Engineering, Iowa State University, Ames, IA, 50011

Phosphate glasses have lower transition temperatures and higher thermal expansion characteristics than silicate or borate materials, which recently sparked considerable interest in their technological properties. We present a comprehensive solid state NMR investigation of the $xZnO + (1-x)P_2O_5$ glasses in the $0.35 \leq x \leq 0.70$ composition range. Standard magic angle spinning (MAS) NMR of ^{31}P is a very useful spectroscopic method for the short-range structural studies of phosphates. It has been shown that the P(n) units (where $n = 0, 1, 2, 3$ denotes the number of connectivities to other PO_4 groups) can be usually distinguished by means of their isotropic chemical shift (δ_{iso}) and the CSA. The quantitative measure of relative concentrations of the $P^{(n)}$ intensities has been obtained from the numerical analysis of the ^{31}P MAS sideband patterns. The $P^{(2)}$ groups, which are dominant in the studied glasses, can form chains and/or rings that cannot be resolved by MAS alone. Therefore, high-resolution double-quantum (DQ) NMR has been used to determine the connectivities between various $P^{(n)}$ species, providing new information about their extended chain structure. This analysis was correlated with the ^{31}P NMR spectra in solution, which were better resolved but not quantitative, and with the results obtained using FTIR and FT-Raman spectroscopies.

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322. ***DEUTERIUM WIDE-LINE NMR STUDIES OF LOCAL MOTION OF BENZENE ADSORBED ON Ca-MONTMORILLONITE.*** Jincheng Xiong, Technical Center, Union Carbide Corp., South Charleston, WV 25303; Gary Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

Deuterium wide-line NMR spectra and interpretations are presented on two samples of deuterium-labeled benzene that have been adsorbed on a major soil component, Ca-montmorillonite clay. Spectra were obtained on the samples with two different benzene loading levels over a wide temperature range, and using two values of quadrupolar echo delay period. Computer simulations of lineshapes resulting from various forms of local motion of C-D moieties provide useful guidelines for interpreting the experimental results. The result suggest that adsorbed benzene molecules first form p-complexes with Ca2+ in the interlayer space of the clay with an adsorption enthalpy of 42±4 KJ/mol at temperatures at or below -75 °C. The adsorbed molecules undergo small-angle wobbling of the C6 axis accompanied by rapid discrete jumps about the C6 axis. At higher temperatures, benzene molecules start to perform large-angle wobbling of the C6 axis with extremely fast jumps around the axis, and eventually desorb from Ca^{2+} to tumble freely in the interlayer space of the clay. The enthalpy and entropy changes between different motional states were obtained from the variable temperature studies. The activation energies of relevant molecular motions were also estimated. This approach is attractive for elucidation of detailed motional behaviors of organic pollutants adsorbed in soil.

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323. ***PROBING ELECTRONIC AND PROTONATION STATES IN A POLYMER: A ^{15}N SSNMR STUDY OF POLYANILINE.*** Tanya Young, Matthew Espe, Department of Chemistry, University of Akron, Akron, OH 44325; Dali Yang, Benjamin Mattes, Santa Fe Science and Technology, Santa Fe, NM 87505.

Upon doping (protonation), polyaniline is converted from its insulating form to a conducting form. In addition to different protonation states, polyaniline can also be poised in different oxidation states as well. Previously, it has not been possible to establish both the specific forms (oxidation and protonation states) of the polymer and the amount of each form present in the solid state. Aniline oligomers have been used as models to optimize the procedures to achieve specific oxidation and protonation states of the polymer. ^{15}N labeled polyaniline has been poised in its fully oxidized and fully reduced forms as well as the fully doped (protonated) and undoped forms and the 15N spectra collected. Characteristic chemical shifts, chemical shift tensors, and linewidths have been observed for the different forms of the polymer. These results have been used to characterize polyaniline films that are formed from solutions containing amines to increase polymer solubility. The ^{15}N solid-state NMR spectra from the films extracted from these solution indicate that the polymer is heterogeneous, containing a mixture of oxidation and protonation states. With this information it has been possible to gain insights into the various forms present after film and fiber formation and SSNMR has proved to be the optimal technique to probe the electronic structure of polyaniline.

NMR Poster Session—Tanya Young, Department of Chemistry, University of Akron, Akron, OH 44325, 330-972-8389, 330-972-7370 (fax), tyoung@chemistry.uakron.edu

324. ***INVESTIGATION OF POLY(LACTIDE) STRUCTURE USING SOLID-STATE NMR SPECTROSCOPY.*** Mark T. Zell, Brian E. Padden, Amanda J. Paterick, Marc A. Hillmyer, Eric J. Munson, University of Minnesota, Department of Chemistry, 207 Pleasant St. S.E., Minneapolis, MN 55455; Khalid A.M. Thakur, Robert T. Kean, Cargill Incorporated, Central Research, P.O. Box 5699, Minneapolis, MN 55440.

Lactic acid based aliphatic polyesters such as poly(lactide) (PLA) are increasingly being explored for use in several applications including biodegradable packaging materials, food containers, bioresorbable medical implants, and drug delivery systems. We are using two-dimensional exchange NMR to probe the microstructure of PLA to understand the conformation and arrangement of the polymer chains. The two-dimensional exchange CP/MAS NMR spectrum of 5% L-lactide ^{13}C labeled at the carbonyl site in unlabeled L-lactide suggests the presence of up to 10 crystallographically inequivalent sites in highly crystalline poly(lactide). We are also using rotor-synchronized two-dimensional exchange NMR experiments to determine the relative torsion angles in the helical crystalline polymer chain, which will aid in elucidation of the crystalline structure of the polymer. ^{13}C CP/MAS NMR spectroscopy is also a powerful technique for probing the incorporation of stereosequence defects into the polymer chain. ^{13}C CP/MAS NMR spectra of poly(D-lactide) containing small amounts (< 10%) of L-lactide ^{13}C labeled at the carbonyl carbon can be deconvoluted to quantitate the relative amounts of stereosequence defects which are incorporated into the crystalline chain versus the amount in the amorphous domain. For a sample containing 3% L-lactide, approximately 50% of the defects are incorporated into the crystalline chain, while the remainder are forced into the amorphous domain. In-situ variable temperature-CP/MAS NMR experiments on PLA containing 5% L-lactide ^{13}C labeled at the carbonyl carbon in 95% D-lactide show that defects are incorporated into the crystalline polymer domain early in the crystallization process.

NMR Poster Session—Mark T. Zell, University of Minnesota, Department of Chemistry, 139 Smith Hall, 207 Pleasant St. S.E., Minneapolis, MN 55455, (612) 625-3098, fax: (612) 626-7541, zell@chem.umn.edu

325. ***THE ROLE OF INTERNET APPLIANCES IN THE MODERN ANALYTICAL LABORATORY.*** Brian N. Radford, Genesis Laboratory Systems, Inc., P.O. Box 1484, Palisade, CO, 81526; Keith W. Ballantyne, Genesis Laboratory Systems, Inc.

The widespread use of the Internet has ushered in an age where the exchange and dissemination of data is global and immediate. This paper explores the use of the same technology in support of centralized data collection and reporting. The authors detail the development of a web-enabled analytical instrument, and show how Internet technology may be used to improve laboratory performance and data handling.

Quality Assurance/Pharmaceutical Analysis Oral Session—Keith Ballantyne, Genesis Laboratory Systems, Inc., 385 1/2 Hill View Drive, Grand Junction, CO, 81503, (970) 241-0889, fax: (970) 245-9593, HYPERLINK mail to: keith@gj.net keith@gj.net

326. ***CLEANING VALIDATIONS: DEVELOPMENT, VALIDATION AND TRANSFER OF ANALYTICAL TEST METHODS.*** David E. Nadig, Sr. Research Scientist, Johnson & Johnson Merck Consumer Pharmaceuticals Co., Fort Washington, PA 19034

Drug products and active pharmaceutical ingredients are required to be manufactured using clean equipment in order to assure they are not adulterated. The cleaning process must be validated to prove it is effective. The cleaning process validation must be supported by trace level analytical methods that are suitable for their intended purpose. Test method validation includes experiments to determine linearity, accuracy, precision, limit of detection, limit of quantitation and recovery from the swab material. Additional validation experiments are required that demonstrate that the swabbing technique yields acceptable recovery from the equipment surface. The analytical development laboratory is responsible for optimizing swabbing protocol parameters including solvent selection, swab materials selection, and swab area optimization. Test methods must be transferred to the appropriate laboratory using suitable strategies. Using method validation results, we have designed successful method transfer protocols. Each cleaning process must be validated to assure that it is effective in removing manufacturing residue without leaving residual cleaning agents. Analytical method validation and transfer procedures provide a scientific foundation to assure effectiveness of manufacturing equipment-cleaning procedures. Suitable validation protocols will be discussed.

Quality Assurance Oral Session—David E. Nadig, Sr. Research Scientist, Johnson & Johnson Merck Consumer Pharmaceuticals Co., Fort Washington, PA 19034

327. ***SELECTION AND USE OF DEFENSIBLE REFERENCE MATERIAL STANDARDS FOR CALIBRATION, VALIDATION AND QUALIFICATION OF UV/VIS ABSORPTION SPECTROPHOTOMETERS.*** Kathy McLain, Aron Shultz and Jerry Messman, SpectroStandards' Analytical, The Centre for Advanced Technology, 2301 Research Boulevard, Suite 105, Fort Collins, CO 80526

Defensible reference material standards are critical for meaningful calibration, validation and qualification of laboratory UV/VIS absorption spectrophotometers. If the reference material standards do not meet stringent certification specifications, and/or if they are not used correctly, however, the apparent "validation" or "qualification" will have minimal scientific defensibility and quality assurance value. This presentation will provide scientific insight into the key issues affecting the selection and laboratory use of defensible UV/VIS reference material standards. This overview will be especially instructive to those analytical and quality control laboratories wanting to strengthen or reinforce their UV/VIS quality assurance and measurement practices which will facilitate timely and cost-effective compliance with regulatory requirements.

Quality Assurance/Pharmaceutical Analysis Oral Session—Jerry D. Messman, SpectroStandards' Analytical, P.O. Box 270334, Fort Collins, CO 80527-0334, (970) 472-9537, fax: (970) 427-9580, spectrostandards@juno.com

328. *"RAMPSCAN—A PORTABLE GAMMA-RAY ANALYSIS SYSTEM FOR MONITORING AIR FILTERS.* Colin G. Sanderson and Norman Latner, U.S. Department of Energy, Environmental Measurements Laboratory, 201 Varick Street, New York, NY 10014-4811

Rampscan is a portable gamma radiation measurement and analysis system designed to rapidly measure and assess freshly collected aircraft filters for fission product likelihood. This can be done on the tarmac, in minutes, by the aircraft crew without the need to remove the filter from its protective envelope.

Rampscan is completely computer driven and offers the user straight-forward menu choices. The results of the measurement are shown in a "Go/No-Go" indication that clearly shows the operator which filters to ignore and which require further analysis.

- *Performs rapid assessment of aircraft filters for fission products by gamma-ray analysis*
- *Based on a 3" x 3" Inline Sodium Iodide Detector, 6.3% fwhm resolution*
- *No preparation of filter is needed*
- *Designed to be used in the field by unskilled operators*
- *User Friendly computer interface*
- *Typical sample count of 2 minutes*
- *Straightforward Go/No-Go indication*
- *On board calibration check source*
- *Powered by rechargeable sealed lead acid batteries, which are physically arranged around the detector to form a virtual shield and thus reduce background count*
- *Battery voltage display, charge indicator and live counting display option*
- *4 hours of continuous operation per charge, charger operates on 120 or 240 VAC*
- *Housed in a rugged aluminum case*
- *Weight: 19.5kgm, Size: L=43cm, W=53cm, H=18cm*

Radiochemistry Oral Session—Colin G. Sanderson, U.S. Department of Energy, Environmental Measurements Laboratory, 201 Varick Street, New York, NY 10014-4811

329. *PROPOSED RADIOCHEMICAL TECHNIQUE FOR RADIUM-224 IN DRINKING WATER SAMPLES.* D.E. McCurdy, A.D. Banavali, J.M. Raimondi, Duke Engineering & Services, Boston, MA 01740

Recent studies conducted by the State of New Jersey, the USEPA and the USGS have discovered that Ra-224 may be found in significant concentrations in potable ground waters throughout the United States. This finding is important for two reasons; the Ra-224 in the water contributes to the radiological dose to the public and the gross alpha-particle concentration results obtained by the screening method recommended by the USEPA Safe Drinking Water Act is directly affected by the presence of Ra-224. As a result of the short half-life of Ra-224, the measured gross alpha concentration of the water containing this isotope will vary according to time. Furthermore, the analytical turnaround-time between sample collection and analysis is somewhat restrictive due to the rapid decay of the isotope.

A classical technique employing ion exchange chromatography for elemental concentration and purification followed by $BaSO_4$ microprecipitation and alpha spectrometry has been refined for the simultaneous quantification of Ra-223, Ra-224 and Ra-226 in a water sample. Thorium in the sample is removed quantitatively by the ion exchange column. The chemical recovery of each sample is determined through the use of a Ba-133 radiotracer.

The FWHM alpha particle resolution for the microprecipitate mounts is typically between 70 and 100 keV. Detctor efficiency for the spectrometry system used is 25%. Ra-224 and Ra-226 are directly quantified via their 5686 keV and 4784 keV alpha energy lines. Ra-223 is quantified using the 7386 keV alpha energy line of Po-215, the second decay product of Ra-223. A MDC value of < 1 pCi / L is easily obtained by this technique using a 250 mL sample, a chemical recovery of ~ 60% and a counting time of 1000 minutes.

An overview of the technique, along with its attributes and disadvantages will be presented.

Radiochemistry Oral Session—D.E. McCurdy, Duke Engineering & Services, Boston, MA 01740

330. *COMPARISON OF MEASUREMENTS OF "FALLOUT" LEVELS OF PU AND AM IN SEDIMENTS.* Pamela Greenlaw, U.S. Department of Energy, Environmental Mesurements Laboratory, 201 Varick Street, New York, NY 10014-4811

No abstract.

331. *EXTRACTION CHROMATOGRAPHY: PRINCIPLES AND THE ACHIEVEMENT OF SEPARATION AND SELECTIVITY.* E. Philip Horwitz, Lawrence Jassin, Eichrom Industries, Inc.

No abstract.

332. ***STATISTICAL COMPARISON OF GROSS ALPHA AND GROSS BETA PARTICLE ACTIVITY IN WATER ANALYZED USING TWO ANALYTICAL METHODS.*** Roy C. Bartholomay, U.S. Geological Survey, WRD, INEEL, MS 1160, Idaho Falls, ID 83403; George M. Hill and Raymond B. Randolph, U.S. Department of Energy, RESL, MS 4149, Idaho Falls, ID 83403

The U.S. Geological Survey, in cooperation with the U.S. Department of Energy, statistically compared results from two analytical methods used to analyze gross alpha- and gross beta-particle activity in 50 pairs of water samples collected from selected wells at the Idaho National Engineering and Environmental Laboratory (INEEL). Water samples were analyzed by the Radiological and Environmental Sciences Laboratory at the INEEL using the current analytical method, alpha scintillation counting and gas-flow proportional beta counting, and a quicker method, liquid scintillation counting, to determine whether changing analytical methods would affect precision of results.

To evaluate the precision of the two methods, the results of 50 pairs of samples were compared statistically for equivalence on the basis of the precision associated with the results. The statistical comparison indicated that results for gross alpha-particle activity in 98 percent of the samples were equivalent; results for gross beta-particle activity in all the samples were statistically equivalent. The study indicates that a change in analytical methods to liquid scintillation counting will not affect precision of results.

Radiochemistry Oral Session—Ann Mullin, USGS/NWQL, Box 25046, Denver Federal Center, Bldg 95, MS 407, Denver CO, 80225-0046

333. ***MARLAP,*** Stan Morton, U.S. Department of Energy, 850 Energy Drive, Idaho Falls, ID 83403

No abstract.

334. ***INTRODUCTION OF EICHROM Sr RESIN CARTRIDGES: Sr-90 ANALYSIS.*** Anil Thakkar, Lawrence Jassin, Michael Fern, Eichrom Industries

No abstract.

335. ***UPDATE ON NELAC.*** Donivan R. Porterfield, Los Alsmos, NM 87545

No abstract.

336. ***CANBERRA INDUSTRIES ANALYTICAL ROLE IN THE ENVIRONMENTAL RESTORATION AND DECONTAMINATION AND DECOMMISSIONING OF ROCKY FLATS ENVIRONMENTAL TECHNOLOGY SITE.*** Larry Umbaugh, Canberra Industries, 800 Research Parkway, Meriden, CT 06450

No abstract.

337. ***A METHOD VALIDATION SOP AT EPA'S NATIONAL AIR AND RADIATION ENVIRONMENTAL LABORATORY.*** Mary Wisdom, U.S. EPA NAREL, 540 South Morris Ave., Montgomery, AL 36115-2601

No abstract.

338. ***ADAPTATION OF EMPORE™ TECHNOLOGY TO FIELD SAMPLING AND ANALYSIS.*** David C. Seely, 3M Filtration Products, 3M Center, Building 209-1C-30, St. Paul, MN 55144-1000

The development of Empore™ membrane technology has lead to a wide variety of analytical solid phase extraction applications in the environmental and bioanalytical fields. Recently this technology has also been formulated into Rad Disks for radiochemistry laboratory use. In a continuing effort to simplify and reduce the cost of testing operations, new research and development has focused on adapting EmporeTM technology for use in the field.

Applications for field use include sampling of aqueous sources and field analysis of Empore™ disks. Earlier work studied sampling for Tc and Pb. Recent studies with Cs, Ra, and Sr have been completed. Disks have been used with attended sampling, composite sampling, and with process monitoring. Field analytical work, using loaded disks, is in the prototype/laboratory development stage.

Radiochemistry Oral Session—David C. Seely, 3M Filtration Products, 3M Center, Building 209-1C-30, St. Paul, MN 55144-1000, dcseely@mmm.com

339. ***A QA CHEMIST GOES TO THE CENTER OF THE MEASUREMENT UNIVERSE: MY WEEK AT NIST.*** Mary Wisdom, U.S. EPA NAREL, 540 South Morris Ave., Montgomery, AL 36115-2601

No abstract.

340. *A COMPARISON OF RA-224 AND RA-226 BY ALPHA SPEC AND GAMMA SPEC.* David Kappleman, U.S. EPA NAREL, 540 South Morris Ave., Montgomery, AL 36115-2601

No abstract.

341. *HOW DO LONG-LENGTH-SCALE SOLVENT DENSITY FLUCTUATIONS AFFECT SOLUTE DYNAMICS IN COMPRESSIBLE SUPERCRITICAL FLUIDS?* G. Goodyear, S. C. Tucker (Invited Speaker), University of California Davis, Davis, CA 95616

Supercritical fluids in the highly compressible region of the phase diagram are unusual in that they exhibit mesoscopic length-scale density inhomogeneities which may dramatically affect solute behavior.We have shown through computer simulation that as a result of these inhomogeneities a solute may experience a mean, local solvent density which exceeds the bulk value. Additionally, we find that a solute may also experience a very broad distribution of local solvent environments. Our newly developed simulation methodologies have enabled us to characterize the detailed microscopic structure of these local environments and to determine their characteristic reorganization times. We find that these local structural reorganizations may be very slow and hence that inhomogeneous broadening effects can be observed for dynamic processes in compressible supercritical fluids. We therefore examine the effects that such solvent density inhomogeneities have on dynamic solute processes, such as vibrational relaxation, diffusion and reaction.

Supercritical Fluids Oral Session—Susan C. Tucker, Associate Professor, Department of Chemistry, University of California, Davis, CA 95616, (530)752-2203, fax: (530)752-8995, sctucker@ucdavis.edu

342. *THE USE OF INTEGRAL EQUATION AND MONTE CARLO TECHNIQUES TO UNDERSTAND THE LIGHT SCATTERING DENSITY PROFILES OF SUPERCRITICAL BINARY MIXTURES.* Frank G. Baglin, Wayne T. Stanbery, University of Nevada, Chemical Physics Program/216, Reno, Nv. 89557; Tasha E. Palmer, University of Nevada, Chemical Engineering Department, Reno, Nv. 89557.

Using interaction induced Raman light scattering (iiRLS) to provide intensity/density (I/d) vs. density (d) profiles for both CH4/CO2 or CO solute-solvent systems, Monte Carlo (MC) and integral equation (IE) techniques have been applied to more fully comprehend the radial distribution functions (rdf) properties that represent the various densities. In particular, the IE calculations have used only single center Lennard-Jones (LJ) parameters whereas the MC use atomic centered LJ parameters and partial Charges on the atom, thus allowing the effects of the dipoles and or quadrupoles to be ascertained. Moreover, the IE results have been used to calculate the local density numbers which, in turn, allow us to reproduce the experimental iiRLS results.

Supercritical Fluids Oral Session—Frank G. Baglin, University of Nevada, Chemical Physics Program/216, Reno, Nv. 89557, phone 775/784-6651, identical then 6804,baglin@chem.unr.edu

343. *A NOVEL APPROACH IN DETERMINATION OF MOISTURE CONTENT IN PLUTONIUM DIOXIDE UTILIZING SUPERCRITICAL CARBON DIOXIDE EXTRACTION AND FOURIER TRANSFORM INFRARED DETECTION.* William K. Hollis, Aaron M. Martinez, Stephen Trujillo, James B. Rubin, and Craig M. V. Taylor (Invited Speaker), Physical Organic Chemistry Group (CST-12), Los Alamos National Laboratory, Los Alamos New Mexico.

Supercritical fluids (SCF's) exist in a unique "state" of matter with properties of both liquids and gasses. Their gas-like viscosity and diffusivity, coupled with liquid-like densities, make them unique, tunable solvents. These unique solvent properties allow for novel solvent substitution applications in areas such as cleaning, materials modification, chemical processing, and analytical chemistry. A novel approach has been developed at the Los Alamos National Laboratory (LANL) for the quantitative determination of moisture in plutonium oxide powders. The method incorporates the use of SuperCritical Carbon diOxide (SCCO2) as an extraction media coupled with Fourier transform infrared (FTIR) spectrometry for quantitative analysis. SCCO2 was chosen for its combination of low viscosity and high diffusivity resulting in an enhanced ability to penetrate microporous media. The use of the SCCO2/FTIR system also benefits the process by its ability to remove and quantitate other hydrogenous materials from the plutonium oxide matrix. A commercial extraction instrument has been modified and interfaced to a commecially available high-pressure FTIR cell. This approach will be implemented as an alternative method for moisture determination for the storage of plutonium oxide at various Department of Energy sites. To certify the SCCO2/FTIR method, we are performing a set of controlled round-robin tests, comparing SCCO2/FTIR with four other moisture measurement methods, Loss-On-Ignition, Interstitial Gas Analysis (IGA), Thermogravimetry (TGA) and neutron moderation, on pure and impure plutonium oxide samples. The results of this study will be discussed.

Supercritical Fluids Oral Session—Craig M. V. Taylor, Physical Organic Chemistry Group (CST-12), Los Alamos National Laboratory, Los Alamos New Mexico.

344. ***THE USE OF SUPERCRITICAL FLUIDS IN ASYMMETRIC CATALYSIS TO TUNE PRODUCT ENANTIOSELECTIVITY AND ISOLATION.*** Dolores C. Wynne (Invited Speaker), University of California at Davis, Department of Chemistry, One Shields Avenue, Davis, CA, 95616; Philip Jessop, University of California at Davis, Department of Chemistry, One Shields Avenue, Davis, CA, 95616

Supercritical fluids (SCFs) have a number of properties which make them attractive media for catalytic asymmetric synthesis. First, the variation of dielectric constant in some SCFs near the critical point can allow one to assess the effect of solvent strength on the selectivity of the reaction. We have shown that in supercritical (sc) fluoroform (scCHF$_3$*, *T_c* = 25.9°C, *P_c* = 48.2 bar), the enantioselectivity of the intermolecular cyclopropanation of styrene and methyl phenyldiazoacetate in the presence of a dirhodium carboxylate catalyst can vary with dielectric constant from 40% e.e. at pressures above 90 bar to almost 80% e.e. at lower pressures closer to *P_c* (Wynne, D. C., Jessop, P. G., Angew. Chem. Int. Ed. Engl., in press). Additionally, SCFs such as scCO*$_2$* and scCHF*$_3$* allow for a potential means of separation by retrograde crystallization (Foster et al., Ind. Eng. Chem. Res., 1991, 30, 1955-1964). This technique requires that the solubilities of the product and the catalyst have opposite temperature dependence. Whether this is likely to be the case will be discussed. This provides an excellent possibility for the separation of organics from the catalyst, which would result in an increase in the purity of the products and would enable the recycling of catalyst. Use of scCO*$_2$* as a reaction medium provides the additional benefits that it is a non-flammable, biologically and environmentally benign solvent. Supported by EPA/NSF Partnership for Environmental Research.*

Supercritical Fluids Oral Session—Dolores C. Wynne, University of California at Davis, One Shields Avenue, Davis, CA, 95616, (530) 754-7541, dcwynne@ucdavis.edu

345. ***SUPERCRITICAL CO2-ASSISTED NEBULIZATION AND BUBBLE DRYING FOR THE PRODUCTION OF MICRON-SIZED DRY POWDERS OF PHARMACEUTICALS FOR INHALATION DRUG THERAPY.*** S.P. Sellers, K.D. Kusek, G.S. Clark, B.J. Korte, R.E. Sievers; University of Colorado, Cooperative Institute for Research in Environmental Science, Boulder, CO 80309-0216.

A new process has been developed for the preparation of fine powders of pharmaceuticals for inhalation therapy. This process involves the use of supercritical CO2-assisted nebulization and bubble drying to form micron-sized spheres of drug or drug/excipient. These powders are suitable for storage and/or later use in metered-dose or dry powder inhalers as most of the particles produced are within the inhalable-size range. With this technique, supercritical CO2 is brought into contact with an aqueous solution of the drug or drug/excipient formulation inside a low-dead-volume tee. The resultant emulsion of supercritical CO2-and aqueous drug solution saturated with CO2 is allowed to expand through a capillary restrictor. Upon decompression, large sheer forces due to the rapid expansion of CO2 produce a very fine aerosol of the aqueous drug solution. The aerosol is immediately combined with warm nitrogen to form dry (potentially hollow) spheres of the drug.

Supercritical Fluids Oral Session—Scott Sellers, University of Colorado-CIRES, Campus Box 216, Boulder, CO 80309-0216, (303) 492-8624, fax: (303) 492-1414, sellers@terra.colorado.edu

346. ***EXTRACTION AND DETERMINATION OF MOISTURE AND ORGANICS FROM PLUTONIUM DIOXIDE USING SUPERCRITICAL CARBON DIOXIDE EXTRACTION AND FOURNIER TRANSFORM INFRARED SPECTROSCOPY.*** Aaron M. Martinez, William K. Hollis, James B. Rubin, Craig M. V. Taylor, Michael N. Jaspersona, and Joseph B. Rodrigueza Physical Organic Chemistry Group, Material Characterization Group (NMT-1), Los Alamos National Laboratory, PO Box 1663, MS 537, Los Alamos, NM, 87545

A quantitative analysis method at Los Alamos National Laboratory has been developed for the verification of moisture content in plutonium oxides. The Department of Energy (DOE) has established a maximum amount of moisture in plutonium oxide bound for long term storage at 0.5% by weight. It has been found that water in the oxide will produce gases by radiolysis. The formation of gases above this initial concentration of water could lead to an over pressurization of the canister resulting in a breach of containment. In order to quantitate this moisture content a new method incorporating supercritical carbon dioxide (SCCO2) as the extraction fluid and an interface to a high-pressure cell that is monitored by a Fourier transform infrared detector (FTIR) has been developed. There are two major advantages to this method, real time analysis for a production scale system and elimination of generated waste. SCCO2 fluid unique physical properties offer extraction behavior as a liquid and diffusion behavior as a gas that makes it beneficial for our selection. It is also non-toxic, non-flammable and environmentally friendly. The data has shown that the SCCO2/FTIR method has performed well in the removal of the water from the plutonium oxide samples.

Commercial extraction and detection systems have been used for this process. The combined system was implemented for use inside a glovebox where radiation control is required. The current DOE standard method is loss on ignition (LOI), where a gravimetric weight loss by thermal stabilization 1000°C is performed. The LOI method has the potential of producing artificially high moisture content due to volatilized inorganic salts. This will directly result in an increase in the cost and time of doing business. Our proposed method, SCCO2/FTIR is also capable of distinguishing hydrogenous material types, water and organics, in the oxide. This method is therefore more specific as to what type of hydrogenous material present. This approach if successful will be implemented as an alternative method for moisture determination that can be used in the Material Identification and Surveillance Program for storage of Plutonium Oxide.

Data will be presented on plutonium oxide and other surrogates has been analyzed and compared to the LOI method. An additional independent method, Interstitial Gas Analysis (IGA), has also been included for comparison. To further determine the boundaries of the methods; elemental analysis data generated by ICP/MS was used to characterize the weight loss of LOI. Additional documentation from this *project showing how the system conformed to the rigorous and strict safety procedural methodologies by facilities, the University of California and the Department of Energy safety guidelines will be supplied.*

Supercritical Fluids Oral Session—Aaron M. Martinez, Los Alamos National Laboratory, Physical Organic Chemistry Group, Box 1663, MS 537, Los Alamos, NM 87545, (505) 667-7673 fax: 5(05) 667-6561, martinezamt@lanl.gov

347. *ALKYLATION OF AROMATICS AT SUPER-CRITICAL CONDITIONS; A PARAMETRIC AND IN SITU SPECTROSCOPIC INVESTIGATION.* Daniel M. Ginosar, Christopher E. Bunker, Robert V. Fox, Kyle Coates, Lockheed Martin Idaho Technologies Co., Idaho National Engineering and Environmental Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2208

The chemical industry produces more than 15 billion pounds per year of alkyl aromatics via the liquid acid catalyzed alkylation of aromatics. Aromatics are combined with olefins over concentrated liquid acid catalysts. These concentrated liquid acids pose serious safety and environmental concerns due to the transport and storage of concentrated liquid acids and disposal of acid-hydrocarbon sludges. A solid acid catalyst could replace liquid acids and eliminate these safety and environmental concerns; however, solid catalysts deactivate rapidly due to the buildup of coke. Supercritical Fluids (SCFs) have unique solubility and transport properties that make them ideal for extraction in porous media, such as solid acid catalysts. By operating a solid catalyst alkylation process at super-critical conditions coke forming compounds can be extracted from the catalyst surface as they are formed resulting in long catalyst lifetimes and high catalyst activity. An experimental program was undertaken to explore the effect of super-critical operation on the heterogeneous catalytic alkylation of toluene with ethylene. Results are presented on catalytic activity, catalyst deactivation and product selectivity at gas, liquid, near- and super-critical conditions. Near- and super-critical conditions showed clear advantages for minimizing catalyst deactivation compared to gas phase conditions and clear advantages for product selectivity compared to liquid phase reaction conditions. In addition, spectroscopic measurements are made in situ to probe the fluid-catalyst interface. The results are discussed within the context of possible catalytic mechanisms and the observed advantages of near- and super-critical conditions over gas and liquid conditions.

Supercritical Fluids Oral Session—Frank G. Baglin, University of Nevada, Chemical Physics Program/216, Reno, NV 89557, baglin@equinox.unr.edu

348. *NMR DETECTION AND IMAGING OF GAS PHASE MICELLES.* David E. Fremgen, Rex E. Gerald II, Robert J. Klingler, Jerome W. Rathke, Argonne National Laboratory, Chemical Technology Division, Argonne IL 60439; Eugene S. Smotkin, Illinois Institute of Technology, Chicago, IL 60616

Microemulsions£ offer several advantages as media for conducting homogeneous catalytic reactions: catalyst recovery via phase separation, and enhanced mass transport rates over conventional phase transfer systems. Microemulsions of water in liquid and supercritical carbon dioxide are being investigated in-situbyhigh pressure nuclear magnetic resonance (NMR) spectroscopy. Interactions between specific surfactant nuclei and a dissolved (micellar) salt have been probed by homonuclear saturation experiments. The longitudinal relaxation rates and line widths of these components are being determined. In addition, an imaging technique, using the radio frequency magnetic field gradient of a toroid cavity detector, allows us to record NMR spectra of localized regions of the reaction vessel. In this manner, we can determine physical properties of the surface and the interior regions of the microemulsion system. The NMR imaging technique can be applied to the determination of diffusion coefficients of the various micellar components: water, water soluble salts, and surfactant. This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under contract No. W-31-109-ENG-38.

Supercritical Fluids Oral Session—David Fremgen , Argonne National Laboratory, Chemical Technology Division, 205/J-137, Argonne, IL 60439-4837, (630) 252-4438, fax: (630) 252-9373, fremgen @cmt.anl.gov

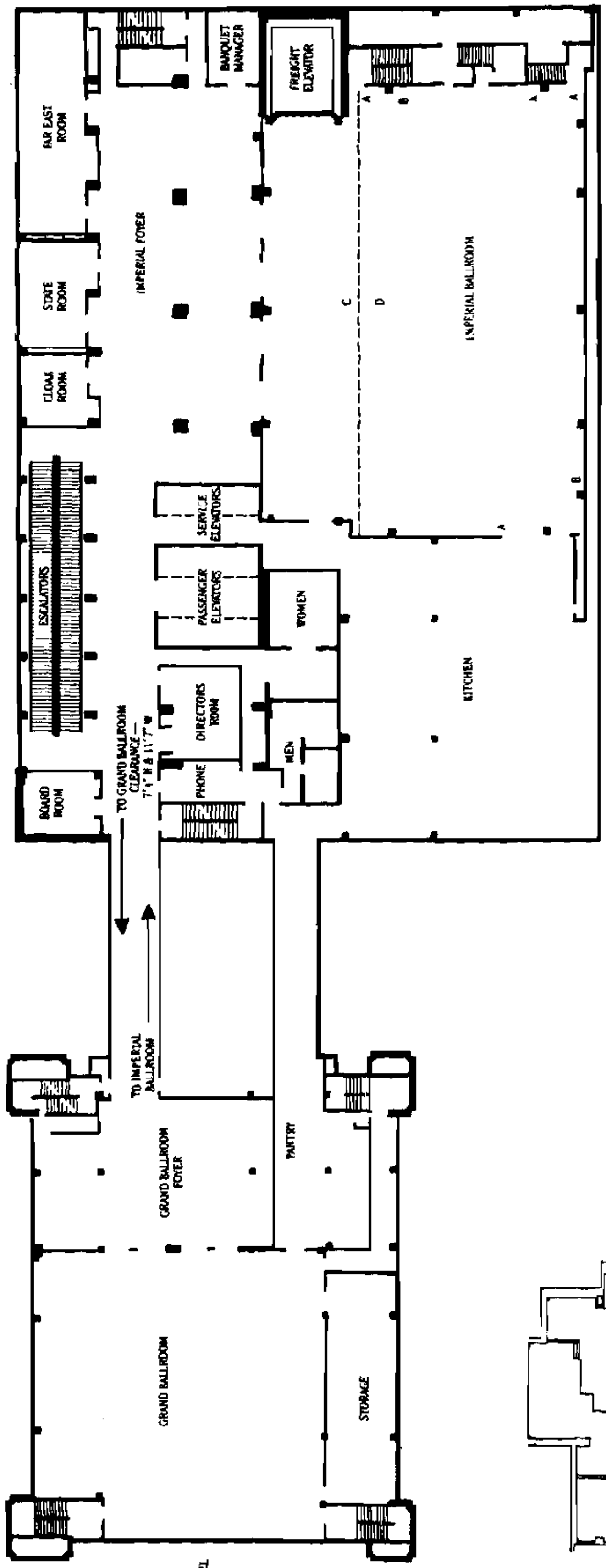
349. *SUPERCRITICAL CARBON DIOXIDE PROCESSING CONSIDERATIONS TO PRODUCE CEMENT-BASED, CHEMICALLY BONDED CERAMICS.* Roger H. Jones, Jr., President, the Supramics company, 14525 Rim Rock Road, Reno, Nevada 89511

Over the last fifty years, ceramics applications became bifurcated between relatively mundane uses, such as serving dishes and ovenware, on the one hand, and, on the other, costly sophisticated products such as electronic packaging and high-temperature aerospace composites. This split resulted from the advent of inexpensive, durable thermoplastics and resins from petrochemical fractions during the last half of this century. A new class of chemically bonded ceramics called, "Supramics®," and formed by supercritical carbon dioxide (CO_2) treatment of final-net-shaped products made from hydraulic cements, offers a way to fill the manufacturing and economic gap between these two product extremes. Once an article has been formed and allowed to hydrate, differing supercritical processing conditions permit significant control over a productís final physical and chemical properties.

As thermally bonded ceramics progressed from simple pottery to complex modern products, empirical data about materials, product forming, firing (temperature, kiln design and kiln-atmosphere chemistry, pressure and duration) and glazing were developed and codified to permit control over final product properties. As with traditional ceramics (and as is still the case with thermoplastics and composites), these new Supramics® materials systems will require the development of similar empirical data to produce ever-more-sophisticated and economical products. The author discusses the current state of the art in this exciting new materials field and outlines its likely course of future research and development.

Supercritical Fluids Oral Session—Roger H. Jones, Jr., President, the Supramics company, 14525 Rim Rock Road, Reno, Nevada 89511

Notes



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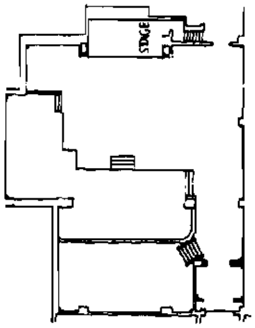

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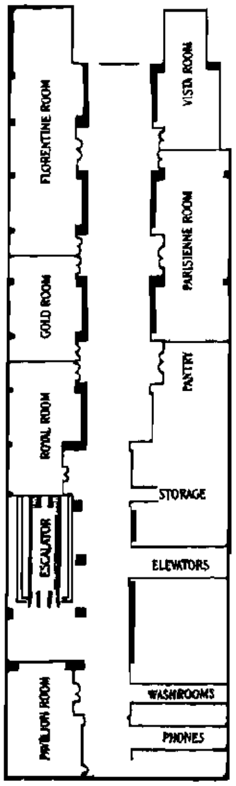

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