

# Rocky Mountain Conference on Magnetic Resonance

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Volume 42 *42nd Rocky Mountain Conference  
on Analytical Chemistry*

Article 1

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7-30-2000

## 42nd Rocky Mountain Conference on Analytical Chemistry

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### Recommended Citation

(2000) "42nd Rocky Mountain Conference on Analytical Chemistry," *Rocky Mountain Conference on Magnetic Resonance*: Vol. 42, Article 1.

DOI

<https://doi.org/10.56902/RMCMR.2000.42.1>

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## 42nd Rocky Mountain Conference on Analytical Chemistry

### Abstract

Abstracts from the 42nd 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 Broomfield, Colorado, July 30 - August 3, 2000.

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# ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

## ABSTRACTS

### Electrochemistry

1. INFLUENCE OF STERIC ACCESSIBILITY ON CHEMICAL REACTIVITY IN MONOLAYERS. Richard Martoglio, University of Wyoming, Department of Chemistry, Laramie, WY 82071; Eli Hvastkovs, University of Wyoming, Department of Chemistry, Laramie, WY 82071; Kristin Jackson, University of Wyoming, Department of Chemistry, Laramie, WY 82071; Daniel A. Buttry\*, University of Wyoming, Department of Chemistry, Laramie, WY 82071

*Immobilized monolayers are increasingly being used for a variety of purposes, ranging from fundamental physical studies to sensing. In many of these applications, it is desirable to use a variety of chemical reactions to couple solution phase reactants onto a pre-formed monolayer. This is especially true in the case of sensing applications, in which a variety of biorecognition elements may be incorporated into monolayers. One classic study of monolayer reactivity that stands out is that by Van Ryswyk and coworkers, in which ester hydrolysis in a monolayer was studied.<sup>1</sup> However, in spite of the obvious need to understand reactivity of solution phase reagents with chemically reactive functional groups in monolayers, and the many uses of reactive monolayers, there is a remarkable paucity of studies on their reactivity. Several different types of reactive functional groups have been immobilized into monolayers. Our interest is in electrophilic groups that allow facile reaction with solution phase nucleophiles, since many such solution phase reagents are known. One particularly interesting class of reagents is 11,11'-dithio-bis(succinimidylundecanoate) (DSU) and its derivatives with different alkyl chain lengths. This compound was first reported by Nakano and coworkers<sup>2</sup>, who showed that it could be reacted with enzymes. Later, Wagner and coworkers<sup>3</sup> reported a more thorough study of the reactivity of monolayers of this reagent with proteins and other amine-containing compounds. In both cases, while reactivity was observed, the authors found it to be considerably lower than expected based on the intrinsic reactivity of the N-hydroxysuccinimidyl (NHS) group. In the present study, we report the dependence of the reactivity of interfacially immobilized NHS esters on their extent of dilution with alkyl disulfides in pre-formed monolayers.*

1. H. Van Ryswyk et al., *Langmuir*, 1996, 12, 6143.

2. K. Nakano, H. Taira, M. Maeda and M. Takagi, *Anal. Sci.*, 1993, 9, 133.

3. P. Wagner, M. Hegner, P. Kernen, F. Zaug and G. Semenza, *Biophys. J.*, 1996, 70, 2052.

**Electrochemistry Symposium Oral Session—Richard Martoglio, University of Wyoming, Department of Chemistry, Laramie, WY 82071. Tel: 307-766-3041, Fax: 307-766-2807, E-mail: ricardo@uwyo.edu**

2. POLYVINYLACETATE ELECTROLYTES: PREPARATION, CHARACTERIZATION AND STABILITY. Renee Henry, University of Colorado at Colorado Springs, Department of Chemistry, 1420 Austin Bluffs Parkway, P.O. Box 7150, Colorado Springs, CO 80933-7150; Radha Pyati, University of Colorado at Colorado Springs, Department of Chemistry, 1420 Austin Bluffs Parkway, P.O. Box 7150, Colorado Springs, CO, 80933.

*Ongoing research and development of new polymer electrolytes is necessary to improve battery technology. To this end, the preparation of polyvinylacetate electrolyte thin films are described. The stability of the film has been studied as a function of time. It was found that the film quality diminishes with repeated cyclic voltammetry scanning and not as a function of the age of the film. The films have been studied under different atmospheres in order to compare the film operation in ambient versus inert atmospheres. These atmospheres include argon, vacuum, air, air saturated with water and air saturated with dimethylsulfoxide. These films were further studied by varying the scan rates to overcome the degradation of the film quality. The contents of the films were studied by spectroscopic means.*

**Electrochemistry Symposium Oral Session—Renee Henry, University of Colorado at Colorado Springs, Department of Chemistry, Colorado Springs, CO 80933-7150. Tel: 719-262-3689, Fax: 719-262-3047, E-mail: rmhenry@brain.uccs.edu**

3. INVESTIGATION OF THE CORROSION OF ALUMINUM CURRENT COLLECTORS IN LITHIUM-ION BATTERY ELECTROLYTES. Mateusz L. Hupert, Utah State University, Department of Chemistry and Biochemistry, Logan, UT 84322-0300; Greg M. Swain, Utah State University, Department of Chemistry and Biochemistry, Logan, UT 84322-0300.

*Aluminum, which is the most commonly used current collector material for the positive electrode in lithium-ion batteries, is susceptible to environmental degradation. At the highly oxidizing potential associated with the positive electrode charge condition, pitting corrosion of bare aluminum occurs. The results from the electrochemical (cyclic voltammetry, chronoamperometry) studies of corrosion of aluminum in different non-aqueous electrolytes, as well as data from microstructural characterization of aluminum surface before and after corrosion will be presented.*

**Electrochemistry Symposium Oral Session—Greg M. Swain, Utah State University, Department of Chemistry and Biochemistry, Logan, UT 84322-0300. Tel: (435) 797-1626, E-mail: e-mail:gmswain@cc.usu.edu**

4. MAPPING ALLOY ELECTRODEPOSITION CONDITIONS ONTO DEPOSIT CHARACTERISTICS FOR MICROELECTRODE ARRAYS. Jason Thomas, and Daniel A. Buttry\*, Department of Chemistry, University of Wyoming, Laramie, (WY) 82071-3838, USA; and John Pope, The Blue Sky Group 365 North Ninth Street, Laramie, (WY) 82072-3380

*Electrochemical processing is well suited to many of the materials needs of integrated circuit fabrication. In particular, it is ideal as a means to deposit various pure metals and alloys onto integrated circuit structures. Our groups have recently been engaged in the development of combinatorial methods for alloy electrodeposition onto microelectrode arrays. One type of array that has been employed in this effort is an analog CMOS circuit containing 1024 individually addressable microelectrodes. It is a goal of the effort to develop electrochemical methodologies to allow use of these arrays with combinatorial methods to search for new materials with improved properties. As part of that effort, several interesting features of the electrodeposition of bimetallic alloys on such arrays have been uncovered. This report will discuss the behavior of the electrodes on the CMOS arrays under various conditions. The experimental protocols used during the electrodeposition and the major problem of displacement reactions will also be discussed.*

*We are grateful to the Office of Naval Research for financial support of the work at U.W.*

**Electrochemistry Symposium Oral Session—Jason Thomas, University of Wyoming, Department of Chemistry, Laramie, (WY) 82071-3838. Tel: (307) 766-3041, Fax: (307) 766-2807, E-mail: jthomas@uwyo.edu**

5. ELECTROCHEMICAL OXIDATION AND DETECTION OF ALIPHATIC POLYAMINES AT BORON-DOPED DIAMOND THIN-FILM ELECTRODES. Malgorzata A. Witek, USU, Department of Chemistry and Biochemistry, Logan, UT 84322-0300, Miles D. Koppang, USD, Department of Chemistry, Vermillion, SD 57069, and Greg M. Swain, USU, Department of Chemistry and Biochemistry, Logan, UT 84322-0300.

*The oxidation of aliphatic polyamines (ethylenediamine, cadaverine, putrescine, spermine and spermidine) was investigated at polycrystalline, boron-doped diamond thin-film electrodes. Cyclic voltammetry and flow injection analysis (FIA) with amperometric detection were performed to evaluate diamond electrode response. Measurements were conducted in carbonate buffer solution (pH10). In the cyclic voltammetry, well-resolved oxidation waves for all the polyamines were observed at potentials about +900 mV vs. Ag/AgCl. FIA results demonstrated that the diamond electrodes can be used for detection of these compounds with a concentration limits of quantitation at 1.0 mM (S/N >3), and a linear dynamic range from 10<sup>-3</sup> to 10<sup>-6</sup> M ( $r^2 > 0.997$ ). An injected concentration of 1.0 mM cadaverine and spermidine yielded signal with relative standard deviation (RSD) of about 5.0% for repeat injections. Detection figures of merit were obtained at constant potential without any prior derivatization. A model for the reaction whereby the polyamine oxidation occurs by oxygen transfer reaction from OH radicals was proposed. Hydroxyl radicals are generated at the non-diamond carbon impurity sites at lower overpotential than surrounding diamond matrix. These sites are believed to be located at the grain boundaries in the polycrystalline diamond lattice. A mechanism is proposed whereby the amine is stabilized by complexation of the nitrogen's free electron pair at surface boron sites, also located in close proximity to the non-diamond carbon impurity phases. Results from these electrochemical studies will be presented.*

**Electrochemistry Symposium Oral Session—Greg M. Swain, USU, Department of Chemistry and Biochemistry, Logan, UT 84322-0300. Tel: (435)-797-1626, Fax: (435)-797-3390, E-mail: gmswain@cc.usu.edu**

6. THE INCORPORATION OF PT PARTICLES INTO BORON-DOPED DIAMOND THIN-FILMS: APPLICATIONS IN ELECTROCATALYSIS. Jian Wang, Utah State University, Department of Chemistry and Biochemistry, Logan, UT 84322-0300; Greg M. Swain, Utah State University, Department of Chemistry and Biochemistry, Logan, UT 84322-0300

*Polycrystalline, boron-doped diamond thin films were co-deposited with Pt particles on either a Si or Pt substrate. The films were fully characterized by scanning electron microscopy, energy dispersive x-ray analysis, atomic force microscopy, auger electron spectroscopy, Raman spectroscopy, powder x-ray diffraction, secondary ion mass spectrometry and cyclic voltammetry. These dimensionally stable and corrosion-resistant electrodes consist of well-faceted microcrystallites with dispersed Pt particles incorporated into the surface. The metal particles are well-anchored into the surface and range from 10 to 500 nm in diameter. Importantly, the Pt particles at the surface are in electronic communication with the current collecting Si or Pt substrate through the boron-doped diamond matrix, and they are electroactive for the UPD of hydrogen. The dispersed Pt particles are extremely stable as no change in the activity was observed after 1000 potential cycles between the oxygen and hydrogen evolution regimes in 0.1 M HClO<sub>4</sub>. The methanol oxidation and oxygen reduction reactions on the Pt incorporated diamond films were investigated and will be reported on.*

**Electrochemistry Symposium Oral Session—Jian Wang, Utah State University, Department of Chemistry and Biochemistry, Logan, UT 84322-0300. Tel: 435-797-1547, Fax: 435-797-3390, E-mail: SL1Z4@cc.usu.edu**

7. ANGLE AND WAVELENGTH DISPERSED SPR SPECTROSCOPY OF ROUGHENED SILVER FILMS. Roger Terrill, Department of Chemistry, San Jose State University, San Jose, CA 95192-0101.

*Surface plasmon resonance (SPR) spectra with both angle- and wavelength-dependent information were obtained in-situ during the electrodeposition of thin, relatively rough Ag films on smooth Ag substrates. Estimates of the optical constants of the smooth and rough Ag films were made and the impact of surface roughness on SPR spectra are discussed. The sensitivity of the SPR spectral response to chemisorption onto the smooth and electrodeposited surfaces are discussed.*

**Electrochemistry Symposium Oral Session—Roger H. Terrill, Department of Chemistry, San Jose State University, CA, 95192-0101. Tel: 408-924-4970, Fax: 408-924-4945, E-mail: rterrill@jupiter.sjsu.edu.**

8. ELECTRONICALLY CONDUCTING POLYMER FILMS WITH TUNABLE WORK FUNCTIONS. Corey J. Bloom, C. M. Elliott, P. G. Schroeder, B. A. Parkinson, Chemistry Department, Colorado State University, Fort Collins, CO 80523

*Recently there has been a great deal of interest in light emitting devices composed of thin film electroluminescent organic polymers or small molecule organics (OLED's). Such systems offer several potential advantages over the more traditional inorganic LED's including relative ease of production and processing. A typical OLED consists of one or more organic layers between a low work function metal cathode such as calcium and a higher work function anode, often indium-tin oxide (ITO). While theoretically many of these systems are very close to ideal, there are indications that in reality the metal cathode-organic interface does not behave so perfectly. The replacement of such highly reactive metals with a low work function polymer may provide significant improvement.*

*With special treatments, electrochemically active films based on substituted tris(bipyridine)ruthenium(II) complexes can be made to electronically conduct much like a very low bandgap intrinsic semiconductor. Used in this manner, important electronic properties are set by the exact chemical nature of the complexes. Through judicious choice of ligands, it is possible to tune parameters of interest such as work function (F) and bandgap of the films. Approximate F of films can be predicted via electrochemical data, and verified with ultraviolet photoelectron spectroscopy. In addition to the fundamental interest of such tailor made materials, they offer the prospect of polymeric LED cathode materials with variable work functions.*

**Electrochemistry Symposium Oral Session—Corey Bloom, CSU Chem. Dept. (970) 491-7348.**

**E-mail: corbloom@lamar.colostate.edu**

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## Environmental Chemistry

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9. **INVITED SPEAKER IN ENVIRONMENTAL CHEMISTRY SPONSORED BY TJA SOLUTIONS** EPA's DRINKING WATER LABORATORY CERTIFICATION AND METHOD APPROVAL PROGRAMS, Richard Reding, United States Environmental Protection Agency, Office of Ground Water and Drinking Water, Technical Support Center (MS-140), 26 West Martin Luther King Drive, Cincinnati, OH 45268.

*To conduct compliance monitoring under the Safe Drinking Water Act a laboratory must be certified for drinking water analyses and use an approved method. Requirements for monitoring chemical contamination at public water systems are outlined. Laboratory certification requirements, the steps involved in an onsite laboratory audit, and key features of an acceptable laboratory quality assurance program are described in detail. The scientific and regulatory steps in the selection and approval of analytical methods for compliance monitoring are also discussed. Although most approved methods are published by government agencies or voluntary consensus standards bodies, method developers may also obtain approval under the Office of Water's alternate test procedure (ATP) program. The ATP program encourages the development and approval of new methods and modifications to currently approved methods that achieve one or more of the following:*

- improve method performance
- overcome matrix interferences
- reduce test complexity and costs
- reduce the amount of hazardous materials used or produced in the laboratory
- increase the protection of human health and the environment

*To improve method flexibility and to more quickly adopt new measurement technologies in water monitoring, OW standardized and reduced ATP application requirements and is developing a framework for the evaluation, approval and use of some methods as screening procedures for determinations of chemical contaminants in drinking water samples.*

**Environmental Chemistry Oral Session—Richard Reding, United States Environmental Protection Agency, Office of Ground Water and Drinking Water, Technical Support Center (MS-140), 26 West Martin Luther King Drive, Cincinnati, OH 45268.**

10. MTBE MITIGATION IN A DRINKING WATER RESERVOIR—A SUCCESS STORY. M.W. Tikkanen, R. Sykes, and M. Wallis, East Bay Municipal Utility District, 375 11th Street, Oakland, CA 94607.

*Methyl tertiary-butyl ether (MTBE), an oxygenate used in gasoline to boost octane and reduce emissions from automobiles, has been detected in both groundwater and surface water in California and nationally. Where motorized recreational activity occurs on surface water reservoirs MTBE has been detected in the water.*

*Over the past 42 months, East Bay Municipal Utility District (EBMUD) has faced the problem of low level contamination of several of its water supply reservoirs from MTBE. This paper discusses the results of EBMUD's continued efforts to evaluate and control this contamination in its water supply reservoirs.*

*To understand the breadth of the problem, MTBE monitoring on the three drinking water reservoirs that permit recreational motorized boating was established. Additionally, monitoring of effluent from the water treatment plants associated with these reservoirs was also conducted. Results of these studies will be detailed.*

EBMUD focused its MTBE control strategy on source prevention. The East Bay Municipal Utility District MTBE Action Plan included restriction of high emission outboard engines on these drinking water reservoirs. Restriction of high-emission outboard engine usage on these reservoirs has been implemented. In 1998-1999, all District-owned and concessionaire-owned 2-stroke high emission engines were replaced with 4-stroke low emission engines. As of January 2000, only 4-stroke outboard engines will be permitted on San Pablo Reservoir. Results and impact of the phased-in restriction of the high emission marine engines on San Pablo Reservoir to date will be discussed in detail.

Finally, recent regulatory and legislative actions, in California and nationally, will be outlined.

**Environmental Chemistry Oral Session—Maria Tikkanen, East Bay Municipal Utility District, Oakland, CA 94607, Tel: 510-287-1561, Fax: 510-287-1530, E-mail: mtikkane@ebmud.com**

11. AN OVERVIEW OF CURRENT QUADRUPOLE ICP-MS PERFORMANCE CRITERIA RELATED TO THE IMPLEMENTATION OF US EPA ENVIRONMENTAL ANALYSIS METHODS. Rob Henry, TJA Solutions, 1812 Mapleton Avenue, Boulder, CO 80304, USA; Sue Woods and Fergus Keenan, TJA Solutions, 27 Forge Parkway, Franklin, MA 02038, USA.

The US EPA has developed a range of ICP-MS methods for use in its various metals measurement programs: Drinking Water, Waste Water, Superfund etc. Since the US EPA ICP-MS methods were developed, advances in Quadrupole ICP-MS technology have been made which allow easier implementation of the methods into routine use. The technology improvements will be discussed relative to the requirements of the different methods.

**Environmental Chemistry Oral Session—Rob Henry, TJA Solutions, 1812 Mapleton Avenue, Boulder, CO 80304. Tel: 303-939-9012, Fax: 303-939-9017, E-mail: robhenry@excelonline.com**

12. ENVIRONMENTAL MONITORING FROM PRECIPITATION RUNOFF. Steven Matthes, Bernard Covino, Jr., Gordon Holcomb, and Sophie Bullard, U.S. Department of Energy, Albany Research Center, 1450 Queen Avenue, S.W., Albany, OR 97321-2152

Precipitation runoff is the water that drains from a surface and contains components from the surface and wet and dry deposited reactants. Analysis of precipitation runoff from sites in Washington DC, Newport OR, and Albany OR was used to characterize these sites and the impact of the environment on the corrosion of metal surfaces. Environmentally significant ions were measured in incident precipitation and in precipitation runoff from zinc, copper, and lead surfaces, as well as a non-reactive (blank) surface. Precipitation runoff data gives valuable information concerning the release of metal ions from structures such as roofs, gutters, siding, bridges, piping and sculpture into the biosphere. Comparison of the chemistry of incident precipitation to the chemistry of the runoff yields information about the impact of environmental constituents and pollutants on metallic corrosion. Predictions about these impacts can be derived from runoff data.

**Environmental Chemistry Oral Session—Steve Matthes, U.S. Department of Energy, Albany Research Center, 1450 Queen Avenue, S.W., Albany, OR 97321-2152. Tel: 541-967-5826, Fax: 541-967-5936, E-mail: matthes@alrc.doe.gov**

13. ARSENIC CYCLING IN THE VERDE RIVER WATERSHED, ARIZONA. Anne-Marie Compton, Richard D. Foust, Jr., Northern Arizona University, Department of Chemistry, Flagstaff, AZ 86011; Prabhudatta Mohapatra

Surface and groundwater samples were collected in the Verde River watershed, Arizona. Total arsenic was measured by electrothermal atomization atomic absorption spectroscopy. Though copper mining was once prevalent in the area, the major source of arsenic is natural, primarily from Montezuma Well, a thermally constant collapsed travertine spring. Arsenic cycling in Montezuma Well was studied extensively, including total arsenic in plants, sediment and soil. Results are reported.

**Environmental Chemistry Oral Session—Anne-Marie Compton, Department of Chemistry, Northern Arizona University, P.O. Box 5698, Flagstaff, AZ 86011. Tel: (520) 523-7494, E-mail: ac23@dana.ucc.nau.edu**

14. METHODS OPTIMIZATION OF MICROWAVE ACCELERATED EXTRACTION TECHNIQUES FOR VARIOUS REGULATORY COMPOUNDS. Greg LeBlanc, Mike Miller, CEM Corporation, POB 200, Matthews, NC 28106-0200, (800) 726-3331.

We have seen a period of rapid growth in the separation sciences, with gas and liquid chromatography as well as the hyphenated techniques becoming commonplace. There is a need to streamline the extraction techniques preceding these chromatographic analyses. Time and solvent usage have become critical factors. In response to this need several new sample preparation technologies have emerged. As a result analysts are faced with the challenge of adapting current methods or developing entirely new ones depending on the extraction technology they use.

Microwave Accelerated Extraction is a new technique that works with existing solvent regimes with minimal modifications and significant solvent reduction. It also has the benefit of reducing the extraction time. This study will review the methods optimization process when using a closed vessel microwave accelerated solvent extraction technique. It will focus on extraction temperature, sample water content and ratios for solvent mixtures. Recovery data will be presented for pesticides from spiked and reference soils and for fungicides from spiked and "real world" vegetable samples.

**Environmental Chemistry Oral Session—Greg LeBlanc, CEM Corporation, POB 200, Matthews, NC 28106-0200, Tel: (800) 726-3331**

- 15.** ANALYSIS OF ENVIRONMENTAL CONTAMINATION SOURCES THROUGH ISOTOPE RATIO MEASUREMENTS. Kimberly A. Givler, Northern Arizona University, Department of Chemistry, P.O. Box 5698, Flagstaff, AZ 86011; Richard D. Foust, Jr., Northern Arizona University, Department of Chemistry, P.O. Box 5698, Flagstaff, AZ 86011

*Atmospheric deposition of heavy metals due to anthropogenic activity is causing natural ecosystems to become contaminated with elevated levels of heavy metals. Combustion of coal in coal-fired power plants releases particulate matter known as fly ash which is known to concentrate such heavy metals. Two of the most common and controversial of these metals are lead and cadmium. One useful means of identifying sources of heavy metal contamination of heavy metals is through analysis of isotopic ratios. Isotopic composition is retained from the originating ore, and generally these compositions are different in ores used in industrial processes than in lead occurring naturally in sediments and soils. Analysis of the lead and cadmium ratios in coal burned in the coal-fired Mohave Power Plant were used to attribute elevated lead levels in the soils to their corresponding pollution source. Coal was prepared for analysis through ashing and a nitric acid/hydrogen peroxide digestion. Concentration and isotope ratios were analyzed using GFAAS and ICP-MS. Isotopic ratios of lead and cadmium were also reported for specific soil and coal Standard Reference Materials.*

**Environmental Chemistry Oral Session—Kim Givler, Northern Arizona University, 1385 W. University Ave. Apt. 10-279, Flagstaff, AZ 86001. Tel: 520-523-7494, Fax: 520-523-8111, E-mail: kag8@dana.ucc.nau.edu**

- 16.** ANALYSIS OF WASTEWATER AND SLUDGES WITH A SCANNING ARRAY ICP EMISSION SPECTROMETER. Randy Hergenreder, 761 Main Ave M/S H67, Norwalk, CT 06859, Joachim Nölte, PerkinElmer, Bodenseewerk PerkinElmer, Postfach 10 17 61, D-88647, Überlingen, Germany

*Wastewater and sludge analyses generally require the determination of many elements and are economically performed using ICP-OES. For this type of application, the concentration of toxicological-relevant metals can be relatively high compared to the detection limits of this technique. However the matrix levels can be quite high and so a sample introduction system tolerant of high sample matrix is important. Array type ICP emission spectrometers supply the user with spectra rather than single data points. This allows the user to utilize the spectral information around an analytical wavelength. A new scanning array ICP-OES instrument has been designed, which is able to handle the various demands of environmental analysis. This paper shows the analytical performance of this instrument for wastewater and digested sludges.*

**Environmental Chemistry Oral Session—Randy L. Hergenreder, 761 Main Ave, M/S H67, Norwalk, CT 06859, Tel: 800-762-4000. Fax: 303-403-1798, E-mail: hergenrl@perkinelmer.com**

- 17. INVITED SPEAKER IN ENVIRONMENTAL MASS SPECTROMETRY SPONSORED BY AGILENT TECHNOLOGIES**  
THE ENVIRONMENTAL ANALYSIS OF PESTICIDES BY HPLC/MS WITH APCI AND ESI IONIZATION. E. Michael Thurman, U.S. Geological Survey, 4821 Quail Crest Place, Lawrence, Kansas 66049

*The evaluation of 30 pesticides from six classes (triazines, organophates, phenylureas, chlorinated phenols, phenoxyacids, and quaternary amines) by high-performance liquid chromatography/mass spectrometry (HPLC/MS) clearly shows that different classes of pesticides are detected more sensitively under either atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) conditions. For example, neutral pesticides in solution often are more sensitive in APCI (especially positive ion), and ionic pesticides in solution are more sensitive in ESI (especially negative ion). These data are expressed graphically in a figure called an ionization-continuum diagram that shows that polarity expressed as proton addition or subtraction (pKa) is useful to predict sensitivity under either APCI or ESI conditions. The importance of protonation and de-protonation within the microdroplet is discussed, as well as the role that this process plays in enhancing sensitivity under APCI or ESI conditions.*

**Environmental Chemistry Oral Session—Mike Thurman, U.S. Geological Survey, 4821 Quail Crest Place, Lawrence, Kansas 66049. 785-832-3559 (office); 785-832-3500 (fax) ethurman@usgs.gov**

- 18.** IDENTIFICATION OF ALKYL DIMETHYLBENZYL AMMONIUM CATIONS IN WATER SAMPLES BY SOLID-PHASE EXTRACTION FOLLOWED BY LC/MS/MS. Imma Ferrer, Edward T. Furlong, National Water Quality Laboratory, U.S. Geological Survey, Denver, CO 80225-0608

*Alkyl (C12, C14 and C16) dimethylbenzyl ammonium chlorides (grouped commercially as benzalkonium chloride, Chemical Abstracts Service number: 8001-54-5) are quaternary ammonium salts with antiseptic properties and uses similar to other cationic surfactants. Their wide-spread use as a disinfectant in many different products has suggested that they should be present in surface water and wastewater. A method based on solid-phase extraction (SPE), that uses C18 cartridges, followed by liquid chromatography/mass spectrometry (LC/MS) detection with an electrospray interface in positive ion mode, was developed for the determination of the alkyl dimethylbenzyl ammonium cations in water samples. The main ions used for LC/MS detection corresponded to the molecular cations at  $m/z = 304$ ,  $332$  and  $360$ , which are equivalent to C12, C14 and C16 in the alkyl chain of the structure, respectively. The structure of this compound in water samples was confirmed by MS/MS after the molecular cations that were isolated and subsequently fragmented. The main fragmentation observed for the three different compounds corresponded to the loss of the benzyl group in the chemical structure, which resulted in the fragment ions at  $m/z = 212$ ,  $240$  and  $268$ . Detection limits for the methodology developed in this work were in the low nanogram-per-liter range. Concentrations of benzalkonium chloride ranged from 0.05 to 1 micrograms per liter in water samples collected from different wastewater treatment plants, or from sites immediately downstream of wastewater discharges. This reflects the input of benzalkonium chloride to wastewater and the potential for its presence in surface water.*

**Environmental Chemistry Oral Session—Edward T. Furlong, National Water Quality Laboratory, U.S. Geological Survey, PO Box 25046, MS 407, Building 95, Denver Federal Center, Denver, CO 80225. Tel: 303-236-3941, Fax: 303-236-3499, E-mail: efurlong@usgs.gov**

19. COMPARATIVE ANALYSIS OF SILCOSTEEL® COATED SAMPLE PATHWAY AND ELECTROFORM NICKEL SAMPLE PATHWAY IN THE TEKMAR 3100 SAMPLE CONCENTRATOR. Glynda Smith, Tekmar-Dohrmann, 7143 E. Kemper Road Cincinnati, OH 45249; Don Harrington, Tekmar-Dohrmann, 7143 E. Kemper Road Cincinnati, OH 45249; Mark Krigbaum, Tekmar-Dohrmann, 7143 E. Kemper Road Cincinnati, OH 45249; Eric Heggs, Tekmar-Dohrmann, 7143 E. Kemper Road Cincinnati, OH 45249

*The Tekmar 3100 Sample Concentrator represents an extension of the 3000 Purge and Trap product line. Silcosteel® -treated sample fittings are used throughout the sample pathway. Silcosteel® treatment involves a process that passivates the active surfaces on metal. A thin, silicon-based coating is applied to the metal surface, which keeps analytes from adsorbing onto active sites on the metal. As a result, there is enhanced inertness, corrosion resistance, and reduced adsorption. Prior to the introduction of Silcosteel®, the sample pathway consisted of electroform nickel and fittings constructed of electroless nickel plating. Difficulties were encountered in the analysis of thermally labile analytes, high boiling compounds, flavor volatile organics, and some environmental compounds such as 1,1,2,2-tetrachloroethane. These compounds are targeted for evaluation because many of them are prone to breaking down and adsorbing onto active metal surfaces. A direct comparison of the 3100 and the 3000 was completed to show the advancement in the product evolution. The evaluation specifically focuses on difficult compounds such as the Polar components of USEPA Method 524.2, the high boiling compounds in USEPA 502.2, Sulfur Compounds & thermal labile compounds. In this paper, the results of a comparison study between samples evaluated using a Silcosteel® sample pathway and an electroform nickel sample pathway will be presented and discussed.*

**Environmental Chemistry Oral Session—Don Harrington, 7143 E. Kemper Road, Cincinnati, OH 4524, Tel: 303-768-0126, Fax: 303-768-0025, E-mail: donhar@tekmar.com**

20. AN ACCELERATED SOLVENT EXTRACTION GC/MS METHOD FOR THE DETERMINATION OF MULTIPLE CLASSES OF PESTICIDES AND PESTICIDE DEGRADATION PRODUCTS IN AMBIENT AIR. D.R. Chase, W.T. Foreman; M.S Majewski; F.W. Wiebe; M.W. Sandstrom; M.E. Stoppel, U.S. Geological Survey, National Water Quality Laboratory, Denver, CO. 80225-0046

*The U.S. Geological Survey (USGS) previously developed a method for the determination of selected high-use pesticides in air that uses a glass fiber filter (GFF)/polyurethane foam (PUF) plug sampler with analysis by gas chromatography with selected-ion mass spectrometry (GC/MS). This method performed well for many of the 47 compounds tested, but some of the more volatile pesticides or pesticide degradates are incompletely collected on the PUF. The method also uses traditional solvent extraction in a Soxhlet apparatus, which consumes time and solvent. A new method has been developed to determine more than 70 parent pesticides and nearly 50 selected pesticide degradation products in ambient air. Compounds are collected by using a medium-volume air sampler that consists of a GFF followed by a PUF/XAD-2 resin/PUF sorbent trap contained in the tube section of an accelerated solvent extraction (ASE) cell. The GFF and sorbent trap are then separately extracted at elevated temperature and pressure by ASE. Extracts are reduced in volume by solvent evaporation, cleaned up with stacked C-18 and Florisil solid-phase extraction columns, and analyzed by GC/MS. Addition of the XAD-2 resin improves collection efficiency versus PUF alone for many of the gas-phase pesticides. Use of the ASE substantially reduces the time and solvent necessary for sorbent trap precleaning and for extraction of the trap following sampling. The new air method is designed to complement two USGS water methods that determine the same suite of pesticides and degradates to facilitate comparison of air data with results obtained for rain and surface-water samples.*

**Environmental Chemistry Oral Session—Daniel R. Chase, U.S. Geological Survey, National Water Quality Laboratory, Denver, CO 80225-0046, Tel: 303-236-3963, Fax: 303-236-3499, E-mail: drchase@usgs.gov**

21. ASSESSMENT OF HUMAN EXPOSURE TO PAH USING GC WITH HIGH RESOLUTION MASS SPECTROMETRY TO DETECT URINARY PAH METABOLITES. Christopher J. Smith, W. Huang, C. Walcott, J. Grainger, and D.G. Patterson Jr., Centers for Disease Control and Prevention, 4770 Buford Hwy., MS F-17, Atlanta, GA 30341

*Human exposure to PAH (polycyclic aromatic hydrocarbons) is universal, and several mechanisms are responsible for the transfer of PAH into the human body. A single PAH metabolite is often used as a biomarker of exposure; however, PAH exhibit differential absorption into the human body. PAH are metabolized into many products including hydroxy-PAH that are excreted in the urine primarily as glucuronide conjugates. Our work focuses on the application of an isotope-dilution method that determines 18 monohydroxy-PAH metabolites arising from eight parent PAH. The quantification of these metabolites enables an accurate evaluation of the range of exposures from background levels to occupational levels. We will present results from method development (solid phase microextraction), isotope-dilution with high resolution mass spectrometry, and sample data. Profiles of the metabolite excretory patterns will be evaluated in terms of the route and source of exposure.*

**Environmental Chemistry Oral Session—Christopher Smith, CDC, 4770 Buford Hwy., MS F-17, Atlanta, GA 30341, Tel: 770-488-4166, Fax: 770-488-4609, cps6**

22. DETERMINATION OF PHARMACEUTICALS IN SURFACE-WATER SAMPLES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY: METHODS AND INITIAL RESULTS. Jeffery D. Cahill, Edward T. Furlong, Mark R. Burkhardt, National Water Quality Laboratory, U.S. Geological Survey, Denver, CO 80225-0608; Larry Anderson Department of Chemistry, University of Colorado, Denver, CO 80217-3364

*A new method has been developed for determining low microgram-per-liter to low nanogram-per-liter concentrations of human pharmaceutical compounds in surface-water samples by using solid-phase extraction (SPE) and high-performance liquid chromatography/mass spectrometry (HPLC/MS). Data for the number of prescriptions and the typical dosages for administration for the most commonly used prescription and over-the-counter pharmaceuticals were collected. These data were used to develop a list of common pharmaceuticals likely to be present in sur-*



face water. Various SPE phases were tested to determine the best phase for the chemically diverse classes of pharmaceuticals in the final analytical list. Average recoveries greater than 60 percent for 12 of 19 compounds tested resulted when an N-vinyl pyrrolidone-modified styrene-divinylbenzene SPE sorbent was used. Mixture separation, compound identification, and quantitative analysis were by HPLC/MS with a positive-ionization electrospray interface and selected ion monitoring. HPLC separation was accomplished by a narrow-bore column that contained an octadecylsilane stationary phase modified to reduce tailing of basic compounds. The mobile phase consisted of a 10-millimolar ammonium formate/formic acid buffer, pH 3.7, and acetonitrile in a stepped gradient. Seventy-seven filtered 1-liter surface-water samples were obtained from various sites across the United States, representing a range of land uses. Nonprescription compounds such as acetaminophen, caffeine, and the nicotine metabolite cotinine were typically the compounds with the highest concentrations, up to 10 micrograms per liter ( $\mu\text{g/L}$ ). Compounds such as gemfibrozil, caffeine, ibuprofen, sulfamethoxazole, and trimethoprim, previously detected in other studies, were measured at median concentrations ranging from 0.30 to 0.55  $\mu\text{g/L}$ . New compounds not previously reported, such as acetaminophen, cotinine, cimetidine, paraxanthine, diltiazem, and dehydronifedipine, were detected at median concentrations ranging from 0.011 to 0.60  $\mu\text{g/L}$ .

**Environmental Chemistry Oral Session—Edward T. Furlong, National Water Quality Laboratory, U.S. Geological Survey, PO Box 25046, MS 407, Building 95, Denver Federal Center, Denver, CO 80225. Tel: 303-236-3941, Fax: 303-236-3499, E-mail: efurlong@usgs.gov**

- 23.** EVALUATION OF USEPA METHOD 524.2 USING A TEKMAR-DOHRMANN 3100/AQUATEK-70 WITH GC/MS. Glynda Smith, Tekmar-Dohrmann, 7143 E. Kemper Road Cincinnati, OH 45249; Don Harrington, Tekmar-Dohrmann, 7143 E. Kemper Road Cincinnati, OH 45249; Mark Krigbaum, Tekmar-Dohrmann, 7143 E. Kemper Road Cincinnati, OH 45249; Eric Heggs, Tekmar-Dohrmann, 7143 E. Kemper Road Cincinnati, OH 45249

Purge and Trap coupled with gas chromatography offers a simple method for the extraction and concentration of Volatile Organic Compounds (VOC) from multiple matrices such as waters and soils. USEPA Method 524.2 monitors a wide range of VOC in drinking water. Due to the wide range and number of compounds analyzed in Method 524.2 there are multitudes of analytical problems that can arise. One of the most common problems is the transfer of water to the analytical column. Excessive water transfer can cause problems both with the chromatography and with the mass spectrometer. An evaluation of different methods of moisture control will be evaluated. Another problem that arises when using purge and trap systems is poor peak shapes of the permanent gases. Since the sample is being transferred to the GC in the gas phase, laminar flow can cause the sample to broaden during transfer to the analytical column thus causing poor peak shape. There are multiple ways to transfer the sample to the analytical column, many of these eliminate or lessen the effects of laminar flow. Different injection techniques will be evaluated to clearly view the advantages and disadvantages of each technique. In this paper, Tekmar-Dohrmann's 3100 Purge and Trap in combination with an AquaTek-70 Liquid Autosampler will be optimized for the analysis of USEPA 524.2 on GC/MS. The optimization will focus on achieving the optimal chromatography with the lowest detection limits and maximum reproducibility. Presentation of results will include calibration curves, sample reproducibilities and detection limits.

**Environmental Chemistry Oral Session—Don Harrington, 7143 E. Kemper Road Cincinnati, OH 45249, Tel: 303-768-0126, Fax: 303-768-0025, E-mail: donhar@tekmar.com**

- 24.** DETERMINATION OF ANIONIC AND NON-IONIC SURFACTANTS, THEIR DEGRADATION PRODUCTS AND ENDOCRINE-DISRUPTING COMPOUNDS IN SEWAGE SLUDGE BY LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY. Damià Barceló and Mira Petrovic, Department of Environmental Chemistry, IIQAB-CSIC, c/Jordi Girona 18-26, 08034 Barcelona, Spain.

A comprehensive analytical method based on reverse-phase liquid chromatography and mass spectrometry using both Atmospheric Pressure Chemical Ionization (APCI) and Electrospray Ionization (ESI) has been developed for the simultaneous determination of anionic and non-ionic surfactants, their polar degradation products and endocrine-disrupting compounds (EDCs) in sewage sludge. Extraction of target compounds, with recovery rates from 86% to nearly 100% for polyethoxylates, and from 84% to 94% for polar degradation products, was achieved applying ultrasonic solvent extraction with a mixture of methanol:dichloromethane (7:3, v/v). Clean-up of sample extracts was performed on octadecyl solid-phase extraction cartridges. Determination of less polar compounds: alcohol ethoxylates (AEOs), nonylphenol ethoxylates (NPEOs), coconut diethanol amides (CDEAs), polyethylene glycols (PEGs) and phthalate esters was accomplished by reversed phase LC-APCI-MS in positive ionization mode, while more polar compounds: nonylphenolcarboxylates (NPEC), nonylphenol (NP), octylphenol (OP) and bisphenol A were analyzed by ion-pair LC-ESI-MS under negative ionization conditions. This protocol was successfully applied to the trace determination of anionic and non-ionic surfactants, polar degradation products and EDCs in sewage sludge collected from different sewage treatment plants (STPs). The analysis revealed the presence of NP at high concentration levels ranging from 25 to 600 mg/kg. Polyethoxylates (AEOs and NPEOs) were also found in all samples at parts-per-million levels (10-190 mg/kg of AEOs and 2-135 mg/kg of NPEOs, respectively).

**Environmental Chemistry Oral Session—Damià Barceló, Department of Environmental Chemistry, IIQAB-CSIC, c/Jordi Girona 18-26, 08034 Barcelona, Spain.**

25. ATMOSPHERIC LEAD DEPOSITION AT THE MOHAVE POWER PLANT NEAR LAUGHLIN, NEVADA. Jens-Uwe Kuhn, Northern Arizona University, Department of Chemistry, Flagstaff, AZ 86011-5698; Kimberly A. Givler, Northern Arizona University, Department of Chemistry, Flagstaff, AZ 86011-5698; Richard D. Foust, Jr., Northern Arizona University, Department of Chemistry, Flagstaff, AZ 86011-5698

*Atmospheric lead deposition at the coal-fired Mohave Power Plant near Laughlin, NV was examined by analyzing surface and sub-surface soil samples. Dried soil samples were sieved to isolate the smallest fraction of particles containing most of the fly ash. These dried and sieved soil samples were prepared for analysis using a mixed-acid digestion procedure. Dried and ashed samples of the coal used to fire the plant were prepared for analysis using a nitric acid / hydrogen peroxide digestion procedure. Both materials were then analyzed for lead concentration and isotope ratios using GFAAS and ICP-MS. The highest lead surface soil concentration of 34.1 µg/g was measured at a distance of 5.3 km from the power plant. The lead content of the surface soil was found to reach a baseline level of approximately 10 µg/g, indicating the natural background level of lead in the soil, at a distance of approximately 20 km from the plant. Regression analysis of the surface soil concentration data determined by GFAAS demonstrates a significant correlation between lead concentration and distance from the power plant. Lead isotope ratios of the coal and soil samples measured by ICP-MS were compared to identify possible sources for the elevated lead levels.*

**Environmental Chemistry Oral Session—Jens-Uwe Kuhn, Northern Arizona University, Department of Chemistry, P.O. Box 5698, Flagstaff, AZ 86011-5698. Tel: 520-523-1721, Fax: 520-523-8111, jk6@dana.ucc.nau.edu**

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## EPR Tuesday Oral Sessions

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26. IN VIVO SPECTROSCOPY AND IMAGING - (PAST/PRESENT). Lawrence J. Berliner, Dept. of Chemistry, The Ohio State University, Columbus Ohio 43210-1185

*The development of in vivo EPR is part of a continuum of developments towards more applications and importance in the biomedical sciences. The initial uses of EPR were in the realm of physics but soon also began to involve chemistry and then biochemistry, especially in regard to metalloproteins. But within ten years of the work of Zavoisky establishing the feasibility of EPR spectroscopy, the technique was applied not only to biological problems, but also directly to biological systems. This talk particularly summarizes both some of the first and early key developments, especially as they relate to the development of in vivo EPR and EPR imaging in vivo through the '80s. By 1990 it became clear that in vivo EPR was a useful and continually developing technique, as indicated by the balance of the talk, which provides summaries of the developments of the last ten years with the next speaker outlining some projections of the future course of in vivo EPR1.*

1. Berliner, L. J. (editor) *In Vivo EPR(ESR): Theory and Applications, Biological Magnetic Resonance, Volume 18*, Kluwer Academic/Plenum Publishing Corp., New York (2000).

**EPR Symposia Oral Session—Lawrence J. Berliner, Dept. of Chemistry, Newman-Wolfrom 1118, 100 W. 18th Ave., The Ohio State University, Columbus Ohio 43210-1185. Tel: (614)292-0134, Fax: (614)292-1532, E-mail: berliner.2@osu.edu**

27. IN VIVO SPECTROSCOPY AND IMAGING: FUTURE EXPERIMENTAL AND CLINICAL APPLICATIONS. Harold M. Swartz, Dartmouth Medical School, Department of Radiology, Hanover, NH 03755

*While the details of developments in the future cannot reliably be forecast, sufficient progress already has occurred with in vivo EPR to make it clear that it will be used significantly and it therefore is plausible to speculate about future directions. It is clear that in vivo EPR can provide very useful information that cannot be obtained as readily by other approaches. The information includes measuring key parameters such as oxygen, redox reactions, pH, and molecular motion. In vivo EPR also has been shown to be able to directly observe free radicals in vivo, a unique and very important capability. The potential limiting factors for applications of these capabilities are sensitivity and potential adverse effects of the procedures. With careful planning these factors should be surmounted in experimental animals. The extent of clinical applications will be very dependent on overcoming these potential limitations. Plausible successful scenarios will be discussed.*

*Supported by NIH Grants RR11602 (NCRR) and GM51630.*

**EPR Symposia Oral Session—Harold M. Swartz, Dartmouth Medical School, Department of Radiology, Hanover, NH 03755. Tel: 603-650-1955, Fax: 603-650-1717, E-mail: harold.swartz@dartmouth.edu**

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

*It will be shown that, contrary to some prior derivations, the sensitivity of EPR measurements is, as expected, the same as for NMR, and that in general comparisons of EPR sensitivity as a function of frequency have been pessimistic by one factor of  $\omega$ . The sensitivity of EPR can increase at lower frequency if the sample size is scaled inversely with frequency. The frequency dependence of sensitivity will be compared for various types of EPR measurements. The characterization of spectrometers needed to compare theory and experiment will be outlined. Some measurements on spectrometers in our lab will be used to illustrate the principles.*

**EPR Symposia Oral Session—Gareth R. Eaton, Department of Chemistry and Biochemistry, University of Denver,**

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DOI: <https://doi.org/10.56902/RMCMR.2000.42.1>

- 29.** EPR IMAGING OF BIOLOGICAL SAMPLES—PRINCIPLES & PROGRESS. Periannan Kuppusamy, Johns Hopkins University, The EPR Center, Division of Cardiology, 5501 Hopkins Bayview Circle, Baltimore, MD 21224

*The developments of low frequency EPR instrumentation and lumped circuit resonators have enabled EPR measurements on large aqueous biological samples. Previous in vivo or ex vivo EPR spectroscopic studies focused on global measurements of free radical metabolism or generation as well as measurements of tissue oxygenation. Studies that require measurements of the spatial distribution of these within the sample volume can be performed by electron paramagnetic resonance imaging (EPRI) techniques. The EPRI can be performed in purely the spatial domain to obtain one, two- or three-dimensional (1-D, 2-D or 3-D) images of free radical distribution. It can provide both qualitative and quantitative information at every spatial location within the object. The image is obtained by reconstruction from projections acquired in the presence of magnetic field gradients. The reconstructions are commonly performed by filtered-backprojection or Fourier reconstruction techniques. In addition, a variety of projection and image data processing techniques, including spectral deconvolution and hyperfine correction are utilized to improve the quality and resolution of the reconstructed images. An alternative and more useful EPRI technique is the spectral-spatial (or spectroscopic) imaging, which provides an EPR spectrum for each voxel in the object, thus enabling to obtain spatially resolved lineshape information. Because the spatial and spectral dimensions are fully separable in the spectroscopic image, information about local linewidth, and hence local oxygen content, can be derived independently from local spin density. The basic concepts of EPR imaging, instrumentation, data acquisition, signal processing, image reconstruction techniques and applications will be discussed.*

**EPR Symposia Oral Session—Periannan Kuppusamy, Johns Hopkins University, 5501 Hopkins Bayview Circle, Baltimore, MD 21224. Tel: 410-550-3229, Fax: 410-550-2448, E-mail: kuppu@welch.jhu.edu**

- 30.** TIME-DOMAIN RADIO FREQUENCY IN VIVO EPR IMAGING. Sankaran Subramanian, Nallathamby Devasahyam, John A. Cook, James B. Mitchell and Murali C. Krishna, Radiation Biology Branch, National Cancer Institute, NIH, Bethesda, MD 20892

*We have designed and built a 300 MHz pulsed EPR spectrometer/imager capable of performing in vivo imaging of small laboratory animals such as mice. The spectrometer operates in a single channel IF mode and uses in vivo paramagnetic spin probes based on the trityl radical. Using short pulses (70 - 120 ns), specially constructed parallel-coil resonators, fast recovery preamplifiers, and an ultra fast digitizer/averager, we are able to record 3D image data from a live mouse within 3 min. (81 projections, each being sum of 100,000 FIDs of 4k data points). All timing sequences are derived from a set of three daisy-chained Stanford Research System DG535 Delay Generators. The data collection is automated using a PC with IEEE-GPIB interface. We use a two stage filtered back-projection algorithm written in C++ for reconstructing the images from profiles which are obtained using volume excitation in presence of constant gradients. Matlab, C++ and Voxelview softwares are used for data processing and image rendering in a Silicon Graphics Indigo2 workstation. Our in vivo results (some involving fiducials to unequivocally confirm anatomical details) show that we can obtain reliable morphological data from the liver, kidneys, bladder, etc. of the mouse where the trityl based spin probes accumulate preferentially. Because oxygen produces a broadening effect on free radicals due to dipolar interaction and shortens the spin-spin relaxation time ( $T_2^*$ ), we can assess in vivo pO<sub>2</sub> from time domain data by processing the same with Relaxation weighting. Our results from phantom objects, in vivo mouse anatomy, tumors, and liver ischemia-reperfusion studies will be presented and quantitative oxymetry modalities discussed.*

**EPR Symposia Oral Session—Sankaran Subramanian, Radiation Biology Branch, National Cancer Institute, Bld. 10, Room B3B69, NIH, Bethesda, MD 20892-1002. Tel: 301-496-7511, Fax: 301-480-2238**

- 31.** RECENT PROGRESS IN FIELD-CYCLED PEDRI IMAGING OF FREE RADICALS. David J. Lurie, Margaret A. Foster, Wiwat Youngdee, University of Aberdeen, Department of Bio-Medical Physics, Foresterhill, Aberdeen AB25 2ZD, UK; Valery V. Khramtsov, Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia; Igor A. Grigor'ev, Institute of Organic Chemistry, Novosibirsk 630090, Russia.

*Proton-electron double-resonance imaging (PEDRI, also known as Overhauser Imaging) is now a well-established method for imaging free radical distributions in biological samples and animals. Based on dynamic nuclear polarisation (DNP), it involves the irradiation of an EPR resonance of the free radical of interest during the collection of a proton NMR image. Since spatial information is obtained via the NMR resonance, only modest gradient strengths are needed to obtain high-resolution images.<sup>1</sup> In field-cycled PEDRI (FC-PEDRI) the EPR irradiation is applied at low field (hence low frequency) to reduce power absorption while the NMR signal is observed at a much higher field to improve the signal-to-noise ratio (SNR). We have built an FC-PEDRI imager with a whole-body sized magnet; typically  $B_0 = 3$  mT during EPR irradiation (~50 MHz) and 59 mT during NMR detection at 2.5 MHz.<sup>2</sup> This instrument has been used to image exogenous free radicals in anaesthetised 2 kg rabbits. Currently we are using it to investigate various pH-sensitive nitroxide probes, and we have performed in vivo measurements of pH-sensitive nitroxides in anaesthetised rats. We are investigating the optimisation of pulse sequences for FC-PEDRI, and have found that the inclusion of a 180° inversion pulse in the NMR pulse sequence increases image contrast and may improve sensitivity. The SNR in FC-PEDRI is proportional to the detection magnetic field strength, so it is useful to field-cycle to as high a field strength as possible. We are presently constructing a small-animal FC-PEDRI imager with a detection magnetic field of 0.5 T. This instrument will use a 0.5 T superconducting magnet with a co-axial actively-shielded resistive magnet to provide the field-cycling capability. It is anticipated that the instrument will have an order-of-magnitude superior sensitivity to our present apparatus, and will allow detection of free radicals in vivo at sub micro-molar concentration.*

1. Lurie D.J. Proton-Electron Double-Resonance Imaging (PEDRI), in: *In Vivo EPR (ESR): Theory and Applications, Biological Magnetic Resonance*, Vol. 18, ed: L.J. Berliner, Plenum, New York. (2000).
2. Lurie D.J., Foster M.A., Yeung D. and Hutchison J.M.S. Design, Construction and Use of a Large-Sample Field-Cycled PEDRI Imager, *Phys. Med. Biol.* 43, 1877-1886 (1998).

**EPR Symposia Oral Session—Dr. David J. Lurie, University of Aberdeen, Department of Bio-Medical Physics, Foresterhill, Aberdeen AB25 2ZD, UK. Tel: +44 1224 554061, Fax: +44 1224 685645, E-mail: lurie@abdn.ac.uk**

32. EPR IMAGING OF FREE RADICALS, REDOX METABOLISM AND FUNCTION IN THE HEART. Jay L. Zweier, Alexandre Samouilov, Guanglong He, Michael Chzhan, and Periannan Kuppusamy, Molecular and Cellular Biophysics Laboratories, Department of Medicine and the EPR Center, The Johns Hopkins University School of Medicine, 5501 Hopkins Bayview Circle, Baltimore, Maryland, 21224

*Free radicals are important modulators of cardiac function and critical mediators of disease. It has been hypothesized that free radical metabolism, oxygenation, and nitric oxide generation in the heart and cardiovascular system, vary over the spatially defined tissue structure and there is evidence that this may be an important factor in the pathogenesis of cardiovascular disease. Therefore, we developed instrumentation optimized for 3D spatial and 3D or 4D spectral-spatial EPR imaging of free radicals in the heart and cardiovascular system. Using this instrumentation at 1.2 GHz and 750 MHz high quality 3D spectral-spatial imaging of redox metabolism was performed in the isolated heart and in living mice, respectively, as well as spatially localized measurements of tissue oxygenation. With 3D spatial imaging using single-line labels, resolutions down to 200  $\mu$ m could be obtained. It was shown that EPR imaging provides important knowledge regarding alterations in oxidant stress and free radical metabolism following ischemia, as occurs during heart attack. Important insights were also obtained regarding the basis of the wave-front evolution of cell death. EPR imaging of nitric oxide with both intrinsic and extrinsic spin traps enabled measurement and imaging of the magnitude and time course of nitric oxide generation following the onset of ischemia in the isolated heart and in vivo whole body mouse. Imaging of specific metabolic pathways of nitric oxide generation was performed using  $^{15}\text{N}$  labeled substrates. With gated cardiac EPR imaging, alterations during the cardiac cycle can be visualized and cardiac contractile function and wall thickening can be measured. Thus, in vivo EPR imaging has emerged as a powerful tool that provides unique information regarding the role of free radicals, oxygen, and nitric oxide in the pathogenesis of cardiovascular disease.*

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33. HOLDING THE LINE: EXTRACTION OF EPR LINE PARAMETERS WITH IN VIVO RADIOFREQUENCY EPR IMAGING (EPRI). Howard J. Halpern, Benjamin B. Williams, Colin Mailer, Valeri E. Galtsev, Eugene D. Barth, G.V.R.Chandramouli, Department of Radiation Oncology and The National Biomedical Center for EPR Imaging for In Vivo Physiology, University of Chicago, Chicago, IL

*Extraction of physiologic information from in vivo EPRI at 250 MHz takes advantage of the very low frequency but, at the same time requires attention to a number of aspects of data acquisition to minimize instrumental spectral or spectral-spatial projection distortion. Single line trityl spin probes markedly improve sensitivity and resolution but increase vulnerability to distortion effects. Fixed frequency operation vs AFC with field frequency lock applied to each data point and automatic coupling control are crucial to minimize distortion. Signal-to-noise issues are also crucial for the extraction of accurate linewidths from in vivo samples. A trade off exists between spatial resolution using higher gradients and signal reduction into noise levels due to the broadening at higher gradients. These issues presented elsewhere in greater detail will be summarized. Images of homogeneous phantoms will be shown to map magnetic fields. High spatial and spectral resolution EPRI gives oxygen maps from tumors in a living mouse. The resolution for these images is verified from phantoms obtained under similar conditions. Further relationship to tissue oxygenation will be explored with oxygenation changes and measurements with needle electrodes. Four dimensional images of phantoms and tumors will be shown. These very low frequency provide proof of principle for measurements in larger human size subjects. Issues pertaining to scaling to larger systems will be discussed including next generation systems. Supported in part by RR12257 and CA 69538.*

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34. UTILIZATION OF NITROXYL PROBES FOR CLINICAL AND PHARMACEUTICAL APPLICATIONS. Hideo Utsumi, Graduate School of Pharmaceutical Sciences, Kyushu University, Higashi-ku, Fukuoka 812-8582, Japan

*The sensitivity of an in vivo ESR spectrometer is unfortunately insufficient to detect trace amount of endogenous radicals. Thus, we utilize nitroxyl radicals as a probe for in vivo free radical reaction and reactive oxygen generation. The nitroxyl probe is reported to react with  $\bullet\text{OH}$ , causing loss of the paramagnetism of the probe, while excretion to urine, adsorption to tissue of the probes, etc, should take part in the in vivo signal decay. We have used this character of nitroxyl radical to analyze ROS generation in experimental disease models, including hyperoxia, ischemia-reperfusion, liver damage induced by  $\text{CCl}_4$  or iron-overload, streptozotocin-induced diabetes,  $\text{NH}_4\text{OH}$ -induced gastric lesions, and arthritis. In these experiments, the loss of paramagnetism was observed as enhanced signal decay, which was suppressed with  $\bullet\text{OH}$  scavengers and antioxidant enzymes. These results demonstrate that in vivo ESR technique with nitroxyl radicals as probes is very useful technique to estimate free radical reactions in living body, their contribution to diseases, and pharmacological effect of medicines. In the present paper, I will present our recent results and discuss the possibility of in vivo EPR/Nitroxyl Probes technique for clinical and pharmaceutical applications.*

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35. C. J. Hsia

36. V. Vallyathan

37. HARD AND SOFTWARE FOR EPR IMAGING. Joost A.B. Lohman, Tian Qing Ye, Bruker UK Limited, Banner Lane, Coventry, CV4 9GH, United Kingdom.

*The principles of EPR imaging have been established for quite some time ("EPR Imaging and In Vivo EPR", G.R. Eaton, S.S. Eaton and K. Ohno, Eds. CRC Press (1991)). In recent years, the number of exciting applications in the fields of in vivo and biomedical EPRI has increased dramatically. The availability of new narrow-line spin-probes has been an important factor in this development. The instrumentation used for these experiments has in general been custom designed for the application and home-built. In this contribution, design criteria for EPRI instrumentation are examined, with some focus on biomedical applications, but otherwise with a wide range of applications and experiments in mind. Elements in the discussion will be: Method of EPR signal measurement, design of the gradient system, adaptability to new techniques and ease of use for routine applications. Particular attention will be paid to the spectral content of EPRI data and a novel approach to spectral spatial imaging will be presented.*

**EPR Symposia Oral Session—Joost A.B. Lohman, Bruker UK Limited, Banner Lane, Coventry, CV4 9GH, United Kingdom. Tel: (+44)-(0)24-7685-5258, Fax: (+44)-(0)24-7646-5317, E-mail: joost.lohman@bruker.co.uk**

38. A NEW SPIN ON PROTEIN STRUCTURE AND DYNAMICS. Wayne L. Hubbell, Jules Stein Eye Institute and Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-7008.

*Site-directed spin labeling (SDSL) has emerged as an important tool for exploring structure and dynamics in membrane and soluble proteins of arbitrary molecular weight. The SDSL strategy involves the introduction of one or two nitroxide side chains (R1) at selected positions in the protein sequence, followed by analysis of the electron paramagnetic resonance (EPR) properties to yield the solvent accessibility ( $\Pi$ ), environment polarity (P), electrostatic potential ( $\Psi$ ), mobility (M), and inter-spin distance (d) as primary experimental quantities. The sequence dependence of P,  $\Pi$  and M identifies secondary structure, while their vector moments reveal tertiary organization. Together with measurements of d, such information provides sufficient constraints to model a protein at the level of the backbone fold. Recent high-resolution crystal structures of R1 in proteins reveal the preferred conformations and interactions of R1, and provide a firm foundation for interpretation of EPR spectra in terms of local structure. In addition, this information enables rational simulations of the EPR spectra aimed at resolving dynamic contributions from protein backbone fluctuations and internal side chain motions. Initial results suggest that SDSL will provide a unique opportunity for mapping backbone dynamics in membrane proteins. SDSL has now been applied to mapping structure, structural fluctuations and conformational changes in a number of membrane proteins. Rhodopsin has been explored most extensively, and a specific model for the light-activated molecular switch has been formulated.*

**EPR Symposia Oral Session—Wayne Hubbell, Jules Stein Eye Institute, UCLA School of Medicine, 100 Stein Plaza, Los Angeles, CA 90095-7008. Tel: 310/206-8830, Fax: 310/794-2144, E-mail: hubbellw@jsei.ucla.edu**

39. MEMBRANE-PROTEIN INTERACTIONS: ELECTROSTATIC SWITCHES AND  $\text{Ca}^{2+}$ -DEPENDENT PROTEIN BINDING INVESTIGATED USING SITE-DIRECTED SPIN-LABELING AND EPR SPECTROSCOPY. David S. Cafiso, Department of Chemistry and Biophysics Program, McCormick Road, University of Virginia, Charlottesville, VA, 22901

*Proteins that are involved in cell-signaling are often active only when attached to the membrane-solution interface. Membrane attachment of these proteins can be mediated by protein acylation, positively charged protein motifs, PH domains or C2 domains. Site-directed spin labeling combined with EPR spectroscopy is being used to investigate the structure and position of several membrane binding domains on the membrane interface. These include charged domains from proteins such as the src-tyrosine kinase and MARCKS, as well as the  $\text{Ca}^{2+}$  regulated C2 domain from cPLA2. For basic protein motifs the work demonstrates that a combination of forces act on these motifs. In addition to a long range Coulombic attractive force, these forces include hydrophobic and short range repulsive forces. For C2 domains, EPR spectroscopy reveals the membrane interacting face, and the position of the domain on the bilayer interface. This work also provides evidence for membrane and  $\text{Ca}^{2+}$ -induced structural changes that may play a role in the  $\text{Ca}^{2+}$ -mediated attachment of proteins involved in cell-signaling.*

**EPR Symposia Oral Session—David S. Cafiso, Department of Chemistry, Tel: (804) 924-3067, Fax: (804) 924-3567, E-mail: cafiso@virginia.edu.**

40. QUANTIFYING MOLECULAR DYNAMICS BY ESR. J. H. Freed, Cornell University

41. SPIN LABEL DISSECTION OF MUSCLE. David D. Thomas, University of Minnesota, Department of Biochemistry, Molecular Biology, and Biophysics, Minneapolis, MN 55455.

*With Wayne's blessing (OK, sometimes cursing), we have used site-directed spin labeling, protein exchange, and reconstitution to obtain intact, functional muscle fibers and membranes with spin labels attached to desired domains of the muscle proteins myosin, actin, the calcium pump, or phospholamban. We then used EPR, saturation transfer EPR, and transient EPR to test models for the motions and associations of these proteins during muscle contraction and relaxation. Our EPR data require the introductions of new features, even new concepts, into the muscle text books. For example, the biochemical states of these proteins are not single "crystal structures," as depicted by the outcome of x-ray crystallography experiments. Rather, these protein states must be characterized as much by their dynamic disorder as by their crystal structures. The release of ATP by laser flash photolysis allows us to synchronize the myosin molecules in a muscle fiber, and thus to reveal their kinetics. Myosin undergoes a dynamic disorder-to-order transition upon generating force, with only a small fraction of myosin molecules exerting force at*

any instant in time. EPR reveals that aging decreases force by oxidation, which decreases the fraction of myosin molecules capable of entering the EPR-detected force-bearing structural state. The calcium pump and phospholamban both exist in dynamic monomer-oligomer equilibria in the membranes of cardiac muscle, in a reciprocal relation: the reversible dissociation of phospholamban oligomers results in association of calcium pump oligomers and inhibition of the pump. We can mimic the effect of adrenalin on the heart by making mutant phospholamban in which oligomers are destabilized.

**EPR Symposia Oral Session—David D. Thomas, University of Minnesota, Department of Biochemistry, Molecular Biology, and Biophysics, Minneapolis, MN 55455. Tel: (612) 625-0957, E-mail: ddt@ddt.biochem.umn.edu**

- 42.** STUDIES OF PROTEIN DYNAMICS USING SITE-DIRECTED SPIN LABELING AND EPR SPECTROSCOPY. Yeon-Kyun Shin, University of California, Department of Chemistry, Berkeley, CA 94720; Iowa State University, Department of Biophysics, Ames, Iowa 50011.

Site-directed spin labeling (SDSL) developed by Wayne Hubbell provides a unique opportunity to monitor protein conformational changes. Rigid-body movements of secondary structural elements such as  $\alpha$ -helices are often considered essential for the functions of many membrane proteins. Experimentally, pairs of nitroxide spin labels are introduced at strategic positions using SDSL. Recent advances in EPR spectroscopy allows us to obtain the inter-spin distances by analyzing the dipolar broadened EPR spectra. Changes in distances permit a simple modeling for the three dimensional displacement of the protein structure. Typically, the time scale of the movement are on the order of 100  $\mu$ sec to 1  $\mu$ sec that is much longer than the EPR time scale. Thus, the protein conformational changes can be recorded in real time by following the time-dependent spectral changes. Using these EPR strategies the nature of the light-induced protein conformational change has been fully characterized for bacteriorhodopsin. Furthermore, the timing of this rigid-body movement has been determined using time-resolved EPR spectroscopy.

**EPR Symposia Oral Session—Yeon-Kyun Shin, University of California, Department of Chemistry, Berkeley, CA 94720. Tel: 510-643-5507, Fax: 510-643-1255, E-mail: shin@cchem.berkeley.edu**

- 43.** EVOLUTION OF STRUCTURE IN THE SMALL HEAT-SHOCK PROTEIN FAMILY: A SITE-DIRECTED LABELING PERSPECTIVE. H. Mchaourab, Vanderbilt University

- 44.** AGGREGATION OF MOLTED GLOBULAR HUMAN CARBONIC ANHYDRASE II MONITORED BY SPIN AND FLUORESCENT CYSTEINE PROBES. Mikael Lindgren, Rikard Owenius, Per Hammarström, Uno Carlsson, Linköping University, Department of Physics and Measurement Technology, Linköping, S-581 83 Linköping, Sweden.

Spin-labeling of systematically mutated proteins<sup>1</sup> in combination with other molecular probe techniques<sup>2</sup> were introduced in the beginning of the nineties in studies of protein folding processes. One question often raised in the context of molecular labeling is to what extent the probe as well as the mutation itself perturbs the system under study. It was shown in a study of chaperone action that the destabilization of the spin-labeled substrate protein actually can be used to give additional thermodynamic information.<sup>3</sup> Another way to determine the impact of the label and mutations is to use several different labels.<sup>4</sup> By detailed studies of the molecular label properties in simple model systems one can increase the resolution of the method.<sup>5</sup> Here we used the L79C/C206S mutant of human carbonic anhydrase II (HCA II) for multiple labeling experiments to investigate the structure at the edge of the hydrophobic core of the protein during unfolding in GuHCl. Two spin-labels were used, IPSL, and MTSSL, and two fluorescent labels, IAEDANS, and BADAN. The spin label IPSL and the fluorescent label IAEDANS reported on a substantial change in mobility and polarity at both unfolding transitions, at a distance of 7.4-11.2 Å, from the backbone. The shorter and less flexible labels BADAN and MTSSL revealed less pronounced spectroscopic changes in the native to intermediate transition, 6.6-9.0 Å from the backbone. At intermediate GuHCl concentrations the occurrence of an irreversibly aggregated structure was identified from refolding experiments. The size and the structure of the aggregates could be varied by changing the protein concentration. EPR measurements and line-shape simulations together with fluorescence anisotropy measurements provided a picture of the aggregate structure as a disordered protein structure with a distribution of compact, dynamic and polar environments at the site of the molecular labels.

1. M. Lindgren et al., J. Chem. Soc., Perkin Trans. 2 (1993) 2003. M. Lindgren, et al., Biophys. J., 69 (1995) 202.

2. M. Svensson et al., Biochemistry 34 (1995) 8606.

3. M. Persson et al., Biochemistry 38 (1999) 432.

4. Rikard Owenius et al., 21st International EPR Symposium at the Rocky Mountain Conference in Denver, USA, July 1998.

5. P. Hammarström, et. al., Proceedings of the 43rd Annual Meeting of the Biophysical Society in Baltimore, USA, February 1999.

Rikard Owenius, et al., 22nd International EPR Symposium at the Rocky Mountain Conference in Denver, USA, August 1999.

**EEPR Symposia Oral Session—Mikael Lindgren, Linköping University, LiTH-IFM, S-581 83 Linköping, Sweden. Tel: + 46 13 282485, Fax: + 46 13 137568, E-mail: milin@ifm.liu.se**

- 45.** RADICAL PAIR GENERATION, STABILIZATION AND REACTIVITY IN B<sub>12</sub> ENZYME CATALYSIS. Andrew S. Utada<sup>a</sup>; Bon E. Fleming<sup>a</sup>; Sandra D. Parsons<sup>b</sup>; and Kurt Warncke<sup>a,b</sup> <sup>a</sup>Department of Physics and <sup>b</sup>Physical, Materials and Computational Sciences Program, Emory University, Atlanta, GA 30322 USA

The family of vitamin B<sub>12</sub> coenzyme- (adenosylcobalamin-) dependent enzymes catalyze radical rearrangement reactions. Substrate binding-triggered thermal cleavage of the cobalt-carbon bond of B<sub>12</sub> generates low spin ( $S=1/2$ ) Co<sup>II</sup> and the 5'-deoxyadenosyl organic radical. In the proposed minimal mechanism, the C<sub>5</sub>, carbon center of the deoxyadenosyl radical abstracts a hydrogen atom from the bound substrate to form a substrate radical, which rearranges to a product radical. The structure and dynamics of the Co<sup>II</sup>-radical pair states in ethanolamine deaminase

from *Salmonella typhimurium* are revealed by using techniques of X-band continuous-wave and high-resolution pulsed-electron paramagnetic resonance (EPR) spectroscopy, in combination with specific  $^2\text{H}$ -,  $^{15}\text{N}$ - and  $^{13}\text{C}$ -labeled reactants, applied to cryotrapped steady-state and transiently-generated states. Pulsed-laser photolysis of the cobalt-carbon bond of coenzyme analogs bound to the enzyme and time-resolved EPR probing is being used to study the early events in radical pair separation. In another study, a novel radical intermediate, formed during turnover on a substrate analog, has been prepared. Based on substrate and coenzyme isotopic substitutions and simulations of EPR and electron spin echo envelope modulation (ESEEM) spectra, we propose that this radical originates from the deoxyadenosyl moiety. Simulation of the ESEEM from dipolar coupling of unpaired electron spin density on the  $\text{C}_1$  carbon of the substrate radical with the three  $\text{C}_5$ , methyl  $^3\text{H}$  nuclei reveals a  $\text{C}_1\text{-C}_5$  distance of 2.4 Å. This indicates that  $\text{C}_5$  of the deoxyadenosyl radical directly abstracts the hydrogen atom from the substrate in the active site, and suggests that the  $\text{C}_5$  methyl group is poised for hydrogen atom reabstraction by the product radical following the rearrangement step. The results merge to provide insight into the principles of high-yield radical pair generation and radical rearrangements in vitamin  $\text{B}_{12}$  coenzyme-dependent enzymes. Supported by NIH DK54514.

**EPR Symposia Oral Session—Kurt Warncke, Department of Physics, 1001 Rollins Research Center, 1510 Clifton Road, Emory University, Atlanta, GA 30322. Tel: 404-727-2975, Fax: 404-727-0873, E-mail: kwarncke@physics.emory.edu**

46. CW AND PULSE EPR AND ENDOR INVESTIGATIONS OF HEME-THIOLATE ENZYME MODELS. Stefan Stoll, Arthur Schweiger, Physical Chemistry Laboratory, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland; Cécile Claude, Wolf-Dietrich Woggon, Institute of Organic Chemistry, University of Basle, St.-Johanns-Ring 19, 4056 Basle, Switzerland

*Fe(III)-heme centres with a thiolate as fifth ligand form the active sites of an important class of enzymes (cytochromes P450, nitric-oxide synthase NOS, chloroperoxidase CPO) catalyzing a wide range of reactions. It has been shown that the molecular environment in the vicinity of the metal centre crucially influences the spin state of Fe(III), the coordination behaviour and the reactivity of the site. An important question is why the resting state of cytochrome P450cam has a low spin resting state whereas all other members of the P450 family are high spin. In order to help understand the impact of steric and dielectric factors on the spin state and to gain more insight into the electronic structure of heme-thiolate centres, we have investigated a series of cytochrome P450cam and chloroperoxidase enzyme models and their complexes with water, OCl- and HOCl using CW and pulse EPR and ENDOR techniques at 9 and 35 GHz.*

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## EPR Tuesday Poster Sessions

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47. ELECTRONIC STRUCTURE OF THE  $\text{Fe(III)}$ -TETRAPHENYLCHLORIN-BIS-IMIDAZOLE COMPLEX AS DETERMINED BY ESEEM AND PULSED ENDOR TECHNIQUES. A.V. Astashkin, Arnold M. Raitsimring and F. Ann Walker, University of Arizona, Department of Chemistry, Tucson, AZ 85721.

Knowing the details of the electronic structure of the complexes of iron with porphyrins and similar compounds (chlorins, isobacteriochlorins, etc.) is essential for understanding their properties as active centers of metalloenzymes. EPR and its high resolution varieties (ESEEM, ENDOR) are the methods of choice for solving this kind of problems. There is a considerable number of studies of the electronic structure of the iron-porphyrin complexes by EPR (and NMR), providing the detailed information on the dependence of the electronic structure on the axial ligands and porphyrin substituents. At the same time, no studies with comparable level of detail has been performed for chlorins. In this work we apply pulsed ENDOR and ESEEM methods to elucidate the details of the electronic structure of the bis-imidazole iron-tetraphenylchlorin ( $\text{Fe}^\bullet\text{TPC}/\text{Im}_2$ ) complex, to establish the orientation of its  $g$ -tensor with respect to the molecular coordinate frame and to find the orientation of the imidazole ligand planes with respect to the  $g$ -tensor. The proton ENDOR and ESEEM spectra indicate that, same as in the corresponding porphyrin (tetraphenylporphyrin), the largest  $g$ -value corresponds to the direction normal to the heme plane. The angle between the axis of the smallest principal  $g$ -value and the plane of the imidazole ligands is about  $40^\circ$ . The financial support of the NSF (BIR-9224431 and DBI-9604939) and the NIH (DK 31038) is gratefully acknowledged.

**EPR Symposia Poster Session—Andrei Astashkin, University of Arizona, Department of Chemistry, 1306 E. University Blvd., Tucson, AZ 85721. Tel: 520-621-9968, Fax: 520-621-8407, E-mail: andrei@u.arizona.edu**

48. ADVANCED ESEEM STUDIES OF THE HIGH- AND LOW-pH FORMS OF CHICKEN LIVER SULFITE OXIDASE. A.V. Astashkin, Arnold M. Raitsimring, Rachel Codd, M.L. Mader, Andrew Pacheco and John H. Enemark, University of Arizona, Department of Chemistry, Tucson, AZ 85721.

Advances in pulsed EPR methodology have enabled the nearby protons of the high pH (hpH) form of the  $\text{Mo(V)}$  center of sulfite oxidase to be directly detected for the first time. An adjustable frequency S/C-band pulsed EPR spectrometer and a three-pulse sequence that refocuses the primary electron spin echo (RP ESE) have been used to produce an ESEEM spectrum with the intensities of the lines due to nearby protons greatly enhanced relative to those due to distant matrix protons. This technique reveals new structural details of the coordination environment of  $\text{Mo(V)}$  center in the hpH form of sulfite oxidase. Simulation of the RP ESEEM spectrum suggests the presence of two nearby protons that have



distributed hyperfine interactions. These protons are ascribed to a Mo-OH group with strong H-bonding to another nearby proton or to an H<sub>2</sub>O ligand. The RP ESEEM technique promises to be generally applicable to the investigation of paramagnetic centers in metalloproteins, where the lines of a nearby proton of interest are often masked by intense lines of much more numerous distant protons. A P-band (~16 GHz) ESEEM study of the low-pH form of the Mo(V) center of sulfite oxidase in ~40% H<sub>2</sub><sup>17</sup>O has allowed direct detection of <sup>17</sup>O coordinated to Mo(V). Together with the observation of a strongly coupled exchangeable proton in the vicinity of the central ion, this indicates an OH group coordinated to Mo(V). This study also shows that higher operational frequencies (Q-band) are needed to obtain resolved quadrupole splittings for <sup>17</sup>O in this system and other systems with large <sup>17</sup>O hfi constants. The financial support by the NSF (BIR-9224431 and DBI-9604939) and the NIH (GM 37773) is gratefully acknowledged.

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- 49.** X-BAND AND W-BAND EPR STUDIES OF BINDING OF COUNTERIONS TO CATIONIC SURFACTANT AGGREGATES IN SOLUTION AND ADSORBED ON SILICA SURFACES. M.G. Bakker,<sup>1</sup> E. L. Granger,<sup>1</sup> T. Morris,<sup>1</sup> A. Smirnov,<sup>2</sup> <sup>1</sup>Department of Chemistry, The University of Alabama, Tuscaloosa, AL. <sup>2</sup>Illinois EPR Research Center, University of Illinois, Urbana, IL

The binding of counterions to surfactant aggregates such as micelles and solloids (on particle surfaces) is of interest in areas as diverse as pollutant transport, chromatography, and synthesis of mesoporous materials. The spin probes peroxyamine disulfonate (PADS) and 4-[N,N-dimethyl-N-(n-hexadecylammonium)-2,2,6,6-tetramethylpiperidyl-N'-oxyl bromide (HTAB\*, an analog of hexadecyltrimethylammoniumbromide (HTAB)) have been used to study the effect of binding of counterions to micelles of HTAB, and to HTAB aggregates adsorbed onto silica particles. Similar studies on cetylpyridinium chloride (CPC) and cetylpyridinium salicylate (CPSA) have probed the effect of replacing chloride with the much larger salicylate (SA) counterion. The spin-probe HTAB\* is displaced from strong binding sites on silica by CPC but not by CPSA. Linewidth analysis suggests that CPSA forms two surfactant domains, with HTAB\* being excluded from one of them. The EPR spectra of PADS show significant differences in rotational mobility between CPC and CPSA in solution, and show evidence of two different micellar environments in CPSA. This work was supported in part by NIH grant P41-RR01811 (AS) and by a NATO travel grant (MGB).

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- 50.** 140 GHz PULSED EPR AND ENDOR STUDIES ON THE TYROSYL RADICAL IN RIBONUCLEOTIDE REDUCTASE FROM YEAST. G. Bar, M. Bennati, Hiep-Hoa T. Nguyen, J. Stubbe, R.G. Griffin, Center for Magnetic Resonance and Dept. of Chemistry, MIT, Cambridge MA 02139 USA

High frequency pulsed EPR and ENDOR are powerful techniques to identify and characterize endogenous radicals in biological systems. For instance ribonucleotide reductase (RNR) utilize a tyrosyl radical (Y•) to catalyze the reduction of ribonucleotides into the corresponding deoxyribonucleotides and therefore plays an essential role in DNA replication and repair processes. The role of Y• is to initiate a long range coupled electron/proton transfer which ends in the formation of a thiyl radical (S•) at the active site. Recently, Stubbe and coworkers (Nguyen 1999, PNAS 96 12339) successfully expressed and purified RNR subunits from Yeast at sufficiently high concentrations (~100mM) to enable studies of 140 GHz pulsed EPR and ENDOR spectra. The 140 GHz pulsed EPR spectrum shows expected spectrum from the stable Y•, that exhibits an anisotropic Zeeman interaction as well as proton hyperfine couplings. An interesting feature of the high frequency spectrum is an upfield shift of the g<sub>x</sub> value relative to that observed for E.coli tyrosyl radical. In previous reports of tyrosyl radicals in proteins, a correlation between the g<sub>x</sub> value and the presence of a hydrogen bond to the oxygen of the tyrosyl ring was proposed. The hydrogen bond is expected to affect the spin density distribution on the tyrosyl ring. In order to demonstrate the existence of such a hydrogen bond in Yeast RNR, we recorded 140 GHz proton and deuterium pulsed ENDOR spectra of the protein in H<sub>2</sub>O and D<sub>2</sub>O. We present the analysis of the ENDOR data along with spectra simulations and compare the results with the characteristic pulsed ENDOR features of the E.coli RNR tyrosyl radical.

**EPR Symposia Poster Session—G. Bar, Center for Magnetic Resonance and Dept. of Chemistry, MIT, Cambridge MA 02139 USA. E-mail: galli@ccnmr.mit.edu**

- 51.** A MULTITUDE OF HOLE-CENTRES IN IRRADIATED ZIRCONIUM SILICATE. WHY SO MANY? R.F.C. Claridge, W.C. Tennant, N.S. Lees and C.J. Walsby, Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

A surprisingly large number of paramagnetic hole centres have been observed and characterized by EPR in zircon, zirconium silicate. The crystal space group is tetragonal I4<sub>1</sub>/amd. The EPR spectra of most of the hole centres reported in zircon reflect point-group symmetry m (C<sub>4</sub>), Laue class 2/m (C<sub>2h</sub>), typical of centres on or interacting with oxygens (Wyckoff positions h) lying in the ac or bc mirror planes. One hole centre, apparently stabilized by an nearby Y atom, has been reported where the site symmetry is lowered to (C<sub>1</sub>). The symmetry of some holes centres is not apparent from the reported EPR data. EPR data suggest that x-irradiation produces a hole which is normally trapped in the non-bonding p<sub>z</sub> orbital of an O<sup>-</sup> ion and is stabilized by a nearby impurity cation acting as a stabilizer although in at least one example a p<sub>z</sub> ground state can be inferred. Often, the compensating ion is a +3 cation which can be identified by its nuclear spin. Thus far B<sup>3+</sup>, Al<sup>3+</sup>, and Y<sup>3+</sup> have been unequivocally identified as such ions. However there are a number of hole centres which either do not involve a compensating ion or are associated with ions with no nuclear spin. Considering that there is but one type of O atom in the ideal zircon lattice, EPR studies of oxygenic holes form a surprisingly complex field. In this poster we present a review of the observed hole-centres and propose a model based on some ten precisely measured centres. Not supported by any New Zealand government research fund, PGSF or Marsden fund.

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- 52. MULTIFREQUENCY EPR STUDIES OF ELECTRON SPIN RELAXATION IN Gd(3+) CHELATES.** R. B. Clarkson, A.I. Smirnov, T.I. Smirnova, H. Kang, R.L. Belford, B.M. Odintsov, Illinois EPR Research Center, University of Illinois, 190 MSB, 506 S. Wright St., Urbana, IL 61801; V. A. Atsarkin, V. V. Demidov, Institute of Radioengineering and Electronics, Russian Academy of Sciences, Moscow 103907, Russia

The technique of EPR measurements at multiple frequencies, or multifrequency EPR, offers a route to study electron spin relaxation in Gd(3+) chelates in aqueous solution at room temperature. Both the effective g-factor and the line width of EPR spectra show a dependence on the experimental frequency that can be analyzed to obtain information on the square of the zero field splitting ( $\Delta^2$ ) and the phenomenological ZFS correlation time ( $\tau_c$ ) in these systems. We have examined several Gd(3+) systems at 9 GHz, 35 GHz, 48 GHz, 96 GHz, and in some instances higher frequencies, and have analyzed spectra in the light of two applications of Redfield theory [1. Hudson, A.; Lewis, J. W. E., *Trans. Faraday Soc.*, 1970, 66, 1297. 2. Poupko, R.; Baram, A.; Luz, Z., *Mol. Phys.*, 1974, 27, 1345.]. Results are compared with values of  $\Delta^2$  and  $\tau_c$  calculated from NMR relaxation theory, as well as to direct measurements of  $T_1$  made by longitudinally detected EPR (LODEPR). Partial support for this work was provided by the NIH (GM42208, TW00998, RBC; RR01811, RLB) and the Russian Foundation for Basic Research (99-02-16024, VAA).

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- 53. ON THE TRUNCATED SPIN HAMILTONIANS USED IN EMR AND MAGNETISM STUDIES — EXAMPLE: Mn<sub>12</sub> S=10 COMPLEX.** Thomas C.Y. Chung and Czeslaw Rudowicz, City University, Department of Physics and Materials Science, Hong Kong

A recent survey of literature has revealed several examples of the truncated forms of the zero-field splitting (ZFS) Hamiltonian of the second- and/or fourth-order. Such forms have been used in (a) HF-EPR (high frequency) as well as macroscopic quantum tunnelling (MQT) studies of the Mn<sub>12</sub> complexes with spin S=10, and (b) magnetic ordering and MQT studies of antiferromagnets. The "truncation" can be classified into three types: (i) some ZFS parameters allowed by symmetry are arbitrarily set to zero thus effecting the fitted values of other parameters, (ii) one ZFS term is omitted leaving the Hamiltonian non-invariant, and (iii) some parts of the spin operators are omitted leading to unusual definitions of ZFS parameters. Examples of the truncated Hamiltonians considered here are, e.g. (type ii) and (type iii). In most cases such truncation is driven by mathematical tractability of the problem. In this paper we will show that the type (ii) and (iii) truncation may have negative implications. This includes (a) inconsistent notation for ZFS parameters hampering direct comparison of data from various sources and, moreover, (b) misinterpretation of the physical properties of the system, e.g. rhombicity and relative values of the ZFS parameters involved. Some numerical examples will be considered utilizing the recently developed Mathematica programs for simulation of the energy levels, EPR transitions of given order and resonance fields. The simulation programs, unlike the existing EPR.FOR program, are applicable to systems with an arbitrary high value of spin. Some recent HF-EPR results for the Mn<sub>12</sub> S=10 complex will be reconsidered yielding better insight into the spectroscopic properties.

**EPR Symposia Poster Session—Thomas C.Y. Chung, City University of Hong Kong, Department of Physics and Materials Science, Hong Kong SAR, Fax: 852-27887937, E-mail: thomas.chung@plink.cityu.edu.hk**

- 54. MSH MODELLING AND SIMULATION OF TRANSITIONS OBSERVED IN HF-EPR OF Fe<sup>2+</sup> AND Mn<sup>3+</sup> WITH SPIN S=2.** Hilda W.F. Sung, Thomas C.Y. Chung, and Czeslaw Rudowicz, City University, Department of Physics and Materials Science, Hong Kong

Recent HF-EPR (high frequency EPR) data for the spin S=2 ions: Fe<sup>2+</sup>(d<sup>6</sup>) at the reduced sites of rubredoxins, and Mn<sup>3+</sup>(d<sup>4</sup>) in porphyrins and MnPcCl are reanalysed. The experimental results have originally been interpreted using an early limited microscopic spin Hamiltonian (MSH) approach. Here we use the extended MSH theory for the S=2 d<sup>4</sup> and d<sup>6</sup> ions developed (by CZR) up to the fourth-order of perturbation theory and an Excel package worked out recently based on the existing MSH Fortran program. The package enables efficient modelling of the zero field splitting (ZFS) parameters, B<sub>k</sub><sup>q</sup>, in the Stevens operator notation, and the electronic Zeeman g<sub>i</sub> components for orthorhombic and tetragonal symmetry. The variation of  $\lambda$ - spin-orbit and  $\rho$ - spin-spin coupling constant,  $\Delta$ - energy level splittings (i=1-4), and s - the mixing coefficient] can be plotted for a specified range of the input values, keeping the five other parameters fixed. Such graphs enable easy modelling of the theoretical predictions and identification of the parameter ranges yielding agreement with experimental data. A set of Mathematica programs, geared specially towards HF-EPR studies of high-spin molecules (e.g. Mn<sub>12</sub> S=10 complex), has also been developed. The programs enable simulation of the energy levels, EPR transitions of given order, and resonance fields. Using these programs the HF-EPR data for Fe<sup>2+</sup> and Mn<sup>3+</sup> in the above compounds are re-considered yielding new insight into their spectroscopic properties. The results may also be useful for interpretation of HF-EPR data for other S=2 d<sup>4</sup> and d<sup>6</sup> ions in various crystals with orthorhombic or axial symmetry.

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- 55. EXTRACTION OF PHYSIOLOGICAL INFORMATION FROM TIME DOMAIN EPR USING SPECTRA-SPATIAL IMAGING.** John A. Cook, Nallathamby Devasahayam, James B. Mitchell, Sankaran Subramanian and Murali C. Krishna, Radiation Biology Branch, National Cancer Institute, NIH, Bethesda, MD 20892.

We have designed and constructed a time domain 300 MHz radio frequency EPR spectrometer/ imager. Using narrow-line non-toxic water-soluble in vivo EPR probes, we are able to routinely perform 2D and 3D imaging of small animals such as mice. In order to obtain physiological information such as in vivo pO<sub>2</sub> we can use the effect of dipolar spin broadening of the narrow-line probes by dissolved oxygen. It is possible to obtain simultaneously both spatial and spectral information using the spectra-spatial imaging modality, which we have implemented and tested in time domain EPR imaging. Both phantom images acquired using this probe under different oxygen concentrations and in vivo images

from mouse anatomy could be analyzed to extract physiological and hence functional information. The scope of in vivo FT EPR spectra-spatial imaging in small animals will be discussed.

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56. NEW TECHNIQUES IN MAGNETIC RESONANCE FORCE MICROSCOPY-HARDWARE, STATISTICS AND ADAPTIVE CONTROL. W.M. Dougherty, S. H. Chao, J. L. Garbini, S. E. Jensen, M. R. Morrell, Department of Mechanical Engineering; J. A. Sidles, Department of Orthopaedics; University of Washington, Seattle, WA 98195-2600

Magnetic resonance force microscopy (MRFM) is a method for observing magnetic resonance at nanometer length scales by the direct mechanical detection of modulated spin-gradient forces. Many of the classic manifestations of NMR and EPR have been observed—spin echoes, nutation, saturation, etc.<sup>1,2</sup> MRFM opens a new window on spin physics in which the external magnetic field gradient can equal or exceed local intramolecular gradients. We will describe recent developments in our laboratory, including a third-generation UHV cryogenic scan head and digital adaptive feedback control of force cantilever dynamics. We will demonstrate a suite of on-line tools we use to evaluate many statistical properties of MRFM signals and noise. We also survey work from the some of the other institutions actively developing MRFM. The National Institutes of Health, the National Science Foundation, and the U.S. Army Research Office support this work.

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57. CERULOPLASMIN IN HUMAN BONE MARROW AND BODY FLUIDS. Anna Bratasz, Tomasz Zajac, Martyna Elas, Jagiellonian University, Institute of Molecular Biology; Igor Goscinski, CMUJ, Institute of Neurology; Aleksander Skotnicki, CMUJ, Haematological Clinic; Stanislaw J. Lukiewicz, Jagiellonian University, Institute of Molecular Biology, Krakow, Poland.

The concentration of ceruloplasmin in blood or serum has been demonstrated to vary in many pathological states, and in particular in the case of infections and malignant or hematological diseases. In contrast, the level of ceruloplasmin has never been studied in cerebrospinal fluid and bone marrow. The cerebrospinal fluid was taken from 46 neurological patients and biopsies of bone marrow from 20 patients with hematological disorders. Blood samples originated from 30 other individuals, 15 among them suffering from leukemias. The highest and most striking levels of ceruloplasmin have been noticed in the cerebrospinal fluid and blood from patients with brain tumors. Such an elevation of ceruloplasmin has never been seen in other brain diseases or hematological disorders. Two of the patients within this group died. The second largest concentration of ceruloplasmin in blood and cerebrospinal fluid is found among the group of cases with severe brain lesions, often associated with bleeding. A few of them developed additionally meningitis. Among 30 patients from this group 3 died. Comparison of the ceruloplasmin level in the blood of healthy individuals and leukemic patients has revealed that in the latter case the amplitude of EPR signals is on average at least 6 times larger. Conclusions: 1. a very significant increase in the level of ceruloplasmin can be observed in a variety of brain dysfunctions; 2. the same is true, though to a lesser degree, in many leukemic patients; 3. a remarkable rise in the concentration of ceruloplasmin is usually associated with an abnormally high accumulation of nitric oxide in body fluids.

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58. ARTIFACTUAL EPR SIGNALS IN POST-OPERATIVE SAMPLES OF HUMAN TUMORS. Joanna Urban, Martyna Elas, Stanislaw J. Lukiewicz, Jagiellonian University, Institute of Molecular Biology, Lab. for Radiospectroscopy of Cancer, 31-120 Kraków, Poland

The present paper describes a simple way of avoiding a common paramagnetic contamination of samples, excised during surgery, which is known in literature as a "fatty tissue signal". The origin of this complex spectra, composed of 5 or 6 lines of hyperfine structure, was explained in 1976 by Antholine et al. who established that they are due to an exogenous low-molecular-weight copper sulphur complex of diethyldithiocarbamate (DETC). Any materials removed surgically from human body may become contaminated with this substance which could bring about confusion and obscure signals characteristic of the examined tissue. The source of such artifacts proved to be the contact with surgical gloves. Induction of a quintet signal in the animal tissue proved to be possible in the case of all brands of gloves examined. The only brand of gloves, which is never able to induce quintet signal, are hypoallergenic (non-powdered) gloves. This is due to a high degree of purity of latex from which this brand of gloves is made. The material is free of both DETC-Cu and even of DETC, which might form this complex after combining with copper present in the tissue. It is interesting to note that artifactual quintet signals can be induced without a direct contact with gloves. A mediator in their transfer may be powder alone, which is often used to cover the surface of gloves. Hypoallergenic gloves are as a rule non-powdered. It is possible to avoid the contamination of post-operative samples of human tumors with the copper complex of DETC giving rise to artifactual quintet EPR signals by using hypoallergenic gloves.

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59. TEMPERATURE DEPENDENCE OF PROTON ELECTRON NUCLEAR DOUBLE RESONANCE SPECTRA OF NITROSYL HEMOGLOBIN — SPECTRAL ANALYSIS AND STRUCTURE OPTIMIZATION. Marco Flores, Eliane Wajnberg, George Bemski, Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro, 22290-180, Brazil; Alan da Silva, Pedro Pascutti, Universidade Federal de Rio de Janeiro, Instituto de Biofísica, Rio de Janeiro, Brazil

Electron nuclear double resonance (ENDOR) spectroscopy has been used to study protons in nitrosyl hemoglobin (HbNO).  $^1\text{H}$  ENDOR spectra were recorded for different settings of the magnetic field at 10K. Detailed analysis of the ENDOR powder spectra using computer simulation,<sup>1-3</sup> based on the "orientation-selection" principle,<sup>4</sup> lead to the identification of the available protons in the heme pocket.<sup>5</sup> It is possible to observe differences between the rhombic and axial symmetries of  $\alpha$  and  $\beta$  chains. We observe hyperfine interactions of the  $\text{Ne}(\text{HisF8})\text{-Fe}^{2+}\text{-N}(\text{NO})$  complex with five protons in axial and seven protons in the rhombic symmetry from a chain, and with four protons in axial and eight protons in the rhombic symmetry from  $\beta$  chain along different orientations including those of the principal axes of the g-tensor. Protons from His-E7 and Val-E11 residues are identified in the two symmetries. The THOR program was used to optimize the proton structure considering the ENDOR derived proton positions.<sup>6</sup> The experimental and theoretical results indicate that both residues are present inside the heme pocket in either conformation. The temperature dependence of  $^1\text{H}$  ENDOR spectra between 5 K and 48 K was partially reproduced by simulations which indicate changes in the hyperfine interactions of several protons and can be associated with protein conformational changes. Two possibilities are proposed, one involves a change in the ligand orientation and the other one involves changes in the positions of the amino acid residues in the heme pocket. Supported by CAPES and CNPq.

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60. INSTRUMENTAL SOLUTIONS FOR LOW FREQUENCY IN VIVO EPR SPECTROSCOPY, OXYMETRY AND IMAGING. Valeri E. Galtsev, Colin Mailer, Benjamin B. Williams, Eugene D. Barth, and Howard J. Halpern, Department of Radiation and Cellular Oncology, University of Chicago, Chicago, IL, 60637

In vivo implementation of narrow line spin probes (e.g., NYCOMED trityl radical, linewidth  $\sim 25 \text{ mG}_m$ ) challenges EPR spectroscopy in several ways. Lossy living object movements cause simultaneous changes in the resonance frequency and coupling of the resonator. We are exploring improvements provided by automatic frequency control (AFC) and automatic coupling control (ACC) for very narrow line spin probes. Possible instrumental solutions will be presented, and their effect on overall spectrometer performance will be described. Operation at a fixed frequency with automatic resonator frequency control was studied. This particular technique is particularly helpful for modulation free EPR absorption, in which the r.f. carrier reflected from the resonator is directly detected. Fixed frequency operation also helps to avoid D.C. baseline drift during the magnetic field scan because a major source such drift is generated by the change of bridge balance produced by any change of source frequency. Supported by NIH grant CA69538 and RR12257.

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61. DETERMINATION OF SIZE OF FERROELECTRIC RESONATORS USED FOR INCREASING SENSITIVITY OF EPR METHOD. Ilia Geifman, Oakton Community College, 7701 N. Lincoln Avenue, Skokie, IL 60077; Iryna Golovina. Institute of Semiconductors Physics Ukrainian Academy of Sciences, Ukraine, 252028 Kiev, pr.Nauki 45.

Using of a ferroelectric resonator leads to increasing of EPR spectrometer sensitivity.<sup>1</sup> Now we show that for irregular forms of resonators (resonators with a hole) it is possible either to take into account the inviolable part of a resonator or take into consideration a whole resonator but with sizes subtracted on the value of the sizes of the hole. In this case the smaller part of the resonator with a hole determines the configuration of the microwave field. We measured temperature dependence of signal/noise ratio enhancement for six resonators made from potassium tantalate and compared with results of calculation. For example, we can consider an object in a form of a right parallelepiped with the dimensions  $2.75 \times 3.5 \times 4.6 \text{ mm}^3$  with hole along its height with diameter 1.9 mm and depth of 3 mm as two resonators. One has sizes  $2.75 \times 3.5 \times (4.6-3) \text{ mm}^3$  – inviolate part of object. The sizes of the other will be  $2.20 \times 2.95 \times 4.6 \text{ mm}^3$ . To get the sizes 2.20 mm and 2.95 mm we subtract from area of object  $2.75 \times 3.5 \text{ mm}^2$  the area of hole  $\pi d^2/4$  and correct sizes according to new value of area. The value of frequency<sup>2</sup> is close to the experimental value when  $m=1$ ,  $n=3$ ,  $\delta=0.718$  for the first resonator and  $m=2$ ,  $n=1$ ,  $\delta=0.877$  for second resonator. Results of such consideration for all six objects will be presented in a table.

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62. STRUCTURAL MODIFICATIONS TO FREE RADICAL INDUCED BY COORDINATION TO A TRANSITION METAL: A SINGLE CRYSTAL EPR STUDY AND DFT INVESTIGATIONS. Michel Geoffroy, Shrinivasa N. Bhat, Helena Sidorenkova, University of Geneva, Department of Physical Chemistry, CH Geneva 1211 (Switzerland).

Interactions between radicals and transition metal ions are of fundamental importance in many fields of modern chemistry (electron transfer, catalysis, molecular electronics...). The purpose of this study is to assess the electronic and structural modifications resulting from coordination of a neutral organic radical to a transition metal. The well-known phosphinyl radical<sup>1,2</sup>  $RR'P\bullet$  is trapped in X-irradiated single crystals or powders of  $\Phi_3P-W(CO)_5$ ,  $\Phi_2PH-W(CO)_5$  and  $\Phi PH_2-W(CO)_5$ . The g as well as the  $^{31}P$  and  $^1H$  hyperfine coupling tensors are measured at room temperature and compared with those already reported for an isolated  $\Phi_2P\bullet$  or  $\Phi PH\bullet$  radical. The main part of the spin remains localized on the phosphorus atom. However, besides the expected increase of the g-anisotropy, the coordination to the transition metal raises the  $^{31}P$  Fermi contact interaction and modifies the coupling to the proton bound to the phosphorus atom. The orientations of the EPR tensors are compared to the bond directions of the diamagnetic precursor as given by the crystal structure. The radical structure and the various hyperfine interactions are discussed in the light of Density Functional Theory (DFT) calculations.

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63. TEMPERATURE DEPENDENCE OF THE  $Al_{Si}$  CENTER EPR IN 6H SiC. Gary J. Gerardi, William Paterson University, Department of Chemistry and Physics, Wayne, NJ 07470; Edward H. Poindexter, Army Research Laboratory, Adelphi, Maryland 20783.

We studied the temperature dependence of the EPR signals due to Al substituting for Si ( $Al_{Si}$ ) in SiC at the three inequivalent sites of the 6H polytype. A sharp decrease in signal intensity is observed, without any measurable signal distortion, over a 2 K temperature range for samples with free-carrier concentration on the order of  $10^{17} \text{ cm}^{-3}$ . High free-carrier concentration samples, near  $10^{19} \text{ cm}^{-3}$ , show an additional broad signal which exhibits the same anisotropy as the  $Al_{Si}$  signals but different temperature dependence. In reviewing possible mechanisms for the temperature behavior of the  $Al_{Si}$  signals, we find that spin depolarization due to hole hopping accounts best for the observed temperature behavior. Analysis of the data based on this mechanism provides a way to determine the degree of nitrogen compensation.

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64. DENDRIMERIC-CONTAINING NITRONYL NITROXIDES AS SPIN TRAPS FOR NITRIC OXIDE: SYNTHESIS, KINETIC AND STABILITY STUDIES. Howard J. Halpern,<sup>1</sup> Supatra Porasuphatana,<sup>2</sup> Pei Tsai,<sup>2</sup> Eugene D. Barth,<sup>1</sup> Valeri Galtsev,<sup>1</sup> and Gerald M. Rosen.<sup>2,3</sup>  
<sup>1</sup>Department of Radiation and Cellular Oncology, University of Chicago, Chicago, IL 60637; <sup>2</sup>Department of Pharmaceutical Sciences, University of Maryland School of Pharmacy, Baltimore, MD 21201; <sup>3</sup>Medical Biotechnology Center, University of Maryland Biotechnology Institute, Baltimore, MD 21201

The in vivo in situ spin trapping of  $NO\bullet$ , secreted by activated murine macrophages, have been successfully detected using the highly charged ferro-di(N-methyl-D-glucaminedithiocarbamate) or the more hydrophilic ferro-di(N-(dithiocarboxy)sarcosine). These iron chelates are, nevertheless, limited in their ability to localize  $NO\bullet$  at defined cellular compartments. Recent studies, however, have suggested that nitronyl nitroxides, such as 2-(4-carboxyphenyl)-4,4,5,5-tetramethylimidazoline 3-oxide 1-oxyl, can react with  $NO\bullet$ . The resulting nitroxide, 2-(4-carboxyphenyl)-4,4,5,5-tetramethylimidazolidine 1-oxyl, exhibits an EPR spectrum that is characteristically distinct from the parent nitroxide. Notwithstanding the chemical flexibility offered by this class of spin traps for  $NO\bullet$ , which would allow detection of this free radical at specific tissue sites, excitement for these nitronyl nitroxides must be tempered by the rapidity by which these spin labels are bioreduced. The spanning structure of dendrimers with terminal functional groups have attracted much interest as models to incorporate a localized high concentration of a specific guest molecule. With this in mind, we have been drawn to the potential of using dendrimeric-linked spin traps as reporters of free radicals. Herein, we report on the preparation of a family of dendrimer-containing nitronyl nitroxides. With these compounds in hand, we determined their kinetics and efficiency of spin trapping  $NO\bullet$  and estimated the stability of nitronyl nitroxides under various experimental paradigms.

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65. PULSED ELDOR DETERMINATION OF RELAXATION PROCESSES IN L-ALANINE. James R. Harbridge, Sandra S. Eaton, and Gareth R. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado 80208

CW-saturation recovery or inversion recovery curves can be fit to a single exponential if the relaxation time,  $T_1$ , is due only to spin-lattice relaxation. For many samples such as irradiated L-alanine, the recovery curve cannot be fit to a single exponential and relaxation processes other than  $T_1$  may dominate the recovery. In this study pulsed ELDOR (Electron-electron double resonance) is used to analyze the multiexponential recovery curves for irradiated L-alanine in terms of individual contributions and determine the processes that dominate relaxation as a function of temperature from room temperature to 77 K. A simulation program that considers 16 energy levels and transitions among these levels due to spin-lattice relaxation, nuclear relaxation, cross relaxation, and spectral diffusion is used to determine the individual relaxation times. The effects of methyl rotations also will be discussed.

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66. THE POSITION OF CYTOCHROME  $B_{559}$  IN PHOTOSYSTEM II STUDIED BY PULSED ELDOR. A. Kawamori, M. Tonaka, and S. Kuroiwa, Faculty of Science, Kwansei Gakuin University, Nishinomiya 662-8501 Japan, and K. Akabori, Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima, 739-8521 Japan.

Field sweep ESE of the ferric ion of heme in Cyt  $b_{559}$  can be observed over the field range from  $g = 3$  to  $1.5$  at X-band. The magnetic field was fixed at  $g = 1.98$  and ELDOR excitation was applied to the reduced plastoquinone ( $Q_A^-$ ) in Zn- substituted PS II oriented membranes. Applying orientation selection in simulation of the time profile of ELDOR, the distance and angle of the vector from Cyt  $b_{559}$  to  $Q_A$  were determined to be  $40 \pm 1 \approx$  and  $80 \pm 5^\circ$  from the membrane normal ( $n$ ). Similarly, by exciting  $Chl_z^+$  trapped in Tris-treated membranes, the distance and angle of the vector from Cyt  $b_{559}$  to  $Chl_z$  were determined to be  $34 \pm 0.5 \approx$  and  $58 \pm 5^\circ$  from  $n$ -axis. Cyt  $b_{559}$  is suggested to be on the stromal side of PS II membranes and separated by more than  $50 \text{ \AA}$  from  $Y_D$  and  $Y_Z$ .

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67. SPATIOTEMPORAL ESR-CT OF MICE WITH RENAL LESIONS USING TEMPO-DX. Shunsuke Kazama, University of Shizuoka, School of Pharmaceutical Sciences, Shizuoka, 422-8526 Japan; Hisashi Yoshioka, Kieko Saito, University of Shizuoka, Institute for Environmental Sciences, Shizuoka, 422-8526 Japan; Hisayuki Tanizawa, Hiroshima Jogakuin University, Department of Life Science, Hiroshima, 732-0063 Japan; Tomohiro Ito, Tateaki Ogata, Yamagata University, Graduate School of Science and Engineering, Yonezawa, 992-8510 Japan; Lawrence J. Berliner, Ohio State University, Department of Chemistry, Columbus, OH 43210-1185, U.S.A.

TEMPO radical has a long half-life in vivo when it is chemically bonded to the glucose chain of dextran. The radical is quenched (i.e., probably bioreduced) while it circulates. Since it cannot pass through the kidney due to its large molecular size, we can measure time dependent ESR-CT images of the radical distribution. In order to assess the effective applications of such a long lived radical, we have measured the excretion/metabolic capacity of the kidney and liver. Recently we synthesized smaller M.W. TEMPO-DX species, i.e., less than  $40 \text{ kDa}$ , in order to reduce the viscosity of injected bolus. We have obtained good relatively high-resolution time dependent CT images of the mouse abdomen after i.v. administration. The  $10 \text{ kDa}$  TEMPO-DX species was rapidly excreted as expected, since the kidneys filter molecules of less than  $40 \text{ kDa}$ . However, its lifetime in the mouse was sufficiently long enough to accumulate good CT images. TEMPO-DXs of  $20 \text{ kDa}$  and  $40 \text{ kDa}$  were excreted into the bladder about  $40 \text{ min}$  after i.v. administration. On the other hand, TEMPO-DXs which were administered to mice with renal lesions induced by  $HgCl_2$  administration were not excreted into the bladder simultaneously with the disappearance of the radical in the kidney, suggesting that the kidney lost function and the TEMPO-DX molecules were metabolized while in the circulation. In conclusion, time dependent ESR-CT images distinguished differences in TEMPO-DX molecular size and some indications of kidney malfunction. Furthermore  $20 \text{ kDa}$  and  $40 \text{ kDa}$  TEMPO-DXs were of suitable size to measure kidney capacity.

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68. ENDOR SPIN TRAPPING STUDIES OF RADICAL INTERMEDIATES IN CHEMICAL AND PHOTO-INDUCED OXIDATION OF CAROTENOIDS. T.A. Konovalova, L.D. Kispert, University of Alabama, Department of Chemistry, Tuscaloosa, AL 35487

Carbon-centered carotenoid radicals were detected by EPR spin-trapping technique upon chemical oxidation of carotenoids by  $FeCl_2$  or  $I_2$  in  $CH_2Cl_2$  solutions. Oxidation of  $\beta$ -ionone,  $8'$ -apo- $\beta$ -caroten- $8'$ -al and other carotenoids with terminal electron-withdrawing groups in the presence of 2-methyl-2-nitroso-propane (MNP) results in the formation of stable spin adducts. Their EPR spectra at RT exhibit triplets of doublets with  $a_N = 13.8 - 14.8 \text{ G}$  and  $a_{\beta-H} = 4.0 \pm 0.2 \text{ G}$ . ENDOR studies of these spin adducts at  $140-160 \text{ K}$  revealed the smaller proton coupling constants (for example, for  $\beta$ -ionone/MNP the  $a_H = 0.6 \text{ MHz}$ ,  $2.6 \text{ MHz}$  and  $4.2 \text{ MHz}$  were obtained). The EPR/ENDOR results permitted the structures of radical intermediates and the mechanism of the carotenoid radical generation via deprotonation of their radical cations or addition of nucleophilic agents to them. Photo-oxidation of carotenoids in  $TiO_2$  colloids in air was found to lead to singlet oxygen generation. An EPR signal of TEMPONE nitroxide radical ( $a_N = 14.8 \text{ G}$ ,  $g = 2.0061$ ) was observed in the presence of 2,2,6,6-tetramethylpiperidin, that is characteristic of the product of singlet oxygen interaction with sterically hindered amines. The mixture of spin adducts of oxygen-centered radicals was detected in the presence of phenyl-tert-butyl nitron (PBN) spin trap. ENDOR measurements at  $180-240 \text{ K}$  aided in identifying the  $PBN/O_2^{\bullet-}$  ( $a_N/2 = 27.6 \text{ MHz}$ ,  $a_{\beta-H} = 4.5 \text{ MHz}$ ) and the  $PBN/OOH^{\bullet}$  ( $a_N/2 = 28.2 \text{ MHz}$ ,  $a_{\beta-H} = 7.8 \text{ MHz}$ ,  $a_H = 1.5 \text{ MHz}$ ) spin adducts. Parameters obtained from ENDOR spectra were used successfully to simulate the EPR spectra. The results explain the mechanism of singlet oxygen generation by the dismutation of the  $O_2^{\bullet-}$ .

Supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Grant DE-FG02-86ER13465.

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69. 1D, 2D-ESEEM AND PULSED ENDOR STUDY OF CHEMICALLY PREPARED CAROTENOID RADICAL CATIONS. T.A. Konovalova, L.D. Kispert, University of Alabama, Department of Chemistry, Tuscaloosa, AL 35487; S.A. Dikanov, Illinois EPR Research Center, University of Illinois, Urbana, IL 61801; M.K. Bowman, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352

The carotenoid radical cations chemically generated on silica-alumina support and in  $\text{AlCl}_3$  solution were studied by the three-pulsed ESEEM and pulsed ENDOR spectroscopies. The observed nuclear modulations were assigned by the two dimensional Hyperfine Sublevel Correlation spectroscopy (HYSCORE). For canthaxanthin radical cation the pulsed ENDOR spectrum consists of two well-resolved doublets with hyperfine couplings of 2.6 and 8.6 MHz (with the same signs) and a broad line with a hyperfine coupling about 14 MHz. These parameters were assigned to three different methyl protons. ENDOR measurements were carried out at 3.3 – 55 K and no spectral changes were found in this temperature region. Apparently, fast rotation of the methyl groups occurs even at low temperatures. The three-pulsed ESEEM spectrum of canthaxanthin complex with  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  solution exhibited an  $^{27}\text{Al}$  line at 3.75 MHz. The HYSCORE analysis yielded the principal values of the hyperfine tensors. The major lines in the HYSCORE spectrum were the proton lines. The assignments were done on the basis of known (from CW ENDOR) isotropic hyperfine couplings. For freely rotating methyl groups the anisotropy is limited and the hyperfine tensor is nearly axial. However, the hyperfine tensors estimated from HYSCORE measurements were much more anisotropic than those which were reported previously for the carotenoid methyl-protons (or  $\beta$ -protons). We assume that the large anisotropy is due to  $\alpha$ -proton couplings.

Supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Grant DE-FG02-86ER13465 (Tuscaloosa).

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70. HIGH FREQUENCY AND FIELD EPR OF NOVEL MANGANESE (III) COMPLEXES. J. Krzystek, National High Magnetic Field Laboratory, Tallahassee, FL 32310; J. Telser, Chemistry Program, Roosevelt University, Chicago, IL 60605; M. J. Knapp, Department of Chemistry, University of California, Berkeley, CA 94720; S. Licoccia, Department of Chemistry and Technology, Università di Roma Tor Vergata, Rome, Italy; D. N. Hendrickson, Department of Chemistry and Biochemistry, University of California, San Diego, CA 92093; B. M. Hoffman, Department of Chemistry and Biochemistry, Northwestern University, Evanston, IL 60208; L. C. Brunel, National High Magnetic Field Laboratory.

We have performed High Frequency and Field Electron Paramagnetic Resonance (HF-EPR) experiments on a series of molecular complexes containing manganese(III) ion. The complexes studied so far were:  $\text{Mn}(\text{Me}_2\text{dbm})_2\text{X}$ , where Me = methyl, Hdbm = 1,3-diphenyl-1,3-propanedione, X = Cl and Br;  $\text{Mn}(\text{acac})_3$  where acac = acetylacetonate;  $\text{Mn}(\text{8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole})$ ;  $\text{Mn}(\text{meso-tetra(4-sulfonatophenyl)porphine})$ ;  $\text{Mn}(\text{meso-octaethylporphine})\text{X}$ , where X = Cl, Br and I; and  $\text{Mn}(\text{tetraphenylporphine})\text{Cl}$ . Some of these complexes have only recently been synthesized. They were investigated both in a solid (powder) form, and as frozen solutions in either water or organic solvents. They are all high-spin ( $S = 2$ ) systems characterized by relatively large zero-field splittings (ca. 1-3  $\text{cm}^{-1}$ ), and are correspondingly 'EPR-silent' at conventional frequencies and fields. Our interest in these complexes is based on their properties as 'building blocks' of molecular magnets, as catalysts, and as mimicking models for Mn(III)-containing biomolecules. They represent varying ligands, and ligand symmetries around the metal ion. The purpose of this study is to obtain spin Hamiltonian parameters for these compounds and correlate them with the electronic structure. Conclusions regarding the latter are drawn and related to geometric structure. In particular, the mutual energy separation between the ground quintet, and the excited triplet state of Mn(III) is evaluated, and linked to spin Hamiltonian parameters.

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71. AN EPR STUDY OF COPPER-EXCHANGED ZEOLITES: THE EFFECTS OF NITROGEN BINDING ON EPR PARAMETERS. Patrick J. Carl, Sandy Baccam, and Sarah C. Larsen, Chemistry Department, University of Iowa, Iowa City, IA 52242

Electron paramagnetic resonance (EPR) spectroscopy was used to investigate adsorption of a series of amines (ammonia, methylamine, triethylamine) on copper-exchanged zeolites. Several changes were observed in the EPR spectra after adsorption of the amine: an increase in spectral broadening, a shift in the copper hyperfine features, and the appearance of nitrogen hyperfine splittings in the perpendicular region of the EPR spectrum for some of the samples. For samples that exhibited resolved nitrogen hyperfine couplings, the EPR spectra were interpreted in terms of the number of coordinated amine molecules. For samples in which resolved nitrogen hyperfine interactions were not observed, the interpretation of the EPR spectrum was more complex. An empirical model correlating the EPR parameters for a series of model compounds to the number of nitrogen ligands and the charge of the copper complex was also used. (Peisach, J.; Blumberg, W. E. Arch. Biochem. Biophys. 1974, 165, 691.) This approach was very effective for determining the number of nitrogen ligands if the charge of the complex was known or vice versa. It was determined that four molecules of ammonia or methylamine bind to the  $\text{Cu}^{2+}$  centers in Cu-ZSM5 and Cu-Beta, but that only one molecule of triethylamine is able to bind to the  $\text{Cu}^{2+}$  centers in these zeolites. For cases in which the charge of the complex and the number of ligands are both unknown, there is more uncertainty in using this empirical approach to interpret the EPR spectra. This empirical approach was further assessed by application to the EPR spectra of NO adsorbed on Cu-ZSM5 and Cu-Beta.

**EPR Symposia Poster Session—Sarah C. Larsen, Chemistry Department, University of Iowa, Iowa City, IA 52242. Tel: 319-335-1346, Fax: 319-335-1270, E-mail: sarah-larsen@uiowa.edu**

- 72.** EPR INVESTIGATIONS OF IRON-EXCHANGED ZEOLITES. Conrad Jones and Sarah C. Larsen, Chemistry Department, University of Iowa, Iowa City, IA 52242

Electron paramagnetic resonance (EPR) spectroscopy was used to investigate the electronic environment of  $\text{Fe}^{3+}$  in iron-exchanged zeolites. Iron-exchanged zeolites, such as FeZSM-5, are active catalysts for the selective catalytic reduction of  $\text{NO}_x$  with hydrocarbons (SCR-HC). The catalytic activity of FeZSM-5 is extremely sensitive to the many factors, such as the exchange procedure, the parent zeolite, and the pretreatment protocol. In this study, a series of FeZSM-5 samples were prepared using three different exchange methods: aqueous exchange, sublimation and solid state exchange. EPR spectra were obtained for each of the iron-exchanged zeolites after different pretreatment protocols and after exposure to reactants. By comparing the EPR spectra of samples that were prepared by different exchange methods, spectroscopic signatures of different  $\text{Fe}^{3+}$  sites were identified. A future goal is to correlate the spectroscopic signatures with catalytic activity in order to determine which sites are responsible for the catalytic activity.

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- 73.** PARAMAGNETIC PHASE RELAXATION DUE TO SURROUNDING METHYLS AND MAGNETIC NUCLEI IN DILUTED SPIN SYSTEMS. Mikael Lindgren, Linköping University, Department of Physics and Measurement Technology, Linköping, S-581 83 Linköping, Sweden; Surendra Mahapatro, Melissa Woltkamp, and Chinh Nguyen, Department of Chemistry, Regis University, Denver, CO; Sandra S. Eaton, Gareth R. Eaton, University of Denver, Department of Chemistry, Denver, CO 80208-2436, USA.

Surrounding magnetic nuclei are known to induce phase relaxation in diluted paramagnetic systems at low temperatures ( $< 100$  K).<sup>1</sup> The phenomena can be explained by flip-flop transitions and certain motions of nuclei in the surrounding lattice; e.g., the presence of rotating methyl groups can increase the relaxation rate by approximately one order of magnitude.<sup>2</sup> Here we present a structure-to-property simulation model, based on a free-radical with a surrounding lattice of nuclei. The relaxation is introduced by various fluctuations of the dipolar interaction with the lattice nuclei. The model can account for local nuclear concentration and spin-diffusion phenomena in the vicinity ( $< 20$  Å) of the unpaired electron. A classical model based on a methyl rotor explains qualitatively the relations between methyl group rotation rate and geometrical parameters such as distance to, concentration and orientation of, proximate methyls in the surrounding lattice. The results of phase memory relaxation simulations are compared with previous and novel experimental data for tempone and trityl radicals in a variety of frozen glasses. Using two differently sized free radicals in various solvents the model is shown to be self-consistent. The geometrical structure of the surrounding lattice determines the relaxation behaviour for a given set of dynamic flip-flop frequency and/or methyl rotation parameters associated with a specific solvent type. The simulations imply that the nearest 'dephasing distance' of the flip-flop process is approximately 5.5 - 6 Å, whereas the rotating methyl groups become important at distances of approximately 4 Å. The model is used to understand dynamic properties of methyl groups in glasses at low temperatures by direct comparison with phase relaxation measurements.

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- 74.** EFFECT OF CIGARETTE TAR AND ITS COMPONENTS ON THE TYROSYL RADICAL OF RIBONUCLEOTIDE REDUCTASE IN JURKAT CELLS. Karen L. Link<sup>1</sup>, Jessica M. McCue<sup>2</sup>, Sandra S. Eaton<sup>1</sup>, and Brian M. Freed<sup>2</sup>, <sup>1</sup>Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado and <sup>2</sup>Department of Allergy and Clinical Immunology, University of Colorado Health Science Center, Denver, Colorado

Cigarette smoking causes profound suppression of pulmonary T cell responses, which has been associated with increased susceptibility to respiratory tract infections and decreased tumor suppression. Hydroquinone and catechol, which are present in substantial concentrations in cigarette smoke, induce profound suppression of T cell responses in the lungs and block DNA synthesis in human T lymphocytes. The tyrosyl radical in the M2 subunit of ribonucleotide reductase is essential for DNA synthesis and is the only stable tyrosyl radical in sufficient concentration to be detectable by EPR in lymphocytes. Cultured human Jurkat T cells were treated for 5 min with cigarette tar extract, or 40mM HQ, catechol or phenol. The cells were then centrifuged into quartz EPR tubes and frozen in liquid nitrogen. EPR spectra were obtained at X-band at 93 K. To improve spectra resolution, some samples also were recorded at 50K. The tyrosyl radical was detected in Jurkat cells with an absolute signal intensity of 0.2 mM. Extracts from a low-tar cigarette (Carlton) quenched the M2 tyrosyl radical by  $<40\%$ , while treatment with high-tar extracts (unfiltered Camel) resulted in  $>95\%$  quenching. 40 mM HQ and catechol quenched the tyrosyl radical by  $>99\%$ , phenol quenched only 25% of the radical, and nicotine (1mM) had no effect. The results indicate that the benzene derivatives, HQ and catechol, block DNA synthesis by quenching the M2 tyrosyl radical and thereby inhibiting ribonucleotide reductase. Supported by NIH grants HL60538 and ES05673.

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## EPR Wednesday Oral Sessions

- 75.** ADVENTURES WITH ELECTRON SPIN ECHOES. Larry Kevan, University of Houston, Department of Chemistry, Houston, Texas 77204-5641

*An overview of applications of electron spin echoes will be given encompassing aspects of ion and atom solvation structure including solvated electron structure, location of photogenerated radicals in model membrane systems such as micelles and vesicles, ion location and adsorbate geometry in microporous and mesoporous oxide materials and the structure of heterogeneous catalytic reaction intermediates.*

**EPR Symposia Poster Session—Larry Kevan, University of Houston, Department of Chemistry, Houston, Texas 77204-5641. Tel: 713-743-3250, Fax: 713-743-2709, E-mail: KEVAN@UH.EDU**

- 76.** DEER MEASUREMENTS OF INHOMOGENEOUS DISTRIBUTIONS OF RADICALS IN IRRADIATED MATERIALS. M.K. Bowman, Pacific Northwest National Laboratory, WR Wiley Environmental Molecular Sciences Laboratory, PO Box 999, Richland, WA 99352-0999; H.M. Mottaz and A.F. Fuciarelli, Battelle Northwest, Toxicokinetic and Bioanalytical Department, 900 Battelle Blvd, Richland, WA 99352; J.D. Zimbrick, Purdue University, School of Health Sciences, West Lafayette, IN 47907.

*Ionizing radiation deposits its energy inhomogeneously in condensed matter. The radiation products are often free radicals whose spatial distribution, before subsequent diffusion and reaction, reflect that inhomogeneous energy deposition. Experimental determination of the inhomogeneity of free radicals provides an important glimpse into the energy deposition mechanisms, subsequent chemistry or it can provide a means to reconstruct doses and determine the energy profile of the ionizing radiation. We report on the use of DEER (double electron electron resonance) to investigate local concentrations of radiation damage products in irradiated frozen glasses and minerals. At low doses, we find both inhomogeneous distributions of free radical products and a marked dependence on the LET (linear energy transfer) of the radiation.*

**EPR Symposia Oral Session—M.K. Bowman, Pacific Northwest National Laboratory, WR Wiley Environmental Molecular Sciences Laboratory, PO Box 999, Richland, WA 99352-0999. Tel: 509-376-3299, Fax: 509-376-2303, E-mail: michael.bowman@pnl.gov**

- 77.** MULTIFREQUENCY PULSED EPR STUDY OF THE CHICKEN LIVER SULFITE OXIDASE. Andrei V. Astashkin, Arnold M. Raitsimring, Rachel Codd, M.L. Mader, Andrew Pacheco and John H. Enemark, University of Arizona, Department of Chemistry, Tucson, AZ 85721.

*Using the multifrequency capabilities of the pulsed EPR spectrometers of the EPR facility of the University of Arizona and the recently developed two-dimensional refocused primary (RP) ESEEM technique that is free from dead time, we have been able to directly detect the nearby protons of the high-pH form of the Mo(V) center of sulfite oxidase. Simulation of the RP ESEEM spectrum has shown the presence of two nearby protons. Their hyperfine interactions are distributed over broad limits, suggesting that their positions with respect to the Mo(V) center are not unique. These protons are ascribed to an H<sub>2</sub>O ligand or to a Mo-OH group with strong H-bonding to another nearby proton. To obtain a more detailed information about the OH-type ligand in various forms of sulfite oxidase, we have initiated studies of the oxygen nucleus of this ligand in <sup>17</sup>O – enriched samples. The results obtained for the <sup>17</sup>O – enriched low-pH form of sulfite oxidase will be presented. The financial support by the NSF (BIR-9224431 and DBI-9604939) and the NIH (GM 37773) is gratefully acknowledged.*

**EPR Symposia Oral Session—Andrei Astashkin, University of Arizona, Department of Chemistry, 1306 E. University Blvd., Tucson, AZ 85721. Tel: 520-621-9968, Fax: 520-621-8407, E-mail: andrei@u.arizona.edu**

- 78.** TOWARD SEPARATING DIPOLAR AND SPIN EXCHANGE INTERACTIONS IN LIQUIDS AT CONSTANT TEMPERATURE. Barney L. Bales, Department of Physics and Astronomy, California State University at Northridge, CA 91330-8268.

*Recent advances in studying EPR line shapes for spin probes tumbling rapidly in liquids have allowed three independent measures of the spin exchange frequency to be extracted from an experimental spectrum as follows: (1) line broadening, (2) line shifts, and (3) the intensity of a spin-exchange induced dispersion.<sup>1</sup> The first effect has been exhaustively studied and the theory verified, the second has been slightly studied and the theory verified within large uncertainties, and the third had not been studied until recently.<sup>1</sup> Since dipolar interactions also lead to line broadening that is proportional to the spin probe concentration, most past experimental efforts to separate the two interactions had to rely on comparing experiment with a Stokes-Einstein temperature dependence. Analyzing all three effects of spin exchange in terms of well established theory is a promising approach to separate the two without the uncertainty of modeling the temperature dependence. Applied to Fremy's salt, the agreement between experiment and theory is astonishingly good and perhaps surprisingly, one may deduce spin exchange frequencies with almost as much precision from line shifts and dispersion as from line broadening. The charge of Fremy's salt makes it difficult to reach conditions of appreciable dipolar interactions. When applied to pd-TEMPONE, the agreement between measured and predicted line shifts breaks down while the agreement for the dispersion term continues to be excellent in the spin-exchange regime. In the dipolar regime a dipolar-induced dispersion is found that is of opposite sign and not yet predicted by theory. In order to quantitatively separate the two interactions a more complete theory for dipolar interactions is needed; nevertheless, adopting a reasonable form for the dipolar-induced dispersion allows the separation.*

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**EPR Symposia Oral Session—Barney L. Bales, Department of Physics and Astronomy, California State University at Northridge, CA 91330-8268, E-mail: barney.bales@email.csun.edu**



**79. EPR STUDIES OF PHOTOREFRACTIVE BaTiO<sub>3</sub>. R.N. Schwartz, HRL Laboratories, Malibu, CA 90265**

The photorefractive effect has been investigated in many electro-optic materials with the hope of understanding the basic physics of the effect. A large body of results supports the view that the "photorefractive centers" originate either from substitutional impurities or intrinsic point defects or possibly some combination of these impurities/defects. The use of EPR and photo-EPR to identify, to probe the electronic structure, and to locate the ionization levels of impurities/defects in BaTiO<sub>3</sub> and to assess their role in the photorefractive effect will be described. Supported by the Defense Advanced Research Projects Agency (DARPA) Photorefractive Information Storage Materials (PRISM) Consortium through Contract No. MDA972-94-2-0008.

**EPR Symposia Oral Session—Robert N. Schwartz, HRL Laboratories, LLC, 3011 Malibu Canyon Road, Malibu, CA 90265. Tel: 310-317-5595, Fax: 310-317-5679, E-mail: rnschwartz@hrl.com**

**80. 1D AND 2D ELECTRON SPIN RESONANCE IMAGING (ESRI) OF NITROXIDE RADICALS IN STABILIZED POLY(acrylonitrile-butadiene-styrene): UV vs THERMAL DEGRADATION. Shulamith Schlick, Mikhail V. Motyakin, Krzysztof Kruczala, Department of Chemistry, University of Detroit Mercy, Detroit, Michigan 48219-0900.**

1D spatial and 2D spatial-spectral electron spin resonance imaging (ESRI) was used in order to deduce the intensity profile and the spatial variation of line shapes for nitroxides formed during accelerated UV irradiation and thermal degradation of poly(acrylonitrile-butadiene-styrene) (ABS) containing a hindered amine stabilizer (HAS). The detection of two dynamically different sites for the HAS-derived nitroxide radicals (Afast@ and Aslow@ components) and the decrease of the relative intensity of the fast component with UV irradiation or heating time point to the butadiene-rich domains as the vulnerable site for degradation.<sup>1</sup> Spatial variation of the nitroxide intensity and of the line shapes was detected in the UV-irradiated samples. The nitroxide signal is strong on the irradiated side, increases with time on the opposite side, and is very weak in the sample interior; these results were taken as evidence for diffusion-limited oxidation. By contrast, the radical concentration and the line shapes are spatially homogeneous in the polymer undergoing thermal degradation at 333 K.<sup>2</sup> This study has demonstrated the potential of imaging methods based on ESR to provide, nondestructively, spatial details on polymer degradation and stabilization. Supported by the Polymers Program of NSF.

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**EPR Symposia Oral Session—Shulamith Schlick, Department of Chemistry, University of Detroit Mercy, Detroit, Michigan 48219-0900, E-mail: schlicks@udmercy.edu**

**81. MULTI-FREQUENCY PHOTO-EPR AND ENDOR STUDIES OF SUBSTITUTIONAL [Cl<sub>3</sub>Ir(NMP)]<sup>2+</sup> COMPLEXES IN AgCl. R.S. Eachus, Th. D. Pawlik, and R. C. Baetzold, Imaging Materials Division, Eastman Kodak Company, Rochester, NY 14650-2021**

Optimum imaging characteristics for many photographic materials are achieved by the addition of polyvalent transition-metal (TM) ion impurities to the silver halide (AgX) microcrystals. These TM ions are incorporated as hexacoordinate complexes substituting for (AgX)<sub>6</sub><sup>5+</sup> or larger lattice sub-units. Complexes in which one ligand is organic comprise a particularly interesting new class of dopants. In this contribution, we will describe X- and Q-band photo-EPR studies of AgCl dispersions doped with [IrCl<sub>3</sub>(NMP)]<sup>2+</sup> (where NMP = N-methylpyrazinium). Calculations predict that this complex substitutes for (Ag<sub>2</sub>Cl)<sub>6</sub><sup>5+</sup>, and that the majority of these centres are charge-compensated by association with four silver ion vacancies arranged in a (101)( $\bar{1}$ 01)(01 $\bar{1}$ )(0 $\bar{1}$  $\bar{1}$ ) geometry. The Cl-Ir-(NMP) axis defines z. During exposure to actinic light, [IrCl<sub>3</sub>(NMP)]<sup>2+</sup> traps an electron. This electron can originate from the conduction band edge (band gap irradiation) or from the valence band edge through a charge-transfer transition (sub-band gap light). Since the dopant's LUMO is primarily a  $\pi^*$  NMP orbital, the photoproduct, [IrCl<sub>3</sub>(NMP)]<sup>2+</sup>, is a ligand-centred, one-electron donor. It gives a relatively simple and uninformative EPR spectrum. However, data from powder ENDOR experiments, particularly those on <sup>13</sup>C and <sup>2</sup>D labelled dopants, in combination with calculations of structure and energy, have facilitated structural assignments. Pseudo-rotation studies allowed the assignment of many of the powder ENDOR signals. The experimentally derived <sup>1</sup>H, <sup>14</sup>N, <sup>13</sup>C and <sup>2</sup>D hyperfine data are consistent with the unpaired electron distribution calculated by Hartree-Fock methods. Kinetic studies suggest that latent image formation involves long-range electron tunnelling from [IrCl<sub>3</sub>(NMP)]<sup>2+</sup> to positive kink sites on surfaces of the AgCl microcrystals. A configuration coordinate model can be used to explain the unexpected sensitivity to long-wavelength light ( $\lambda \geq 600$  nm) of the [IrCl<sub>3</sub>(NMP)]<sup>2+</sup> centre.

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**82. NIST ACTIVITIES IN DEVELOPMENT OF INDUSTRIAL EPR APPLICATIONS. Vitaly Nagy, James Puhl and Marc F. Desrosiers, National Institute of Standards & Technology, Gaithersburg MD 20899-8460**

In developing industrial applications of EPR, NIST focuses its efforts mostly on two areas: EPR dosimetry with alanine and EPR quantitations. The technique developed at NIST for determining high radiation doses used in industrial radiation processing (sterilization, materials processing), is currently the most accurate in the world and provides doses with the overall uncertainty of as low as 1.2% (2s), of which only about 0.5% is due to the inaccuracy of EPR measurements. This technique is currently used on a regular basis for calibrating industrial radiation sources against the national standard radiation source maintained by NIST. The critical elements of this procedure that provide such high accuracy will be discussed. The new system of remote EPR dose determination using the Internet, which is currently being developed by NIST (in cooperation with Bruker Instruments), will be briefly described. In the area of EPR quantitations, the efforts are focused on developing a general-purpose concentration standard that would meet the strict NIST requirements for analytical standard reference materials and could be used

in industrial and research applications that involve absolute measurements of concentrations of paramagnetic centers. The strategy that has been used in selecting prospective paramagnetic materials will be described on the basis of the general methodology of EPR quantitation, and the available results will be reported. The status of EPR among other contemporary methods of quantitative chemical analysis will be discussed, its strong points and weaknesses will be analyzed, and the most promising areas of its future industrial applications will be outlined.

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- 83.** APPLICATION OF ELECTRON PARAMAGNETIC RESONANCE TO PROBLEMS IN MICROELECTRONIC ENGINEERING. P.M. Lenahan, The Pennsylvania State University, University Park, PA 16802

Most solid state technology in use today is based upon insulated gate field effect transistors. The most important of these devices is the metal-oxide-silicon-field effect transistor. Satisfactory operation of these devices requires the control of trapping centers within the insulators and at the insulator/semiconductor interface. The most important of the insulator and interface defects have been identified in studies involving electron paramagnetic resonance (EPR) and other "electronic" measurements. Studies involving collaboration of our university laboratory with industrial research organizations has lead to a fundamental but incomplete understanding of the role of about a dozen paramagnetic defects in technologically important device problems. In several cases, this understanding has lead directly to approaches in device processing which have ameliorated the device problems.

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- 84.** AZULENYL NITRONES: COLORIMETRIC DETECTION OF OXYRADICAL END PRODUCTS IN MODELS OF ALS AND STROKE. John S. Althaus, Parke-Davis Research, Neuroscience Therapeutics, Ann Arbor, MI 48105; Edward D. Hall, Parke-Davis Research, Neuroscience Therapeutics, Ann Arbor, MI 48105; David A Becker, Department of Chemistry, Florida International University, Miami, FL 33199

EPR in combination with nitron spin trapping agents are used to measure oxyradical production in models of human disease. This approach has limited utility because many research laboratories are not equipped with spectrometers and lack the expertise required to interpret EPR spectra. We developed a method for measuring nitroxide spin trapped by-products which does not require EPR-based technology. The method is based on the azulanyl nitron which possesses unique spectral properties which can be adapted to a simple, sensitive and straight forward HPLC-UV assay. The method was used in a gerbil transient forebrain ischemia/reperfusion model and in a transgenic mouse model of familial amyotrophic lateral sclerosis (FALS). Electrochemical oxidation of the azulanyl nitron (AZN) produced the corresponding azulanyl aldehyde (AZA) which was identified as a fragmentation product of azulanyl nitroxide formation. Both AZN and AZA exhibited UV-absorption maximum at 390nm which was used in detection following separation by HPLC. As a percentage, measurement of AZA was normalized to measurement of AZN found in the same tissue via the mass ratio expression AZA/AZN (%). AZN was administered to mice which expressed the transgene SOD1-G93A, a mutant gene found in humans which causes FALS. AZA/AZN measured in spinal cords was nearly eight times higher in transgenic mice compared to control mice. In ischemia/reperfusion experiments with gerbils, brain AZA/AZN was nearly 3-times greater with injury compared to sham-treatment. We found that the HPLC-UV assay of AZN conversion to AZA in brain tissue to be a simple, sensitive and inexpensive alternative to EPR-based technology.

**EPR Symposia Oral Session—John S. Althaus, Parke-Davis Research, Neuroscience Therapeutics, Ann Arbor, MI 48105**

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## EPR Wednesday Poster Sessions

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- 85.** A QUANTITATIVE RADIATION CHEMICAL STUDY OF HYDROXYL RADICAL SPIN TRAPPING BY DMPO. ROLE OF THE DMPO-HYDRATED ELECTRON SPIN ADDUCT. Keith P. Madden, Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556-0579, U.S.A.; Hitoshi Taniguchi, Department of Veterinary Radiology, Faculty of Agriculture, Yamaguchi University, Yamaguchi 753-8515, Japan

Time-resolved in situ radiolysis EPR studies have shown that the scavenging of radiolytically-produced hydroxyl radical in nitrous oxide-saturated aqueous solutions containing 2 mM DMPO (5,5-dimethyl-1-pyrroline-N-oxide) is essentially quantitative (94% of the theoretical yield) at 100 μsec after the electron pulse (Madden and Taniguchi, J. Phys. Chem. 1995, 100, 7511). This result appeared to conflict with earlier results using continuous cobalt-60 radiolysis, where a factor of 35% was obtained (Carmichael, Makino, and Riesz, Radiat. Res. 1984, 100, 222). In the current studies, nitrogen-saturated aqueous solutions containing 15 mM DMPO were cobalt-60 irradiated (dose rate = 223 Gy/min) for period of 0.25-6 minutes, and observed within 30 seconds of irradiation. The apparent discrepancy between the results of pulsed and continuous irradiation is due to the rapid, pseudo-first-order termination reaction of the DMPO-hydrated electron adduct (from  $e^- + \text{DMPO} + \text{H}^+ \rightarrow \text{DMPO-H}$ ; also  $\text{DMPO} + \text{H}\cdot \rightarrow \text{DMPO-H}$ ) with DMPO-OH. In low dose experiments, this reaction lowers the observed yield of DMPO-OH to 45% of the radiation-chemical OH radical yield ( $G=2.8$ ), in good agreement with the earlier results.

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- 86.** EXCHANGE COUPLED QUANTUM-MIXED SPIN FERRIC HEMES. Martin M. Maltempo, University of Colorado at Denver, Department of Physics, P.O. Box 173364, Denver, CO 80217-3364  
*The quantum-mixed spin state of ferric heme occurs when the crystal field energy separation between the  ${}^6A_1$  ( $S=5/2$ ), and  ${}^4A_2$  ( $S=3/2$ ) states is comparable to, or smaller than, the spin-orbit coupling ( $\sim 300\text{ cm}^{-1}$ ). The ground state Kramers doublet then contains significant admixtures of the  ${}^6A_1$  and  ${}^4A_2$  states, resulting in magnetic properties (g-values, magnetic susceptibility) intermediate between those of the two pure spin states. The quantum-mixed spin state has been studied in peroxidases, the cytochromes c', and various inorganic complexes, and theoretical work reported for the case in which there is no exchange coupling with neighboring spins. In this study calculations are reported for the magnetic properties of a pair of exchange coupled quantum-mixed spins.*  
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- 87.** INDOLINIC NITROXIDE RADICALS STUDIED WITH A NEW HIGH-FREQUENCY EPR SPECTROMETER. G.G. Maresch, C.A. Saylor, and L.C. Brunel, Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, Florida State University, 1800 E Paul Dirac Dr., Tallahassee, FL 32310  
*Nitroxide free radicals are a wide class of paramagnetic molecules which are extensively studied by EPR. With a new high-frequency EPR spectrometer high-resolution spectra have been acquired at a resonance frequency of 220 GHz (D-band). The indolinic nitroxides belong to a class of uncommon nitroxides, which are stable both in the solid and in solution, though they have a benzene  $\pi$  system which is conjugated with the N-O group. In fact, their spin density is distributed on a system of eight atoms. It is emphasized that the needed precision of the g-factors can only be achieved with the elaborate field calibration of the superconducting magnet. This is demonstrated in comparison to the g-values of other nitroxide molecules.*  
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- 88.** ACCURATE HYBRID DENSITY FUNCTIONAL COMPUTATIONS OF THE HYPERFINE CONSTANTS OF PERSISTENT RADICALS: TEMPONE AND THE NEUTRAL MONO-, BI- AND TRICYCLIC DITHIAZOLES. Saba M. Mattar and Alyson D. Stephens, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada. E3B 6E2.  
*In the past, due to the failure of Hartree-Fock techniques to yield accurate wave functions, the hyperfine constants of radicals had to be estimated indirectly via McConnell Q relationships. Here, the UBILYP hybrid density functional and Barone's triple- $\zeta$  EPR-III basis sets are used to directly calculate the hyperfine tensor components of the TEMPONE spin label in its chair, boat and twisted forms at a moderate computational expense. Very good agreement between the computed  ${}^1\text{H}$ ,  ${}^{13}\text{C}$ ,  ${}^{14}\text{N}$  and  ${}^{17}\text{O}$  hyperfine tensor components and those determined by EPR, NMR and ENDOR spectroscopy is obtained provided the effects of the solvent, NO vibrational bending modes and twisting of the ring are taken into account. In addition, the hyperfine tensor components of six neutral mono-, bi- and tricyclic dithiazole radicals are also computed using the same method. These molecules are building blocks for neutral  $\pi$ -type molecular conductors. All the  ${}^1\text{H}$ ,  ${}^{13}\text{C}$ ,  ${}^{14}\text{N}$  and  ${}^{33}\text{S}$  hyperfine coupling constants are in very good quantitative agreement with those determined experimentally by EPR spectroscopy (less than 0.5 G). Thus, for the first time, the hyperfine tensors of large bicyclic and tricyclic hetero radicals that contain sulfur linked to nitrogen are accurately calculated without resorting to post Hartree-Fock techniques. As predicted, the computed total hyperfine tensors show that all these  $\text{C}_{2v}$  molecules have no magnetically equivalent atoms.<sup>1</sup>*  
 Supported by NSERC Canada.  
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- 89.** DETECTION OF THE EPR SPECTRUM OF  $\text{NO}\cdot$  IN RUTHENIUM(II) COMPLEXES. Bruce R. McGarvey, School of Physical Sciences, Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada; Alessandro Acacio Ferro and Elia Tfouni, Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto-USP, Av. Bandeirantes, 3900, 14040-901, Ribeirão Preto-SP, Brazil; Cicero Wellington Brito Bezerra; Izilda Bagatin and Douglas W. Franco, Instituto de Química de São Carlos-USP, Av. Dr. Carlos Botelho, 1465, 13560-970, São Carlos, SP, Brazil  
*The EPR of  $\text{NO}\cdot$  can be detected in the liquid and solid state when crystal fields are sufficient to remove the axial symmetry and separate the  $(\pi^*)_{\sigma}$  and  $(\pi^*)_{\pi}$  orbitals by a few hundred  $\text{cm}^{-1}$ . The theory of the EPR spin-Hamiltonian of bound  $\text{NO}\cdot$  is reviewed, further developed, and then applied to the observed frozen liquid spectra of  $\text{NO}\cdot$  bound to Ru(II) obtained from Ru(II)( $\text{NO}^+$ ) complexes by reduction. Analysis of the spin-Hamiltonian indicates that the unpaired spin resides in the nitrogen p orbital about 70% and the energy separation between the  $(\pi^*)_{\sigma}$  and  $(\pi^*)_{\pi}$  orbitals is around  $1700\text{ cm}^{-1}$ , indicating a Ru-N-O bond angle of much less than  $180^\circ$ . Comparisons to earlier reports on the observation of the EPR spectra of  $\text{NO}\cdot$  will be made.*  
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90. MICROWAVE AMPLITUDE MODULATION TECHNIQUE: CALCULATIONS INCLUDING THE TRANSVERSE COMPONENT OF MAGNETIZATION WITH AN ARBITRARY MODULATION COEFFICIENT. Sushil K. Misra, Concordia University, Montreal, Quebec, Canada H3G 1M8 and Gareth R. Eaton and Sandra S. Eaton, University of Denver, Denver, Colorado, 80208-2436.

The original Herve and Pescia microwave modulation amplitude technique for estimating electron spin  $T_1$  involved measuring the longitudinal component of magnetization ( $M_z$ ) in a pick-up coil with its axis parallel to the Zeeman field, with a small extent of modulation. An alternative measurement technique is proposed in which the transverse ( $M_x$  and  $M_y$ ) components of the magnetization will be measured. To predict the EPR signal for this experiment, the Bloch equations have been extended to theoretically take account of an arbitrary coefficient of modulation,  $m$ . Series expansions for  $M_x$  and  $M_y$  have been obtained in  $m$ , allowing for the possibility of strong modulation (large modulation index  $m$ ). This generalization of the Herve and Pescia method to transverse as well as longitudinal magnetization, and to deeper modulation index, is expected to extend the range of relaxation times that can be measured accurately by this technique.

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91. DOMAIN FORMATION AND PHASE TRANSITIONS IN THE PLASMA MEMBRANE OF LISTERIA MONOCYTOGENES AS STUDIED BY SPIN EXCHANGE AND DIFFERENTIAL SCANNING CALORIMETRY. Reef (Philip D., II) Morse\*, Scott Jones\*, Siqing Liu\*\*, Tonia Wooldridge\*\*, Brian Wilkinson\*\*, and N. Dennis Chasteen\*\*\*, Departments of Chemistry\* and Biological Sciences\*\*, Illinois State University, Normal, IL 61790-4160 and Department of Chemistry, University of New Hampshire, Durham, NH 03824

*Listeria monocytogenes*, the foodborne gram positive psychrotroph responsible for listeriosis, is a concern to the food industry and those with weakened immune systems because it grows in food at refrigeration temperatures. This study looks at both cold growing and cold sensitive strains of *L. monocytogenes* in order to determine whether micro-domains of lipids occur in the plasma membrane. In order to determine if temperature-dependant lipid domain formation occurs in the plasma membrane of *L. monocytogenes*, the oxazolidine probe 7N14 was inserted into isolated plasma membranes. To compare nitroxide behavior in the isolated plasma membranes with its behavior in bilayers of known properties, a test lipid system consisting of 1,2 dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), and 1,2-dipalmitoyl-sn-glycero-3-[phospho-rac-(1-glycerol)] sodium salt (DPPG) in a 4:1 ratio was used. The nitroxide probe was used to label and evaluate exchange broadening both the isolated plasma membranes and DPPC/DPPG liposomes. EPR spectra were taken at various concentrations of 7N14 and various sample temperatures to determine exchange in both systems. The data indicate that there are no apparent regions where 7N14 is selectively soluble in the plasma membranes of *L. monocytogenes*. However, 7N14 does appear to sequester in liposomes made from DPPC/DPPG. If local lipid domain formation does exist in plasma membranes of *L. monocytogenes*, it is not being detected by EPR using 7N14. However, we did observe the possibility of a phase transition in the plasma membrane of *L. monocytogenes* as evidenced by 7N14 central peak to peak width narrowing as a function of temperature. This narrowing occurs at the gel to liquid crystal phase change in DPPC/DPPG. In *L. monocytogenes* this narrowing correlates to the range of temperatures over which *L. monocytogenes* grows. Confirming DSC studies are underway.

Supported by grants from the US Department of Agriculture and the Illinois Council for Agricultural Research.

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92. SPIN LATTICE RELAXATION TIMES OF SPIN PROBES IN DISPERSIONS OF HYDROGENATED CASTER OIL. Kouichi Nakagawa, Fukushima Medical University, RI Research Center, 1 Hikarigaoka, Fukushima, 960-1295, Japan.

Electron spin lattice relaxation times ( $T_{1e}$ ) of spin probes in 5 ~ 10 wt % dispersions of poly-(oxyethylene) (10) hydrogenated castor oil (HCO-10) were investigated by saturation recovery. Degassing was achieved by passing  $N_2$  gas over a teflon tube containing the sample solution.  $T_{1e}$  was measured for dispersions in  $H_2O$  or  $D_2O$  as a function of temperature (22 ~ 50°C) for signals from probes in either the aqueous or vesicle phases. For DTBN spin probe,  $T_{1e}$  in the vesicle phase was shorter than that in the aqueous phase. For TEMPO,  $T_{1e}$  of vesicle and aqueous phase were similar. In the aqueous phase DTBN and TEMPO showed similar relaxation times.  $T_{1e}$  of DTBN in the vesicle phase was slightly shorter than that of TEMPO, which is attributed to faster tumbling of DTBN than of TEMPO. For doxylstearic acids (DSA),  $T_{1e}$  was more than an order of magnitude longer than for DTBN. As the nitroxyl group in DSA was moved further down the membrane chain,  $T_{1e}$  became shorter. The shorter  $T_{1e}$  indicates flexibility of the membrane chain in the vesicle. No significant difference in  $T_{1e}$  between  $H_2O$  and  $D_2O$  solutions was observed for TEMPO, DTBN, or various DSA. It is concluded that steric effects and/or local rotational mobility of the nitroxyl moiety influence the  $T_{1e}$ 's obtained.

Supported in part by Grant-in-Aid for Scientific Research (C) (No. 10640562) from the Ministry of Education, Science, Sports and Culture of Japan.

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93. FERROELECTRIC CAVITY INSERTION: ENHANCING EPR SIGNALS OF AQUEOUS SAMPLES. Y. Nesmelov and D. D. Thomas, University of Minnesota, Department of Biochemistry, Minneapolis, MN 55455

The high dielectric constant and small losses of some ferroelectrics in the GHz range make them attractive for developing new resonance devices for EPR. In particular, it has been suggested that a ferroelectric insertion into the cavity might increase the EPR signal intensity.<sup>1</sup> In the present study, a cylindrical  $KTaO_3$  ferroelectric insertion for an X-band cavity was designed, based on calculations that permitted optimization of reso-

nance frequency and dimensions. The insertion was tested with aqueous samples in a Bruker SHQ cavity, and its performance of this cavity plus insertion was compared with that of a loop gap resonator.<sup>2</sup> Measurements at a constant microwave field amplitude ( $H_1 = 0.012$  G) showed that the insertion increased signal/noise by a factor of 3 and  $H_1/(\text{Power})^{1/2}$  by a factor of 5 compared to the SHQ cavity. The resulting performance was at least comparable to that of a loop-gap resonator. These results suggest that this ferroelectric insertion will be of great value in experiments on aqueous EPR samples, especially those requiring saturating levels of  $H_1$ . We thank Dr. L.A. Boatner (Oak Ridge National Laboratory, TN) for providing  $\text{KTaO}_3$  monocrystals, and we thank Roberta Bennett for helpful discussions.

We acknowledge also the support of University of Minnesota Supercomputing Institute.

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- 94.** EFFICIENT COMPUTER SIMULATION OF PULSED ELECTRON PARAMAGNETIC RESONANCE POWDER SPECTRA. Christopher J. Noble, Graeme R. Hanson, Centre for Magnetic Resonance, Level 2 Gehrman Laboratories, University of Queensland, St Lucia, Queensland, 4072, Australia; Kevin E. Gates, Kevin Burrage, Department of Mathematics, University of Queensland, St Lucia, Queensland, 4072, Australia.

The XSophe computer software suite<sup>1</sup> allows the simulation of single crystal and powder continuous wave EPR spectra for a general spin system with any number of electron and nuclear spins. An extension to this simulation package is currently being developed for the simulation of pulsed EPR spectra with a general spin system. This program is also completely general so that an arbitrary pulse sequence can be simulated but an emphasis is placed on efficient techniques for the simulation of the common two and three pulse ESEEM experiments and HSCORE. 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 can also be greatly reduced if the calculations are performed in the frequency domain.<sup>2</sup> Techniques have been developed for the efficient integration of distributions both in the orientation of the crystallites and also of the Hamiltonian parameters. The theoretical basis for these calculations will be presented with representative examples of spectra and simulations.

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- 95.** MODELLING STRAIN BROADENING IN THE EPR SPECTRA OF HIGH SPIN  $\text{Fe(III)}$  METALLOPROTEINS. Christopher J. Noble, Graeme R. Hanson, Centre for Magnetic Resonance, Level 2 Gehrman Laboratories, University of Queensland, St Lucia, Queensland, 4072, Australia; Gerhard Schenk, Department of Biochemistry, University of Queensland, St Lucia, Queensland, 4072, Australia.

The linewidths in high spin  $\text{Fe(III)}$  metalloproteins are often determined by 'strain' broadening involving a distribution of the zero field splitting (zfs) parameters,  $D$  and  $E$ . The accurate determination of the spin Hamiltonian parameters and spin concentration require a rigorous treatment of these distributions in the computer simulation of the EPR spectra.<sup>1</sup> For small distributions of these parameters, first order perturbation theory may be used to calculate the linewidths used in the simulation. In general, a numerical summation over the entire distribution must be used to accurately reproduce the experimental spectrum, however, this method is computationally expensive. We look at various strategies for the efficient and accurate simulation of strain broadened high spin iron spectra. We present results from a recent study of a purple acid phosphatase from sweet potatoes (SPPAP) and show that some features in the EPR spectrum of this centre can only be explained using a correct treatment of these spin Hamiltonian parameter distributions.<sup>2</sup>

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- 96.** INTERACTIONS OF WATER AT THE SURFACE OF ACTIVATED CARBON CHARS. B.M. Odintsov, R. B. Clarkson, P. M. Ceroke, R. L. Belford, Illinois EPR Research Center, University of Illinois, Urbana, IL 61801; R. Sh. Vartapetian, Institute of Physical Chemistry, Russian Academy of Sciences, Moscow 117915, Russia

Carbon chars synthesized from wood provide very strong signals for use in EPR oximetry [1. EPR and DNP of Char Suspensions: Surface Science and Oximetry, Clarkson, Odintsov, Ceroke, Ardenkjær-Larsen, and Fruianu, Belford, Phys. Med. Biol., 1998, 43, 1907-1920; 2. Solid-Liquid Electron Density Transfer:  $^1\text{H}$  Pulsed DNP in Aqueous Suspensions of Chars at Low Magnetic Field, Odintsov, Belford, Ceroke, and Clarkson, J. Am. Chem. Soc., 1998, 120, 1076-1077]. By proper choice of starting materials and synthesis conditions, variations of EPR line width with

oxygen can be tailored to meet differing measurement requirements (e.g. oxygen-rich brain, hypoxic tumors), thus providing a very flexible array of sensor materials for in vivo oximetry. These materials also usually exhibit low toxicity, and thus offer many attractive possibilities for the development of oxygen measurement techniques in living systems. To be useful for in vivo oxygen measurements made over a period of days or months, the materials must have stable properties in biological environments. Virtually all oxygen sensitive materials (chars, coals, lithium phthalocyanine) can exhibit sensitivity variations when placed in living tissue. If the nature and cause of changes can be understood, oxygen sensors can be treated or conditioned prior to use, calibrated, and their performance in vivo will be stable. Biological environments are aqueous, so we have studied the effects of water on char oxygen sensitivity. Results from multi-frequency EPR, NMR, DNP, and classical adsorption experiments are presented. The data suggest that changes in the oxygen sensitivity of chars due to water interactions are caused at least partially by strongly adsorbed surface water molecules, which reduce the effective interaction of oxygen molecules with the paramagnetic centers located on the char surface. Partially supported by the NIH (P41 GM51630). Collaborative work was facilitated by NIH (FIRCA) and NATO grants.

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97. COMPARISON OF METHODS TO DETERMINE DISTANCES BETWEEN DEEPLY BURIED POSITIONS IN HUMAN CARBONIC ANHYDRASE II. Malin Persson<sup>1</sup> James R. Harbridge<sup>2</sup>, Ragheed Mitri<sup>2</sup>, Per Hammarström<sup>1</sup>, Uno Carlsson<sup>1</sup>, Gareth R. Eaton<sup>2</sup>, and Sandra S. Eaton<sup>2</sup>, <sup>1</sup>Department of Chemistry, University of Linköping, Linköping, Sweden, <sup>2</sup>Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado

Spin labels were attached to cysteines at deeply-buried positions in the hydrophobic cluster of human carbonic anhydrase II (N67C/C206, V121C/C206, N67C/V121C/C206S, and I59C/A174C/C206S). Distances between the labels were determined from the relative intensity of the half-field transition (Eaton et al. (1983) J. Am. Chem. Soc. 105, 6560), Fourier analysis of line-shape broadening (Rabenstein and Shin (1995) Proc. Natl. Acad. Sci. U.S. 92, 8239), lineshape simulation (Hustedt et al. (1997) Biophys. J. 74, 1861) and 4-pulse DEER (double electron-electron resonance) (Pannier et al. (2000) J. Magn. Reson. 142, 331). The nitroxyl-nitroxyl distances are in the range of 7 to 20 Å. Good agreement was obtained from the half-field transition, Fourier deconvolution, and lineshape simulation for distances in the range of 7-9 Å. At distances between 18 and 20 Å Fourier deconvolution and DEER gave distances in good agreement. The best working range of each method will be discussed.

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98. IDENTIFICATION OF PROTEIN-DERIVED TYROSYL RADICAL IN THE REACTION OF CYTOCHROME *c* AND HYDROGEN PEROXIDE: CHARACTERIZATION BY ESR SPIN-TRAPPING, HIGH PERFORMANCE LIQUID CHROMATOGRAPHY AND MASS SPECTROMETRY. Steven Y. Qian, Yeong-Renn Chen, Yang C. Fann, Colin F. Chignell, and Ronald P. Mason, Laboratory of Pharmacology and Chemistry; Leesa J. Deterding, and Kenneth B. Tomer, Laboratory of Structural Biology, National Institute of Environmental Health Sciences, National Institutes of Health, P.O. Box 12233, Research Triangle Park, NC, 27709

The protein-derived tyrosyl radical from the reaction of horse heart cytochrome *c* with hydrogen peroxide was investigated using the ESR spin-trapping technique with 2-methyl-2-nitrosopropane (MNP). After nonspecific proteolysis, the protein-derived radical adduct had a three-line spectrum with MNP and a multi-line spectrum with perdeuterated MNP-*d*<sub>9</sub>. Identical ESR spectra were observed from the oxidation of tyrosine by HRP-H<sub>2</sub>O<sub>2</sub>. However, the structure of MNP/tyrosyl adduct had not been correctly determined [David P. Barr, J. Biol. Chem, 271:15498-15503, 1996]. In this study, a series of <sup>13</sup>C-labeled tyrosines was examined by ESR spin-trapping to determine this radical structure, i.e., the MNP trapping site. Additional hyperfine couplings observed from experiments with <sup>13</sup>C-labeled tyrosines suggested that the radical site was located on C-3 of the tyrosine phenyl ring instead of on C-1 as was previously proposed. To confirm this C-3 structure, we photochemically synthesized an authentic MNP/tyrosyl radical adduct in which the MNP/tyrosyl radical adduct at the C-3 position was generated by UV irradiation of 3-iodo-tyrosine in the presence of MNP. The superfine couplings of the authentic MNP-*d*<sub>9</sub>/tyrosyl adduct were identical to that of cytochrome *c*-derived MNP/tyrosyl adduct, demonstrating again that C-3 is the trapping site for MNP/tyrosyl adduct. When HPLC was coupled with ESR on-line, the ESR-active HPLC peaks (MNP/tyrosyl adduct) from tyrosine oxidation via HRP-H<sub>2</sub>O<sub>2</sub> and UV-irradiated 3-iodo-tyrosine had the same retention time, suggesting that they are identical. To further identify the MNP adducts, the HPLC fractions which possess ESR activity were analyzed by electrospray mass spectrometry (ESI/MS) and tandem mass spectrometry (MS/MS). We conclude that the tyrosyl radical trapping with MNP that leads to a persistent radical adduct occurs at the C-3 position of the tyrosine phenyl ring.

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99. IN VIVO ESR MEASUREMENTS OF FREE RADICAL REACTIONS BY HYPOXIC-ISCHEMIC BRAIN DAMAGE IN WHOLE MICE. Hiroaki Sano<sup>1</sup>, Masaichi Naruse<sup>1</sup>, Tetsuo Oi<sup>1</sup>, <sup>1</sup>Daiichi Radioisotope Laboratories Ltd., Research Center, Chiba, 289-1592, Hideo Utsumi<sup>2</sup>, <sup>2</sup>Kyushu University, Graduate School of Pharmaceutical Sciences, Fukuoka, 812-8582, Japan

Hypoxic-ischemic (HI) brain damage is one of the causes by free radicals and reactive oxygen species (ROS). There have been, however, few reports on direct determination of free radicals generated in vivo in the brain. Nitroxyl radicals are widely used as probes for in vivo ESR measurement and their signals decrease gradually in living animals. The interactions of nitroxyl radicals with reducing enzymes, ascorbic acid and reactive oxygen species cause loss of their paramagnetism, and in vivo signal decay of nitroxyl radical depends on physiological and pathological conditions such as streptozotocin-induced diabetes and iron overload etc. Quite recently, we developed new nitroxyl probe, which is highly retained in the brain after intravenous administration.<sup>1</sup> In the present paper, we applied this probe to HI brain damage. Any infarct was

observed in sham operated brains and the brains treated 3 h HI, which was determined with 2,3,5-triphenyl-H-tetrazolium chloride (TTC) staining, but severe infarct was occurred 3 days after the 3 h HI treatment in the regions of brains as remained unstained. In vivo ESR signal decay of the nitroxyl probe was monitored in the head of mice after the intravenous. The signal decay rate just after 3 h HI treatment group was significantly smaller than that of sham group, but that of 3 days after HI treatment did not differ from sham one. These suggest that ESR measurement of the nitroxyl probe detects ROS generation in early stage of HI injury.

1. Sano et al., *Free Radic. Biol. Med.*, in press.

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- 100.** MULTIFREQUENCY HIGH-FIELD QUASIOPTIC HOMODYNE EMR SPECTROMETER. Charles. A. Saylor, NHMFL, Tallahassee, FL, Guenter G. Maresch, Tallahassee, FL, Johan van Tol, NHMFL, Tallahassee, FL, Jureck Krzystek, NHMFL, Tallahassee, FL, Richard. Wylde, Thomas Keating Ltd., West Sussex, UK, L.C. Brunel, NHMFL, Tallahassee, FL, USA

The NHMFL, in collaboration with Thomas Keating Ltd., has developed a new High-Field Multifrequency Quasioptic EMR spectrometer. This spectrometer uses quasioptical techniques, including elliptical focusing mirrors, flat mirrors, polarizing grids and a corrugated waveguide, to propagate millimeter waves in the frequency range from 180 to 360 GHz. This permits the millimeter waves to propagate in a broadband, low loss, polarization conserving mode. The spectrometer can therefore operate in a broad frequency range with increased sensitivity while using phase sensitive homodyne techniques to selectively detect either the absorptive or dispersive component of the EMR signal. Introductory results on nitroxides, MgO and Al<sub>2</sub>O<sub>3</sub> showing the flat background and phase control will be discussed.

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- 101.** POSSIBLE INTERFERENCE OF ACCIDENTAL AND X-RAY DENTAL DOSES IN EPR DOSIMETRY WITH TEETH. S.V. Sholom, V.V. Chumak, E.V. Bahanova, Scientific Center of Radiation Medicine, Melnikova str., 53, Kiev-50, Ukraine, 04050

Threshold values of reconstructed dose in EPR dosimetry with teeth today are lower than 100 mGy.<sup>1</sup> Such sensitivity covers the entire range of doses being of practical interest for dosimetric support of radiation effect epidemiological studies. The main interest in this regard has the accidental dose  $D_{acc}$ , which, in general case, is related to cumulative dose  $D_{cum}$  via equation:  $D_{acc} = D_{cum} - D_{uv} - D_{bg} - D_{x-ray}$  where  $D_{uv}$  – dose from ultraviolet solar exposure,  $D_{bg}$  – dose from background environmental exposure,  $D_{x-ray}$  – dose from possible x-ray diagnostic procedures. First component is displayed mainly on front teeth. This was the reason why such teeth were excluded from dosimetry. Second component may be determined by multiplying of enamel age on environment dose rate typical for the area where tooth donor lives. Thus, the component dose from x-ray examination is the main source of uncertainties for accidental dose determination. In previous study<sup>2</sup>, teeth of different types were exposed in vitro in different geometries using x-ray facilities most common in Ukraine, and then <sup>137</sup>Cs-equivalent doses were reconstructed separately for lingual and buccal parts of each tooth. In such way the empirical values of doses per single x-ray examination were obtained. In the present study, doses of few tens of Chernobyl liquidators' teeth were measured separately for lingual and buccal parts. For most cases the excess of buccal doses comparing with lingual was seen. For some cases this excess was higher than 100 mGy. The measuring of control teeth confirmed that observed effect is not related to Chernobyl exposure. The method of accidental component dose evaluation is proposed. This method is based on the modelling of found effects using Monte-Carlo simulation.

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- 102.** PROPERTIES OF SOME THERMOACTIVATED EPR CENTERS IN TOOTH ENAMEL. S.V. Sholom, V.V. Chumak, Scientific Center of Radiation Medicine, Melnikova str., 53, Kiev-50, Ukraine, 04050

Tooth enamel is known as a unique biomineral that has found widespread application in EPR dosimetry and dating because of the properties of some carbonic radicals. Radiological properties of CO<sub>2</sub><sup>•-</sup> centers are usually exploited although enamel contains other paramagnetic radicals<sup>1,2</sup> as well, including radiation-sensitive. Paramagnetic centers of enamel, arising in previously irradiated samples after their heating to certain temperatures, have been studied in the present work. Enamel was carefully purified by chemical treatment (100-250 mm grains in KOH 60°C solution under ultrasound) from dentine and microimpurities, which gave possibility to reduce significantly the intensity of the strong signal, usually dominating in untreated samples after heating to high temperatures and caused by the organic component of enamel. EPR signals were studied in the range of temperatures from ambient to 900°C and dose from zero to 200 Gy. Few strongly overlapping EPR signals were seen around g-factor of 2.0. Using the difference in saturation properties of these signals, it was possible to isolate their separate components and determine spectroscopic parameters. Assumptions concerning possible localization of corresponding centers in the structure of enamel were proposed. Suggestions about possible application of observed signals for the purposes of retrospective dosimetry are given.

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- 103. DIELECTRIC RESONATOR-BASED RESONANT STRUCTURE FOR SENSITIVE ESR MEASUREMENTS AT HIGH HYDROSTATIC PRESSURES.** Andrzej Sienkiewicz, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland; Slaven Garaj, Institut de Génie Atomique, Département de Physique, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland; Marek Jaworski, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland; Charles P. Scholes, Chemistry Department, SUNY at Albany, Albany, NY 12222, USA; László Forró, Institut de Génie Atomique, Département de Physique, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

We report a novel miniature microwave probehead for performing sensitive ESR measurements at high hydrostatic pressures. The system combines two sub-assemblies: 1) the double-stacked dielectric resonator (DR) resonant structure, and 2) the modified sapphire-anvil pressure cell (SAC). The BeCu-made body forms the outer shell of the probehead and accommodates the resonant structure, as well as provides a precise guidance for movable metallic parts of the SAC. The microwave resonant structure is designed around commercially available high dielectric ( $\epsilon_r \approx 30$ ) ceramic DRs from MuRata-Erie North America. A pair of such DRs resonates in the lowest cylindrical  $TE_{018}$  mode at 9.28 GHz while being separated by a distance of 4.9 mm. This rather large spacing between the DRs easily accommodates two conical sapphire pistons and the metallic gasket of the SAC. The microwave power is routed to and from the high pressure ESR probehead via a section of 0.141" coaxial cable. The sapphire-anvil gasketed cell is ruby-calibrated and operates in a similar way to more commonly used diamond-anvil pressure cells (DACs), reaching pressures up to 2 GPa. The newly developed apparatus was used for high-pressure Conduction Electron Spin Resonance (CESR) studies of anorthorhombic phase conducting polymer,  $K_3C_{60}$ . The CESR linewidth ( $\Delta H_{pp}$ ) of the metallic-phase  $K_3C_{60}$  broadens considerably with increasing hydrostatic pressure, thus supporting the one-dimensional model for this compound. While using our high-pressure ESR system we could follow the  $\Delta H_{pp}$  broadening up to the pressures in the range of  $\sim 1.5$  GPa. We also performed preliminary high-pressure ESR measurements of aqueous samples containing stable nitroxide radicals. Satisfactory S/N was obtained for 500 mM aqueous solution of TEM-POL contained in 0.35 mL volume of the SAC gasket. The ESR study of liquids under the high-hydrostatic pressure has its rationale since pressure is becoming an increasingly useful tool for studying the structure and function of proteins.

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- 104. CHARACTERIZATION OF AGGREGATES FORMED BY NOVEL ANIONIC ISOINDOLINE NITROXIDES IN LIQUID AND FROZEN SOLUTIONS BY W-BAND (95 GHz) EPR SPECTROSCOPY.** S. E. Bottle, A. S. Micallef, CIDC, School of Physical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, Q4001, Australia; D. Gilles, Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, United Kingdom; D. L. Hughes, Biological Chemistry Department, John Innes Centre, Norwich Research Park, Colney, Norwich NR4 7UA, United Kingdom; L. H. Sutcliffe, Institute of Food Research, Norwich Research Park, Colney, Norwich NR4 7UA, United Kingdom; A. I. Smirnov, Illinois EPR Research Center, University of Illinois, 190 MSB, 506 S. Mathews, Urbana, IL 61801, USA.

Isoindoline-based nitroxides are known to be very useful spin probes because of the narrow EPR line width and excellent thermal and chemical stability. Recently, several new derivatives of isoindoline-based nitroxides have been synthesized that significantly extended applications of these spin labels particularly in studies of aqueous systems<sup>1,2</sup>. Here we characterize one of the newly synthesized isoindoline nitroxides, 5-carboxy-1,1,3,3-tetramethylisoindolin-2-yloxy (CTMIO), with W-band (95 GHz) EPR spectroscopy. We have found that CTMIO aggregates in toluene solutions. In liquid solutions, the EPR spectra of the monomer and dimer are different due to dipolar broadening and differences in the rotational correlation time. The latter effect is amplified by High Field EPR spectroscopy thus allowing us to separate the spectra by least-squares simulation and to estimate the enthalpy of the dimer formation ( $-43 \pm 8$  kJ/mol). W-band spectra from frozen solutions demonstrated resolved dipolar splitting in the z-manifold that gave us a measure for the NO group separation in the dimer. The EPR data are compared with results of X-ray analysis.

Supported by CIDC, Australian Research Council, Laporte Centenary Scholarship from the Sir Robert Menzies Centre for Australian Studies, QUT Vice Chancellor's Initiative Scholarship, Australian Postgraduate Award, BBSRC, and NIH (RR01811).

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- 105. MOLECULAR OXYGEN ARTIFACTS IN EPR EXPERIMENTS AT X-BAND AND AT HIGH MAGNETIC FIELDS (W-BAND, 95 GHz) — IMPLICATIONS FOR METALLOPROTEIN STUDIES.** A.I. Smirnov, R.B. Clarkson, R. L. Belford, Illinois EPR Research Center, University of Illinois, 190 MSB, 506 S. Mathews, Urbana, IL 61801, USA

Although molecular oxygen is paramagnetic, its X-band (9.5 GHz) EPR spectrum in air at normal atmospheric pressure is so broad that it can be ignored for many practical purposes. At Q-band (35 GHz), the peak-to-peak intensity of molecular oxygen in air is still rather weak; however, it is known to be useful for a simple and convenient test of spectrometer sensitivity. We have observed that with a further increase in microwave frequency to 95 GHz (W-band), molecular oxygen in air at room temperature gives rise to a complex multi-line spectrum which might cause significant artifacts in experiments with samples exhibiting broad EPR lines. Even more surprising was the observation of X-band EPR signals at cryogenic temperatures (around 10 K) from molecular oxygen in frozen water. Similar signals were also observed at 10 K from frozen air samples. Both samples exhibit a strong EPR signal at ca. 1.15 T that is characteristic for molecular oxygen in a nitrogen matrix<sup>1</sup>. This indicates that upon freezing and storing the sample in open EPR tubes, some cavities formed in the ice are filled with molecular nitrogen and nitrogen. In addition to the 1.15 T signal, we also observed some weak EPR signals in the "high-spin" metalloprotein region (effective g-factor around 2.0). These signals could lead to some misinterpretation of metalloprotein spectra if are not recognized. The intensity of



these molecular oxygen EPR signals is significant for samples that form a poor quality glass and upon prolonged storage of open EPR tubes at 77 K. The artifacts are easily avoided by sealing the EPR tubes. In addition, the presence of 1.15 T serves as a reliable indication of possible molecular oxygen artifacts. Supported by the NIH (RR01811, RLB).

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- 106.** MULTI-FREQUENCY TIME-RESOLVED (TR) EPR ANALYSIS OF THE CHARGE-SEPARATED RADICAL PAIR STATE  $P^+Q^-$  IN PHYLOQUINONE BIOSYNTHETIC PATHWAY MUTANTS OF PHOTOSYSTEM I. Dietmar Stehlik, Stephan Zech, Free University Berlin, Department of Physics, D14195 Berlin; John Golbeck, Don Bryant, Penn State University, Department of Biochemistry, University Park, PA 16802

TREPR spectroscopy proved to be a powerful tool to study structural and functional properties “in action” for the primary photosynthetic process of charge separation to the first stabilized radical pair (RP) state  $P^+Q^-$ , which typically evolves in the EPR accessible time range of longer than  $10^{-8}$ s. A wealth of structural and functional information can be extracted from the magnetic interaction tensors (g-tensors, spin-spin RP interaction and hyperfine tensors, including their relative orientations) and can be supplemented by kinetic and dynamical parameters. Obviously, the most conclusive information comes from a determination of decisive relative changes in spectral and dynamic parameters associated with specific changes of the cofactor molecules and/or of the binding site determined by protein environment. The genetic identification and engineering capability of the biosynthetic pathway of the quinone acceptor phyloquinone ( $VK_1$ ) of photosystem I (PS I) in cyanobacteria *Synechocystis* sp. PCC 6803<sup>1</sup> opens a great tool box to introduce specific cofactor changes. The enzymes naphthoate synthase, phytyl transferase and methyl transferase (coded by the genes *MenB*, *MenA* and *MenG*, resp.) catalyse the last three steps in the  $VK_1$  synthesis. Deletion of any of these genes leads to specific changes in the quinone acceptor site  $A_1$  of PS I. For the *MenB*- and *MenA*-mutants  $VK_1$  is blocked to be synthesized. Instead a substitute quinone (plastoquinone PQ9, available during bacterial growth) is recruited into the  $A_1$  site, as characterized by TREPR and biochemical methods.<sup>2</sup> The *MenG*-mutant is expected to synthesize demethylated  $VK_1$  quinone as readily recognized by the corresponding change in the observed hyperfine pattern. In a further step *MenB*-mutants have been used for quinone feeding experiments. Depending on the choice of the supplemented quinones different cofactors could be realized in the  $A_1$ -site. Feeding quinones like naphthoate,  $VK_3$  or  $VK_2$  result in reconstitution of original  $VK_1$  in the  $A_1$  site. New cofactors are observed in the case of feeding with straight naphthoquinone as well as other substitutes. The recent characterisation results will be presented. The potential to study details of the binding site and the protein-cofactor interactions in connection with function will be discussed.

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- 107.** GENERALIZED FREQUENCY-DOMAIN CALCULATION OF PULSE EPR SPECTRA OF DISORDERED SYSTEMS. Stefan Stoll, Arthur Schweiger, Physical Chemistry Laboratory, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland

Pulse EPR spectra of powders can be calculated numerically using time-domain or frequency-domain approaches. The former are general but rather slow, the latter faster, but up to now limited to special experiments (two-pulse and three-pulse ESEEM, HYSCORE) and special spin systems. We present a generalized and fast frequency-domain approach applicable to arbitrary pulse sequences and arbitrary spin systems. It directly calculates the positions and amplitudes of spectral peaks for selected orientations of the paramagnetic species and uses an interpolation scheme to obtain the full powder spectrum. The method is suited for experiments of arbitrary dimension. We show its special advantage for 2D correlation and separation experiments.

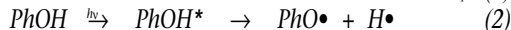
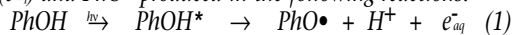
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- 108.** BOUND STATE CONFORMATION AND DISAGGREGATION OF MODEL PEPTIDE SUBSTRATES OF THE CHAPERONE SecB: ESR AND FLUORESCENCE STUDIES. Pia D. Vogel, Wolfgang E. Trommer, Department of Chemistry, University of Kaiserslautern, D-67653 Kaiserslautern, Germany; Vikram G. Panse, Raghavan Varadarajan, Molecular Biophysics Unit, Indian Institute of Science, Bangalore 560012, India

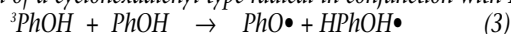
SecB is a homotetrameric chaperone that forms part of the protein translocation machinery in *E. coli*. We have investigated the bound state conformation of the model substrate bovine pancreatic trypsin inhibitor (BPTI) as well as the conformation of SecB itself by using proximity relationships based on site-directed spin labeling and pyrene fluorescence methods. The data suggests that SecB binds a collapsed coil of reduced unfolded BPTI, which then undergoes a structural rearrangement to a more extended state upon binding to SecB. In addition, ESR shows that also SecB undergoes a conformational change during this process. Similar studies using the insulin B chain revealed that SecB does not act as a catalyst in the dissociation of aggregated B chains but rather binds to a small population of free B chains with high affinity, thereby shifting the equilibrium from the aggregate towards individual B chains.

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- 109.** *pH AND WAVELENGTH DEPENDENCE OF THE PHOTOCHEMISTRY OF PHENOLS. A FT-EPR STUDY.* Alejandro Bussandri and Hans van Willigen, Department of Chemistry, University of Massachusetts at Boston, Boston, MA 02125, United States
- The pH and excitation wavelength (308, 266 and 193 nm) dependence of the photochemistry of phenol, p-cresol, and tyrosine in aqueous solution was studied using Fourier Transform Electron Paramagnetic Resonance (FT-EPR). In basic solution (pH 11), the excitation of phenolates (PhO<sup>-</sup>) with 308, 266 and 193 nm laser light leads to photoionization. Resonance signals from the hydrated electron (e<sub>aq</sub><sup>-</sup>) and phenoxyl radical (PhO•) develop with instrument-controlled rise time (~ 50 ns). On the other hand, the photochemistry in neutral and acidic (pH 2-7) solutions of phenol and p-cresol shows a remarkable wavelength dependence. Excitation to S<sub>1</sub> (266 nm) and S<sub>2</sub> (193 nm) gives FT-EPR signals of the H-atom, (e<sub>aq</sub><sup>-</sup>) and PhO• produced in the following reactions:



Chemically Induced Dynamic Electron Polarization (CIDEP) effects provide strong evidence that whereas reaction (2) occurs via the singlet excited state upon excitation into S<sub>2</sub>, the triplet excited state is involved when excitation is into S<sub>1</sub>. Furthermore, excitation into S<sub>1</sub> gives rise to formation of a cyclohexadienyl type radical in conjunction with PhO• via the triplet state reaction:



This reaction is not observed if excitation is into S<sub>2</sub>. Apparently, intersystem crossing to the triplet state under these conditions is strongly attenuated.

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- 110.** *MAPPING TISSUE PERFUSION, ISCHEMIC RISK REGION AND REDOX STATE IN THE RAT HEART USING EPR IMAGING.* M. Velayutham, H. Li, P. Kuppusamy, Jay L. Zweier, The EPR Center and Department of Medicine, The John Hopkins University School of Medicine, 5501 Hopkins Bayview Circle, Baltimore, MD 21224
- With the advent of thrombolytic and other revascularization therapies, reperfusion of ischemic tissues has become a common event in the treatment of major human diseases such as heart attack and stroke. To study the pathogenesis of these diseases, it is of critical importance to have methods capable of measuring tissue perfusion, as well as localized regions at risk of injury. The usual way of determining myocardial risk region and cell death is based on histologic sections of cut tissue, however, this precludes assessment of the time course of this process. Therefore, it would be preferable to have a non-invasive technique for obtaining this critical information. EPR imaging techniques have been developed to study biological organs and tissues at L-band, 1-2 GHz. In order to map myocardial risk region and tissue redox state as a possible index of cell viability 2D and 3D EPR image data were obtained for isolated rat hearts before and after the onset of regional ischemia using nitroxide spin labels. With left anterior descending coronary artery occlusion, 2D and 3D image data clearly show the risk region as a void of lower intensity in the image and upon reperfusion this void is largely reversed. The presence of this void and the rate of its appearance are influenced by the structure of the nitroxide label used with the rate of nitroxide reduction and its cellular partitioning affecting the image data obtained. We observe that EPR imaging enabled mapping of the ischemic risk region with a resolution of better than 0.5 mm. The unique information obtained regarding the time course of changes in redox metabolism of the risk region and normal myocardium can provide unique insights regarding the basic mechanisms of myocardial injury during and following heart attack.

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- 111.** *PULSED EPR AND AB INITIO CALCULATIONS ON TETRACYANO NICKELATE (I) IN NaCl AND KCl HOST LATTICES.* Alexandre A. Leitão, José A. Coelho Neto, Nelson M. Pinhal, Carlos E. Bielschowsky and Ney V. Vugman, Instituto de Física - Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brazil, 21945-970.
- Combination of accurate measurements and high quality calculations of magnetic and quadrupolar hyperfine interactions, in paramagnetic molecules in the solid state, is not usually found in literature. Good agreement is achieved in cases of gaseous phase measurements. However, for paramagnetic complexes inserted in crystal host lattices, the matrix actively participates on molecular structure, demanding severe additional efforts to take it into account in the calculations. X-ray irradiation on diamagnetic Ni(II) 3d<sup>8</sup> cyanide complexes in KCl or NaCl host lattices gives rise to paramagnetic 3d<sup>9</sup> [Ni(CN)<sub>4</sub>]<sup>-</sup> molecules (unpaired electron in a d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital). The magnetic and quadrupolar hyperfine interactions with the four nitrogens, hidden in the CW EPR linewidth, are revealed by ENDOR, 2D-ESEEM and ESEEM angular variation studies. Pulsed EPR experiments were performed at X-band (9.724 GHz) on a Bruker ESP380E CW/FT spectrometer at 16K. Stimulated echo was optimized by power variation of a sequence of three 16 ns pulses. ESEEM spectra were obtained as a result of a sum projection of a 512x256 2D spectrum, varying the distances between the second and the third pulses with a 8 ns step. The geometry, electronic structure and isotropic hyperfine interaction with the nitrogens are determined by Mollet-Plesset perturbation theory based on ab initio unrestricted spin Hartree-Fock calculations (UMP2) embedded cluster calculations. These calculations, besides confirming the unpaired electron orbital assignment and providing precise localization of cyanides and axial chlorines, are in excellent agreement with measured hyperfine and quadrupole values.

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- 112.** PHOTOLYSIS OF CAGED-DIOXYGEN DRIVES SUPEROXIDE PRODUCTION BY XANTHINE OXIDASE IN A MODEL SYSTEM FOR RADICAL DAMAGE IN ISCHEMIA-REPERFUSION INJURY. Manjula Rao and Kurt Warncke, Department of Physics, Emory University, Atlanta, GA 30322 USA

Cell and tissue injury induced by reperfusion of dioxygen,  $O_2$ , following ischemia in biological cells and tissues is a medical problem of broad scope. An interval of anaerobiosis in cells enhances levels of xanthine oxidase and substrate xanthine, which, upon reintroduction of  $O_2$ , is oxidized to uric acid with concomitant production of superoxide radical ( $O_2^{\bullet-}$ ). The "primary" superoxide radical has been proposed to initiate cell destruction through a radical damage cascade. Our immediate aim is to characterize these reactions in vitro by using pulsed-laser-induced photolytic release of dioxygen from a caged-dioxygen molecule, followed by time-resolved electron paramagnetic resonance (EPR) spectroscopic probes of the radical intermediates. We use a  $\mu$ -peroxo-bridged bis-cobalt(III) complex that releases  $O_2$  upon irradiation with the 355 nm output of a pulsed-Nd YAG laser. Dioxygen consumption measurements ( $O_2$  electrode) show that concentrations of caged-dioxygen complex up to  $10^{-3}$  M do not inhibit xanthine oxidase activity under dark aerobic conditions. Superoxide generation by xanthine/xanthine oxidase following photolysis of the caged-dioxygen complex in anaerobic solution is evinced by optically-detected (550 nm), superoxide dismutase-sensitive reduction of cytochrome c. Under comparable conditions in the presence of spin traps, X-band continuous-wave EPR spectroscopy reveals the prompt light-dependent formation of both superoxide and hydroxyl radical adducts. These results demonstrate that the caged-dioxygen complex is capable of initiating superoxide radical generation by xanthine/xanthine oxidase in response to light. Time-resolved EPR studies of photogenerated radicals using the anaerobic xanthine/xanthine oxidase/caged-dioxygen complex system will be reported.

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- 113.** AN EFFECTIVE FIELD-FREQUENCY LOCK FOR VLF EPR IN VIVO SPECTROSCOPY. Benjamin B. Williams, Colin Mailer, Eugene D. Barth, Valeri E. Galtsev, and Howard J. Halpern, University of Chicago, Dept. Radiation Oncology, Chicago, IL 60637.

The focus of our effort is the in vivo measurement of oxygen concentration based on changes in the linewidth of narrow lined spin probes. Any animal movement during a scan or image will cause the resonant frequency of the cavity to change and result in a confounding shift or distortion of the acquired spectrum. We account for animal movement by adjusting the RF frequency using an automatic frequency control circuit, (discussed elsewhere), and binning our spectral data on a point-by-point basis. The main magnetic field is generated and swept using Helmholtz-type coils whose current is supplied by a Kepco BOP. The resulting magnetic field is known to 16 bit resolution over a range on the order of 10 Gauss, providing magnetic field accuracy better than 1 mG. The frequency of the reference RF signal from an HP8640B source is measured using an HP5334B frequency counter. The measured frequency is accurate to 1 kHz, consistent with a field accuracy of .35 mG. Operationally, at each field sweep value the EPR signal is collected along with a measurement of the current frequency. In software, the difference between the frequency read at each point and an initial frequency collected at the beginning of the scan or image is used to calculate the effective field sweep value. The collected EPR signal is then binned according to this effective value. Without a lock of this type changes in the frequency will cause distortions of the line shape that could be misinterpreted or produce inconsistent data for EPRI. Spectra collected with and without the bin shifting algorithm in place will be presented demonstrating the ability of the algorithm to correct for spectral distortions caused by sample motion.

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- 114.** AN ANALYSIS OF SIGNAL HEIGHT DEPENDENCE ON GRADIENT STRENGTH, SPATIAL SPIN DISTRIBUTION, MODULATION AMPLITUDE IN CW EPRI. Benjamin B. Williams, Colin Mailer, Eugene D. Barth, Valeri E. Galtsev, and Howard J. Halpern, University of Chicago, Dept. Radiation Oncology, Chicago, IL 60637.

In CW EPRI projections of a spatial-spectral object are collected by acquiring spectra in the presence of varying magnetic field gradients. These gradients act to decouple the spectral and spatial characteristics of the object. The application of a field gradient over a distribution of spins reduces the number of spins at resonance at a given field sweep value. As the distances along the field sweep over which changes in absorption occur fall below the field modulation amplitude the signal is further reduced. Assuming a constant noise floor, as the gradient strength increases the scan time must be increased in order to maintain the signal-to-noise ratio among the projections. However, data acquisition times in EPRI are a major limiting factor of image quality in 3 and 4 dimensional spectral-spatial in vivo imaging. A quantitative understanding of the dependence of signal height on the spatial spin distribution, gradient strength and modulation amplitude in EPRI will lead to more time efficient image acquisition methods that will facilitate high resolution in vivo imaging in biologically relevant times. A mathematical discussion of the effects of gradient strength, modulation amplitude and spatial spin distribution on signal height will be presented. The conclusions will be demonstrated through simulated projections and experimental data.

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- 115.** *IN VIVO EPR IMAGING STUDIES OF SPATIOTEMPORAL CHANGES OF NITROXIDE LEVEL IN TUMOR BEARING MICE.* Ken-ichi Yamada, Mahadevan Subramoni, Nallathamby Devasahayam, Radiation Biology Branch, Division of Clinical Sciences, National Cancer Institute, National Institutes of Health, Bethesda, MD 20892; Periannan Kuppusamy, EPR Laboratories, Johns Hopkins University School of Medicine, Baltimore, MD 21224; Janusz W. Koscielniak, SAIC-Frederick Cancer Research and Development Center, Frederick, MD 21702; James B. Mitchell, Sankaran Subramanian, and Murali C. Krishna, Radiation Biology Branch, National Cancer Institute, Division of Clinical Sciences, National Institutes of Health, Bethesda, MD 20892

Nitroxide spin probes undergo reduction to the corresponding hydroxylamine in vivo depending on the redox status and oxygen status of the tissue. In this study, we investigated in vivo pharmacokinetics of nitroxides in tumor bearing mice by Continuous Wave Electron Paramagnetic Resonance (CW EPR) imaging spectrometer operating at 300 MHz. Mice were injected with tumor cells on the hind leg and the tumor was allowed to grow to about 10-15 mm<sup>3</sup> in dimension. 3D and 2D EPR imaging experiments on tumor bearing mice were performed by acquiring spectral projections under static magnetic field gradients after nitroxide administration. Results from 3D EPR imaging experiments after intravenous injection of nitroxide suggest that the level of nitroxide was much higher in tumor bearing leg than in normal leg, presumably because of the larger tissue volume sampled in tumor bearing leg. Nitroxide clearance rates in tumor leg from 2D images exhibited heterogeneous behavior than in normal leg. If the imaging of these clearance rates can be reconstructed from the time dependent change of EPR imaging, the image should reflect the redox status. The decay constants for each pixel were estimated from the slopes of semilogarithmic plots of image intensity versus time after injection, and then reconstructed into 2D images of clearance rate constants. These studies suggest that EPR imaging can provide information related to redox status differences between normal tissue and tumors, non-invasively.

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- 116.** *THE STUDY OF INTERACTION OF TAMOXIFEN AND GENISTEIN WITH BREAST CANCER CELLS.* Jingfen Lu, Bolati, Gulinuer, and Bo Xu, National Key Laboratories of Natural and Biomimetic Drugs, Peking University, Beijing 100083; Jun Jie Yin, Instrumentation and Biophysics Branch, FDA, Washington DC, 20204, USA.

It has been shown that tamoxifen and genistein can kill breast cancer cells through the experiment of cell screening. In order to understand the molecular mechanism of anticancer, we studied comparatively the interactions of tamoxifen and genistein with breast cancer cells, using spin labeling- ESR method. Spin label 5DS and 16DS were used for checking the fluidity of membrane bilayer of breast cancer cells and Maleimide was used for checking the conformation and rotational correlation time  $\tau_c$  of membrane proteins. The results revealed that both tamoxifen and genistein induce to decrease the fluidity of membrane lipid of breast cancer cells and the change induced by genistein is more obvious than tamoxifen's under the same concentrations. Meanwhile, the  $\tau_c$  was decreased after adding tamoxifen and genistein to breast cancer cells. It means there is a similar molecular mechanism for the interactions of tamoxifen and genistein with cancer cells. The one of targets in the prevention and treatment breast cancer might be in the cell membrane. The anti-oxidation experiments indicated that the scavenging ability of genistein on super-oxygen ions and hydrogen is more stronger than tamoxifen's, using spin trapping-ESR method. The genistein extracted from natural soybeans shows a good application for prevention and treatment of some cancers.

**EPR Symposia Poster Session— Jun Jie Yin, Instrumentation and Biophysics Branch, FDA, Washington DC, 20204, USA**

- 117.** *WIDE RANGE MEASUREMENTS OF LOW MAGNETIC FIELDS BY A LONGITUDINALLY DETECTED ESR METHOD.* Hidekatsu Yokoyama, Hiroaki Ohya, and Hitoshi Kamada, Institute for Life Support Technology, 2-2-1 Matsuei, Yamagata 990-2473, Japan; Toshiyuki Sato, Yamagata Research Institute of Technology, 2-2-1 Matsuei, Yamagata 990-2473, Japan.

For absolute magnetic field measurements in low fields, a new magnetometer utilizing a longitudinally detected ESR (LODESR) method was developed. A probe head of the LODESR magnetometer consists of paramagnetic species, an irradiation coil, and a pickup coil. The irradiation coil is a single-turn coil (8 mm in diameter) which has a very wide bandwidth because the reactance of the coil is always smaller than the resistance of the transmission line (50 ohms) at frequency less than 700 MHz. Thus an absolute magnetic field could be measured over a wide range (2 to 9 mT) by using this magnetometer without changing the probe head.

**EPR Symposia Poster Session—Hidekatsu Yokoyama, Institute for Life Support Technology, 2-2-1 Matsuei, Yamagata 990-2473, Japan. Tel: +81-236-47-3132, Fax: +81-236-47-3149, E-mail: yokohide@fmu.ac.jp**

## EPR Thursday Oral Sessions

- 118.** A NEW HIGH-FIELD MULTI-FREQUENCY TRANSIENT EPR SPECTROMETER. J. van Tol, L.C. Brunel, Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, Florida State University, 1800 E Paul Dirac Dr., Tallahassee, FL 32310  
*High-frequency/high-field electron paramagnetic resonance continues to expand rapidly due to the gain in resolution and sensitivity, and the possibility to study high-spin systems with relatively large zero-field splittings. We have constructed a new transient superheterodyne EPR spectrometer operating at 120, 240, and 360 GHz in order to exploit also the possible gain in time-resolution that is inherent to the use of higher frequencies, and one of our objectives is to study systems with life-times shorter than 1 ns. The spectrometer uses Schottky mixers/detectors and has an operating bandwidth of 2 GHz. In order to limit losses and to have maximum sensitivity at these high frequencies, the spectrometer design is almost completely quasi-optical. Details of the experimental setup and the first results will be presented. This research is supported in part by the NSF grant CHE-9601731.*

**EPR Symposia Oral Session—Hans van Tol, National High Magnetic Field Laboratory, Florida State University, 1800 E Paul Dirac Dr, Tallahassee, FL 32310, Tel: 850 644 1187, Fax: 850 644 1366, E-mail: vantol@magnet.fsu.edu**

- 119.**  $Mn^{2+}$  EPR LINEWIDTH IN  $MnSO_4 \cdot H_2O$  : 10/3-EFFECT NARROWING AND g-ANISOTROPY BROADENING IN GOING FROM 9.5 TO 249.9 GHz. Sushil K. Misra, Physics Department, Concordia University, 1455 de Maisonneuve Blvd. West, Montréal (Québec), Canada H3G 1M8; Yves Servant, CPMOH, Université Bordeaux-I, 351 cours de la Libération, F-33405 Talence Cedex, France; Cyclicia Triratna Kereh, Physics Department, Concordia University, 1455 de Maisonneuve Blvd. West, Montréal (Québec), Canada H3G 1M8; Keith A. Earle and Jack H. Freed, Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853, U.S.A.  
*We have measured the peak-to-peak linewidth of the first derivative of the EPR absorption for  $Mn^{2+}$  in an  $MnSO_4 \cdot H_2O$  powder sample at X-band (~ 9.5 GHz) and at 249.9 GHz. The linewidths are found to be  $192 \pm 5$  G and  $1820 \pm 50$  G at 9.5 and 249.9 GHz, respectively. The spectra at 249.9 GHz (1 mm) were taken at Cornell University, while those at 9.5 GHz at Concordia University. The 250-GHz instrument uses a transmission Fabry-Perot cavity. Two main independent mechanisms influence the EPR linewidth. One of them increases linewidth due to g-anisotropy and/or g-strain, being directly proportional to the strength of the external Zeeman field; while the other narrows the dipolar linewidth due to the exchange interaction by a factor of 10/3 as one goes to higher frequencies, say from 9.5 GHz to 249.9 GHz. Finally, taking into account the resonance condition:  $f/GHz = 2.8$  B/kG, the relative spread of the g values is calculated to be:  $\Delta g/g = 0.0204$ . Thus, the absolute spread of the g value is  $\Delta g = 0.0408$ . The influence of the unresolved fine and hyperfine structures has been neglected in this estimation. Detailed computer simulations will be presented for a more detailed discussion and interpretation of the experimental data to shed more light on the EPR linewidth at high frequencies.*

**EPR Symposia Oral Session—Sushil K. Misra, Physics Department, Concordia University, 1455 de Maisonneuve Blvd. West, Montréal (Québec), Canada H3G 1M8. Tel: 514-848-3278, Fax: 514-848-2828, E-mail: skmisra@vax2.concordia.ca**

- 120.**  $T_{1e}$  MEASUREMENTS USING RF-LONGITUDINALLY DETECTED ESR (LODESR) AND APPLICATIONS IN OXIMETRY. Ioannis Panagiotelis, Ian Nicholson, James M. S. Hutchison, Department of Bio-Medical Physics and Bio-Engineering, University of Aberdeen, Foresterhill, Aberdeen, AB25 2ZD, UK.

*In this work we have confirmed the relationship between  $T_{1e}$  and LODESR signal amplitude at radio-frequencies<sup>1</sup> and predicted theoretically, with experimental verification, the LODESR signal phase dependence on modulation frequency. These methods are valid for inhomogeneous lines provided  $T_{1e} \gg T_{2e}$ . We have also developed a new approach for measuring  $T_{1e}$ , valid for inhomogeneous spectra, when  $T_{1e} \approx T_{2e}$ . The method is based on measuring the spectral area as a function of modulation frequency.  $T_{1e}$  dependence on oxygen and free radical concentration was measured for Triarylmethyl (Nycomed Innovations, Sweden) and TEMPOL.  $T_{1e}$  remains independent of free radical concentration<sup>3</sup>, a major advantage for oxygen mapping. Measurements were also performed on TAM in human blood for  $T_{1e}$  as a function of temperature and free radical concentration. We also investigated char suspensions, where  $T_{1e} \gg T_{2e}$ . In this slow motion situation,  $T_{1e}$  oximetry possesses an advantage because the percent change in  $T_{1e}$  due to interaction with oxygen is much greater than that for  $T_{2e}$ . This work, together with the ability of LODESR to provide images of exogenous free radicals in-vivo, presents an attractive alternative to the conventional ESR linewidth based methods.<sup>2</sup>*

1. A. Colligiani et al., Appl. Magn. Reson. 3, 107-129 (1992).

2. I. Nicholson et al., J. Magn. Reson., series B 113, 256, (1996).

3. J.J. Yin et al., Proc. Nat. Acad. Scien. USA. Vol. 84, 964, (1987).

**EPR Symposia Oral Session—Ioannis Panagiotelis, Department of Bio-Medical Physics and Bio-Engineering, University of Aberdeen, Foresterhill, Aberdeen, AB25 2ZD, UK. Tel: +44 7967 013815, Fax: +44 1224 685645, E-mail: i.panagiotelis@biomed.abdn.ac.uk**

- 121.** NOVEL EPR RELAXATION MECHANISMS IN MAGNETIC RESONANCE FORCE MICROSCOPY. J.A. Sidles, Department of Orthopaedics; W. M. Dougherty, S. H. Chao, J. L. Garbini, S. E. Jensen, M. R. Morrell, Department of Mechanical Engineering; University of Washington, Seattle, WA 98195-6500

*As reviewed by Orbach,<sup>1</sup> the study of relaxation mechanisms in EPR has historically followed a repetitive cycle in which theorists predict relaxation rates, experimentalists measure faster-than-predicted relaxation rates, which leads theorists to recognize new relaxation mechanisms. Magnetic resonance force microscopy (MRFM) affords new opportunities for continuing this historical cycle, mainly by virtue of the uniquely strong gradients in which resonance is observed. This talk reviews the theoretical predictions and experimental status of the following classes of EPR relaxation mechanisms: (1) thermal magnetic noise from conduction-band electrons, (2) ferromagnetic noise from thermally excited magnons and coherent ferrodynamical precession, and, (3) spectral-spatial diffusion and cross-relaxation of nuclear and electron spin polarization in the high-gradient MRFM environment. The engineering relevance of these mechanisms to the goals of single-spin imaging and solid-state quantum computing will be discussed. The National Institutes of Health, the National Science Foundation, and the U.S. Army Research Office support this work.*

1. R. Orbach and H. J. Stapleton in "Electron Paramagnetic Resonance" (S. Geschwind, Ed.), pp. 121–216, Plenum Press, New York (1972).

**EPR Symposia Oral Session—John A. Sidles, University of Washington, Department of Orthopaedics, Seattle, WA 98195-6500, (206) 543-3690, Fax: (206) 685-3139, E-mail: sidles@u.washington.edu.**

- 122.** CHARACTERISTICS OF A HOMODYNE W-BAND PULSED/CW SPECTROMETER. Peter E. Doan, Clark E. Davoust, and Brian M. Hoffman, Department of Chemistry and BMBCB, Northwestern University, Evanston, IL 60208

*We have constructed a W-band EPR/ENDOR spectrometer with the titled configuration, which has not been used previously at this frequency; its use here has been prompted by the recent availability of low-noise amplifiers for detection purposes. We will describe the bridge and discuss its performance, relating this in particular to the progression in frequency from 9 to 35 to 95 GHz.*

**EPR Symposia Oral Session—Brian M. Hoffman, Department of Chemistry & BMBCB, Northwestern University, 2145 Sheridan Road, Evanston, IL, 60208. Tel: 847-491-3104, Fax: 847-491-7713, E-mail: bmh@northwestern.edu**

- 123.** ON THE MECHANISMS GOVERNING THE INTERACTION OF TRIPLETS AND DOUBLETS IN LIQUID SOLUTIONS. Aharon Blank and Haim Levanon, Department of Physical Chemistry and the Farkas Center for Light-Induced Processes, The Hebrew University of Jerusalem, 91904 Israel.

*When photoexcited triplets and stable radicals interact in solution, the radical's EPR spectrum changes from its normal Boltzmann spin distribution to a spectrum, which is in enhanced absorption or emission. The magnetization generated by triplet-doublet interaction in high viscosity solvents at room temperature was measured by FT-EPR spectroscopy. The stable radical was found to generate high spin-polarized magnetization (more than ten times larger than the Boltzmann magnetization). Moreover, the polarization, which is in emission, lasts for long a period of time after laser excitation (> 100ms). The experimental results were treated by a theoretical model, based on numerical and analytical solutions of the stochastic Liouville equation, which combines the following two mechanism: 1) Electron spin polarization transfer (ESPT), where the triplet, which interacts with the radical, is spin polarized (previously this mechanism was treated only semi-empirically); and 2) Radical triplet pair mechanism (RTPM), where the triplet levels are in thermal equilibrium. We can predict the radical's polarization following an encounter with a triplet of arbitrary polarization (thermal or non-thermal) and determine the temporal behavior of the radical's magnetization, not only in its initial stage (in-cage encounters). The theory also explains the long lasting polarization, which we attribute to the inefficient quenching of the photoexcited triplets by the radicals.*

*This work was partially supported by the Israel Ministry of Science, by a US-Israel BSF grant and by the Volkswagen Foundation (I/73 145). The Farkas Research Center is supported by the Bundesministerium für die Forschung und Technologie and the Minerva Gesellschaft für Forschung GmbH, FRG.*

**EPR Symposia Oral Session—Aharon Blank, Department of Physical Chemistry and the Farkas Center for Light-Induced Processes, The Hebrew University of Jerusalem, 91904 Israel. Tel: +972-53-357914, Fax: +972-2-5618033 E-mail: blanka@chem.ch.huji.ac.il**

- 124.** CW- AND PULSED EPR OF TRANSITION METAL IONS IN SOME SILICATE AND FLUORIDE GLASSES. Simon C. Drew; John R. Pilbrow, Department of Physics, PO Box 27, Monash University, Victoria, Australia 3800.

*EPR of transition metal ion probes in glasses remains an important source of information to understand aspects of the microstructure of ordinary glasses. Most commercial glasses contain small concentrations of one or more transition metal ions as natural spin probes and sometimes alkali ions as charge compensators and stabilisers. The aim of the present investigation is to determine whether the combination of CW-EPR, Echo-Detected EPR [ED-EPR], spectral simulations and measurements of spin-lattice relaxation times at very low temperatures can lead to firm conclusions concerning the microstructure of different glasses – whether they are either intrinsically random network structures or consist of microcrystallites. Computer simulations of CW- and some of the ED-EPR spectra are based on a strategy that covers a stochastic model in which each site has a unique spin Hamiltonian at one limit to a 'powder' model to test for microcrystallite structures at the other extreme. Data will be presented for a number of commercial silicate glasses containing Fe<sup>3+</sup>, Ti<sup>3+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup> ions and for fluorozirconate and fluoroaluminate glasses containing some of the following ions, Cu<sup>2+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Gd<sup>3+</sup>, Eu<sup>2+</sup> and Ce<sup>3+</sup>. Preliminary ESEEM results particularly for the fluoride glasses will also be presented. Experiments reported are necessarily limited to temperature ranges in which echoes may be observed, typ-*

ically below 10K. Thanks are due to Mr Peter Lowe, Pilkington Glass, Melbourne for providing the commercial glass samples and to Dr Peter Newman and Professor Doug Macfarlane, Department of Chemistry, Monash University, for providing the doped fluoride glasses.

**EPR Symposia Oral Session—Prof John R Pilbrow, Dept of Physics, PO Box 27, Monash University, Clayton, Victoria, Australia 3800, Tel: +61-3-9905-3630, Fax: +61-3-9905-3637, E-mail: john.pilbrow@sci.monash.edu.au**

- 125.** BIOPHYSICAL AND BIOCHEMICAL APPLICATIONS OF DIELECTRIC RESONATOR-BASED SENSITIVE PROBEHEADS: FROM ULTRA-RAPID MIXING STOPPED-FLOW EPR TO OPEN RESONANT STRUCTURES FOR ORIENTED MUSCLE FIBERS AND HIGH-HYDROSTATIC PRESSURE EPR. Andrzej Sienkiewicz, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland; P. G. Fajer, National High Magnetic Field Laboratory, 1800 E. Paul Dirac Drive, Tallahassee, FL 32306; László Forró, Institut de Génie Atomique, Département de Physique, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland; Charles P. Scholes, Chemistry Department, SUNY at Albany, Albany, NY 12222, USA.

We present novel biophysical and biochemical applications of microwave EPR probeheads that are designed around a double-stacked Dielectric Resonator (DR). We employ commercially available cylindrical DRs to achieve specialized EPR systems. Simple single and double-stacked DRs resonating in their lowest cylindrical  $TE_{018}$  mode offer better isolation of the microwave electric component from the sample space than regular metallized cavities. This isolation leads to considerably higher S/N for lossy aqueous samples. Miniature DR-based resonant structures are easily combined with rapid mixing devices, making it possible to perform sensitive Stopped-Flow (SF) EPR experiments on microliter sample volumes. We report applications using a Wiskind grid mixer and the DR-based SF system to measure folding/unfolding kinetics of spin-labeled protein; the time resolution of such SF measurements is several milliseconds. (An EPR flow system using a mini ball mixer intimately integrated to a DR and having 150 microseconds dead time has recently been developed by V. Grigoryants in the Scholes lab.) Additional, synchronized triggering of rapid field scans provides spectroscopic information that is complementary to kinetic data obtained at single fields. Kinetics of free radical build up or decay can also be followed using these both techniques. The open structure of the double-stacked DR with a finite separation between the cylindrical resonators enables one to design side-access resonators that are particularly amenable for sensitive EPR study of small bundles of oriented muscle fibers. Moreover, the modular design of the double-stacked DR can easily accommodate a complete Diamond- or Sapphire-Anvil Pressure Cell (DAC or SAC). This offers a relatively user-friendly combination of the high-hydrostatic pressure with EPR. We will present technical details of these unique DR-based EPR probeheads. We will also discuss the potential of their applications for EPR study of phase transitions in solids, as well as for such challenging applications as pressure-induced denaturation of proteins.

**EPR Symposia Oral Session—Andrzej Sienkiewicz, Institute of Physics, ON-4.3, Al. Lotników 32/46, 02-668 Warsaw, Poland. Tel: (48-22) 843 70 01 ext. 2963, Fax: (48-22) 843 09 26, E-mail: sienk@delta.ifpan.edu.pl**

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## General Poster Sessions

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- 126.** A FAST RP-HPLC/UV METHOD FOR PURITY DETERMINATION OF DIVERSE COMBINATORIAL LIBRARIES. Kevin P. Ash, Kathy A. Halm, Madalene D. Fetsch, Adam W. Cook, Conrad W. Hummel, Alan S. Florjancic, Gary P. Hingorani, John A. Josey, Array BioPharma, Inc., 1885 33rd St., Boulder, CO 80301.

The challenge to develop faster, more efficient analytical methods is omnipresent when analyzing the vast number of molecules created by combinatorial chemistry. Our goal to develop a high throughput RP-HPLC/UV method for purity analysis of combinatorial libraries has been met with a few basic changes to our historical methodology. Column chemistry has been maintained (Waters YMC-Pack™ ODS-AQ™, 4.6x50mm), but particle size has decreased from 5mm to 3mm. Utilization of faster TFA/acetonitrile gradients, incorporation of 1% isopropyl alcohol in the mobile phase to decrease column equilibration time, and optimization of HPLC hardware have all contributed to decrease our sample analysis time without sacrificing resolution or peak shape. Using the new methodology, we have been able to decrease our analysis time 50% from 10 min. to 5 min. per sample, doubling our throughput and allowing us to keep pace with the productivity of our combinatorial chemists.

**General Poster Session—Kevin P. Ash, Array BioPharma, Inc., 1885 33rd St., Boulder, CO 80301. Tel: 303-381-6664, Fax: 303-381-6652, E-mail: kash@arraybiopharma.com**

- 127.** NONEXPONENTIAL "BLINKING" KINETICS OF SINGLE CDSE QUANTUM DOTS AND SINGLE BIOMOLECULE KINETICS. E.B. Jochnowitz, M. Kuno, D.P. Fromm, H.F. Hamann, A. Gallagher, and D.J. Nesbitt, JILA, National Institutes of Standards and Technology and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440;

Single molecule confocal microscopy is used to study the fluorescent blinking behavior of individual ZnS overcoated CdSe quantum dots excited at 488 nm. A distribution of "on" and "off" times are measured, and are found to conform to power law behavior in the distribution of off times that extends for over 9 orders of magnitude in dynamic range. Similar laser-induced fluorescence techniques are also applied to a variety of individual biological macromolecules. By using such techniques the activity of single biological molecules are studied unmasked by ensemble averaging.

**General Poster Session—Evan Jochnowitz, JILA, Department of Chemistry & Biochemistry, University of Colorado, Boulder, Colorado 80309-0440. Tel: 303-735-2159, E-mail: jochnowi@ucsub.colorado.edu**

- 128.** CONCURRENT DETERMINATION OF FOUR FLUOROQUINOLONES; CIPROFLOXACIN, ENROFLOXACIN, SARAFLOXACIN AND DIFLOXACIN IN CATFISH, SHRIMP AND SALMON BY LC WITH FLUORESCENCE DETECTION. José E. Roybal, Calvin C. Walker, Allen P. Pfenning, Sherri B. Turnipseed, Steve A. Gonzales, U.S. Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, P.O. Box 25087, Denver, CO 80225 and Jeffrey A. Hurlbut, Department of Chemistry, Metropolitan State College of Denver, P.O. Box 173362, Denver, CO 80217

A liquid chromatographic (LC) method with Fluorescence detection is presented for the concurrent analysis of four fluoroquinolones, Enrofloxacin (ENRO), Ciprofloxacin (CIPRO), Sarafloxacin (SARA) and Difloxacin (DIFLX) in catfish, shrimp and salmon. The procedure consists of extraction of fish tissue 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 (16+84) mobile phase and a PLRP-S polymer column with fluorescence detection, EX-278nm and EM-450nm. A target level (x) of 20ppb for each of the four fluoroquinolones has been established for this method. Fortified and incurred fish sample results are based on a five point standard curve calculation (10-160ppb). Overall percent recoveries (%RSD) from fortified catfish were 78 (10), 80 (11), 70 (9.4), 78 (10); from fortified shrimp were 69 (5.9), 85 (4.9), 79 (5.9) and 90 (4.5) and from fortified salmon were 56 (15), 93 (5.6), 61 (11) and 87 (5.0) for CIPRO, ENRO, SARA and DIFLX, respectively. Data from the analysis of fluoroquinolone incurred catfish, shrimp and salmon are presented.

**General Poster Session—José E. Roybal, U.S. Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, P.O. Box 25087, Denver, CO 80225. Tel: (303)236-3073, Fax: (303)236-3100, E-mail: jroybal@ora.fda.gov**

- 129.** LC/MS CONFIRMATION OF IONOPHORES IN ANIMAL FEEDS. Sherri B. Turnipseed, José E. Roybal, Allen P. Pfenning, Steve A. Gonzales, Animal Drugs Research Center, ORA/FDA, Denver, CO 80225

An LC/MS electrospray confirmation method has been developed to confirm four ionophores (monensin, lasalocid, salinomycin, and narasin) in a variety of animal feed using a single quadrupole mass spectrometer. The sodium ions of these compounds are dominant in the electrospray mass spectrum. Using optimized "in-source" collision induced dissociation, characteristic fragment ions seen previously using MS/MS can be observed. The drugs were extracted from the feed matrix using hexane/ethyl acetate and isolated using a silica solid phase extraction cartridge. These four ionophores were confirmed in both medicated feeds and non-medicated feeds fortified with these drugs at the 1-50 ppm level. In addition, this method was used to confirm residues of monensin in a non-medicated feed which was collected from a feed mill immediately after the production of a similar feed that was medicated with high levels of monensin.

**General Poster Session—Dr. Sherri B. Turnipseed, FDA, Denver Federal Center P.O. Box 25087, Tel: 303-236-3072, Fax: 303-236-3100, E-mail: sturnips@ora.fda.gov**

- 130.** TOC ANALYSIS OF LOW LEVEL SAMPLES: A CATALYTIC COMBUSTION APPROACH. Brian Wallace, Don Harrington, and Ken O'Neal, Tekmar-Dohrmann, 7143 E. Kemper Rd., Cincinnati, OH 45249

For low level TOC analysis, few techniques are suitable for all of the challenging demands of its diverse applications. Historically, most research has been done using the UV/Persulfate technique for TOC analysis. However recently, new low-level TOC applications have hinted that different techniques may be more appropriate for certain types of samples.

Improvements made in new catalytic combustion TOC analyzers have lowered their detection limits to low ppb levels, becoming comparable to UV/Persulfate systems. Also, there is a strong argument made for the use of the catalytic combustion TOC analysis in cleaning validation applications because of better recoveries on proteins and peptides in comparison to other techniques.

Data will be presented to demonstrate the improved sensitivity of the catalytic combustion technique and recoveries of challenging compounds in comparison to other techniques.

**General Poster Session—Brian Wallace, Tekmar-Dohrmann, 7143 E. Kemper Rd., Cincinnati, OH 45249. Tel: 513-247-7068, Fax: 513-247-7045, E-mail: briwal@tekmar.com**

- 131.** TOC ANALYSIS: ANALYTICAL AND MAINTENANCE CONSIDERATIONS FOR SEAWATER AND OTHER SALT WATER APPLICATIONS. Brian Wallace, Don Harrington, and Ken O'Neal, Tekmar-Dohrmann, 7143 E. Kemper Rd., Cincinnati, OH 45249

The concentration of organic and inorganic carbon in samples containing sodium chloride is of considerable interest. Dissolved Organic Carbon (DOC) concentrations in the world's oceans must be known to elucidate the effect of organics on the global carbon cycle. Coastal cities find the intrusion of seawater into their fresh water supplies and many industries must analyze process and outfall water that contains salt. A combustion-type Total Organic Carbon Analyzer provides the best way to measure TOC in salty waters. Other methods of oxidizing carbon experience interference by the chloride ion. However, the catalysts that aid in the combustion of carbon can also experience interference from the deposition of salts onto their surfaces. This paper focuses on the analytical dependability of the combustion oxidation technique for this difficult application as well as the maintenance issues.

**General Poster Session—Brian Wallace, Tekmar-Dohrmann, 7143 E. Kemper Rd., Cincinnati, OH 45249. Tel: 513-247-7068, Fax: 513-247-7045, E-mail: briwal@tekmar.com**



- 132.** TOC ANALYSIS OF PARTICULATED SAMPLES: MEETING ISO 8245. Brian Wallace, Don Harrington, and Ken O'Neal, Tekmar-Dohrmann, 7143 E. Kemper Rd., Cincinnati, OH 45249

Total Organic Carbon (TOC) analysis has become a very significant component of water quality determination. TOC analysis has broadened from drinking water and purified water to other environmental applications such as surface and wastewater analysis. However with all of the expansion of applications, there are also some challenges associated with the analysis. One specifically troublesome matrix is liquid suspensions containing incompletely dissolved particulate matter. These suspensions are commonly encountered in TOC applications such as wastewater effluents and surface water.

Recently, an international standard draft, ISO/FDIS 8245, has developed a suitability test for TOC analysis of samples containing particles. This test calls for the TOC analysis of a 100mg C/l test solution of 100 µm particle size cellulose. For an instrument to be considered suitable, the mean of a triplicate analysis must be between 90 and 110 mg C/l. The repeatability variation coefficient should be less than 10%.

Because of the inherent nature of these samples, it is essential for an analyzer to provide optimal homogenization through agitating of the samples. Also, meet the demands of the ISO 8245, an analyzer must have the ability to include particulates in the TOC analysis. Results will be presented using normal operating conditions and under optimal conditions for cellulose samples ranging from 20 to 500 µm particle size at concentration of 100 to 1000 mgC/l.

**General Poster Session—Brian Wallace, Tekmar-Dohrmann, 7143 E. Kemper Rd., Cincinnati, OH 45249.**  
**Tel: 513-247-7068, Fax: 513-247-7045, E-mail: briwal@tekmar.com**

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## ICP-MS and Radionuclide Detection by ICP-MS

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- 133.** INVESTIGATIONS INTO THE MASS SPECTRAL ANALYSIS OF NON-METALS USING INDUCTIVELY COUPLED PLASMA AS ION SOURCE BY HIGH RESOLUTION ICP-MS. Rob Henry, TJA Solutions, 1812 Mapleton Avenue, Boulder, CO 80304, USA; Dagmar Koller and Phil Miller, TJA Solutions, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, England.

The analysis of the non-metals across a wide range of concentrations is required in many application areas: from the relatively high levels measured in environmental samples to the very low levels needed by the semiconductor industry. Analysis of non-metals by inductively coupled plasma mass spectrometry is hampered in many cases by their high ionization potential and by the presence of polyatomic interferences. Together, these factors increase the detection limits for the non-metallic elements above those required by many analysts. Alteration of any of the 3 main plasma parameters: plasma power, plasma gas and sample matrix can change plasma conditions, which have been shown to be very useful for improving the ionization efficiency and thus analytical conditions for analytes of high ionization potential. High resolution ICP-MS can be used to remove interferences at up to 15,000 Resolving Power, which gives access to clear mass spectral interpretation. This paper will describe the use of high resolution ICP-MS with varying plasma and sample introduction parameters to significantly improve the analytical performance for the non-metallic elements.

**ICP-MS Oral Session—Rob Henry, TJA Solutions, 1812 Mapleton Avenue, Boulder, CO 80304. Tel: 303-939-9012, Fax: 303-939-9017, E-mail: rhenry@tjasolutions.com**

- 134.** EVALUATION OF AN HR-ICP-MS SYSTEM FOR ANALYSIS OF AMMONIA HYDROLYSIS SAMPLES. G.W. Johnson, J. O. Proctor and V. H. Houlding, Matheson Tri•Gas, 1861 Lefthand Circle, Longmont, CO 80501.

A High Resolution Inductively Coupled Plasma - Mass Spectrometer (HR-ICP-MS) system has been evaluated for analysis of ammonia hydrolysis samples. The instrument is an Axiom HR-ICP-MS manufactured by VG Elemental. The evaluation criteria included elemental coverage, freedom from spectral interference effects, method detection limits, speed, precision, and accuracy of analysis. Elemental coverage was found to be excellent, with seventy-two isotopes providing quantitative results on sixty-eight elements. Freedom from interference effects was also excellent, with results for fourteen elements made at resolution settings ranging from 2420 to 10440; effectively eliminating potential spectral overlap problems due to spectra from background and/or concomitant species. Method Detection Limits (MDL's) were evaluated using two statistical procedures. A weighted least squares approach was used initially and is being adopted as a once-per-year procedure (Semiconductor Equipment and Materials International (SEMI) Method C10-0698). In addition, each day of use MDL's were calculated as confidence intervals at the 99.74% level, using standard deviations of repetitive measurements on the zero concentration calibration standard run four times throughout the analysis sequence. MDL's using both methods were comparable, with MDL's at lower than one part per trillion in solution (<1 ng/L) obtained for ten to twenty elements. At present, the speed of analysis is approximately forty-five minutes per sample. It includes the time necessary to examine all test solutions (i.e., calibration standards, controls, and sample solutions) necessary to complete a run sequence. Approximately fifteen minutes is required to run one test solution. Generally, precision and accuracy are within the ±25% guideline promulgated by SEMI. It was concluded that the analytical capabilities of the Axiom HR-ICP-MS instrumentation manufactured by VG Elemental were found to meet or exceed elemental analysis demands of even the highest purity ammonia categorized by SEMI (<1 mg analyte per liter concentrated NH<sub>3</sub>(aq) solution, i.e. <1ppb).

**ICP-MS Oral Session—Greg W. Johnson, Matheson Tri•Gas, 1861 Lefthand Circle, Longmont, CO 80501,**  
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- 135.** OVERVIEW OF ATOM COUNTING TECHNIQUES FOR ROUTINE RADIONUCLIDE MEASUREMENTS. Rob Henry, TJA Solutions, 1812 Mapleton Avenue, Boulder CO 80304, USA
- During the 1999 National Institute of Science & Technology (NIST) Workshop on Standards, Intercomparisons and Performance Evaluations for Low-level and Environmental Radionuclide Mass Spectrometry and Atom Counting, the range of available atom counting techniques was considered and a summary of each technique's capabilities was produced by the workgroup. The attributes of each technique relative to the requirements of the analysis of radionuclides was tabulated and the current state of the art of atom counting as a viable alternative to traditional counting methods will be discussed. Methods evaluated include ICP-MS, TIMS, FT-ICR-MS, ICP-Ion Trap-MS, AMS, RIMS, FTA & TOF-SIMS. The results of the workshop indicated that ICP-MS in its current forms provided a cost effective solution for many common radionuclide measurements.*
- Radionuclide Detection by ICP-MS Oral Session—Rob Henry, TJA Solutions, 1812 Mapleton Avenue, Boulder, CO 80304, Tel: 303-939-9012. Fax: 303-939-9017, E-mail: rhenry@tjasolutions.com**
- 136.** ULTRATRACE AND ISOTOPIC ANALYSIS OF LONG-LIVED RADIONUCLIDES USING A DIRECT INJECTION HIGH EFFICIENCY NEBULIZER WITH DOUBLE FOCUSING SECTOR FIELD INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Akbar Montaser, John A. McLean, J. Sabine Becker, and Hans-Joachim Dietze. Department of Chemistry, 725, 21st Street, NW., The George Washington University, Washington, DC 20052
- The ultratrace and isotopic analysis of long-lived radionuclides is required in many areas ranging from radiobioassay and nuclear waste management to nonproliferation and monitoring for clandestine activities. Double-focusing, sector field, inductively coupled plasma mass spectrometry (DF-ICP-MS) is useful for such analysis owing to low instrumental background and high sensitivity in low resolution ( $m/\Delta m = 300$ ) operation. To reduce exposure to the operator and minimize investigative derived waste, a reduction in the sample size is desirable. In this report, the analytical performance of DF-ICP-MS in the analysis of long-lived radionuclides ( $^{226}\text{Ra}$ ,  $^{230}\text{Th}$ ,  $^{232}\text{Th}$ ,  $^{233}\text{U}$ ,  $^{237}\text{Np}$ ,  $^{238}\text{U}$ , and  $^{241}\text{Am}$ ) using two types of direct injection high efficiency nebulizers (DIHENS) was evaluated. The DIHEN is a low sample consumption (<100 mL/min) micronebulizer designed to inject 100% of the sample into the plasma for analysis, thus investigative derived waste is minimized. The first device is a standard borosilicate construction (DIHEN) and the second from quartz (Q-DIHEN). Relative sensitivity obtained for the analysis of long-lived radionuclides ranged from 1570 MHz/ppm ( $^{226}\text{Ra}$ ) to 2560 MHz/ppm ( $^{241}\text{Am}$ ) and 1180 MHz/ppm ( $^{226}\text{Ra}$ ) to 1420 MHz/ppm ( $^{241}\text{Am}$ ) for the DIHEN and Q-DIHEN at solution flow rates of 40 and 60 mL/min, respectively. This is similar to, or improved, over conventional sample introduction systems operated at mL/min solution flow rates. In terms of absolute sensitivity this represents at least a factor of 2 to 12 improvement over other micronebulizer and conventional sample introduction devices. The accuracy of DIHEN-DF-ICPMS was evaluated in the analysis of standard reference materials having certified  $^{235}\text{U}/^{238}\text{U}$  ratios of 0.00725, 0.02081, and 0.9995. The method was further applied in the isotopic ratio analysis of radioactive waste samples where good agreement was found for  $^{234}\text{U}/^{238}\text{U}$ ,  $^{235}\text{U}/^{238}\text{U}$ , and  $^{236}\text{U}/^{238}\text{U}$  ratios (down to 10<sup>-5</sup>) with values obtained by alternative methods.*
- Radionuclide Detection by ICP-MS Oral Session—Department of Chemistry, 725, 21st Street, NW, The George Washington University, Washington, DC 20052. Tel: 202-994-6480, Fax: 202-994-2298, E-mail: montaser@gwu.edu**
- 137.** LABORATORY-CONSTRUCTED CONVENTIONAL AND DIRECT INJECTION NEBULIZERS FOR RADIONUCLIDE DETERMINATIONS BY ICP-MS. Michael E. Ketterer and David D. Hudson, Department of Chemistry, Northern Arizona University, Box 5698, Flagstaff, AZ 86011-5698
- Low-cost concentric pneumatic nebulizers are described. These devices can be built, disassembled and reassembled in any laboratory without any specialized skills such as machining, injection molding, or glassworking. Commercially available fused silica tubing is used as an inner (liquid) capillary, and glass pipets are used as outer capillaries.*
- The cost of these nebulizers is US \$5-30 depending upon which specific components are used. The performance characteristics of the conventional nebulizer compare favorably to a commercially available concentric glass nebulizer (Glass Expansion). A design is presented for a lab-constructed, low-cost, working concentric direct injection nebulizer. The disassemble-able direct injection nebulizer operates effectively at 5-50 mL/min sample uptake rate and at ordinary gas pressures (30-60 psig). The applications of these nebulizers to the determination of  $^{232}\text{Th}/^{230}\text{Th}$  and  $^{234}\text{U}/^{238}\text{U}$  in environmental samples are presented.*
- Radionuclide Detection by ICP-MS Oral Session—Michael E. Ketterer, Department of Chemistry, Northern Arizona University, Box 5698, Flagstaff, AZ 86011-5698. Tel: (520) 523-7055, Fax: (520) 523-8111, E-mail: michael.ketterer@nau.edu**
- 138.** DETERMINATION OF THORIUM AND URANIUM BY ISOTOPE DILUTION ICP-MS USING LABORATORY-PREPARED SPIKE SOLUTIONS. Michael E. Ketterer, Scott C. Szechenyi, and Brandon J. Cruickshank, Department of Chemistry, Northern Arizona University, Box 5698, Flagstaff, AZ 86011-5698
- Thorium and uranium are commonly determined in many types of samples by ICP-MS. Isotope dilution is well-known as a high accuracy procedure for use in conjunction in mass spectrometry. We have developed isotope dilution procedures for determining Th and U in a variety of sample types using isotope dilution ICPMS; spikes are produced in-house. A  $^{230}\text{Th}$  spike (~ 3%  $^{230}\text{Th}$ , 97%  $^{232}\text{Th}$ ) is prepared by extraction from a uranium ore; a commercially available solid-phase extraction resin (TRU-Spec, Eichrom) is used to separate Th from the ore digest. The spike is calibrated by reverse isotope dilution vs. a commercially available Th quantitative standard. This  $^{230}\text{Th}$  spike is effective since Th*

in most geological samples consists of  $\sim 100\%$   $^{232}\text{Th}$ . The Th isotope dilution method is applied to a variety of rock standards. Uranium is determined by isotope dilution using a "depleted" uranium stock solution purchased commercially. This spike is calibrated by reverse isotope dilution using a commercially available natural U standard. The U isotope dilution method is based upon mixing of sample-derived natural U ( $\sim 0.7\%$   $^{235}\text{U}$ ) with spike-derived depleted U ( $\sim 0.2\%$   $^{235}\text{U}$ ). Uranium is determined in natural waters using this method. These procedures allow for the accuracy of isotope dilution to be attained in any ICP-MS lab without purchasing any special spike solutions and without any special NRC license being required.

**Radionuclide Detection by ICP-MS Oral Session—Michael E. Ketterer, Department of Chemistry, Northern Arizona University, Box 5698, Flagstaff, AZ 86011-5698. Tel: (520) 523-7055, Fax: (520) 523-8111, E-mail: michael.ketterer@nau.edu**

- 139.** ADVANCES IN INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (ICP-MS) FOR ROUTINE MEASUREMENTS IN THE NUCLEAR INDUSTRY. Rob Henry, TJA Solutions, 1812 Mapleton Avenue, Boulder, CO 80304, USA. Dagmar Koller, M. Liezers, TJA Solutions, Ion Path, Road 3, Winsford, Cheshire, England. O.T. Farmer III, C. Barinaga, D.W. Koppelaar, J. Wacker, PNNL, PO Box 999, Richland, WA, USA.

Traditional methods of quantitation of radioactive isotopes include radioactivity counting ( $\alpha, \beta, \gamma$ ) and Thermal Ion Mass Spectrometry (TIMS). These techniques require extensive matrix separation and sample purification methods before unequivocal identification of specific isotopes and their relative abundance is possible. Counting techniques become very time consuming when the half-life of the target analyte is very long or the concentration of the analyte low, e.g. environmental and bioassay measurements.

Atom counting using ICP-MS meets the nuclear industry requirements for many actinides and their daughter products. The argon plasma provides a rich, stable source of ions, which are introduced through an interface into the mass spectrometer for isotopic analysis. Recent improvements in quadrupole ICP-MS signal-to-background have resulted in attogram mass detection capability and improved analysis of shorter half-life isotopes. Magnetic sector mass spectrometers permit analysis of radionuclides to  $\sim 0.002\%$  accuracy and precision. Examples of ICP-MS productivity relative to 'accepted' techniques for both trace bioassay and environmental analysis as well as definitive isotope ratio measurements will be presented.

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## Lasers & Materials Chemistry

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- 140.** MOLECULAR SCALE CHARACTERIZATION OF POLYMER FILMS AT ROOM TEMPERATURE BY SINGLE MOLECULE SPECTROSCOPY. Yanwen Hou, Angela M. Bardo, and Daniel A. Higgins, Department of Chemistry, Kansas State University, Manhattan, KS 66506

As a result of recent advances in optical microscopy, the detection and spectroscopic characterization of single molecules is now possible. New applications of these methods in materials science continue to be demonstrated. One common class of experiments involves the use of single molecule fluorescence spectroscopy as a means to characterize the nanometer-scale environment in which the molecule resides. Previously, such methods have provided only qualitative results. In this presentation, a model based on the work of Marcus (Marcus, R. A.; J. Phys. Chem. 1990, 94, 4963) is used to obtain more quantitative information. The method is applied in studies of poly(methyl methacrylate) (PMMA) and poly(vinyl alcohol) (PVA) thin films. Specifically, parameters related to the local polarity and rigidity of the material are obtained, using the highly solvent-sensitive emission characteristics of Nile Red. The statistical results indicate a broad inhomogeneous distribution exists in PVA while two distinct classes of environments exist in PMMA. The analysis shows these environments differ in rigidity, rather than polarity. The effect of the environment on the time-dependent single molecule emission characteristics is also explored. It is demonstrated that the hydration level of the PVA film plays an important role in determining the rate of "blinking", as well as the rate of molecular rotation and translation.

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- 141.** CHARACTERIZING PROBE-TARGET BINDING INTERACTIONS USING CAPILLARY ELECTROPHORESIS WITH SINGLE MOLECULE SPECTROSCOPY DETECTION. Lisa Kolodny and Alan Van Orden, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

The application of laser-based spectroscopy techniques for the detection and characterization of individual molecules is leading to dramatic improvements in the speed and sensitivity of biochemical analysis. For example, we have developed a single molecule spectroscopy technique for a capillary electrophoresis system that enables us to determine analyte concentration without the need to perform a chemical separation. Analysis times of only a few seconds or less are routinely achieved, compared to the minutes to tens of minutes needed to perform the analysis by conventional capillary electrophoresis. We are applying this technique to the rapid characterization of probe-target binding interactions in biochemical systems. The electrophoretic mobilities of fluorescently labeled probe molecules, such as peptides or DNA hybridization probes, are determined as the probe molecules flow through an electrophoresis capillary one at a time. The presence of target receptor molecules, such as

drug candidates or DNA fragments alters the electrophoretic mobilities of the probes. The extent to which this occurs depends upon the binding affinity of the probe for the receptor. Applications for this technique in such areas as genomics research, high throughput screening, and environmental monitoring are anticipated.

**Lasers & Materials Chemistry Oral Session—Alan Van Orden, Department of Chemistry, Colorado State University, Fort Collins, CO 80523. Tel: 970-491-6286, Fax: 970-491-1801, E-mail: vanorden@lamar.colostate.edu**

- 142.** IMAGING AND SPECTROSCOPY AT THE SINGLE MOLECULE LEVEL WITH CARBON NANOTUBE PROBES. Charles M. Lieber, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138

Scanning probe microscopies, such as atomic force microscopy, represent important tools for investigating phenomena at the nanometer scale, although the resolution and sensitivity are limited by the nature of the probe tip. Carbon nanotubes are materials that can overcome the limitations of conventional probe tips and thus offer great potential for the future. In this presentation the fabrication, properties and applications of carbon nanotube probes will be reviewed. First, chemical vapor deposition approaches will be described which allows simple and reproducible fabrication of individual single-walled nanotube tips with radii less than 2 nm. The mechanical properties and resolution of these tips will be discussed. Second, application of single-walled nanotube tips for high resolution imaging of complex soft matter, such as large proteins and protein nucleic acid complex will be presented. Third, highly selective strategies for the modification of nanotube probe ends have been developed and used to probe intermolecular forces in a detailed manner. The use of modified nanotube tips for mapping spatial variations in chemical functionality down to the molecular scale will be described. Future directions and challenges with nanotube probe tips will be discussed.

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- 143.** THE USE OF ATOMIC FORCE MICROSCOPY TO IMAGE THE DNA POLYMERASE $\alpha$ -PRIMASE COMPLEX. Jessica A. Ekhoﬀ, K. L. Rowlen, University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO 80309

Atomic Force Microscopy (AFM) is a powerful technique, which can be used to obtain nanometer scale images under a variety of experimental conditions. One of the most significant advances in the field of AFM has been the ability to image biological molecules under physiologically relevant conditions. We have utilized AFM to obtain images of the DNA polymerase  $\alpha$ -primase complex both in air and under fluid conditions. Polymerase  $\alpha$ -primase is a four subunit protein that is known to be essential for the initiation of DNA replication in eukaryotic organisms. At present, the high resolution structure of the protein is not known and there are still many uncertainties surrounding the mechanism of initiation. Various subunit combinations of the protein have been prepared and imaged under identical conditions while bound to DNA. A comparative analysis of the images has been done to acquire architectural information of the entire protein molecule. Preliminary data has indicated that obtaining structural information of subunit assembly is feasible using this technique. Information from this research may then be used in biochemical studies to further understand the mechanistic role of polymerase  $\alpha$ -primase.

**Lasers & Materials Chemistry Oral Session—Jessica Ekhoﬀ, University of Colorado, Department of Chemistry and Biochemistry, Campus box 215, Boulder CO 80309. Tel: 303-492-3631, Fax: 303-492-5894, E-mail: ekhoﬀ@ucsub.colorado.edu**

- 144.** KINK DYNAMICS AND STEP GROWTH KINETICS ON BARIUM SULFATE (001) USING HYDROTHERMAL SCANNING PROBE MICROSCOPY. Steven R. Higgins, Dirk Bosbach, Carrick M. Eggleston, and Kevin G. Knauss, Department of Geology and Geophysics, University of Wyoming, Laramie, WY 82071. Dirk Bosbach, Institut für Mineralogie, Universität Münster, Corrensstrasse 24, 48149 Münster, Germany; Kevin G. Knauss, Earth Sciences Division, Lawrence Livermore National Laboratory, Livermore, CA 94550

We have measured step growth kinetics on barium sulfate (001) as a function of step length, supersaturation, and temperature. Using a one-dimensional nucleation model, we report kink detachment coefficients for  $\langle 120 \rangle$  monolayer steps of:  $v = 114 (\pm 14)$ ,  $187 (\pm 17)$ , and  $357 (\pm 43) \text{ s}^{-1}$ , at 90, 108, and  $125^\circ\text{C}$ , respectively, giving an activation energy,  $E_a = 0.39 (\pm 0.05) \text{ eV}$ . The kink formation energy,  $e$ , was found to be  $0.15 (\pm 0.02) \text{ eV}$ . The lack of increase in experimental kink density with increase in temperature points to surface diffusion limitations in the experiments. Due to the kinetic limitations, whether from mass transport or attachment to kink sites, our results demonstrate that knowledge of the kink kinetics as a function of temperature is important prior to application of the classical Gibbs-Thomson thermodynamic model to kinetic data. The implications of these findings are of fundamental interest in the fields of crystal growth and heterogeneous reactions.

**Lasers & Materials Chemistry Oral Session—Steven R. Higgins, Department of Geology and Geophysics, University of Wyoming, Laramie, WY 82071. Tel: (307) 766-3318, E-mail: shiggins@uwyo.edu**

- 145.** ATOMIC FORCE MICROSCOPY FOR THE ANALYSIS OF GAS-SOLID REACTION OF CARBONACEOUS PARTICLES. Amy E. Michel, University of Colorado, Department of Chemistry & Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), Boulder, CO 80309-0215; Kathy L. Rowlen, University of Colorado, Department of Chemistry & Biochemistry, Boulder, CO 80309-0215; John W. Birks, Department of Chemistry & Biochemistry and CIRES, Boulder, CO 80309-0215

Carbonaceous particles may play a significant role in many atmospheric processes. For example, soot particles absorb and scatter radiation and can act as cloud condensation nuclei, thereby affecting climate. Once placed in the atmosphere by combustion processes, soot particles are

exposed to a variety of reactive gases. The reaction between individual carbonaceous particles and a reactive gas can be monitored with atomic force microscopy (AFM) by following the size decrease of the particle as the reaction progresses. It is believed that studying the reactions of various  $sp^2$ -hybridized carbonaceous particles, such as polycyclic aromatic hydrocarbons and graphite, will lead to an improved understanding of the reactions of soot in the atmosphere. Currently in this research, the reactions of ozone with anthracene nanocrystals and graphite have been investigated in order to develop a new method for quantifying gas-solid reaction rates. The results from these reactions will be discussed.

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- 146.** 3-D SINGLE MOLECULE ORIENTATIONAL MICROSCOPY. Andrew P. Bartko and Robert M. Dickson, Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Single molecule microscopy has enabled nanoscopic probing of environmental dynamics. Available tools, however, remain rather limited with respect to information content and interpretation. Here we report our unique ability to visualize single molecule dipole emission patterns and, from these intensity patterns, extract true three-dimensional orientations of individual molecules. Intrinsically anisotropic light sources, individual fluorescent molecules near a dielectric boundary produce orientation specific fluorescence images. The observation of such emission patterns provides non-destructive confirmation of single molecule observation at room temperature. Simultaneous tracking of many individual molecules' orientation as a function of time provides dynamic local environmental information specific to each individual molecule. Spatially nanoscopic, single molecule dynamics can then probe physical interactions encountered within heterogeneous polymeric systems. These techniques are among the most direct and most readily interpretable reporters on single molecule behavior.

**Lasers & Materials Chemistry Oral Session—Robert M. Dickson, Georgia Institute of Technology, Department of Chemistry and Biochemistry, Atlanta, Georgia 30332-0400. Tel: 404-894-4007, Fax: 404-894-7452, E-mail: dickson@chemistry.gatech.edu**

- 147.** LUMINESCENT QUANTUM DOTS AND SERS-ACTIVE NANOPARTICLES FOR ULTRASENSITIVE BIOLOGICAL IMAGING AND DETECTION. Shuming Nie, Department of Chemistry, Indiana University, Bloomington, IN 47405

Recent research in our group has identified a new class of metal colloidal nanoparticles that are able to enhance the efficiencies of surface optical processes (e.g., surface-enhanced Raman scattering or SERS) by 14-15 orders of magnitude. This enormous enhancement allows vibrational Raman spectroscopy of single molecules adsorbed on a single particle at room temperature. Also, we have developed a new type of ultrasensitive detection labels by covalently coupling luminescent quantum dots (ZnS-capped CdSe) to biological molecules. These nanometer-sized conjugates are water soluble and biocompatible. In comparison with traditional organic dyes, this type of luminescent labels offers significant advantages such as size-tunable emission, spectral symmetry, and simultaneous excitation at a single wavelength. This talk will highlight recent advances in the fundamental studies of these optically active nanoparticles and their applications to bioanalytical and biophysical chemistry.

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- 148.** ATOMIC LAYER DEPOSITION OF TUNGSTEN ON  $Al_2O_3$  STUDIED USING AUGER ELECTRON SPECTROSCOPY. Robert K. Grubbs, C.E. Nelson, S.M. George, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309

The fundamental chemical processes that govern film growth typically occur within the first ten atomic layers. These processes are dictated by the nucleation of film growth on the substrate. Recently, tungsten atomic layer deposition (ALD) was reported using alternating  $WF_6$  and  $Si_2H_6$  exposures. Understanding the nucleation of metallic tungsten on insulating oxides is of scientific and technological importance. The nucleation and initial growth of tungsten metal on aluminum oxide was monitored during tungsten ALD using Auger electron spectroscopy (AES). The AES results observed distinct chemical differences between nucleation and growth. The AES measurements have also provided insight into the nucleation mechanism and resulting growth mode.

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- 149.** FLUORESCENCE ANISOTROPY ON THE SUBMICRON LENGTH SCALE: A NEAR-FIELD SCANNING OPTICAL MICROSCOPY (NSOM) STUDY OF LUMINESCENT POLYMER THIN FILMS. David A. Vanden Bout, Chemistry Department, University of Texas, Austin, TX, 78712

Polyfluorene is a luminescent conjugated polymer that is an excellent candidate for the fluorescent material in polarized light-emitting devices. Its rigid rod structure and thermotropic liquid crystalline properties allow for the possibility of generating highly aligned luminescent films. However, making such films can be complicated by the fact that highly aligned films tend to have increased interpolymer interactions leading to lower emission yields. Near-field scanning optical microscopy (NSOM) is used to study both pristine and annealed films of polyfluorenes with varying alkyl-substituents to determine how these interpolymer interactions affect the film's emission. By varying the side-chain length we can influence how the polymer chains pack in pristine films and the extent of liquid crystalline ordering in annealed films. Polarized fluorescence NSOM images reveal two distinct types of nanoscale ordering in the pristine films that can be correlated with interpolymer emission species. A new method of image math is presented that allows for quantification of polymer chain ordering by calculating the in plane fluorescence

anisotropy. This new anisotropy method allows for characterizing order in amorphous materials. NSOM anisotropy data for pristine films reveal that the films are comprised entirely of small (50-200 nm) domains of polymers that are preferentially ordered in the same direction. These domains are found throughout the films and show emission from both individual polymers and interpolymer excimeric species. NSOM anisotropy images are also used to show how changes in the substituent lengths affect the packing of the polymer chains in the annealed films. Interpolymer emission species are further characterized by wavelength imaging and time-resolved fluorescence data. Initial data has been collected using the new technique of fluorescence lifetime imaging NSOM (FLI-NSOM).

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- 150.** SINGLE MOLECULE PROBES OF LIPID MEMBRANE MICROENVIRONMENTS. Christopher W. Hollars, Sarah A. Vickery, and Robert C. Dunn, Department of Chemistry, Malott Hall, University of Kansas, Lawrence, KS 66045

Near-field scanning optical microscopy (NSOM) is an emerging scanning probe technique capable of optically probing samples at the nanometric scale. We are currently using NSOM combined with other high resolution techniques such as atomic force microscopy and confocal microscopy to study the structure and dynamics of artificial membranes formed using the Langmuir-Blodgett (LB) technique. Single molecule studies using both far-field and near-field techniques provide complementary information on the structure and dynamics of these films. For instance, using the unique properties of the field emerging from the near-field tip, the three-dimensional orientation of probe molecules doped into lipid films can be used to determine the microscopic order in the membrane. Results such as these provide a bridge between bulk experimental studies that measure average properties and theoretical investigations that yield a molecular view of membrane structure.

We have also begun using modified near-field and atomic force tips to create new imaging methods and chemical sensors. For example, we have recently demonstrated the feasibility of a new fluorescence imaging technique based on energy transfer from a donor dye in a sample to an acceptor dye attached to a near-field tip. We have also begun experiments functionalizing near-field tips with films containing dyes sensitive to the presence of  $\text{Ca}^{2+}$ . Progress in probing membrane microenvironments and using modified tips to create novel new sensors will be reported.

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- 151.** ATOMIC LAYER DEPOSITION OF BN USING SEQUENTIAL EXPOSURES OF  $\text{BCl}_3$  AND  $\text{NH}_3$ . John D. Ferguson, Stephen J. Ferro and Steven M. George, Department of Chemistry, University of Colorado, Boulder, CO 80309-0215.

BN is a relatively inert insulating material with a very high thermal conductivity. These BN films are desirable for many applications. Atomic layer deposition (ALD) has become an ideal method for depositing ultrathin and conformal films. A technique for BN ALD was developed by separating the binary reaction  $\text{BCl}_3 + \text{NH}_3 \rightarrow \text{BN} + 3 \text{HCl}$  into two half-reactions. The BN film was grown on high surface area  $\text{SiO}_2$  particles using alternating exposures of  $\text{BCl}_3$  and  $\text{NH}_3$  at 700 K. The sequential surface chemistry was monitored in a vacuum chamber using in situ transmission Fourier transform infrared vibrational spectroscopy. The initial  $\text{SiO}_2$  surface contained  $\text{SiOH}^*$  surface species. The first  $\text{BCl}_3$  exposure reacted with the  $\text{SiOH}^*$  species to form  $\text{SiOBCl}_x^*$  species. The subsequent  $\text{NH}_3$  exposure converted the surface species to  $\text{BNH}_2$ . The following  $\text{BCl}_3/\text{NH}_3$  exposures converted the surface to  $\text{BCl}_x/\text{BNH}_2^*$  species, respectively. By repeating the sequential surface reactions, BN bulk vibrational modes on the  $\text{SiO}_2$  particles increased with number of reaction cycles. Transmission electron microscopy images will show the conformality of the BN film on the  $\text{SiO}_2$  particles. Spectroscopic ellipsometry studies of BN deposited on Si(100) will also provide growth rates and kinetics of BN ALD.

**Lasers & Materials Chemistry Oral Session—John Ferguson, Department of Chemistry, University of Colorado, Boulder, CO 80309-0215. Tel: 303-492-6590, Fax: 303-492-5894, E-mail: John.Ferguson@Colorado.edu**

- 152.** DEVELOPMENT OF A FLUORESCENCE BASED SINGLE VIRUS DETECTOR. Matthew M. Ferris, K. L. Rowlen, University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO 80309.

Viral contamination of water is not only a health related issue but is also of great concern for industrial applications requiring ultra-pure solvents. For example, the semiconductor industry uses ultra-pure water for rinsing of surfaces in the manufacturing process. Any particulate contamination of this solvent, including viruses, can cause product defects and eventually failures. While current water purification techniques, such as filtering, are able to reduce viral concentrations to around 1000 viruses per milliliter this number remains relatively high for applications desiring ultra-pure solvents. A limiting issue in the development of improved filtering technologies is that conventional viral analysis by plaque titering is relatively insensitive at low concentrations. Therefore a novel technique able to detect individual viral particles is being developed utilizing laser induced fluorescence and flow cytometry. Design considerations, instrument characterization and preliminary results will be discussed as well as future goals and applications.

**Lasers & Materials Chemistry Oral Session—Matthew M. Ferris, University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO 80309. Tel: 303-492-3631, Fax: 303-492-5894, E-mail: ferrism@colorado.edu**

- 153.** ORIENTATION INSENSITIVE SECOND HARMONIC GENERATION MEASUREMENTS OF ADSORPTION ISOTHERMS AND ADSORPTION/DESORPTION KINETICS. Sarah, G. Westerbuhr, University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO 80309-0215; Garth J. Simpson, Stanford University, Department of Chemistry, Stanford, CA 94305-5080; Kathy L. Rowlen, University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO 80309-0215
- When measuring adsorption isotherms or the kinetics of adsorption/desorption by second harmonic generation, the detected signal is dependent on both the surface coverage and the molecular orientation. Therefore, the second harmonic signal must be corrected to account for the orientation angle as a function of surface coverage. Recently in our lab, an experimental method that is relatively insensitive to molecular orientation has been developed, allowing for the direct measurement of surface coverage. The orientation insensitive methodology will be presented, as will adsorption isotherms and kinetics measurements for an example molecular system.*
- Lasers & Materials Chemistry Oral Session—Sarah Westerbuhr, University of Colorado, Department of Chemistry and Biochemistry, Campus Box 215, Boulder, CO 80309-0215. Tel: 303-492-3631, Fax: 303-492-5894, E-mail: westerbu@colorado.edu**
- 154.** SPECTROMETRY AND IMAGING VIA DIGITAL MICROMIRROR ARRAYS (DMAS). Richard A. DeVerse, Three LC, Inc., 74-5599 Luhia Street Unit D-6, Kailua-Kona, HI 96740 USA; Robert M. Hammaker, Daniel J. Asunsis, and William G. Fateley, Three LC, Inc. 8459 River Valley Drive, Manhattan, KS 66502 USA; Ronald R. Coifman, Fast Mathematical Algorithms and Hardware Corporation, 1020 Sherman Avenue, Hamden, CT 06514 USA; Jinguang Wu, Department of Chemistry, Peking University, Beijing, 100871, China
- Micro-optoelectromechanical systems (MOEMS) have moved from the laboratory to commercial success. The potential applications of MOEMS in analytical spectroscopy and imaging are just being realized. This new MOEMS technology is demonstrated by the digital micro-mirror array (DMA) present in many commercially available digital light projector systems. The DMA is a logical choice for a spatial light modulator (SLM) to serve as both one-dimensional (1D) and two-dimensional (2D) encoding masks for spectrometry and imaging, respectively, due to the following features: (1) size, (2) reflectivity, (3) speed, (4) reliability in position, (5) variable mask dimensions, (6) virtual solid state device, (7) mirror drive options, and (8) high radiation tolerance. Included in a wealth of new ideas for spectrometric instrumentalists are: (1) infrared and Raman spectrometers with no macroscopic moving parts, (2) hyperspectral imaging cameras for infrared and Raman spectroscopy, (3) use of single detectors with echelle grating instruments to identify and quantify metal atom emissions, (4) use of a single detector in direct coupled plasma instruments for the selective identification of nonmetal atomic emissions in the near-infrared spectral region, and (5) use of mirror modulations to transmit spatial information in spectrometry and imaging.*
- Lasers & Materials Chemistry Oral Session—Robert Hammaker, Kansas State University, Department of Chemistry, Manhattan, KS 66506-3701. Tel: (785)532-1454, Fax: (785)532-6666, E-mail: rmh3008@ksu.edu**
- 155.** DYNAMICS STUDIES OF DYE-DOPED POLYMER-DISPERSED LIQUID CRYSTALS BY NEAR FIELD OPTICS. Xiangmin Liao, Erwen Mei, and Daniel A. Higgins, Department of Chemistry, Kansas State University, Manhattan, KS, 66506
- The dynamics of dye doped polymer-dispersed liquid crystal thin films are studied by near-field scanning optical microscopy (NSOM). BODIPY dye is doped into E7 (a nematic mixture); the liquid crystalline phase is then dispersed as droplets in a poly(vinyl alcohol) film. A modulated voltage is applied between the aluminum-coated NSOM probe and a conductive indium-tin-oxide-coated substrate, upon which the sample is supported. The resulting local electric field causes reorientation of the dye and the liquid crystal. The transmission characteristics (using crossed polarization) and the fluorescence from the sample are recorded simultaneously in time. Use of the dye as a means to monitor the dynamics allows for the results to be more readily interpreted, compared to previous transmitted-light methods. The results show spatial variations in the reorientation dynamics; the dynamics are observed to differ between locations near the polymer surface, near disclination points present within the nematic phases, and in the center of the droplet.*
- Lasers & Materials Chemistry Oral Session—Xiangmin Liao, Department of Chemistry, Kansas State University, Manhattan, KS, 66506. Tel: (785) 532-6079, Fax: (785) 532-6666, E-mail: xli8614@ksu.edu**
- 156.** AN INTEGRATED NSOM/AFM BASED ON LIGHT TRANSMISSION THROUGH AN AFM CANTILEVER. Peter C. Andersen, Kathy L. Rowlen, University of Colorado at Boulder, Department of Chemistry and Biochemistry, Boulder, CO 80309-0215
- The optical properties of nanometer scale materials can be studied directly by modern microscopic and spectroscopic techniques. Near-field scanning optical microscopy (NSOM) allows for the direct correlation of surface topographic features to the optical properties of the sample. However, conventional NSOM has low optical throughput, limiting its use with inefficient optical processes such as Raman scattering. An integrated NSOM/AFM is currently being developed based on light transmission through the tip of an AFM cantilever. The larger taper angle of the AFM tip allows higher optical throughput than conventional probes. In addition, the atomic force feedback produces topographical images that are more easily interpreted and the flexibility of the probe reduces damage to both the probe and the sample. The design of the instrument will be presented along with preliminary results.*
- Lasers & Materials Chemistry Oral Session—Peter C. Andersen, University of Colorado at Boulder, Department of Chemistry and Biochemistry, Boulder, CO 80309-0215. Tel: 303-735-0246, Fax: 303-492-5894, E-mail: andersep@colorado.edu**

## Luminescence Oral Sessions

- 157.** LIFETIME IMAGING WITH AN INTERLINE-TRANSFER CCD CAMERA FOR PRESSURE-SENSITIVE-PAINT APPLICATIONS. James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103; Larry P. Goss and Gregory J. Fiechtner, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638; Thomas F. Drouillard, Chad W. Fisher, Mark A. Linne, and Nigel T. Middleton, Center for Commercial Applications of Combustion in Space, Colorado School of Mines, Golden CO 80401

*Pressure- and temperature-sensitive paints have emerged as valuable diagnostic tools for characterizing aerothermodynamic flows. Paint technology has been applied to a vast array of systems that includes wind-tunnel models, gas turbine engine compressors, skyscrapers, race cars, and the family minivan. Pressure determination is achieved by measuring the oxygen-concentration dependence of luminescence produced through photoexcitation of lumiphores embedded in the paint layer. Measurements of luminescence intensity or lifetime reveal the oxygen partial pressure and, therefore, the total pressure on the painted surface under study. During lifetime-based PSP measurements, the temporal decay of the luminescence signal is recorded rather than the total luminescence intensity. This approach features a number of advantages over the intensity-based approach, which requires acquisition of both "wind-on" (experimental) and "wind-off" (reference) images. Time-domain impulse techniques and frequency-domain phase techniques have been applied to lifetime-based PSP imaging. The merits of these approaches and recent lifetime measurements achieved with a novel interline-transfer CCD camera will be discussed during this presentation.*

**Luminescence Symposium Oral Session—James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103. Tel: 937-255-7431, Fax: 937-656-4570, E-mail: james.gord@wpafb.af.mil**

- 158.** PRESSURE SENSITIVE PAINT (PSP) AT LOW SPEEDS. Patricia B. Coleman, Ford Motor Company, P.O. Box 2053, M/D 3083/SRL, Dearborn, MI 48121-2053

*Oxygen quenching of luminescence has been utilized as a method for measuring oxygen concentration or partial pressure in a wide variety of applications. One such application, called Pressure Sensitive Paint (PSP), measures the surface pressure on a model in an airflow. In the last ten years PSP has gained wide acceptance for experimental pressure measurements in the aircraft industry. For automotive testing the desired velocity range is 70 - 100 mph. Whereas PSP works very well at high velocities used for aircraft testing, it is more difficult to obtain good results at slower velocities. Because of this, it becomes essential to optimize every aspect of the PSP test, to identify all of the possible sources of error in the measurement and reduce them as much as possible. A number of laboratory experiments were carried out using a controlled environment chamber, which had been designed and built for evaluating the sensors in the fluorescence spectrometer sample compartment. In the lab chamber 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. These experiments allowed the chemistry and physics of the PSP system to be better understood. One of the critical issues for low speed PSP testing is temperature control. Two approaches to address this issue are being investigated. One is to run the PSP test in an automotive tunnel where the temperature can be controlled. The other is to add an additional luminophore, which only responds to temperature change, to the PSP system. This second approach would be desirable in non-temperature-controlled automotive tunnels and in aircraft tunnels. This paper will discuss both aspects of temperature control.*

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- 159.** ROTATIONAL ANISOTROPY DECAY IN SUPERCRITICAL FLUIDS AND LIQUID SOLVENTS: INVESTIGATING PHASE TRANSITIONS. Christopher E. Bunker and James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

*Next-generation, high-performance military aircraft will fly faster, higher, and farther than anything currently in use. Fueling such aircraft is no simple task. To maintain reasonable logistics and minimize costs, the Air Force intends to field a single fuel capable of both high-temperature operation (above the critical temperature) with low thermal degradation characteristics and low-temperature operation (at or below the fuel freezing temperature) with excellent flow properties. Achieving such a goal will require a much-improved fundamental understanding of the physical and chemical properties of fuels under these extreme operating conditions. We have accomplished laser-based measurements of rotational anisotropy decay using time-correlated single-photon counting to probe local densities and viscosities about fluorescent probes in model fuels. Results were obtained for the phase transitions experienced on going from gas-like to liquid-like conditions in a supercritical fluid by manipulating pressure and from liquid to fluid and from liquid to solid by manipulating temperature. The data will be discussed within the context of our current understanding of supercritical-fluid and liquid solvent structure.*

**Luminescence Symposium Oral Session—Christopher E. Bunker, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638. Tel: 937-255-1945, Fax: 937-656-4570, E-mail: cbunker@ward.appl.wpafb.af.mil**



- 160.** DENSITY-DEPENDENT SPECTRAL SHIFTS OF PYRENE IN SUPERCRITICAL FUELS. Donald K. Phelps, Christopher E. Bunker, and James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

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

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- 161.** NEW SPECTRAL SOURCES FOR STUDYING COMBUSTION AND FUELS. James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103; Gregory J. Fiechtner and Michael S. Brown, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638; Angus Henderson, Pam Roper, and Roy Mead, Aculight Corporation, 11805 North Creek Parkway South, Suite 113, Bothell WA 98011; J. V. Rudd, David Zimdars, and Matthew Warmuth, Picometrix, Inc., P.O. Box 130243, Ann Arbor MI 48113

Detailed studies of combustion and fuels demand the development and application of non-intrusive measurement techniques for quantifying species concentrations and fluid-dynamic parameters. Laser-based and other optical approaches are well-suited to these tasks. These approaches do little to disturb the reacting flows under study while providing the physical and chemical information required for computational modeling. Much of the optical-diagnostics effort to date has involved laser sources and measurement schemes that operate in the ultraviolet, visible, and near-infrared spectral regimes. While a wealth of information could be obtained through measurements in the mid- and far-infrared regions, suitable coherent radiation sources have been largely unavailable. To address this need in the mid-infrared, we have developed a continuous-wave optical parametric oscillator (OPO) based on periodically poled lithium niobate (PPLN) technology. This 2.3-mm OPO, which is the very first of its kind, has been used to record continuous frequency scans through absorption features of carbon monoxide, an important combustion product. These developments demonstrate the potential of such devices as room-temperature, low-cost, compact mid-infrared sources with numerous spectroscopic and species-detection applications. Novel sources of far-infrared radiation have been achieved through the marriage of ultrafast (femtosecond) lasers and semiconductor materials such as low-temperature-grown gallium arsenide (LT-GaAs). Ultrafast excitation and gated detection with these and other materials has enabled the development of millimeter-wave, terahertz-radiation systems for spectroscopic studies. Terahertz radiation features a number of ideal characteristics for diagnostic studies of aviation fuels and combustion. While kerosene-based fuels do not absorb radiation in this spectral regime, trace water dissolved in fuels interacts strongly with terahertz radiation. This situation permits the quantification of water in fuel while providing an opportunity for the study of water/fuel phase behavior and chemical dynamics. Similarly, soot particles are transparent to terahertz radiation while some key combustion species absorb in this spectral region. Furthermore, some ceramic materials pass terahertz radiation, suggesting the possibility of diagnostic studies in ceramic windowless combustors.

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- 162.** LUMINESCENCE OF BIOMOLECULES ENTRAPPED WITHIN REVERSE MICELLES. Michael Nicholson and Mark P. Heitz, SUNY College at Brockport, Department of Chemistry, Brockport, New York, 14420-2971.

Functionality and stability of biological molecules such as proteins and enzymes depend on specific interactions that occur between the amino acid residues and the immediate microenvironment. A variety of factors (e.g., pH, ionic strength, polarity, hydrogen bonding, etc.) influence overall protein conformation and thus performance. One factor, hydration, plays an essential role in determining protein structure and performance. Reverse micelles offer a novel aqueous environment in which one has the ability to simultaneously solubilize a hydrophile and control the extent of hydration. We report on the entrapment of several different proteins within aerosol-OT (AOT) reverse micelles formed in n-heptane. We address changes that occur when the protein is starved for water by limiting its hydration shell. These results demonstrate the importance of hydration on protein behavior in environments where water is limited such as biosensor interfaces and sol-gel-derived biocomposites.

**Luminescence Symposium Oral Session—Mark P. Heitz, SUNY College at Brockport, Department of Chemistry, 350 New Campus Drive, Brockport, New York, 14420-2971. Tel: 716-395-5586, Fax: 716-395-5805, E-mail: mheitz@brockport.edu**

- 163.** ISSUES ON CHARACTERIZING OPTICAL DEGRADATION OF PHOTOVOLTAIC MODULE ENCAPSULANT EVA UNDER INTERFERENCE FROM SUBSTRATE MATERIALS. E.J. Pern and S.H. Glick. National Center for Photovoltaics, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401

We conducted experiments investigating the photothermal stability of various encapsulation materials for photovoltaic modules under accelerated exposure testing (AET) conditions. One of the objectives was to analyze and quantify the optical loss of superstrate/encapsulant layers and to correlate it with the electrical loss of the encapsulated crystalline Si solar cell from AET-induced degradations. The primary encapsulants studied are ethylene vinyl acetate (EVA) copolymers formulated with various stabilization additives. When transparent superstrates and substrates of glass plates or polymer film materials were used in the laminate configurations, integrated transmittance, color indices, and fluorescence were easily measured; optical changes were subsequently determined. When EVA did not show visible discoloration, fluorescence analysis could differentiate the extent of EVA degradation between different EVA formulations. Difficulties arose when opaque polymer films were used as substrates. Although changes in the integrated transmittance could be determined using reflection measurement modes, results of fluorescence analysis to assess EVA degradation and corresponding color indices were ambiguous or uncertain when the discolored EVA and/or substrate film fluoresced. More difficulties were encountered if the polymer substrate film had a layer of special coating that was browned rapidly under AET treatment. The browned coating layer could result in false interpretation of degradation of the EVA layer; in fact this layer was only slightly degraded when examined by fluorescence analysis. Details about these analytical issues will be presented and discussed in the meeting. This work was performed at NREL under U.S. Department of Energy Contract No. DE-AC36-99-GO10337.

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- 164.** Invited Paper SYNTHESIS AND CHARACTERIZATION OF A CLASS OF LANTHANIDE CHELATES FOR CANCER DETECTION. Darryl J. Bornhop, Steven Robertson, Garry E. Kiefer<sup>1</sup>, David Morgan<sup>2</sup>, Barbara C. Pence<sup>2</sup>, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-106, <sup>1</sup>Dow Chemical Company, Freeport TX 77541, <sup>2</sup>Department of Pathology, Texas Tech University Health Sciences Center

A new class of exogenous marker, based on polyazamacrocyclic chelates of Tb (III) or Eu (III) have been shown to be useful for improving imaging contrast or enhanced tissue-site visualization when fluorescence detection is employed.<sup>1-5</sup> It will be shown that these chelates are non-toxic, have good water solubility and high stability constants and exhibit attractive spectral properties. Physical, chemical, spectroscopic and physiological properties of these unique chemical markers will be discussed in detail and it will be shown that these molecular probes can be used for quantitative minimally invasive tissue imaging and solute transport investigations using an endoscopic fluorimeter.<sup>4,5</sup> One of these chelates, Tb-PCTMB (Tb-3,6,9-tris(methylene phosphonic acid n-butyl ester)-3,6,9,15-tetraaza-bicyclo[9.3.1]pentadeca-1(15),11,13-triene) shows a preference to bind to abnormal tissue allowing the potential for enhanced disease detection.<sup>3</sup> These observations were quantified in multi-animal early cancer detection study using Tb-PCTMB and the Sprague Dawley Rat DMH-induced colon cancer model. Sensitivity and specificity were found to be greater than 85%. Additionally, recent observations suggest that the presence and activity of M-cells (antigen transporting cells), previously not identified as carcinogen transporters, may be involved in the chemical carcinogenesis process, particularly in this animal colon cancer model. Tb-PCTMB transport to tissues associated with M-cells and the pathological implications of these observations will be discussed. Furthermore it will also be shown that the polyazamacrocyclic lanthanide chelates can be detected using time-resolved imaging to further enhance selectivity. Finally we will discuss the potential of constructing bi-functional markers for co-registration mechanism investigations (fluorescent and NMR active).

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2. D.S. Hubbard, et al., *Bioimaging*, 6:63-70, (1998).
3. D.J. Bornhop, et al., *Anal. Chem.* 71, 2607 (1999).
4. M.P. Houlne, et al., *J. Biomed. Opt.* 3: 145-153, (1998).
5. M.P. Houlne, et al., *Anal. Chim. Acta*, 397:267-278, (1999).

**Luminescence Symposium Oral Session—Darryl J. Bornhop, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409. Tel: 806-742-3142, Fax: 806-742-1289, E-mail: djbornhop@ttu.edu**

- 165.** 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, A. Periasamy, Keck Center for Cellular Imaging, 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<sup>8</sup> systems Ru(II), Re(I), and Os(II) with  $\alpha$ -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. Fluorescence microscopy will be shown to be a powerful tool in sorting out the complexities of these systems. However, we will show that these areas are still in their infancy and that the ultimate goal of a totally rational design of probes, luminescence enhancers, and polymer-supported sensors is as yet an imperfectly realized goal.

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- 166.** DEVELOPMENT OF LUMINESCENCE-BASED pH SENSORS EMPLOYING RHENIUM(I) TRICARBONYL COMPLEXES. William D. Bare, Nathan H. Mack, J. N. Demas, University of Virginia, Department of Chemistry, McCormick Road, Charlottesville, VA 22904
- Rhenium(I) tricarbonyl complexes typically contain one bidentate and one monodentate ligand, and are thus particularly attractive for the investigation and development of luminescence-based sensors. These complexes, with two very different ligand sites, provide a simple system for the investigation of interplay between the two ligands and their effect on pH-sensing properties. We have synthesized and studied complexes with deprotonatable sites on either the monodentate or bidentate ligand and will discuss the differences in the pH-dependent luminescence properties of these two classes of complexes. Both sensor types may be applied to pH sensing, although different sensing systems must be employed.*

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- 167.** RECENT DEVELOPMENTS ON SOLID-PHASE EXTRACTION SOLID-MATRIX LUMINESCENCE AND LASER-EXCITED SHPOL'SKII SPECTROMETRY FOR THE ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS. Andres D. Campiglia, Adam J. Bystol, Andrea F. Arruda, Jennifer Parker, Travis Martin, North Dakota State University, Department of Chemistry, Fargo, ND 58105; Gregory D. Gillispie, Dakota Technologies, Inc., 2201A 12th St. N., Fargo, ND 58102-1803.

*The combination of solid phase extraction (SPE) and solid matrix luminescence (SML) provides a promising tool for screening polycyclic aromatic hydrocarbons (PAHs) in environmental samples.<sup>1,2</sup> The organic pollutants are extracted on octadecyl membranes and room-temperature luminescence measurements (fluorescence and/or phosphorescence) are directly performed on the extraction membrane. Synchronous excitation and emission matrices can improve, to some extent, the selectivity of SPE-SML. However, substantial improvement in spectral resolution is observed by performing laser-excited luminescence measurements in Shpol'skii matrices at 77K<sup>3</sup> and 4.2K. We will present recent improvements in both, SPE-SML and laser excited Shpol'skii spectrometry (LESS) for the analysis of PAHs in environmental samples. The methods and instrumentation presented have applications in research areas that take advantage of time-resolved imaging and spectral identification on solid surfaces, and luminescence probes in organized media such as cyclodextrins and micellar solutions.*

1. Hagestuen and Campiglia, *Appl. Spectrosc.*, 1998, **52**, 1096.
2. Hagestuen and Campiglia, *Talanta*, 1999, **49**, 547.
3. Bystol, Gillispie and Campiglia, *Appl. Spectrosc.*, 2000, **54**(6), in press.

**Luminescence Symposium Oral Session—Andres D. Campiglia, Department of Chemistry, North Dakota State University, Fargo, ND 58105. Tel: 701-231-8702, Fax: 701-231-8831, E-mail: campigli@prairie.nodak.edu**

- 168.** LASER INDUCED FLUORESCENCE IMAGING OF COVALENTLY LABELED SILICA NANOPARTICLES; CHARACTERIZATION OF PARTICLE SIZE AND LABELING DISTRIBUTIONS. David C. Hanley and Joel M. Harris, University of Utah, Department of Chemistry, 315 S. 1400 E., Salt Lake City, UT, 84112-0850

*Incorporation of organic materials into the solid matrices of silica particles is of interest in many areas including laser materials, biosensors, optical memories, and thin films. To better understand the covalent incorporation of organic molecules into silica particles, and in an effort toward development of colloidal surface analysis techniques, we are investigating colloidal labeling statistics for silica colloids which have been "internally" labeled with covalently bound fluorescent dye. The silica particles are synthesized in house by the Stober synthesis<sup>1</sup>, as modified by van Blaaderen<sup>2</sup>, which introduces functionalized fluorescent dye molecules during the nucleation and growth of silica particles. The fluorescent dye, Rhodamine-B, is attached through an isothiocyanate linkage to 3-(aminopropyl)triethoxysilane, which participates directly in the synthesis of silica particles. Individual particles are imaged under laser irradiation both in flowing sample streams, and stationary, at a glass/solution interface. Fluorescence is collected with a high numerical aperture inverted microscope, and imaged with a low noise, thermoelectrically cooled, CCD detector. Information is yielded on the number of labels per particle and the distribution of labels among particles, from which information on particle size and the distribution of sizes among a population of particles can be established. Through a union of single molecule sensitivity with imaging, we are developing tools toward the inspection of silica colloidal particles on an individual basis, yielding information of both chemical composition and physical size, as well as physical parameters associated with fluorescent tags in an interfacial environment and restricted in a solid matrix.*

1. Stober, W. et al., *J. Colloid Interface Sci.*, 1968, **26**, 62.
2. van Blaaderen, A. and Vrij, A., *Langmuir*, 1992, **8**, 2921.

**Luminescence Symposium Oral Session—David C. Hanley, University of Utah, Department of Chemistry, 315 S. 1400 E., Salt Lake City, UT, 84112-0850**

- 169.** THE EFFECTS OF RELATIVE HUMIDITY ON PHOSPHORESCENCE LIFETIMES AND INTENSITIES OF POLYAROMATIC HYDROCARBONS ON PARTIALLY HYDROPHOBIC AND NORMAL FILTER PAPER. Amanda H. Ackerman and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, University Station Box 3838, Laramie, Wyoming 82071-3838.

*Phosphorescence lifetimes and intensities were determined for phenanthrene, phenanthrene-d<sub>10</sub>, and benzo[e]pyrene adsorbed onto Whatman #1 and IPS papers. Data were acquired at various relative humidities to determine some of the properties of the papers that affected the phosphorescence parameters of the phosphors and to better understand the nature of moisture quenching in the filter paper systems. For all the compounds, loss of rigidity of the cellulose matrix of the paper, due to water sorption, led to significant decreases in phosphorescence intensity. However, the phosphorescence lifetimes of phenanthrene and benzo[e]pyrene changed very little with relative humidity. For phenanthrene-d<sub>10</sub>,*

which has a lifetime of several seconds under dry conditions, significant dynamic quenching of the phosphorescence was observed. The trends in the data were explained based on Knudsen diffusion of water vapor in cellulose at low relative humidity, and surface diffusion at higher relative humidity. In addition, dynamic phosphorescence quenching and matrix quenching models were considered to explain the changes in the phosphorescence intensities and lifetimes.

**Luminescence Symposium Oral Session—Amanda H. Ackerman, Department of Chemistry, University of Wyoming, University Station Box 3838, Laramie, Wyoming 82071-3838. Tel: 307-766-4844, Fax: 307-766-2807, E-mail: ackerman@uwyo.edu**

- 170.** MICRO-ENVIRONMENTAL STUDY OF GLUCOSE GLASSES FOR SOLID-MATRIX LUMINESCENCE VIA MOISTURE QUENCHING, GLASS TRANSITION TEMPERATURES AND A POLARITY PROBE. Shaun D. Mendonsa and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071

Solid-matrix phosphorescence (SMP) and solid-matrix fluorescence (SMF) of trace organic compounds are readily obtained in glucose glasses. Glucose glasses can be prepared using either crystalline glucose or a glucose melt. In general, model compounds give higher SMP and SMF signals in glasses prepared from a glucose melt compared to crystalline glucose glasses. An understanding of the reasons for the enhanced signals with the glucose-melt glasses is important for improving sensitivity and selectivity, and also for the development of new solid matrices. In this work, the micro-environments of the lumiphors in the glasses were investigated. The model compounds employed were two heterocyclic aromatic amines (HAA). The HAA are a class of mutagenic/carcinogenic substances found in cooked meat, fish, and other environmental samples. In the first set of experiments, the effects of moisture on the SMP intensities and lifetimes of the two HAA were studied. A near-infrared method was developed to determine the moisture contents of the glucose glasses prepared using solvents containing different proportions of methanol and water. The SMP intensities and lifetimes obtained in the glucose glasses were then related to the moisture contents of the glasses using various luminescence quenching models. The data for both types of glasses indicated that dynamic and matrix quenching occurred in the glasses. Consequently, the data were fit to a modified form of the Stern-Volmer equation that accounted for both types of quenching mechanisms. In other experiments, the glass transition temperatures of the glucose glasses were determined using differential scanning calorimetry. The glass transition temperatures were related to the SMP intensities and lifetimes of the HAA and to the rigidities of the glasses. Lastly, the fluorescence properties of pyrene were utilized to probe the micro-environmental polarity of the glasses.

**Luminescence Symposium Oral Session—Shaun D. Mendonsa, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838. Tel: 307-766-4844, Fax: 307-766-2807, E-mail: shaunm@uwyo.edu**

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## MS, GC/MS, LC/MS and Pharmaceutical Analysis Oral Sessions

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- 171.** STRATEGIES FOR CHARACTERIZATION OF COMBINATORIAL LIBRARIES BY LC/MS. Kathy A. Halm, Meg Hermann; Adam W. Cook; Conrad W. Hummel; Alan S. Florjancic; Gary P. Hingorani and John A. Josey, Array BioPharma, Inc., 1885 33rd St., Boulder, CO 80301.

In the drug discovery process, combinatorial chemistry or parallel synthesis is used to generate large numbers of compounds for high throughput screening. Fast, efficient analytical methods are required to characterize the thousands of compounds produced from such high speed synthesis. LC/MS utilizing a ballistic gradient on a short, efficient HPLC column provides specificity, sensitivity and speed. Data was acquired using electrospray ionization on a Finnigan LCQ ion trap mass spectrometer in full scan or MS/MS mode. An alternative mobile phase modifier to trifluoroacetic acid, HFBA (heptafluorobutyric acid) was investigated. In conjunction with the change in mobile phase modifier, a 2x30mm YMC ODS-AQ, 3 micron particle size column was used for the separation. Instrument method control of the LCQ 6-port divert valve enabled flow injection FIA/MS or LC/UV/MS analysis in an automated fashion. Based on valve position, either the sample bypassed the HPLC column for FIA/MS or the sample was injected on column, and the HPLC eluent detected by UV and MS. Both FIA/MS and LC/UV/MS samples acquired on the same 96-well plate could be analyzed and viewed graphically using the Finnigan Xcalibur Discovery software.

**MS, GC/MS, LC/MS Oral Session—Kathy A. Halm, Array BioPharma, Inc., 1885 33rd Street, Boulder, CO 80301. Tel: 303-381-6622, Fax: 303-449-5376, E-mail: khalm@arraybiopharma.com**

- 172.** THE USE OF THE AGILENT 100 SERIES LC/MSD TRAP FOR RAPID IDENTIFICATION OF IMPURITIES, STRUCTURAL ELUCIDATION AND QUANTITATION. Jennifer V. Smith, Agilent Technologies, 2850 Centerville Road, Wilmington, DE 19808

Complementing the very successful Agilent 1100 LC/MSD, the new LC/MSD TRAP uses the same proven source, but with the added capability to do MS/MS and MS<sub>n</sub> experiments using the ion trap. The basic fundamentals of LC/MS will be discussed along with a comparison of the utility of an ion trap versus a single quadrupole instrument. Application examples will include the identification of target and unknown compounds in complex matrices, structural elucidation of proteins and the analysis of natural products. Examples of using the LC/MSD Trap for quantitation will be discussed.

**MS, GC/MS, LC/MS Oral Session—Jennifer Smith, Agilent Technologies, 2850 Centerville, Road, Wilmington, DE 19808. Tel: 302-633-8827, Fax: 302-633-8902, E-mail: jennifer\_smith@agilent.com**

- 173.** A PENTAFLUOROPHENYLPROPYL STATIONARY PHASE: A BETTER STATIONARY PHASE FOR THE HPLC/ESI/MS ANALYSIS OF DRUGS WITH BASIC GROUPS. Shane Needham, Alturas Analytics, Inc., 1282 Alturas Drive, Moscow, ID 83843

The use of a pentafluorophenylpropyl (PFPP) stationary phase to provide optimum signal and peak shape for the high performance liquid chromatography/electrospray ionization/mass spectrometry (HPLC/ESI/MS) of basic pharmaceutical compounds is presented. A PFPP stationary phase gives retention factors (*k*) greater than 4 for various basic drugs with the use of 90% acetonitrile mobile phase. The PFPP phase also provides good peak shape (asymmetry factor  $\approx 1$ ) for a variety of basic pharmaceuticals. C18 and other phenyl ring phases require less than 40% acetonitrile in the mobile phase to provide similar retention of the basic drugs. The increased concentration of acetonitrile in the mobile phase with the PFPP stationary phase provides better desolvation in the ESI interface and leads to a >10x increase in the MS signal when compared to a C18 phase. The PFPP phase was successful in the HPLC/ESI/MS analysis of many different classes of basic drugs with the use of one mobile phase composition. The drugs ranged in p*K*<sub>a</sub> (7.2-14.2), polarity and molecular weight (227.7-385.5 Daltons). To demonstrate the broad applicability of the PFPP stationary phase in the pharmaceutical industry, this phase was used for the validation of cocaine and its metabolite, ecgonine methyl ester assay in human urine by HPLC/ESI/MS/MS. The assay was accurate and precise. In addition, due to the better peak shape and use of 90% acetonitrile mobile phase, the limit of detection was 4 times lower than that obtained on a C18 stationary phase which could use only 12% acetonitrile mobile phase to provide a retention factor greater than 4.

**MS, GC/MS, LC/MS Oral Session—Shane Needham, Alturas Analytics, Inc., 1282 Alturas Drive, Moscow, ID 83843, Tel: 208-883-3400, Fax :208-882-9246, E-mail: sneedham@alturasanalytics.com**

- 174.** ION EXCHANGE SOLID-PHASE EXTRACTION METHOD FOR THE DETERMINATION OF ACIDIC AND BASIC DRUG IN RAT PLASMA BY LC/MS/MS. Claude R. Mallet, Waters Corporation, 34 Maple St., Milford, MA 01757-3696

Today, automated LC-MS-MS systems are constantly pushed to their limits. For example, an increasing number of pharmaceuticals are demanding higher throughput and selectivity in drug discovery programs. In response for higher throughput, it is clear that solid phase extraction, in 96-well plate format, has the potential to reach the thousand analyses-a-day barrier. As for selectivity, Cheng and co-worker<sup>1,2</sup> recently introduced a new clean-up procedure for acidic, neutral and basic drugs using Waters Oasis<sup>TM</sup> HLB sorbent. By varying organic strength, pH and number of washes, more interference can be removed from the matrix. If higher selectivity is required, a new type of Oasis<sup>TM</sup> sorbent, the mixed mode cation exchange (MCX) or anion exchange (MAX) provides a second mechanism of retention. With MAX and MCX, basic or acidic drug can be isolated by using the ion exchange or reversed phase mechanism. Also, the retention mechanism can be switched from one mode to the other during the extraction when better clean up conditions are needed. The final elution step consists of a high or low pH in 100 % organic to elute basic or acidic drug respectively. In situations, when a silica base column is used for the analysis, an evaporation and reconstitution steps must be added to the protocol in order to bring the sample in the working pH range of these stationary phase. Recently, Waters introduced the Xterra<sup>TM</sup> column<sup>3</sup>, which combines the advantages of silica and polymer particles. These columns exhibit a wider working pH range (pH 1 to pH 12). Therefore, the final elution can be directly injected, thus shortening the sample preparation time.

1. Y-F Cheng, D.J. Phillips, U.D. Neue, M. Capparella, L.L. Bean, *Am. BioTech* December (1997) 14.

2. Y-F. Cheng, D.J. Phillips, U.D. Neue, L.L. Bean, *J. Liq. Chromatogr.* 20 (1997) 2461

3. U.D. Neue, T.H. Walter, B.A. Alden, Z. Jiang, R. P Fisk, J.T. Cook, K.H. Glose, J.L Carmody, J.M. Grassi, Y-F. Cheng, Z. Lu, R.J. Crowley, *Am. Lab.* November (1999)

**MS, GC/MS, LC/MS Oral Session—Claude R. Mallet Ph.D., Senior Applications Chemist, Waters Corporation, 34 Maple St., Milford, MA 01757-3045. Tel: 508-482-3045, Fax: 508-482-3100, E-mail: claudemallet@waters.com**

- 175.** USING PROTEOMICS TO DISSECT SIGNALING PATHWAYS. Katheryn A. Resing, Timothy Lewis, Lauren Aveline, William Old, Micah Eades, Sonia Martinez, Natalie G.Ahn. Univ. Colorado, Dept. Chem. & Biochem., Boulder CO 80309

Biochemical, molecular biological, and genetic studies have led to a increasingly complex picture of cell signaling mechanisms. However, cell phenotypes are typically assessed by assays of growth rate, cell shape, motility, adhesion, sensitivity to apoptosis, etc. which are difficult to directly or quantitatively connect these functional assays to specific signaling events. More precise ways of delineating changes in signaling processes that are quantifiable and directly related to the underlying signaling status would be useful. Functional proteomics is often proposed as a solution to this problem, because altered expression and/or post-translational modifications in the major proteins underlie the cell's phenotype, and these events are regulated by signaling-dependent transcriptional activation, message stability, and/or modifying enzymes. Thus, the proteome should reflect the signaling status of that cell type. Using the immobilized dry strip method for isoelectric focusing and two-dimensional gel electrophoresis (2D) and in-gel digestion of "spots" followed by identification of the proteins by mass spectrometry, we have analyzed the changes induced in K562 proteome by phorbol ester treatment or constitutively active MAP kinase kinase (MKK). Ninety-one phorbol ester induced changes were identified, almost all of which represented post-translational modifications. A subset of these are MKK responsive. In many cases, substrate/product relationships were identified, and kinetic analysis of these identified several different signaling patterns. Most of these likely represent phosphorylation, and comparison of the results with known phosphorylation events regulated by MKK provides information about the flux of information through this pathway.

**MS, GC/MS, LC/MS Oral Session—Katheryn Resing, University of Colorado, Dept. of Chemistry and Biochemistry, Denver CO 80303. Tel: 303-492-8273, Fax: 303-492-2439, E-mail: resing@stripe.colorado.edu**

- 176.** EVALUATION OF SOLUTION BEHAVIOR OF ERK2 USING DEUTERIUM EXCHANGE MASS SPECTROMETRY. Andrew N. Hoofnagle, Kathryn A. Resing, Elizabeth Goldsmith, and Natalie G. Ahn, Dept of Chemistry and Biochemistry, Univ. Colorado, Boulder, CO 80309, and Dept. of Biochemistry, Univ. Texas Southwestern Medical Center, Dallas, TX 75235.

*Deuterium exchange mass spectrometry (DE/MS) enables measurement of rates of hydrogen-deuterium exchange from protein backbone amides. The polypeptide samples are diluted into D<sub>2</sub>O (to 90%) and incubated for varying times to allow exchange of deuterium for hydrogen. The reaction is quenched with acid and low temperature. The protein is then cleaved with pepsin and the resulting peptides are separated using a reverse phase HPLC column kept on ice to minimize back exchange from polypeptide backbone amide deuterons. This protocol provides information about protein solution conformation and dynamics of large proteins. Previous studies on MAP kinase kinase 1 (MKK1) using DE/MS revealed altered exchange rates in the N-terminal domain upon activation, interpreted as flexibility changes in the ATP binding domain. In the current study, we extend this method of analysis to the MAP kinase, ERK2, comparing inactive unphosphorylated to active diphosphorylated forms. The results show significant differences between MKK1 and ERK2 in the extent of exchange over several hours, revealing a stable core of nonexchanging hydrogens in ERK2 compared to MKK1. Comparison of exchange rates for unphosphorylated vs diphosphorylated ERK2 reveals changes at amides contained within the ATP binding loop, the hinge, helices  $\alpha$ F and  $\alpha$ G, the  $\alpha$ L14 MAP kinase insert, and the activation lip. Analysis of peptides with overlapping sequences allows models for exchange at individual amides to be constructed, and interpreted in relation to the hydrogen bonding environment predicted from X-ray information. Deviations between observed rate behavior and those expected from X-ray conformation pinpoint sites of protein flexibility changes that may be important for kinase activation. Thus, DE/MS provides information about localized protein dynamics complementary to information from X-ray crystallography.*

Supported by NIH grants GM48521, AR39730, and GM08497

**MS, GC/MS, LC/MS Oral Session—Andrew Hoofnagle, University of Colorado at Boulder, Department of Chemistry & Biochemistry, Boulder, CO 80309. Tel: 303-492-7794, Fax: 303-492-2439, E-mail: andrew.hoofnagle@uchsc.edu**

- 177.** PROTEOMICS STUDIES WITH A NOVEL MALDI TIME-OF-FLIGHT TIME- OF -FLIGHT TANDEM MASS SPECTROMETER. Jennifer M. Campbell, Marvin L. Vestal, Kevin M. Hayden, Peter Juhasz. PE Biosystems, 500 Old Connecticut Path, Framingham MA 01701

*A novel tandem mass spectrometer with a MALDI source, the TOF/TOF (See Analytical Chemistry 72, pp. 552—557), has been constructed. This instrument provides an ideal platform for the study of protein identity, as high quality peptide mass maps and MS/MS spectra can be recorded in rapid succession. Several recent design changes have resulted in a substantially improved performance, generating resolutions in the range of 2000-7000, mass accuracy of greater than 100 ppm, and sensitivity in the low femtomole range. Collision induced dissociation in the TOF/TOF is achieved using high energy (i.e., 1 kV) collision energies, leading to rich fragmentation patterns, including strong sequence coverage, charge remote fragments, and abundant low mass (i.e., immonium) ions. Subsequently, TOF/TOF spectra provide a high probability of success in the de novo sequencing of peptides. When the fragment spectra are used with protein databases, protein identity of low levels of samples can be routinely, rapidly, and unambiguously determined. The rich immonium and internal ion region can be used to prefilter potential protein candidates in a "sequence tag" based search. The use of the TOF/TOF for identifying sites of post translation modifications will be demonstrated, as will the use of MALDI, MS/MS with non specific digests.*

**MS, GC/MS, LC/MS Oral Session—Jennifer M. Campbell, PE Biosystems, Framingham, MA 01701. Tel: (508) 383-7926, Fax: (508) 383-7883**

- 178.** IDENTIFICATION OF CHLORINATED DIMETHOXYSTILBENE ISOMERS AND HOMOLOGUES IN BLEACHED PAPER PRODUCTS BY GC/MS. Jeffrey G. McDonald, Ronald A. Hites, Indiana University, School of Public and Environmental Affairs and Department of Chemistry, Bloomington, IN 47405

*We report here the identification of a novel class of compounds, the chlorinated dimethoxystilbenes (pinosylvins), in bleached paper products by GC/MS. Pinosylvins are naturally occurring compounds in wood that deter infections and predators. These compounds are being chlorinated during the pulp bleaching process. Two dichlorinated pinosylvins have previously been identified in bleached paper pulp, but we have identified other isomers and more highly chlorinated homologues in various bleached paper products. These compounds are present at concentrations on the order of 100's of ppb. Based on the mass spectra of synthesized standards, we can distinguish the isomers in which the chlorines are located on the ethylene moiety from those in which the chlorines are located on the aromatic ring with the methoxy groups. In addition, we predicted the chlorine substitution patterns on both rings for these compounds using linear relationships between retention indexes and calculated dipole moments. The toxicity of these compounds is not known; however, isomers related to the pesticide methoxychlor are pro-estrogenic.*

**MS, GC/MS, LC/MS Oral Session—Jeff McDonald, Indiana University, Geology 541, Bloomington, IN 47405. Tel: 812-855-8486, Fax: 812-855-1881, E-mail: jemcdona@indiana.edu**

- 179.** USE OF MOLECULAR BEAM MASS SPECTROMETRY TO ASSESS CATALYST PERFORMANCE IN THE STEAM REFORMING OF BIO-OIL. Richard J. French, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401; Lucía Garcia, Chemical and Environmental Engineering Department, University of Zaragoza, 50009 Zaragoza, Spain; Stefan Czernik, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401; Esteban Chornet, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401.

*Catalytic steam reforming of condensable vapors (i.e. bio-oils) derived from pyrolysis of biomass is a technically viable process for hydrogen pro-*

duction. In this study the aqueous fraction of bio-oil, generated from fast pyrolysis, was catalytically steam reformed at 825 and 875°C, high space velocity (up to 126,000 h<sup>-1</sup>) and low residence time (26 ms). Using a fixed-bed micro-reactor interfaced with a molecular-beam mass-spectrometer (MBMS). This provided a relatively short test in which changes to the full slate of products could be monitored. A variety of research and commercial nickel-based catalysts were tested. The cobalt-promoted nickel and chromium-promoted nickel supported on MgO-La<sub>2</sub>O<sub>3</sub>-alpha-alumina catalysts showed the best results of the research catalysts. At the reaction conditions used progressive catalyst deactivation was observed leading to a decrease in the yields of hydrogen and carbon dioxide and an increase in carbon monoxide. The loss of activity also resulted in the formation of higher amounts of methane, benzene and other aromatic compounds. Commercial steam-reforming catalysts proved to be more efficient for hydrogen production from bio-oil than most of the research catalysts mainly due to the higher water-gas shift activity. Supported by the U.S. DOE Hydrogen Program and the Secretaría de Estado de Universidades, Investigación y Desarrollo (Spain).

**MS, GC/MS, LC/MS Oral Session—Shane Needham, Alturas Analytics, Inc., 1282 Alturas Drive, Moscow, ID 83843, Tel: 208-883-3400, Fax :208-882-9246, E-mail: sneedham@alturasanalytics.com**

- 180.** SURFACE ENHANCED RAMAN IMMUNOASSAY (SERIA): MEASUREMENT OF PHARMACEUTICALS AND DISEASES. Jason Guicheteau, Roberta Sulk, Keith Carron, Robert Corcoran, University of Wyoming, Department of Chemistry, Laramie WY 82071-3838

Surface Enhanced Raman scattering (SERS) spectroscopy offers a unique approach to immunoassays through its highly localized enhancement of materials at the surface of the metal substrate. The localized enhancement allows us to perform sandwich or competitive assays in the presence of normally interfering species. In particular we are able to perform assays in the presence of excess reporters since only those bound directly to the antibody/antigen complex will be observed in the SERS spectrum. The aspect of our approach is very important as it eliminates the washing steps that introduce error and spread biohazardous waste in conventional immunoassays. We will discuss the instrumentation involved in the SERIA measurements and the methodologies. Appropriate dyes for tagging antibodies will be presented. Partial Least Squares (PLS) techniques were used for data quantization. Particular systems that will be discussed are human growth hormone, thyroid stimulating hormone, pesticides, illicit drugs, and prion diseases.

**MS, GC/MS, LC/MS Oral Session—Keith Carron, University of Wyoming, Department of Chemistry, Laramie, WY 82071-3838. Tel: 307 766-2811, Fax: 307 766-2807, E-mail: carron@uwyo.edu**

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## MS, GC/MS, LC/MS Poster Sessions

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- 181.** BIOCHEMICAL INVESTIGATION OF A SEQUENCE-SPECIFIC, SINGLE-STRANDED DNA BINDING PROTEIN AT THE TELOMERE. E.M. Anderson<sup>1</sup>, R.M. Mitton-Fry<sup>1</sup>, T.R. Hughes<sup>2</sup>, V. Lundblad<sup>2</sup>, D.S. Wuttke<sup>1</sup>, <sup>1</sup>Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309 and <sup>2</sup>Dept. of Molecular and Human Genetics, Baylor College of Medicine, Houston, TX, 77030

Telomeres are the nucleoprotein structures that protect the ends of eukaryotic chromosomes. Telomere length regulation is controlled by the replicative enzyme, telomerase, and a suite of telomere binding proteins. Anomalous telomeric replication and regulation are implicated in many forms of cancer, while telomeric shortening contributes to cellular aging. Cdc13p is an essential protein from *S. cerevisiae* that binds to the single-stranded ends of telomeres with high specificity and affinity. Genetically, Cdc13p has been shown to protect the end of the chromosome from degradation and to load telomerase. Biochemically, Cdc13p binds yeast single-stranded telomeric DNA (sstelo DNA) in vitro with high affinity (K<sub>d</sub>=0.3 nM). We are investigating the structural basis for high affinity binding and sequence specificity of the single-stranded DNA binding domain. We have expressed and purified the isolated ssDNA binding domain in high yield. Its binding affinity and specificity have been examined with libraries of sstelo DNA randomized at each position. In vitro photocrosslinking experiments have been performed using 5-iodouracil substituted for various thymines. Trypsin digestion of the crosslinked products along with micro peptide sequencing and MALDI mass spectrometry have allowed us to identify sites in the protein critical for sstelo DNA binding. These experiments complement high resolution NMR studies of the protein/DNA complex in progress in our laboratory.

**MS, GC/MS, LC/MS Poster Session—Emily Anderson, Dept. of Chemistry and Biochemistry, University of Colorado at Boulder, Campus Box 215, Boulder, CO, 80309-0215. Tel: (303) 492-2369, Fax: (303) 492-5894, E-mail: Emily.Anderson@colorado.edu**

- 182.** HIGH THROUGHPUT ANALYSIS OF COMBINATORIAL LIBRARIES BY FIA AND LC\MS ANALYSIS. Meg Hermann, Kathy Halm, Kevin Ash, Adam Cook, Mark Munson, Alan Florjancic, Gary Hingorani; Conrad Hummel; Greg Miknis; John Josey, Array BioPharma Inc., 1885 33rd Street, Boulder, CO 80301

Traditional sequential medicinal chemistry methods have been augmented by combinatorial synthesis methods yielding a higher number of compounds for high throughput screening against a disease targets and consequently a greater number of compounds that need to be analyzed. Initially, the analysis of compounds was accomplished by flow injection mass spectrometry of all wells in a 96-well plate. A well was passed or failed based on the presence of the molecular ion with at least 25% base peak intensity. In trying to coordinate library information with the RP-HPLC/UV purity data it became obvious that having LC/UV/MS data on libraries was crucial. Therefore, LC/UV/MS analysis was performed on the same wells that were being analyzed in parallel by RP-HPLC/UV for purity. The sampling protocol for purity determination at Array BioPharma is three columns per plate. This work was performed using a Gilson 215 autosampler with a TSP 4000 pump and TSP 2000



UV detector coupled with a Finnigan LCQ ion trap mass spectrometer. The column used was a 2.0 by 50mm Waters YMC-Pack™ ODS-AQ™ with 3-micron particle size. Samples were run FIA or LC/UV/MS in an automated manner.

**MS, GC/MS, LC/MS Poster Session—Meg Hermann, Array BioPharma, 1885 33rd Street, Boulder, CO 80301. Tel: 303-381-6628, Fax: 303-449-5376, E-mail: mhermann@arraybiopharma.com**

- 183.** IDENTIFICATION OF PROTEINS ASSOCIATED WITH THE YEAST PAF1P/RNA POLYMERASE II COMPLEX USING MASS SPECTROMETRY. Cherie L. Mueller, University of Colorado–Health Sciences Center, Department of Biochemistry and Molecular Genetics, 4200 E. 9th Ave, Denver, CO 80262; Judith A. Jaehning, University of Colorado–Health Sciences Center, Department of Biochemistry and Molecular Genetics, Denver, CO 80262

Our laboratory has identified an RNA polymerase II complex distinct from the Srbp-Medp containing holoenzyme. This complex contains the general transcription factors TFIIF and TFIIB, Gal11p and Sin4p and several novel proteins including Paf1p, Cdc73p, Hpr1p and Ccr4p. The Paf1p complex is involved in the expression of subsets of yeast genes including some of those involved in cell wall biosynthesis controlled by the protein kinase C/MAP kinase pathway. To learn more about the composition of the Paf1p complex and its role in yeast cells we have used ion-exchange, affinity and gel filtration chromatography to purify proteins associated with GST-tagged Cdc73p. The tagged protein copurifies with complexes of 1.7 and 0.5 MDa both of which contain Paf1p. Using the technique of mass spectrometry we have confirmed the presence of Rpb1, Sin4p, and Hpr1p in the 1.7 MDa Paf1p complex. We have also identified potential new components of the alternative RNA polymerase II complex. We will present the current composition of the Paf1p complex based on mass spectrometry analysis of the additional factors that copurify with Cdc73p and Paf1p.

**MS, GC/MS, LC/MS Poster Session—Cherie Mueller, University of Colorado-Health Sciences Center, Biochemistry, BRB452, 4200 E. 9th Avenue, Denver, CO 80262. Tel: 303-315-7927, Fax: 303-315-3326, E-mail: cherie.mueller@uchsc.edu**

- 184.** IDENTIFICATION OF ERIOGLAUCINE (BRILLIANT BLUE) AS A WASTEWATER MARKER BY LIQUID CHROMATOGRAPHY/ELECTROSPRAY MASS SPECTROMETRY. Colleen E. Rostad and Jerry A. Leenheer, U.S. Geological Survey, Building 95, Mail Stop 408, Denver Federal Center, Denver, CO 80225 USA

A distinctive characteristic blue color was isolated from tertiary treated wastewater by adsorption at neutral pH on XAD-8 resin in the hydrophobic neutral fraction. The blue color remained after isolation on XAD-8 resin, purification by ion-pair extraction of the tetrabutyl ammonium salt into chloroform, fractionation of this salt by normal phase chromatography on silica gel, and conversion by anion exchange to the sodium form. This wastewater extract was analyzed by flow injection analysis, using 25/75 water/methanol as the mobile phase, with positive and negative electrospray ionization and quadrupole mass spectrometry and for ultraviolet absorbance maxima. Extracts were then separated by reverse-phase liquid chromatography (water/methanol gradient) on an octadecylsilyl column. Negative ion spectra were much simpler than positive ion spectra for these complex wastewater extracts. A series of ions from alkyl phenol ethoxylate carboxylates were present (confirmed with standards) along with other ions. Standards for several fluorescent whitening agents were analyzed under similar conditions. None of the characteristic ions for these compounds were present in the sample spectra. Other widely used fluorescent whitening agents were considered. Possibilities were narrowed based on the ultraviolet spectra, which maximized at 279 and 625 nm. Standards for several coloring agents, as their sodium salts, were selected for analysis based on their UV spectra. In negative ion electrospray, sodium was lost from the standards of fluorescent whitening agents and coloring agents, resulting in strong negative ions, including  $[M-2Na]^{-2}$ ,  $[M-2Na]^{-}$  and  $[M-Na]^{-}$ . Liquid chromatographic separation allowed for identification of mass peaks characteristic of erioglaucine (Brilliant Blue, FD&C Blue No. 1), with the  $[M-2Na]^{-2}$  at 373 m/z and  $[M-Na]^{-}$  at 769 m/z. Identification was confirmed by matching retention time and mass spectra with the authentic standard.

**MS, GC/MS, LC/MS Poster Session—Colleen E. Rostad, U.S. Geological Survey, Building 95, Mail Stop 408, Denver Federal Center, Denver, CO 80225, USA. Tel: 303-236-3971, Fax: 303-236-3934, E-mail: cerostad@usgs.gov**

- 185.** FULLY AUTOMATED PROTEIN/PEPTIDE CHARACTERIZATION AT THE ONE DIGIT FEMTOMOL LEVEL. Jean-Pierre Salzmann, Jean-Pierre Chervet, Hans Vissers, LC Packings (Inc.), 80 Carolina Street, San Francisco, CA, 94103, USA

The analysis of small quantities of protein is of utmost importance in the rapidly growing field of proteomics. The term proteomics involves the study of proteins that are expressed by a genome and it has become an indispensable part of many drug discovery programs. In a practical sense proteomics allows for the determination of: (i) when and where the final gene products (proteins) are translated, (ii) the relative concentration of the proteins, (iii) the type and extent of post-translational modifications and (iv) the phenotype of multigenic phenomena. The current recognized approach in the identification of complete protein maps combines several techniques, including two-dimensional (2-D) gel electrophoresis, image analysis of the 2-D gels with subsequent identification and extraction of potential targets, and identification of the target proteins by mass spectrometry.

Although 2-D gel electrophoresis is able to generate reproducible protein expression patterns, there is still the remaining problem of identifying several thousands proteins. Mapping and sequencing of proteins after in-gel digestion and extraction can be performed either by means of matrix-assisted laser-desorption-ionization time-of-flight mass spectrometry (MALDI-TOF/MS) or on-line liquid chromatography/ electrospray ionization-mass spectrometry (LC/ESI-MS). MALDI is mainly used for high throughput screening of known peptides or simple peptide mixtures, where LC in conjunction with ESI tandem mass spectrometry is the preferred technique in terms of "de-novo sequencing", or in case of complex peptide mixtures that cannot be easily identified by way of data-base searching.



Peptides that are generated after tryptic in-gel digestion of the proteins are often in the low femtomol range, which places high demands on analytical procedures. In order to analyze these minute sample amounts, smaller inner diameter (I.D.) LC columns—such as capillary and nanoscale LC columns—have been implemented. The increased sensitivity of smaller I.D. LC columns is a result of the reduced chromatographic dilution, leading to lower achievable limits of detection. In addition, the coupling of capillary and nanoscale LC columns to a mass spectrometer provides better compatibility compared to conventional column LC/MS because of the strongly reduced column flow-rates.

In this lecture, a dedicated Nano LC system will be presented for fully automated sequencing utilizing nanoscale LC-NanoSpray/MS/MS. Sample preparation, separation and introduction to a mass spectrometer of small sample quantities (1 fmol level) can be performed fully automated on a routine basis with high sample throughput. In addition special features such as peak parking to allow for increased MS/MS acquisition time as well as nanospray interface requirements will be discussed.

**MS, GC/MS, LC/MS Poster Session—Jean-Pierre Salzmann, LC Packings (Inc.), 80 Carolina Street, San Francisco, CA, 94103, USA**

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## NMR Oral Sessions

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- 186.** PEPTIDE STRUCTURE DETERMINATION WITH HIGH FIELD DIPOLAR RECOUPLING. C.M. Rienstra, M. Hohwy, L.J. Mueller, C.P. Jaroniec, B. Reif, M. Hong, M. Baldus, J. Lansing, and R.G. Griffin, Francis Bitter Magnet Lab and Dept of Chemistry, MIT, Cambridge, MA 02139

One of the principal promises of dipolar recoupling during MAS is the possibility of determining the structure of peptides and proteins in solid and membrane environments. We discuss a series of 2D and 3D hetero- and homonuclear experiments involving spectral assignments and distance and torsion angle measurements aimed at accomplishing this goal. The experiments are applied to tripeptides and proteins to full and partially constrain their structure.

**NMR Symposium Oral Session—R.G. Griffin, MIT, Cambridge, MA Tel: 617-253-5597, Fax: 617-253-5405, E-mail: rgg@mit.edu**

- 187.** STRUCTURAL DETERMINATIONS BY SOLID-STATE NMR. K. Takegoshi, Kyoto University, Department of Chemistry, Graduate School of Science, Kyoto 606-8502, Japan

With the aim of applying mainly to biological molecules, several methods for dipolar recoupling under magic-angle spinning (MAS) have been developed. While the non-selective measurements of dipolar couplings by broadband recoupling methods do not currently provide any quantitative structural information, selective measurements are practical and useful for obtaining local geometrical structures. I will discuss the application of selective  $^{13}\text{C}$ - $^{13}\text{C}$  recoupling experiments (R2TR<sup>1</sup>) under MAS to determine the three-dimensional (3D) structure of uniformly  $^{13}\text{C}$ ,  $^{15}\text{N}$ -labeled glycylisoleucine.<sup>2</sup> The R2TR approach does not assume applications to peptide main chains, thus being applicable to side chains and also to general organic molecules. This method allows us to determine one dihedral angle by one R2TR experiment in a uniformly labeled sample, but if we limit a problem to determination of dihedral angles in a peptide main-chain, more efficient experiments can be developed. A recently proposed  $^{13}\text{C}$ - $^1\text{H}$  recoupling sequence operative under fast MAS<sup>3</sup> is applied to observe  $^{13}\text{C}$ - $^1\text{H}$  and  $^{15}\text{N}$ - $^1\text{H}$  dipolar powder patterns in the  $^1\text{H}$ - $^{15}\text{N}$ - $^{13}\text{C}$ - $^1\text{H}$  system of a peptide bond. Both patterns are correlated by  $^{15}\text{N}$ -to- $^{13}\text{C}$  cross polarization to observe one- or two-dimensional (1 or 2D) correlation spectra, which can be simulated by using a simple analytical expression to determine the H-N-C-H dihedral angle.<sup>4</sup> Further, several applications of modulatory resonance<sup>5</sup> to recouple  $^{15}\text{N}$ - $^{13}\text{C}$ ,  $^{14}\text{N}$ - $^{13}\text{C}$ , and  $^{13}\text{C}$ - $^{13}\text{C}$  will be discussed.

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4. K. Takegoshi et al. *Solid State Nucl. Magn. Reson.* in press.
5. K. Takegoshi et al. *Chem. Phys. Lett.*, 260, 331 (1996); *Chem. Phys. Lett.*, 307, 295-302 (1999).

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- 188.** THROUGH-BOND HETERONUCLEAR CORRELATION SPECTROSCOPY IN ROTATING SOLIDS. Anne Lesage, Patrick Charmont, Sabine Hediger, Dimitri Sakellariou, Lyndon Emsley; Ecole Normale Supérieure de Lyon, Lyon, France 69364.

We recently introduced a new approach to obtaining high-resolution through-bond heteronuclear correlation spectra in ordinary organic solids using scalar proton - carbon-13 (or nitrogen-15) couplings under magic angle spinning (the MAS-J-HMQC experiment). Scalar couplings constitute an interesting alternative to dipolar couplings since they provide through-bond correlations, and since they are not modulated by MAS or molecular motion. Like in liquid-state NMR, several alternative pulse sequences can be derived, i.e., MAS-J-HMQC or MAS-J-HSQC, to obtain

heteronuclear through-bond correlations in powdered samples. We evaluate each approach in terms of artifacts and proton resolution. Second, we show that the observation of multiple-bond correlations through two- or three-bond J couplings is feasible, which constitutes an important step towards the assignment of complex MAS spectra. By combining various MAS-J-HMQC experiments, we report the complete proton, carbon-13 and nitrogen-15 assignment of MAS NMR spectra of a natural abundance tripeptide. Finally, we show that through-bond correlation experiments are practicable on disordered solids. We have developed a one-bond wideline correlation spectroscopy for rotating solids. This new technique is applied to the analysis of hydration effects in the wideline proton spectra of complex carbohydrate systems.

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- 189.** SOLIDS NMR OF UNIFORMLY LABELED MACROMOLECULES AT HIGH FIELDS. Kurt W. Zilm, Rachel Wagner, Eric Paulson, James Hartling, George Coker, John Gehman and Xiaoling Wu, Yale University, Department of Chemistry, P.O. Box 208107, New Haven, CT 06520-8107.

Solids NMR is well suited for the study of several important classes of problems in chemical biology and drug design, providing information complimentary to that obtained by solution NMR or X-ray crystallography. In order to be generally competitive with these more traditional and widely accepted techniques, solids NMR methods must be readily applicable to samples containing less than 1 micromole of protein or ligand. In typical cases this translates to 1 to 10 mg contained in a sample volume of less than 10 microliters. This talk will describe the ongoing development of variable temperature triple resonance solids NMR instrumentation at 800 MHz in our laboratory for such applications. Issues in probe design and performance specific to 800 MHz operation will be discussed. Since spin rates in excess of 19 kHz are required at this field strength, achieving efficient  $^{13}\text{C}$ - $^{13}\text{C}$  and  $^{13}\text{C}$ - $^{15}\text{N}$  magnetization transfer at high spinning speeds is very important for obtaining optimal sensitivity in 2D and 3D solids NMR experiments needed for macromolecular spectral assignment. Comparisons of several approaches to these problems will be presented, as well as methods for utilizing  $^1\text{H}$ - $^1\text{H}$  dipolar couplings in establishing connectivity and distance constraints in solids.

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- 190.** ORGANIC REACTIONS IN ZEOLITES: DETERMINING THE ROLE OF CATION BINDING IN ASYMMETRIC CATALYSIS. John P. Osego and Clare P. Grey, Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400; V. Ramamurthy, Department of Chemistry, Tulane University, New Orleans, LA 70118.

The reaction of alkenes with singlet oxygen to produce hydroperoxides, the 'ene' or Schenk reaction, results in a 1:1 ratio of singlet to tertiary hydroperoxides when performed in solution. However, when the reaction is performed in the pores of alkaline earth cation exchanged Y-type zeolites, the primary product is the secondary hydroperoxide.<sup>1</sup> The conformational selectivity provided by the zeolite is thought to be the source for this selectivity. One and two-dimensional solid state NMR techniques have been performed to help understand the role of the cation in the binding and selective reactivity of a phenyl substituted alkene in NaY (Si/Al = 2.6). The population of sodium cation positions within the supercage upon adsorption of the substrate and the presence or absence of specific binding of the cation to the aromatic ring and the alkene moiety has been determined from  $^1\text{H}$ → $^{23}\text{Na}$  CP and HETCOR. The high-resolution proton spectra of the adsorbed molecule, obtained from Lee-Goldburg decoupled HETCOR experiments, will be presented. These results will be correlated with the motional behavior of the substrate as determined from 2H MAS NMR.

1. Rebecca J. Robbins and V. Ramamurthy Chem. Comm., 1997, 1071-1072.

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- 191.** MODERN SOLID STATE NMR METHODS IN CATALYSIS SCIENCE. Subramanian Ganapathy, Solid State NMR Group, National Chemical Laboratory, Pune 411 008, India

Two major areas of research in catalysis science are the synthesis of novel materials and their detailed characterization at the molecular level. The intricate relationship between the catalytic performance and the structural characteristics brings in new challenges in the development of analytical techniques. In our laboratory, there has been a continuing effort to introduce modern solid state NMR methods for a more effective characterization of catalytically important materials. We have addressed the problem of isomorphous heteroatom substitution and T-site ordering in the zeolite framework by monitoring and studying the disruption of tetrahedral symmetry through experimental determination and theoretical quantum chemical calculations of  $^{29}\text{Si}$  shielding tensors. We have used  $^{23}\text{Na}$  MQ-MAS and  $^{29}\text{Si}$ - $^{23}\text{Na}$  REAPDOR experiments and cation modeling to study the cation site distribution and location in molecular sieves. This is demonstrated in the novel titanosilicate ETS-10. We have employed MQ- $\tau$  REDOR in  $^{27}\text{Al}$ - $^{31}\text{P}$  and  $^{27}\text{Al}$ - $^1\text{H}$  double resonance experiments to provide structural characterization of framework T-sites and acidic proton sites in molecular sieves. In heteropolyacids (HPA's), which are solid acids that have broad applications in catalysis, we have used  $^1\text{H}$ - $^{31}\text{P}$ / $^1\text{H}$  REDOR NMR, aided by Density Functional Theory (DFT) quantum chemical calculations, to determine the proton locations within the primary structure building and thermally stable Keggin unit of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ .

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- 192.** DISPERSION CHEMICAL SHIFTS IN SOLID SOLUTIONS. Gerard S. Harbison, University of Nebraska at Lincoln, 508 Hamilton Hall, UNL, Lincoln, NE 68588-0304

The  $^{87}\text{Rb}$ ,  $^{133}\text{Cs}$  and  $^{207}\text{Pb}$  NMR spectra of ionic solid solutions display shifts which arise from the replacement of the cationic nearest neighbors by ions of different polarizability. In favorable cases, complex spectra are obtained in which resolved signals can be observed from nuclei with each possible combination of like and unlike neighbors. The origin of these shifts apparently lies in dispersion effects.<sup>1</sup> Polarizable ions have transient electric dipole moments, and while the field from these ions time-averages to zero, the squared field does not. Thus, terms of the form  $B_1\langle E^2 \rangle$  contribute to the chemical shift. The magnitude of  $B_1$  (the shielding hyperpolarizability) has been determined empirically for  $^{207}\text{Pb}^{2+}$ ,  $^{133}\text{Cs}^+$  and  $^{87}\text{Rb}^+$ ; as might be expected, it depends strongly on atomic number. The dispersion shift is proportional to the polarizability difference between neighboring ions, and to the inverse sixth power of the distance between them. This effect allows us to quantitate not just the intensities of the resolved signals from ionic solid solutions (which allows us to determine ion clustering) but also to interpret their chemical shifts.

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- 193.** RELAXATION OF  $^{207}\text{Pb}$  IN SOLID LEAD SALTS. Peter Beckmann, Bryn Mawr College, Department of Physics, Bryn Mawr, PA 19010-2899; Cecil Dybowski, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716-2522; John Grutzner, Purdue University, Department of Chemistry, West Lafayette, IN 47907-1393; Mike Lumsden, Dalhousie University, Department of Chemistry, Halifax, NS, Canada B3H 4J3; Kevin Stewart, Purdue University, Department of Chemistry, West Lafayette, IN 47907-1393; Rod Wasylshen, Dalhousie University, Department of Chemistry, Halifax, NS, Canada B3H 4J3.

$T_1$  Relaxation times in ionic lead solids are commonly found to be of the order of seconds. None of the standard relaxation paths (dipole-dipole, CSA, paramagnetic impurities) can account for these unusually short values in "rigid" solids. A novel Raman scattering mechanism is being developed. Experimental data on the field and temperature dependence of relaxation in lead nitrate will be presented as a test of the proposed mechanism. Application of the model to other salts and other high Z nuclei will be discussed.

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- 194.** ELECTRONIC STRUCTURES AND GAS ADSORPTION IN SINGLE-WALLED CARBON NANOTUBES STUDIED BY NMR. X.-P. Tang, A. Kleinhammes, H. Shimoda, L. Fleming, K. Y. Bennoune, S. Sinha, C. Bower, O. Zhou, Y. Wu, Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255

A single-walled carbon nanotube (SWNT) can be either metallic or semiconducting depending on its diameter and chirality. Here we report a preliminary NMR study of SWNTs.<sup>1</sup> The  $^{13}\text{C}$  powder pattern of SWNTs is characteristic of aromatic carbons with an isotropic shift at 120 ppm in agreement with MAS spectra. In all the samples studied two types of SWNTs are observed with very different  $T_1$ . The fast-relaxing component is attributed to metallic tubes and the slow-relaxing component is attributed to semiconducting tubes. The measured  $1/T_1$  of the fast-relaxing component is proportional to  $T$  as expected for metallic systems. Assuming a relaxation mechanism via dipolar coupling with electron spins, the density of states at the Fermi level  $g(E_F)$  can be calculated based on  $T_1$  measurements. Such  $g(E_F)$  value agrees very well with the theoretical prediction. It was found that exposure of SWNTs to various gases has a dramatic effect on  $T_1$ . This is true for oxygen as expected from the paramagnetic nature of  $\text{O}_2$ . This is also true for He as such small atoms could diffuse into the interstitial sites of SWNT bundles. Transport measurements, such as electrical conductivity, also revealed a dramatic effect upon exposure to gases. This study has an important implication to the future application of SWNTs as electronic materials. Finally, we'll report  $^1\text{H}$  NMR study of hydrogen adsorption in SWNTs related to the issue of  $\text{H}_2$  storage. This work is supported by ONR-MURI and NSF.

1. X. -P. Tang et al. Science 288, 492, 2000, in press.

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- 195.** NMR STUDIES OF PLATINUM ELECTROCATALYSTS. Eric Oldfield, YuYe Tong; Cynthia Rice; Andrezej Wieckowski, University of Illinois at Urbana-Champaign, Department of Chemistry, 600 South Mathews Avenue, Urbana, IL 61801-3364

I will describe our recent progress in investigating the structure and function of platinum catalysts, used primarily in fuel cell applications, using  $^{195}\text{Pt}$  and  $^{13}\text{C}$  NMR. Topics to be covered may include: correlations between  $^{195}\text{Pt}$ ,  $^{13}\text{C}$  NMR and IR spectroscopy; observation of  $^{195}\text{Pt}$  NMR surface shifts with different adsorbates, and correlations with adsorbate electronegativity; Friedel-Heine invariance; oscillations in the Ruderman-Kittel-Kasuya-Yosida coupling; diffusion in a parabolic magnetic field; and how Ru enhances CO tolerance in Pt catalysts.  $^{195}\text{Pt}$  and  $^{13}\text{C}$  NMR offer detailed new insights into catalyst electronic structure, in both conventional and electrochemical environments which are not otherwise readily available, and help solve problems such as the origins of the Stark tuning effect, seen in IR spectroscopy, which will also be described.

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- 196.** SOLID-STATE REDOR NMR INVESTIGATION OF THE ACTIVE SITE OF KDO8P SYNTHASE. Lilia Kaustov, Shifi Kababya, Schoucheng Du, Timor Baasov, Sara Grooper,<sup>1</sup> Yuval Shoham,<sup>1</sup> and Asher Schmidt, Technion – Israel Institute of Technology, Department of Chemistry and Department of Food Engineering & Biotechnology<sup>1</sup>, Haifa, Israel 32000

Solid state NMR is employed to identify the active site of 3-deoxy-D-manno-2-oxulosonate-8-phosphate synthase (KDO8PS). This enzyme, being vital for the biosynthesis of lipopolysaccharides in Gram negative bacteria, is an attractive target for the development of selective antibacterial drugs. Today, neither its crystal structure nor its enzymatic mechanism are known, and therefore rational drug design, the underlying goal of this study, is impaired. Identification of active site residues of KDO8PS is accomplished by applying rotational-echo double-resonance (REDOR) solid-state NMR experiments to lyophilized binary complexes of uniformly <sup>15</sup>N-labeled KDO8PS with each of its two natural substrates. Its complex with a mechanism-based bisubstrate inhibitor, the most potent known to date ( $K_i = 0.4 \mu\text{M}$ ), is studied as well and its binding is compared to that of the natural substrates. <sup>15</sup>N[<sup>31</sup>P] REDOR NMR data show that phosphoenolpyruvate, the first substrate in a sequentially ordered mechanism, is bound by KDO8PS via a structurally and chemically unique set of lysine and arginine residues. A different set of lysine and arginine residues is found to bind arabinose-5-phosphate (ASP, the second substrate), implying that these two sets of enzyme residues correspond to two (adjacent) subsites capable of independent and sufficiently strong binding. REDOR NMR data of the enzyme-inhibitor complex suggest that the inhibitor can be best characterized as an ASP-based substrate-analogue inhibitor of KDO8PS. Four out of five point mutations of highly conserved arginine residues that were prepared in view of the NMR results showed substantial inactivation. While the above results provide the first direct structural and chemical evidence on KDO8PS active site, current work focuses also on the elucidation of its mechanism.

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- 197.** SOLID-STATE NMR DISTANCE MEASUREMENTS PROBE MECHANISMS OF TRANSMEMBRANE SIGNALING IN BACTERIAL CHEMOTAXIS RECEPTORS. Owen J. Murphy III, Frank A. Kovacs, Binu James, Yael S. Balazs, Jesse Charette, Erin Sicard, and Lynmarie K. Thompson, Department of Chemistry, LGRT 701, University of Massachusetts, Amherst, MA 01003-4510

The bacterial chemotaxis receptor family is thought to undergo a ligand-induced conformational change during signaling; based on crystal structures of soluble receptor fragments, it has been proposed that ligand-binding induces either a piston motion of one helix<sup>1</sup> or a pivot motion across the dimer interface.<sup>2</sup> We are using site-directed solid-state NMR distance measurements in the intact, membrane-bound serine receptor to map local structure in the ligand-free and ligand-bound signaling states. <sup>13</sup>C-observed, <sup>19</sup>F-dephased REDOR measurements have detected a ligand-induced change in the distance between the  $\alpha 1$  and  $\alpha 4$  helices of the periplasmic domain: the p-<sup>19</sup>F-Phe163 to <sup>13</sup>CO-Cys56 distance changes from  $5.8 \pm 0.1$  to  $6.8 \pm 0.1$  Å. In contrast, the <sup>19</sup>F-Phe163 to <sup>13</sup>CO-Cys164 distance is unchanged, indicating that the measured 1 Å distance change is due to a ligand-induced motion of the backbone and not of the Phe side chain. Additional interhelical distance measurements to p-<sup>19</sup>F-Phe163 are in progress in order to discriminate the type of helical motion which occurs upon ligand binding. Site-directed rotational resonance is being used in a similar fashion to measure interhelical distances in the transmembrane domain, in order to follow propagation of the signal. The ability of these solid-state NMR techniques to provide high-resolution distance measurements is the unique contribution of this approach. Thus we are involved in efforts to improve the reliability<sup>3</sup> and to quantify the precision of the measurements. The distance constraints measured in intact, membrane-bound bacterial chemoreceptors should yield a picture of the ligand-induced structural change which occurs in the native signaling system. This research was supported by U.S. Public Health Service Grant GM47601, an award from Research Corporation, and a National Science Foundation Young Investigator Award to L.K.T.

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- 198.** SOLID-STATE NMR STUDIES OF ALZHEIMER'S  $\beta$ -AMYLOID FIBRIL STRUCTURE. John J. Balbach, National Institutes of Health, 9000 Rockville Pike, Bldg. 5 Room B2-27, Bethesda, MD 20892-0505, USA; Robert Tycko, National Institutes of Health, 9000 Rockville Pike, Bldg. 5 Room 112, Bethesda, MD 20892, USA; Oleg N. Antzutkin, Division of Inorganic Chemistry, Luleå University of Technology, S-971 87 Luleå, Sweden

Solid state NMR is ideally suited to analyze the structure of amyloid fibrils, which have very low solubility and as fibrils are noncrystalline. We have applied multiple-quantum <sup>13</sup>C NMR techniques to the fibrils formed by the full-length (40-residue)  $\beta$ -amyloid peptide of Alzheimer's disease and also to smaller fragments of that full-length peptide, including a seven-residue fragment. Our data show that the fibrils of the full-length peptide are formed by parallel, in-register  $\beta$ -sheets. The seven-residue fragment of the full-length peptide also fibrillizes, but appears instead to be in an antiparallel configuration. We are continuing this study with REDOR measurements.

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- 199.** 3D MOTIF OF ALZHEIMER'S  $\beta$ -AMYLOID FIBRILS. Tammie L. S. Benzinger, David M. Gregory<sup>1</sup>, Timothy S. Burkoth, Hélène Miller-Auer, David G. Lynn, Stephen C. Meredith and Robert E. Botto<sup>1</sup>, <sup>1</sup>Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, and the Departments of Pathology and Chemistry, The University of Chicago, Chicago, Illinois 60637

$\beta$ -Amyloid (Ab) peptides are the main protein component of the pathognomonic plaques found in the brains of patients with Alzheimer's disease. These heterogeneous peptides adopt a highly organized fibril structure both in vivo and in vitro. We have used solid-state NMR on stable, homogeneous fibrils of Ab<sub>10-35</sub>. Specific interpeptide distance constraints are determined with dipolar recoupling NMR on fibrils prepared from a series of singly labeled peptides containing <sup>13</sup>C-carbonyl-enriched amino acids, and skipping no more than three residues in the sequence. From these studies, we demonstrate that the peptide adopts the structure of an extended parallel  $\beta$ -sheet in-register at pH 7.4. Analysis of DRAWS data indicates interstrand distances of  $5.3 \pm 0.3$  Å (mean  $\pm$  standard deviation) throughout the entire length of the peptide. Intrastrand NMR constraints, obtained from peptides containing labels at two adjacent amino acids, confirm these findings. Using peptides with <sup>13</sup>C incorporated at the carbonyl position of adjacent amino acids, structural transitions from  $\alpha$ -helix to  $\beta$ -sheet were observed at residues 19 and 20, but using similar techniques, no evidence for a turn could be found in the putative turn region comprising residues 25-29. Implications of this extended parallel organization for Ab<sub>10-35</sub> for overall fibril formation, stability, local disorder, and morphology based upon specific amino acid contacts will be discussed.

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

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- 200.** SOLID-STATE NMR EVIDENCE FOR A PREDOMINANT  $\beta$  SHEET CONFORMATION OF THE MEMBRANE-BOUND HIV-1 FUSION PEPTIDE. Jun Yang, Charles M. Gabrys and David P. Weliky, Department of Chemistry, Michigan State University, East Lansing, MI 48824.

Fusion peptides representing the 23 N-terminal residues of the HIV-1 envelope protein gp41 were synthesized and structurally characterized with MAS solid state NMR. For the HIV-1 virus, this sequence is critical for viral fusion with target host cells. The free fusion peptide also induces fusion of liposomes and erythrocytes and the site-directed mutagenesis/fusion activity relationship of the free peptide is comparable to that of the intact virus. Measurements were made on the Val-2, Phe-8, Phe-11, Ala-15, and Ala-21 residues of the membrane-bound fusion peptide. 2-3 ppm linewidths of the <sup>13</sup>C carbonyls of the Val-2, Phe-8, Phe-11, and Ala-15 residues showed that membrane-bound fusion peptide is well-structured at the N terminus and central region, while a 5 ppm linewidth at the Ala-21 carbonyl showed that the C-terminal region is disordered. The chemical shifts of the structured residues suggest that these labeled residues adopt an extended conformation. Two-dimensional rotor-synchronized MAS exchange measurements on membrane-bound peptide that was <sup>13</sup>C labeled at the carbonyl carbons of Leu-7 and Phe-8 were best fit by a  $\beta$  sheet conformation at Phe-8. These data suggest that an N-terminal  $\beta$  sheet conformation is at least one structural requirement for fusion peptide-induced membrane fusion. The  $\beta$  sheet conformation may be related to formation of oligomeric peptides in the membrane. Solid state NMR measurements on the conformation of a synthetically oligomerized fusion peptide and on the membrane orientation of fusion peptides will also be presented. In addition, <sup>2</sup>H and <sup>31</sup>P measurements on lipid motion in the presence of fusion peptide will be presented.

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- 201.** STRUCTURE AND DYNAMICS OF PROTEINS AND PEPTIDES AT BIOMATERIAL INTERFACES STUDIED BY SOLID-STATE NMR. Wendy J. Shaw<sup>1</sup>, Joanna R. Long<sup>2</sup>, Nathan Oyler<sup>1</sup>, Peter Bower<sup>1</sup>, Michelle Gilbert<sup>2</sup>, Ruti Clark<sup>2</sup>, Patrick S. Stayton, and Gary P. Drobny<sup>1</sup>, <sup>1</sup>Department of Chemistry, <sup>2</sup>Department of Bioengineering, University of Washington, Seattle WA 98195

The construction of elaborate inorganic structures is developmentally controlled in organisms ranging from marine coccoliths to higher vertebrates. Proteins directly control the nucleation and growth of biominerals but the details of molecular recognition at the protein-biomineral interface remain poorly understood. The elucidation of recognition mechanisms at this interface may provide design principles for advanced materials development in medicine and ceramics/composites technologies. Here, we describe the use of solid-state NMR dipolar recoupling techniques and multiple quantum spectroscopy to provide the first high-resolution structural and dynamic characterization of a hydrated biomineralization protein, salivary statherin, on its relevant hydroxyapatite (HAP) mineral surface. Backbone  $\phi$  angles measured for the N-terminal pentadecyl region are characteristic of  $\alpha$ -helical structure and were measured near the N-terminus, the middle portion, and near the C-terminal end of this domain. Direct determination of the (i) to (i+4) carbonyl-amide hydrogen bond distances in this domain confirm a largely helical secondary structure. Dynamic NMR studies demonstrate that the highly anionic N-terminus is strongly adsorbed and immobilized on the HAP surface, while the middle and C-terminal regions of this domain display slow motions. Application of solid state NMR to the study of the structure of other biopolymers adsorbed onto crystalline surfaces, synthetic polymer surfaces and attached to self-assembled monolayers on colloidal gold particles will also be described.

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- 202.** DYNAMIC NUCLEAR POLARIZATION AND ELECTRICALLY DETECTED MAGNETIC RESONANCE IN TWO-DIMENSIONAL ELECTRON SYSTEMS IN THE REGIME OF THE QUANTUM HALL EFFECT. C. Russell Bowers, Eugene Olshanetsky, Manyam Pilla, Sergey Vitkalov, Jerry A. Simmons<sup>1</sup> and John L. Reno<sup>2</sup>; Chemistry Department and National High Magnetic Field Laboratory, University of Florida, Gainesville, Florida ; <sup>1</sup>Sandia National Labs, Albuquerque, New Mexico

*Electrically detected ESR (EDESER) is a remarkable technique first discovered by the Nobel Laureate K. von Klitzing. In our hands electrical detection provides an astonishing sensitivity of better than 10,000 electron spins per Gauss line width. No other method is available for selectively probing the delocalized electron spins and nuclei in hyperfine contact with them in a two-dimensional electron system in a quantum well. Furthermore, EDESER can be used to probe the nuclear spin relaxation times, hyperfine interactions and nuclear magnetic resonance spectra. The method is selective to nuclei in hyperfine contact with the delocalized electron states. Thus, electrically detected magnetic resonance techniques provide the most direct way to probe the spin dynamics and novel quantum states in the regime of the quantum Hall effect. We have exploited EDESER to characterize the electron-nuclear interaction, electron spin dynamics, and formation of collective excitations in GaAs quantum wells in the regime of the integer and fractional quantum Hall effect (QHE). To investigate the 2D electron spin dynamics and EDESER conductivity mechanism, EDESER line width studies were conducted as a function of cyclotron level filling factor (at fixed field or fixed ESR frequency) and temperature in the 0.3 - 4 K range. We have also investigated the enhancement of the Zeeman energy of the 2D electrons resulting from microwave and optical dynamic polarization of GaAs quantum well nuclei. In the case of optical pumping at 815nm, the electron-nuclear cross-relaxation leads to an unusual antiphase relationship between the satellite and central nuclear spin transitions which is associated with the creation of an octupole polarization of the spin system. Using microwave dynamic nuclear polarization, we demonstrate that the change in the Zeeman energy of the 2D electron system due to the enhanced hyperfine field can be substantial enough to induce an observable change in the dc electrical conductivity via thermal deactivation. We have exploited this effect in the development of an electronic transport/ESR hybrid method for determination of the g-factor enhancement due to the formation of collective excitations in the 2D electron system. The results of our new method will be compared to transport in tilted fields and NMR Knight shift measurements under similar QHE conditions.*

**NMR Symposium Oral Session—C. Russell Bowers, Chemistry Department, University of Florida, Gainesville, Florida 32611-7200. Tel: (352) 846-0839, Fax: (352) 392-8758, E-mail: bowers@chem.ufl.edu**

- 203.** DYNAMIC POLARIZATION AT 9 TESLA AND BEYOND. Christian T. Farrar, Kenneth E. Kreischer, Robert G. Griffin, Richard Temkin, and Jeffrey Vieregg, MIT Plasma Science and Fusion Center and MIT Francis Bitter Magnet Laboratory, Cambridge, MA 02139.

*During the last decade, the repertoire of methods to perform structural studies with solid state NMR (SSNMR) has expanded considerably. There are now multiple methods to measure distances, torsion angles, and otherwise constrain molecular structure. Furthermore, many promising applications of these methods have appeared. Nevertheless, when compared to solution NMR, the sensitivity of SSNMR experiments is lower by two to three orders of magnitude per unit time, primarily because they involve direct detection of low g nuclei – <sup>13</sup>C, <sup>15</sup>N, <sup>31</sup>P, etc. – rather than indirect detection via the more sensitive <sup>1</sup>H spin as in solution NMR. To address this problem we are exploring the possibility of performing dynamic nuclear polarization (DNP) experiments to improve the sensitivity of SSNMR. With a spectrometer operating at 5 T (140 GHz for e-, 210 MHz for <sup>1</sup>H) we have successfully enhanced signal intensities by factors of 50-400 in a variety of samples, including amino acids, polymers, proteins, and virus particles. We are now engaged in efforts to conduct these experiments at higher field strengths (9-18 T) where SSNMR is commonly performed today. We have constructed a 9 T DNP-NMR spectrometer (250 GHz for e-, 380 MHz for <sup>1</sup>H) because we anticipate that not only will the resolution be improved at higher fields, but similar size DNP enhancements as those obtained at 5 T should be achievable. The instrument consists of a 9.0 T/125 mm bore NMR magnet with a ±1.0 T superconducting sweep coil, static and MAS DNP probes, and a 250 GHz gyrotron microwave source. The critical factor that has previously impeded the extension of DNP experiments to higher fields has been the paucity of microwave sources with adequate power. We have addressed this problem with the development of a compact, 250 GHz CW gyrotron that reliably generates up to 25 W. We have completed initial DNP experiments with 60 mM 4-amino TEMPO doped into 40:60 glycerol/water at low temperatures (30-150 K). A preliminary enhancement of 43 was observed at 36 K with 2.4 W microwave power incident on the sample. The dependence of the DNP enhancement on operating conditions, including magnetic field strength, microwave power, radical concentration, and temperature will be presented.*

**NMR Symposium Oral Session—Christian T. Farrar, MIT Plasma Science and Fusion Center, Cambridge, MA 02139. Tel: 617-253-8107, Fax: 617-253-5405, E-mail: cfarrar@ccnmr.mit.edu**

- 204.** APPLICATION OF CROSS POLARIZATION FROM HYPERPOLARIZATION XENON TO SURFACE SPECIES. Jay Smith, Luis J. Smith, Kevin Knagge, and Daniel Raftery, Purdue University, Department of Chemistry, 1393 Brown Laboratory, West Lafayette, IN 47907
- Spin polarization induced nuclear Overhauser effect (SPINOE) is the most commonly used method for transferring polarization from hyperpolarized xenon to surface nuclei. Cross polarization (CP) had been previously examined as a polarization transfer method but thought to be possibly limited by adsorbed Xe mobility or low surface coverage at temperatures above 150 K. Recently, we have observed cross polarization to surface protons of silica from hyperpolarized xenon under continuous flow and magic angle spinning over a large temperature range (136 K to 317 K). While this somewhat unexpected result does decrease with increasing temperature, <sup>129</sup>Xe-<sup>1</sup>H CP signal is easily observable at temperatures up to 320K, much higher than necessary for effective SPINOE polarization transfer. As the observed CP signal only originates from nuclei in contact with the hyperpolarized <sup>129</sup>Xe, the resulting signal is truly surface selective. Since the recycle delay for the CP experiment is only dependent on the effective Xe T<sub>1</sub> (i.e. the surface replenishment rate, typically < 1s), the resulting experiment times are short, allowing for faster signal acquisition than the SPINOE experiment particularly for samples with long surface T<sub>1</sub> relaxation times. The <sup>129</sup>Xe-<sup>1</sup>H CP experiment also makes it possible to do heteronuclear correlation (HETCOR) experiments, where the large Xe chemical shift range can be used*

as a discriminating tool for investigating surface species. We have applied this methodology to separating overlapping  $^1\text{H}$  spectra in macroscopically heterogeneous samples.

**NMR Symposium Oral Session—Jay Smith, Purdue University, Department of Chemistry, 1393 Brown Laboratory, West Lafayette, IN 47907. Tel: (765) 494-9134, Fax: (765) 496-1200, smithjay@purdue.edu**

- 205.** LASER-POLARIZED GASES FOR LUNG MRI AND FOR SENSITIVITY ENHANCEMENT. Mark Conradi, Department of Physics-1105, One Brookings Drive, Washington University, St Louis MO 63130-4899

The techniques of optical pumping and spin exchange have been developed over the past 35 years. With the advent of high-power diode laser arrays, it is now easy to polarize a liter of He-3 or Xe-129 to an absolute nuclear spin polarization of order 40%. This yields an increase in NMR signal strength of  $10^4$ – $10^5$  compared to thermal equilibrium. One application of these enormous spin signals is He-3 MR imaging of human lungs. The enhanced polarization more than makes up for the low density of gases, allowing the gas space to be imaged in real time for the first time. Our emphasis has been on temporal resolution, to map the ventilatory function of the lungs. A second application is the enhancement of the sensitivity of OTHER nuclei, like H-1, C-13 and N-15, in solution-state NMR. The key issue is to transfer the intense polarization from the gas to spins in organic or biological molecules. If successful, this could allow NMR to be used on samples  $\sim 1000\times$  smaller than at present. Progress will be reported with supercritical hyperpolarized xenon solutions containing small organic solute molecules.

**NMR Symposium Oral Session—Mark Conradi, Tel: 314-935-6418 (office), 314-935-6292 (lab), Fax: 314-935-6219, E-mail: msc@howdy.wustl.edu**

- 206.** WHAT TYPES OF INFORMATION CAN INTERMOLECULAR NMR CHEMICAL SHIFTS PROVIDE? Cynthia J. Jameson, University of Illinois at Chicago, Department of Chemistry M/C 111, Chicago IL 60607-7061.

The NMR chemical shift is extremely sensitive to intermolecular effects. We present some examples of the types of information that can be obtained directly and those that can be inferred. For example, Xe atoms are trapped in the alpha cages of some zeolites for times sufficiently long that it is possible to observe individual peaks in the NMR spectrum for each occupation number, whilst other molecules such as  $\text{CO}_2$ , CO, or  $\text{CH}_4$  are in fast exchange between the cages and also with the gas outside. We show that the Xe chemical shifts provide information about the zeolite environment, the nature of the averaging for some number of Xe atoms within the same cavity, as well as the distribution among the cavities. The  $^{129}\text{Xe}$  nucleus reports on the changes in the structure of the zeolite cage, cation-induced differences between cages, average number of coadsorbed molecules in a cage with  $n$  Xe atoms. The assumption of pairwise-additive shielding contributions permits computation of average chemical shifts in a Grand Canonical Monte Carlo simulation which can be compared directly with experiment.

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- 207.** NMR SPECTROSCOPY AT GEORGETOWN UNIVERSITY. Joyia E. Rich, Marlon N. Manalo, Chiyu Ni, Thomas Pilkington, Colby A. Foss and Angel C. de Dios, Department of Chemistry, Georgetown University, 37th and O Sts., NW Washington, DC 20057

This work is composed of two parts, one theoretical and one experimental. In the first part, theoretical calculations of shielding in two antibiotics, ampicillin and penicillin-V, will be discussed. Calculated results are compared with solid state experimental nuclear magnetic resonance data. Using the known x-ray structures of these antibiotics, it is demonstrated that the computed shieldings compare favorably with experiment such that, in some cases, calculations can now be utilized in assigning shielding tensor data. The second part will describe recently obtained experimental data at Georgetown University.

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- 208.** INDIRECT NUCLEAR SPIN-SPIN COUPLING CONSTANTS: NEW INFORMATION FROM SOLID-STATE NMR, HIGH-RESOLUTION ROTATIONAL SPECTROSCOPY AND COMPUTATIONAL CHEMISTRY. David L. Bryce; Klaus Eichele; Myrlene Gee; Michael D. Lumsden; Guy M. Bernard; Scott Kroeker; Robert W. Schurko; Michelle Forgeron; Roderick E. Wasylshen, Dalhousie University, Department of Chemistry, Halifax, Nova Scotia, B3H 4J3

Using high-resolution solid-state NMR, we have been able to measure some of the first indirect spin-spin coupling constants involving quadrupolar nuclei (e.g.  $^1\text{J}(^{31}\text{P}, ^{17}\text{O})$ ,  $^1\text{J}(^{207}\text{Pb}, ^{35}\text{Cl})$ ,  $^1\text{J}(^{99}\text{Ru}, ^{31}\text{P})$ ). Furthermore, solid-state NMR allows one to measure spin-spin coupling constants for "frozen" structures. That is, spin-spin coupling constants can be measured in the absence of both intramolecular and intermolecular exchange. In addition, nuclear spin-spin coupling information is available for numerous diatomic molecules from high-resolution microwave and molecular beam spectroscopy. This source of isotropic  $J$  data and  $J$  anisotropy has been almost entirely overlooked by NMR spectroscopists. Finally, it is now clear that modern *ab initio* methods can be used to calculate reliably indirect spin-spin coupling tensors in small molecules containing first- and second-row elements.

In 1969, Jameson and Gutowsky (J. Chem. Phys. 1969, 51, 2790) published a classic paper on indirect spin-spin coupling constants involving directly bonded nuclei. This paper was important because it presented a valuable summary of the data available at that time and more importantly it provided theoretical insight into periodic trends in  $J$ . Thirty-one years later, the combined available information on indirect spin-spin



coupling from solid-state NMR, rotational spectroscopy, and computational chemistry permit re-examination of periodic trends in J. As well, a number of general conclusions about the importance of various coupling mechanisms will be discussed.

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- 209.** THE MAGIC ANGLE TURNING (MAT) EXPERIMENT WITH TIGER PROCESSION TO MEASURE CHEMICAL SHIFT TENSORS AND DIPOLE-DIPOLE INTERACTIONS IN SOLID POWDERS. David M. Grant, Don W. Alderman, James K. Harper, Dewey H. Barich, Jian Z. Hu, Flavian Guenneau, and Ronald J. Pugmire; Department of Chemistry, University of Utah, Salt Lake City, UT 84112

The recent development of MAT experiments has allowed multidimensional solid state spectra of high quality to be obtained. These data are free from the serious overlapping of broad bands common to solid NMR spectra and provide chemical shift tensors and the dipolar interactions present in powders. The earlier triple-echo MAT and PHORMAT variants of MAT spectra suffered greatly from serious sensitivity problems that have been removed by the new and very efficient FIREMAT<sup>1</sup> (Five- $\pi$  Replicated MAT) variant of this series of experiments. The creation of software to analyze the errors with the automated FIREMAT software now allows one to assess the degree of ill conditioning present in overlapping tensors and near axially symmetrical tensors. Further, these data test the propagation of FIREMAT errors through the TIGER<sup>2</sup> data processing software. The impact of the data replication scheme in FIREMAT appears to be no greater than the typical inaccuracies of this type of determination. The FIREMAT/TIGER methodology allows organic molecules with 40 to 70 different carbon atoms to be studied on a 400MHz spectrometer. At higher fields, the size of the molecules can be expected to increase accordingly. A 3D separated-local-field experiment introduces dipolar evolution dimension in the conventional 2D FIREMAT sequence and provides good values for the dipolar coupling constants along with spatial relations between the dipolar axes and the shift tensor orientations. Examples from unusual aromatic hydrocarbons and from natural products will be presented.

1. D.W. Alderman, G. McGeorge, J.Z. Hu, R.J. Pugmire, D.M. Grant; *Mol. Phys.*, 95, 1113 (1998).
2. G. McGeorge, J.Z. Hu, C.L. Mayne, D.W. Alderman, R.J. Pugmire, D.M. Grant; *J. Mag. Reson.*, 129,134 (1997).

**NMR Symposium Oral Session—David Grant, Department of Chemistry, University of Utah, Salt Lake City, UT 84112. E-mail: grant@chemistry.chem.utah.edu**

- 210.** RECENT DEVELOPMENTS ON NMR STUDY OF LIQUID CRYSTALS. Bing M. Fung, Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019-0370

Several aspects of recent NMR study of liquid crystals performed in our laboratory will be discussed. (1) Development of efficient broadband decoupling. Because of the presence of extensive dipolar interactions in liquid crystals, efficient broadband decoupling must cover a wide of proton resonance frequency. We found that this can be achieved by using multiple frequency excitation in the rotating frame through programmed phase alternation schemes. The results are very satisfactory for liquid crystals, and can be applied to solids as well. (2) Magnetization transfer through dipolar interactions. The classical description of "spin diffusion" has been challenged recently by Bruschweiler and Ernst and by Waugh. We have verified their computer simulations experimentally by studying the proton polarization transfer of benzene in a liquid crystal solution. (3) Determination of long-range dipolar couplings by using 1D NMR. It has been well established that 1- and 2-bond <sup>1</sup>H-<sup>13</sup>C dipolar couplings in liquid crystals can be obtained by using separated local field spectroscopy, and the 3D version can yield some long range couplings. Our recent work on the use of monodeuterated liquid crystals to obtain long-range <sup>2</sup>H-<sup>13</sup>C dipolar couplings using 1D <sup>13</sup>C NMR will be described. (4) The use of quadrupole nuclei for quantum logic gates. The use of NMR for quantum computing is an intriguing and controversial idea. We have demonstrated that an I = 3/2 system in a liquid crystal can be used to construct a 2 qubit quantum logic gate. The use of an I = 7/2 system as a 3-qubit quantum logic gate and other related ideas will be described.

**NMR Symposium Oral Session—Bing M. Fung, Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019-0370. E-mail:bmfung@chemdept.chem.ou.edu**

- 211.** 2H NMR STUDIES OF ANISOTROPIC MOTIONS IN MOLECULAR MATERIALS. Kenneth D.M. Harris, Simon J. Kitchin, Linda Lai; School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom; Arnaud Desmedt, François Guillaume, Laboratoire de Physico-Chimie Moléculaire, UMR No. 5803 CNRS Université de Bordeaux I, F-33405 Talence, France

To obtain a detailed understanding of the dynamic properties of molecules in the solid state, we require to apply a range of experimental and computational techniques, each of which can probe different aspects of the dynamics on different characteristic timescales. The techniques that we use in our research in this field includes several solid state NMR methods (particularly 2H NMR), incoherent quasielastic neutron scattering and molecular dynamics simulation techniques, with emphasis on the advantages to be gained by applying appropriate combinations of these techniques. Using this approach, our recent research on molecular motion in solids has focused on two main classes of materials: (i) the dynamics of guest molecules included within host solids, and (ii) the dynamics of hydrogen bonding arrangements in solids. Solid state 2H NMR spectroscopy has been a particularly significant component of this research. The lecture will focus mainly on recent results obtained from our studies of molecular motion in solid inclusion compounds that contain one-dimensional tunnel host structures, typified by urea and thiourea inclusion compounds and certain zeolitic materials. 2H NMR experiments on both powder samples and oriented single crystals will be described, and, where appropriate, the results will be discussed in conjunction with conclusions from the application of other complementary techniques for investigating the dynamic properties. Inter alia, the lecture will introduce new aspects relating to the automated fitting of 2H NMR lineshapes.

**NMR Symposium Oral Session—Kenneth D.M. Harris, School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom**



- 212.** NMR OF WEAKLY ALIGNED MACROMOLECULES. Gabriel Cornilescu, Frank Delaglio, Markus Zweckstetter, Ben Ramirez, Georg Kontaxis, James Chou, and Ad Bax, Laboratory of Chemical Physics, NIDDK, NIH, Bethesda, MD 20892-0520

Biomolecular structure determination by NMR to date has been based almost exclusively on very local parameters such as interproton distances obtained from NOE measurements and torsion angles, derived from J couplings. In contrast, dipolar couplings measured in macromolecules that are weakly aligned with the magnetic field provide information on the orientation of individual bond vectors relative to the molecular alignment tensor. Next to restraining local geometry, they therefore also have an intrinsic global character and can constrain the relative orientation of parts of a structure that are not connected by NOEs. In order to retain the simplicity of the isotropic high-resolution NMR spectrum in the aligned state, it is essential that the degree of alignment is sufficiently weak ( $\leq 10^{-3}$ ). At higher degrees of alignment broadening caused by  $^1\text{H}$ - $^1\text{H}$  dipolar couplings make the spectra generally intractable. Such weak degrees of alignment can be obtained either as a result of the macromolecule's magnetic susceptibility anisotropy, or by using a very dilute liquid crystalline phase consisting of large, disc-shaped phospholipid particles, commonly referred to as bicelles. Alternatively, transient binding to large, oriented particles can be used to "spy" on the conformation of the molecule in the bound state. In favorable cases, both the magnitude and orientation of the alignment tensor are under experimental control. Measurement of dipolar couplings for two different orientations of the solute relative to the liquid crystal director yields discrete orientations of the corresponding internuclear vector relative to the molecular frame. Dipolar couplings obtained in this manner are shown to contain highly precise information on the macromolecular structure and also carry information on its dynamic properties. We demonstrate that if measurements are sufficiently complete, they can be used to define the conformation of a protein backbone with remarkably high accuracy, even in the absence of any hydrogen bonding, J coupling, or NOE information.

**NMR Symposium Oral Session—Ad Bax, Laboratory of Chemical Physics, NIDDK, NIH, Bethesda, MD 20892-0520, E-mail: bax@nih.gov**

- 213.** NMR INSIGHTS CONCERNING MOLECULAR ORDER: SOFT MATERIALS IN EQUILIBRIUM AND UNDER DEFORMATION. Paul T. Callaghan, Institute of Fundamental Sciences-Physics, Massey University, Palmerston North, New Zealand.

The mechanical properties of soft materials are of practical importance in industrial processing, in the plastics and petroleum industries, in biotechnology and in food technology. The really interesting questions often concern the relationship of molecular organization and dynamics to macroscopic constitutive behavior. Unfortunately there is a lack of good experimental data concerning the molecular/mechanical link. Through terms in the spin Hamiltonian which are sensitive to order and dynamics, NMR spectroscopy gives us access to the molecules. Through the use of magnetic field gradients, NMR microscopy and velocimetry gives us access to the mechanics. As will be shown in this lecture, these two approaches are highly complementary. The main focus of this talk will be the study of molecular order, traditionally achieved in NMR by studies of proton dipolar or deuterium quadrupolar interactions. However in soft matter these weak interactions are often masked by chemical shifts or, in systems where the sample shape is non-ideal, by susceptibility inhomogeneity. Simple spin echo schemes enable such problems to be circumvented and examples will be presented concerning the equilibrium behavior of polymer melts and networks, and phenomena associated with deformational flow, such as the "spurt effect", shear banding, and stress-induced polymer chain alignment.

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2. P.T. Callaghan and E.T. Samulski, *The molecular weight dependence of nuclear spin correlations in PDMS networks, Macromolecules*, (in press).
3. P.T. Callaghan and E.T. Samulski, "The molecular weight dependence of nuclear spin correlations in entangled polymeric liquids", *Macromolecules* 31, 3693-3705, (1998).

**NMR Symposium Oral Session—Paul T. Callaghan; Institute of Fundamental Sciences- Physics, Massey University, Palmerston North, New Zealand. Tel: 64-6-3505164, Fax: 64-6-3505682, E-mail: P.Callaghan@massey.ac.nz**

- 214.** MAGNETIC RESONANCE AND LIGHT SCATTERING STUDIES OF ELECTRICALLY ALIGNED SOLUTIONS. Scott A. Riley and Matthew P. Augustine; Department of Chemistry, University of California, Davis, California 95616

Elimination of isotropic molecular orientation in liquid phase reintroduces the typically absent effects of through space nuclear spin dipolar and quadrupolar coupling as well as chemical shift anisotropies into an NMR spectrum. As is well known, measurement of these residual spectral features leads to refinement of molecular structure. Recent experiments in our laboratory aimed at aligning molecules with an externally applied electric field both parallel and perpendicular to the large Zeeman magnetic field have met with some success. A variety of multiple rf pulse sequences in both static and pulsed DC and AC  $\sim 60$  kV/cm electric fields are presented. These sequences compensate for molecular convection induced by charge injection as measured via exchange effects on one-dimensional magnetic resonance images. Magnetic resonance imaging velocimetry studies in aqueous solutions under intense DC and AC magnetic fields along with magneto-electric birefringence experiments indicate that electrical alignment of electrically anisotropic virus particles may be in part due to charge flow, a property that can be controlled in an NMR experiment.

**NMR Symposium Oral Session—Matthew P. Augustine; Department of Chemistry, University of California, Davis, CA 95616. E-mail: augustin@indigo.ucdavis.edu**

- 215.** NMR IMAGING OF A LIQUID CRYSTALLINE POLYMER FLOWING THROUGH AN ABRUPT CONTRACTION. Jeffrey A. Reimer, Materials Sciences Division, Lawrence Berkeley National Laboratory and Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462 USA

*The processing of structured fluids in industrially relevant flow geometries, such as an abrupt contraction, represents a significant theoretical and experimental challenge. I will report on the progress of my colleagues towards measuring and modeling the flow of liquid crystalline polymers into abrupt axisymmetric contractions. At the very least I will discuss imaging data which reveal unusual features in the steady-state axial velocity profiles acquired both up and downstream of the contraction. I will show how local order parameter is a particularly important marker for the underlying physics, and discuss strategies and preliminary results for elucidating this parameter in lyotropic and thermotropic polymers. If all goes well in my lab in the time between preparing this abstract and delivering the talk, we will have accomplished spatially resolved spectroscopy (probably MQ-filtered imaging) in the contraction flow.*

Supported by the Director, Office of Energy Research, Office of Basic Energy Science, Materials Science Division, U.S. Department of Energy, under contract No. DE-AC03-76SF00098.

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2. Gentzler et. al., *Solid State NMR*, 12, 97 1998.

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- 216.** LARGE ALUMINUM QUADRUPOLE COUPLING CONSTANTS AND FIELD-SWEPT AND FREQUENCY-SWEPT NMR SPECTROSCOPY. Les Butler, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804

*In aluminum chemistry, large quadrupolar interactions are frequent and the spectra are difficult to acquire with "standard" techniques like high-speed MAS at high-field. At times, we have accepted the broad resonances of a static sample, and have acquired either field-swept or frequency-stepped NMR spectra. The former can yield quite nice spectra on a resistive magnet at the NRMFL. The latter yields decent spectra on a supercon system in our own lab. The data processing trick of Gil Clark of co-adding frequency-shifted FIDs in the time domain adds considerably to the signal-to-noise and spectral resolution of both field-swept and frequency-stepped NMR spectra. In comparison to field-swept spectra, the frequency-stepped spectra have some distortions due to magnitude processing but easily retain isotropic chemical shift values.*

**NMR Symposium Oral Session—Les Butler, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804. Tel: 225-388-4416, Fax: 225-388-3458, E-mail: lbutler@lsu.edu**

- 217.** ENHANCED SITE RESOLUTION AND QUANTITATION FROM "ULTRA-HIGH" FIELD NMR SPECTROSCOPY OF GLASSES. Scott Kroeker and Jonathan F. Stebbins, Stanford University, Department of Geological and Environmental Sciences, Stanford, CA, U.S.A. 94305-2115

*NMR spectroscopy has played an important role in the development of structural and dynamical models of amorphous materials. Where quadrupolar nuclei are concerned, however, limitations in peak resolution and sensitivity are often encountered, owing – in part – to the distribution inherent in disordered systems of quadrupolar coupling interactions. The utilization of higher magnetic fields for NMR (e.g., 14.1 and 18.8 T) enhances both resolution and sensitivity in such cases, and when used in conjunction with fast magic angle spinning (MAS), can yield structural information not always available from NMR experiments at lower fields. Examples will include site distinction of multiple trigonal boron groups in  $^{11}\text{B}$  MAS NMR spectra of borate glasses, the spectroscopic observation of low concentrations of five- and six-coordinate aluminum species in  $^{27}\text{Al}$  MAS NMR spectra of aluminosilicate glasses, and new insight into magnesium coordination environments in silicate glasses using  $^{25}\text{Mg}$  MAS NMR. Comparisons of spectral data collected at 18.8 T with those at lower fields will demonstrate these principles and provide an indication of the potential of high-field MAS NMR applications to quadrupolar nuclides once thought inaccessible by these means.*

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- 218.** HIGH-RESOLUTION MULTIPLE QUANTUM MAGIC ANGLE SPINNING NMR OF HALF-INTEGGER NUCLEI VIA MIXED MULTIPLE QUANTUM COHERENCE. Alexej Jerschow, John W. Logan, and Alexander Pines, Chemistry Department, University of California, Berkeley, CA 94720-1460.

*A new experiment to perform high-resolution multiple quantum magic angle spinning (MQMAS) NMR spectroscopy of half-integer quadrupolar nuclei is demonstrated. This experiment exhibits improved resolution over current state-of-the-art experiments. The second-order quadrupolar broadening is refocused for  $I = 5/2$  spins by a five quantum to three quantum coherence transfer during  $t_1$ . A full echo acquisition is used to acquire pure phase data. Additional sensitivity is achieved by using fast amplitude modulated (FAM) pulses.<sup>1,2</sup> Similar experiments with a much improved resolution over the conventional MQMAS experiments can also be used for half integer spins with  $I > 5/2$ . Linewidth-limiting factors are discussed for the experiment.*

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2. Goldbourt, Madhu, and Vega, *Chem. Phys. Lett.* 2000, 320, 448.

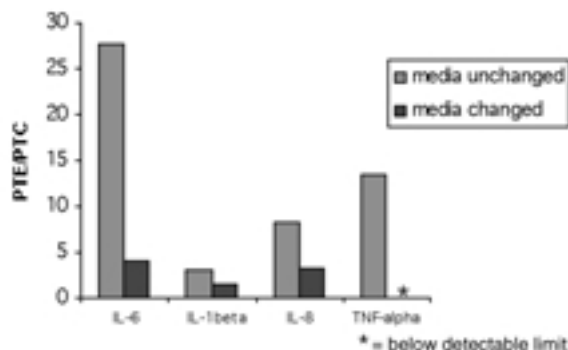
**NMR Symposium Oral Session—Alexej Jerschow, C/O Pines, Chemistry Department, University of California, Berkeley, CA 94720-1460. Tel: 510-486-7442, Fax: 510-486-5744, E-mail: AJerschow@lbl.gov**

- 219.** SOLID-STATE NMR OF METALS OF BIOLOGICAL INTEREST. Andrew S. Lipton, Jesse A. Sears, and Paul D. Ellis, Pacific Northwest National Laboratory, PO Box 999, MSIN K8-98, Richland, WA 99352.
- Historically it has not been possible to directly observe the native metals of metalloproteins by liquid- or solid-state NMR methods. In the case of  $Zn^{+2}$  for example, the NMR resonance frequency is modest, 25.03 MHz, in a field of 9.4 T (400 MHz for  $^1H$ ), a nuclear spin of 5/2, and a magnetic moment (0.214 of that for  $^1H$ ) the size of which implies low sensitivity. The accepted paradigm has been to substitute the native metal with a "spin-spy" (typically  $^{113}Cd$ ) which has more favorable spectroscopic properties. With almost thirty years of literature behind it cadmium substitution seems to be working and is well understood. Recently there has been renewed interest in the direct observation of solid-state NMR spectra of the native metals (i.e.  $^{25}Mg$  and  $^{67}Zn$ ) in model complexes utilizing both MAS and static spin echo methods. We present here examples of our work observing  $^{67}Zn$ ,  $^{25}Mg$  and  $^{43}Ca$  in several model complexes and metalloproteins.*
- NMR Symposium Oral Session—Andrew S. Lipton, Battelle PNNL, PO Box 999, MSIN K8-98, Richland, WA 99352. Tel: 509-376-6633, Fax: 509-376-2303, E-mail: as\_lipton@pnl.gov**
- 220.** MULTINUCLEAR SOLID-STATE NMR INVESTIGATIONS OF COBALAMINS — BASE-ON VS. BASE-OFF. Christopher W. Kirby,<sup>1</sup> David W. Cescon, Jennifer R. Garbutt, and William P. Power. Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, Department of Chemistry, University of Waterloo, Waterloo, ON, N2L 3G1, CANADA <sup>1</sup>Present Address: Department of Chemistry, University of Western Ontario, London, ON N6A 5B7, CANADA
- One of the debates in cobalamin biochemistry deals with the conformation of the molecule when it binds to an enzyme. Previously, we and others have characterized the cobalt centre of cobalamins in base-on form using  $^{59}Co$  powder and single crystal NMR. In this study, we forced by chemical means the tail of cyanocobalamin and methylcobalamin to adopt a base-off conformation, where the dimethylbenzimidazole tail becomes disengaged from the cobalt, and is replaced by CN. Three aspects of the structural features of the cobalamin have been studied in both base-on and base-off forms: 1) the cobalt centre via  $^{59}Co$  powder NMR of the cobalt site, 2) the tail via  $^{31}P$  NMR of the phosphate moiety, and 3) the cap via  $^1H$  NMR of methyl- $d_3$ -cobalamin. The results lead us to believe that we have several reliable nuclear probes with which direct study of conformation in enzyme-bound cobalamins is feasible using only polycrystalline samples, permitting ready identification of the cobalamin conformation.*
- NMR Symposium Oral Session—Christopher W. Kirby, Department of Chemistry, University of Western Ontario, London, ON N6A 5B7, CANADA. Tel: (519)661-2111 ext. 86301 Fax: (519)661-3022, E-mail: cwkirby@julian.uwo.ca**
- 221.** NMR OF PARAMAGNETIC ENZYMES. Ann McDermott, Tatyana Polenova, HyeRim Lee, Columbia University, Department of Chemistry; 3000 Broadway MC-3113; NY NY 10027
- Lineshape fitting of deuterium NMR spectra allow us to derive conformational exchange rates and ligand-metal distances for model compounds and for P450- substrate complexes. We will discuss the basis of these lineshape algorithms. A recent proposal for the mechanism of polarization in photocycling photoreaction centers will also be discussed.*
- NMR Symposium Oral Session—Ann McDermott; Columbia University, Department of Chemistry; 3000 Broadway MC-3113; New York NY 10027, E-mail: mcdermot@chem.columbia.edu**

## NMR Poster Sessions

- 222.** 7-DEHYDROCHOLESTEROL (VITAMIN D<sub>3</sub>) INCREASES SENSITIVITY OF HD-INDUCED CYTOKINES RELEASE. ELISA AND NMR STUDIES. Carmen M. Arroyo, Robert J. Schafer, David W. Kahler, David A. Sartori and Clarence A. Broomfield, U.S. Army Medical Research Institute of Chemical Defense, 3100 Ricketts Point Road, Aberdeen Proving Ground, MD 21010-5400; HOak Ridge Institute for Science and Education, Research Participation Programs, Oak Ridge, TN 37831

Keratinocytes possess the Vitamin D Receptor (VDR), and respond to 1  $\alpha$ , 25-dihydroxyvitamin D<sub>3</sub> (1,25(OH)<sub>2</sub>D<sub>3</sub>) by increasing proliferation and differentiation of keratinocyte clonogenic cells. 7-Dehydrocholesterol acts as a hormone precursor of 1,25(OH)<sub>2</sub>D<sub>3</sub>, which requires two stages of metabolism before reaching actual hormonal form. In the first stage, 25-hydroxycholecalciferol is formed and in the second stage the 1  $\alpha$ , 25-dihydroxyvitamin D<sub>3</sub> is formed. Treatment of human epidermal keratinocytes (HEK) with 7-dehydrocholesterol (10<sup>-6</sup> -10<sup>-8</sup> M) followed by exposure to sulfur mustard (HD, 100 mM) without changing the pretreated media increases production of interleukin-1b (IL-1b), interleukin-6 (IL-6), interleukin-8 (IL-8) and tumor necrosis factor- $\alpha$  (TNF- $\alpha$ ).



HISTOGRAM I: Typical representative data obtained when HEK were treated with 7-dehydrocholesterol (10<sup>-6</sup> -10<sup>-8</sup> M). [ PTE/PTC: ratio of cytokine release (pg/mL) from HEK pretreated with 7-dehydrocholesterol and then exposed to HD / pretreated HEK non-exposed

However, pretreatment of HEK with 7-dehydrocholesterol (10<sup>-6</sup> -10<sup>-8</sup> M) for 24 hours followed by removal of the media and then exposure to HD exposure suppressed the observed cytokines release (HISTOGRAM I.). The results suggest that HD reacts with 7-dehydrocholesterol, precursor of the hormonal form, to produce a more potent activation of the VDR receptor. The by-products of the reaction of HD with 7-dehydrocholesterol increase the cytotoxicity to HEK as measured by cytokine changes. Nuclear magnetic resonance (NMR) techniques are being used to elucidate the by-products formed in the reaction of 7-dehydrocholesterol with HD. A possible explanation of the reported feedback mechanism by which 7-dehydrocholesterol controls cytokine levels by inducing an increase in cytokine release and/or limiting cytokine release will be discussed.

**NMR Symposium Poster Session—Carmen M. Arroyo; U.S. Army Medical Research Institute of Chemical Defense, 3100 Ricketts Point Road, Aberdeen Proving Ground, MD 21010-5400. Tel: (410) 436-4454, E-mail: Carmen.Arroyo@apg.amedd.army.mil**

- 223.** REDOR NMR OF AMIDINE INHIBITORS OF FACTOR Xa. Lynda M. McDowell, Department of Chemistry, Washington University, St. Louis, MO 63130; Margaret A. McCarrick, Berlex Biosciences, 15049 San Pablo Avenue, Richmond, CA 94804; Daniel R. Studelska, and Jacob Schaefer, Department of Chemistry, Washington University, St. Louis, MO 63130.

Berlex Biosciences has patented a large number of amidine compounds as potential anticoagulants. The best oral drug candidates exhibit high selectivity for inhibition of Factor Xa (a serine protease found in the blood) over trypsin (a digestive enzyme that is also a serine protease). Our collaborators at Berlex have synthesized carbon-13 and nitrogen-15 labeled inhibitors (which also contain fluorine) to enable solid-state NMR studies of these potential drugs in enzyme complexes. Rotational Echo Double Resonance (REDOR) experiments provided restraints that have been used in combination with the results of Berlex x-ray crystallography to model the bound structure of amidine inhibitors of Factor Xa and trypsin.

**NMR Symposium Poster Session—Lynda M. McDowell, Department of Chemistry, Washington University, St. Louis, MO 63130. Tel: 314-935-5780, Fax: 314-935-4481, E-mail: mcdowell@wuchem.wustl.edu.**

- 224.** SOLID-STATE NMR OF METAL — NUCLEOTIDE COMPLEXES. Christopher V. Grant, Dan McElheny, Veronica Frydman, Enrico de Vita and Lucio Frydman; Department of Chemistry (M/C 111), University of Illinois at Chicago, Chicago, IL 60607-7061

Magnesium and sodium ions play many important roles in the structure and function of nucleic acids. Both <sup>23</sup>Na and <sup>25</sup>Mg are half-integer spin quadrupolar nuclei, a class of nuclei for which high-resolution solid-state NMR techniques have been recently developed. These NMR techniques have been used to study the coordination environments of <sup>23</sup>Na and <sup>25</sup>Mg complexed with adenosine 5'-triphosphate (ATP). Aside from the biological interest in ATP structure and metal binding, these complexes serve as models for the interaction of sodium and magnesium with RNA. MQMAS allows for distinguishing the four crystallographically inequivalent sodium sites of the Na<sub>2</sub>-ATP complex. MQ-REDOR and phosphorus observed REAPDOR experiments have been used to investigate the <sup>23</sup>Na - <sup>31</sup>P dipolar interaction. Additionally, the application of

<sup>25</sup>Mg NMR to study the interaction of magnesium with ATP in labeled polycrystalline samples is presented.

**NMR Symposium Poster Session—Christopher V. Grant; Department of Chemistry (M/C 111), University of Illinois at Chicago, Chicago, IL 60607-7061, E-mail: grant@penelope.chem.uic.edu**

- 225.** SOLID-STATE PROTON MR SPECTROSCOPY IN POLYSACCHARIDES: STRUCTURE INVESTIGATIONS. L. Y. Grunin, Mari State Technical University, Department of Physics, Lenin sq. 3, Yoshkar-Ola, Mari El, 424000, Russia

The problem of polysaccharides (PS) structure determining becomes very actual in recent years. Chitin and chitosan films find their application in different branches of human activity such as drug production, cosmetics, food industry, ecology and many others. There is also a fast growth of consumption of starch and cellulose fibers. These factors make necessary the creation of methods, which would be able to appreciate fast and exactly the main structural properties of the sample. Of all the methods which are used for the investigation of polysaccharides structure, NMR is proved to be the most elegant due to its invasiveness. More over, it is much faster and sometimes more exact then any chemical method. Strong magnetic dipolar interactions make impossible direct measuring of high resolution NMR in solid PS. This is the main reason for NMR not to have broad use for polysaccharides structure investigations. Nevertheless, measurements of NMR relaxation times found applications for determining the correlation times of molecular motions. In our work we applied various modern pulse proton magnetic resonance (PMR) approaches to solve some problems of physical chemistry of polysaccharides. Careful fourier spectra acquisition gave us opportunity to distinguish signals from solid lattice and relatively mobile radicals and bounded water, so we are able to determine crystallinity and sorption properties. The intensity of double and triple quantum transitions allowed to carry out the investigations of side radicals. We used the non ideality of pulse suppression of dipolar interactions to provide additional information about the structure amorphous regions. The results indicate wide opportunities of proton MR spectroscopy in investigations of solid-state structure of polysaccharides.

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- 226.** STRUCTURAL MOTIF OF A  $\beta$ -HEXAPEPTIDE DETERMINED BY SOLID-STATE NMR. Anil K. Mehta and Jacob Schaefer, Department of Chemistry, Washington University, St. Louis, Missouri 63130; Daniel Bierbaum and Dieter Seebach, Laboratorium für Organische Chemie, Universitätstrasse 16, Eidgenössische Technische Hochschule, ETH-Zentrum, CH-8092 Zürich, Switzerland

Beta-amino acids are unnatural amino acids that have an additional backbone carbon. Peptides composed of  $\beta$ -amino acid residues are potential therapeutics because they can mimic natural peptidic hormones and are resistant to degradation by proteolytic enzymes. Short oligopeptides consisting of four to seven  $\beta$ -amino acids may form pleated sheets, helices, turns or hairpins. Understanding the principles involved in the various structures exhibited by these  $\beta$ -peptides will aid in elucidating their biological function. Using specific <sup>13</sup>C, <sup>15</sup>N, <sup>19</sup>F isotope labeling at four positions of the hexapeptide of 3-amino-2,2-dimethylpropanoic acid and REDOR, we have examined whether aggregated  $\beta$ -hexapeptide chains adopt a hairpin conformation.

**NMR Symposium Poster Session—Anil K. Mehta, Department of Chemistry, Washington University, St. Louis, Missouri 63130. Tel: 314-935-5780, Fax: 314-935-4481, E-mail: anil@wuchem.wustl.edu**

- 227.** SOLID-STATE NMR STRUCTURE DETERMINATION OF A U-<sup>13</sup>C,<sup>15</sup>N-LABELED TRIPEPTIDE BY MULTIDIMENSIONAL TORSION ANGLE METHODS. Chad M. Rienstra, Morten Hohwy, Bernd Reif, Leonard J. Mueller, Christopher P. Jaroniec, Lisa Tucker-Kellogg, Bruce Tidor, and Robert G. Griffin, Department of Chemistry and Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139

We present a series of structural constraints obtained by 3D solid-state NMR projection angle measurements. Techniques for determining <sup>1</sup>H-<sup>15</sup>N-<sup>13</sup>C-<sup>13</sup>H and <sup>1</sup>H-<sup>13</sup>C-<sup>13</sup>C-<sup>13</sup>H torsion angles are extended to higher MAS rates (~9 kHz) by combining the recently developed heteronuclear local field recoupling technique, T-MREV,<sup>1</sup> with efficient means of transferring polarization (SPC-5 for <sup>13</sup>C-<sup>13</sup>C transfer<sup>2</sup> and SPECIFIC CP for <sup>15</sup>N-<sup>13</sup>C transfer<sup>3</sup>). This strategy facilitates application to U-<sup>13</sup>C,<sup>15</sup>N-labeled samples, in which <sup>13</sup>C-<sup>13</sup>C homonuclear dipolar couplings impede efforts to make such measurements at lower MAS rates. To simplify the polarization transfer dynamics, we have employed a band-selective version of SPC-5, which increases transfer efficiency and reduces the effective size of <sup>13</sup>C spin clusters. These characteristics permit a tractable analysis of the multi-spin dynamics, so that projection angles over multiple C-C bonds may be determined. This feature breaks the symmetry of single torsion angle measurements, which are always two-fold and often four- or six-fold degenerate, by selecting a unique conformational solution that satisfies three or more projection angle values depending on two or more torsion angles. We demonstrate an overall precision for most measurements of better than  $\pm 5$  degrees. The 3D experiments are applied to formyl-[U-<sup>13</sup>C,<sup>15</sup>N]-Met-Leu-Phe-OH, and together with <sup>15</sup>N-<sup>13</sup>C-<sup>13</sup>C-<sup>15</sup>N and <sup>1</sup>H-<sup>15</sup>N-<sup>15</sup>N-<sup>1</sup>H measurements, yield in excess of 20 independent structural constraints. The data is used to calculate the complete backbone and partial sidechain structure of the peptide. This research was supported by NIH grants RR-00995 and GM-23403 (MIT).

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- 228.** DEUTERIUM NMR STUDY OF SODIUM HYDROGEN BIS(4-NITROPHENOXIDE) DIHYDRATE. Paolo Rossi, Joanna Clark, Valeri Barsegov and Gerard S. Harbison, Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304.

A class of molecules known as the Speakman-Hadzi compounds, characterized by a very short and symmetrical O-H-O hydrogen bond with an unusual IR absorption spectrum, have often served as model compounds for fundamental studies of strong hydrogen bonds. The crystalline compound sodium hydrogen bis(4-nitrophenoxide) dihydrate is a typical member of this class. A strong H-bond is formed between a phenol and a phenolate base moiety in the unit cell; two more weakly hydrogen bonded water molecules complete the cluster. Recent NMR work on this compound by Klug et al. reported an unexpected result — a two bond anisotropic  $^{13}\text{C}$ - $^2\text{H}$  J coupling of 160 Hz, which is orders of magnitude larger than either empirical or theoretical considerations would permit. We have therefore conducted variable-temperature  $^2\text{H}$  NMR experiments, obtaining the asymmetry parameters and quadrupole coupling constants for both the water and the phenol-phenolate H-bond deuterons as a function of temperature. The electric field gradient of the strongly hydrogen-bonded deuteron is highly unusual, with a quadrupole coupling constant of less than 100 kHz over the range  $-100^\circ\text{C}$  and  $50^\circ\text{C}$ , and an asymmetry parameter of 0.3.  $T_1$  values remain greater than 10 s over this temperature range, confirming that it does not undergo activated jumps, but rather sits in a flat, broad and symmetric potential. Most curiously of all, we find that the quadrupole coupling constant decreases with temperature. We attribute this anomalous decrease to a shortening of the O—O distance, resulting in a lengthening of the nominal O-D single bond, which both empirical evidence and *ab initio* calculations suggest should greatly reduce the field gradient at the deuteron, and which apparently overwhelms the usual increase in the electric field gradient that results from a reduction in thermal averaging. Lineshape analysis also allows us to determine the temperature-dependent rate of the water molecule two-fold hops, yielding the activation energy. These hops cause the broadening previously observed in the MAS spectrum, and dipolar coupling to a water deuteron in intermediate exchange may explain the anomalous REDOR results without the necessity of invoking an anisotropic J tensor.

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- 229.** PHOSPHORUS CHEMICAL SHIFT AND INDIRECT SPIN-SPIN COUPLING IN  $[\text{Ph}_3\text{PPPh}_2][\text{GaCl}_4]$  AND  $[\text{Ph}_2\text{ClPPPh}_2][\text{GaCl}_4]$ : A SOLID-STATE NMR AND *Ab INITIO* INVESTIGATION. Myrlene Gee, Edgar Ocando, Roderick E. Wasylishen, and Neil Burford, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J3

The indirect spin-spin coupling (J) interaction is extremely useful for the elucidation of molecular structure. In solution NMR studies, however, J may be zero or averaged as a consequence of intermolecular and intramolecular exchange. For example,  $^1\text{J}(^{31}\text{P}^{31}\text{P})$  coupling is not observed in solution at room temperature for  $[\text{Ph}_3\text{PPPh}_2][\text{GaCl}_4]$  and  $[\text{Ph}_2\text{ClPPPh}_2][\text{GaCl}_4]$ ; however, this parameter is measured in a solid-state NMR investigation of powdered samples. In addition, the phosphorus chemical shift and the dipolar coupling tensors for both compounds were characterized using  $^{31}\text{P}$  CP NMR on MAS samples as well as stationary powder samples combined with 2D spin-echo NMR and rotational resonance experiments. Upper limits on the P-P bond lengths are determined from the dipolar coupling constants. To further characterize the indirect spin-spin coupling interaction as well as the chemical shift tensors, *ab initio* calculations are carried out on model systems.

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- 230.** RING-CHAIN TAUTOMERISM IN SOLID PHASE ERYTHROMYCIN A: EVIDENCE BY SOLID-STATE NMR. Joseph B. Davis, and Robbie J. Iuliucci, Washington and Jefferson College, Washington PA, 15301; Jian Zhi Hu, Mark S. Solum, and D. M. Grant, University of Utah, Salt Lake City UT, 84116

The macrolide erythromycin A, a 14-member lactone aglycoside with an amino sugar (D-desosamine) attached to the lactone at C5 and a neutral sugar (L-cladinose) attached to the lactone at C3, is considered to be one of the safest and effective antibiotics manufactured. Ring-chain tautomerism has been known to readily occur in the liquid state of erythromycin A and some of its derivatives.<sup>1</sup> Hence, in solution erythromycin A exists as a mixture of the 9-ketone, 6,9- cyclic hemiacetal and 9,12- cyclic hemiacetal. With the formation of the hemiacetal, the C9 protonated carbon of the ketone is converted into a quaternary carbon, which is characterized by a 107-110 ppm  $^{13}\text{C}$  NMR shift in the liquid phase. Upon dehydration of the solid phase erythromycin A dihydrate, the CPMAS spectrum reveals a new resonance at 110 ppm. Through spectral editing techniques it will be demonstrated that this resonance is a quaternary carbon, suggesting the formation of a cyclic hemiacetal in the solid phase. A  $^{13}\text{C}$  chemical shift analysis of this modified structure will be conducted by utilizing the slow magic-angle-turning technique of FIREMAT and the TIGER 2D processing method.<sup>2</sup> Chemical-shift modeling of the tensor data at the DFT level will be presented.

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**NMR Symposium Poster Session—Robbie J. Iuliucci, Washington and Jefferson College, Washington PA, 15301. Tel: 724-223-8539, E-mail: riuliucci@washjeff.edu**

- 231.** DEUTERON NMR STUDIES OF RATES AND ACTIVATION ENERGIES OF INTRAMOLECULAR MOTION IN POLYAMIDOAMMONIUM CHLORIDE DENDRIMERS. Dariya I. Malyarenko, Robert L. Vold and Gina L. Hoatson, Departments of Applied Science and Physics, The College of William and Mary, P.O.Box 8795, Williamsburg, VA 23187-8795

For polyamidoammonium dendrimer salts, the multiexponential Zeeman relaxation behavior can be analyzed as the sum of contributions from interior and terminal deuterated sites. This permits characterization of the geometry, rates, and activation energies of motion for low (G2) and

high (G9) dendrimer generations. Planar librations of interior secondary amide ( $R_2ND$ ) and protonated tertiary amine ( $R_2ND^+$ ) deuterons are simulated by six-site jumps on an arc. Motion of terminal ammonium ( $RND_3^+$ ) group is modeled as a two-frame process:  $ND_3^+$  rotation proceeds by  $120^\circ$  jumps about R-N axis, which in turn jumps among four sites in a cone. At the  $R_2ND$  sites the relatively high activation energy of planar libration,  $E_A=44\pm5$  kJ/mol, is generation independent. The activation energy of the  $RND_3^+$  groups decreases for higher generation dendrimers, from  $64\pm10$  kJ/mol for G2 to  $14\pm3$  kJ/mol for G9. There are two types of ammonium deuterons with different rotational rates. For the "slow" component the relaxation time anisotropy and rotational rate are temperature and generation independent. For all deuteron sites the observed trends for rates and activation energies of all functional groups support a structural transition of the dendrimers: from extended interpenetrating branches of low generations to a backfolded architecture for high generations,  $G>3$ .

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- 232.** INVESTIGATION OF THE CRYSTALLINE STRUCTURE OF POLYLACTIDE USING SOLID-STATE NMR SPECTROSCOPY. Eric J. Munson, Jessica E. Jorvig, Mark T. Zell, JennySue Abbott, and Marc A. Hillmyer, 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.

The structure and morphology of polymers synthesized from chiral monomers are highly dependent on the configuration of the chiral centers in the polymer chain. We are studying the influence of the chiral center configuration on the crystalline structure of polylactide. Polylactide (PLA) is a biodegradable polymer synthesized from the cyclic dimer of lactic acid. Lactide has three stereoisomers, L-(S,S), D-(R,R), and meso-(S,R) lactide. In the crystalline region of poly(L-lactide), the polymer chain forms a  $10_3$  helix. The  $^{13}C$  CP/MAS NMR spectrum of this polymer has five peaks for the carbonyl carbon, suggesting at least five crystallographically inequivalent sites for this carbon. We have been using two-dimensional exchange of isotopically labeled PLA to assign the peaks. Fast MAS ( $>30$  kHz) and high-power  $^1H$  decoupling ( $>250$  kHz) is necessary to resolve each of the peaks in the  $^{13}C$  CP/MAS NMR spectrum of PLA synthesized using 5% uniformly  $^{13}C$  labeled L-lactide and 95% unlabeled L-lactide. We have also been investigating the incorporation of stereodeflect sites into the crystalline region of an almost ( $>90\%$ ) enantiomerically pure polymer. Stereodeflect sites were produced by synthesizing poly(D-lactide) with a small amount of L-lactide as a stereodeflect.  $^{13}C$  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 the stereodeflect incorporated into the crystalline region of the polymer. For a polymer synthesized with 3% L-lactide as a stereodeflect, approximately 50% of the stereodeflect is incorporated into the crystalline region. We are currently synthesizing poly(D-lactide) containing from 1-10% L-lactide to better understand the incorporation of stereodeflects into the crystalline region of the polymer. We are also using in-situ variable temperature-CP/MAS NMR to study when stereodeflects are incorporated into the crystalline region during the crystallization process.

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- 233.** A SOLID-STATE NMR STUDY OF ADSORBED POLYETHYLENE-CO-ACRYLIC ACID RANDOM COPOLYMERS. Victor Nasreddine and Linda Reven; Chemistry Department, McGill University, 801 Sherbrooke Street West, Room: 447, Montreal-Quebec-Canada. H3A 2K6  
Polymer coatings on surfaces have a wide variety of industrial and technological applications. The relationship between the polymer chain conformation and mobility to important properties such as adhesion and wettability is of interest to these applications. The bulk properties of a polyethylene-co-acrylic acid random copolymer are investigated. One and two dimensional solid-state NMR experiments (CP-MAS and 2D-WISE) are performed to characterize mobility, chain conformation and morphology. Spin diffusion experiments (Dipolar Filter) are used to determine the domain sizes. Variable temperature NMR experiments are performed on samples of different mobilities to get more insight into the dynamics of these systems. The copolymer is then adsorbed on a surface (zirconia) via sticker groups (carboxylic acid functionality) which alter the bulk properties. The effect of copolymer loading and acrylic acid content is also discussed.

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- 234.** DIPOLAR COUPLING AND INTERNUCLEAR DISTANCES IN FLUORINE SOLID-STATE NMR. Ulrich Scheler, Institute for Polymer Research Dresden, Hohe Strasse 6, D-01069, Dresden

Inter-nuclear distances, which can effectively be probed via the direct dipolar coupling, provide important information for structural refinement. Homonuclear distances can be probed in zero-quantum experiments (spin exchange) or in double quantum experiments. In both cases the dispersion of chemical shifts has to be taken into account.

The frequency of dipolar oscillations in the built-up curve of  $^1H$ - $^{19}F$  cross polarization is determined by the heteronuclear dipolar coupling strength. Averaging by spin diffusion is circumvented by spin lock at the magic angle which suppresses the homonuclear dipolar coupling. The heteronuclear coupling is retained when the rf amplitudes match the Hartman-Hahn condition (Lee-Goldburg cross polarization). From the frequency of the oscillation in the built-up curve the strength of the dipolar coupling and thus the distance is derived. This approach selects for each fluorine nucleus, that can be resolved in the spectrum, the distance to the closest proton.

Fluorine spin diffusion has a clear effect on  $T_1$  and lead to a single  $T_1$  in perfluorinated systems even at spinning rates of 35 kHz. It can be quenched by fast MAS in because of the chemical shift separation. While a short  $T_1$  (0.5 s) for  $CF_3$  is observed at all spinning speeds,  $T_1$  for an isolated CF can be longer than 60 s.

Applications include partially fluorinated derivatives of benzoic acid, and semicrystalline polymer, PVDF, with high proton and fluorine density. The results are confirmed by NMR simulations.

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- 235.** TRIAD DISTRIBUTIONS IN POLY(ETHYLENE-CO-1-HEXENE). Mark R. Seger and Gary E. Maciel; Colorado State University, Department of Chemistry, Fort Collins, CO 80523

The triad distributions of two poly(ethylene-co-1-hexene) copolymers are analyzed from high signal-to-noise 126 MHz carbon-13 spectra of the copolymers dissolved in deuterated 1,2,4-trichlorobenzene at 398K. Errors involved in applying various algorithms for determining triad concentrations from carefully integrated spectral regions are compared, including the effects of both random and systematic sources of error. The resultant triad mole fractions are compared to sequence statistics expected by Bernoullian, first-order Markovian and Coleman-Fox Two States models.

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- 236.** NMR CHARACTERIZATION OF C<sub>30</sub> SELF-ASSEMBLED MONOLAYERS ON MATERIALS USED FOR HPLC: POROUS SILICA, TITANIA AND ZIRCONIA. D.L. VanderHart, Polymers Division, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, M. Pursch, Dow Deutschland Inc., Werk Rheinmuenster, Industriestr. 1, 77836 Rheinmuenster, Germany and L.C. Sander, Analytical Chemistry Division, NIST, Gaithersburg, MD 20899

Self assembled monolayers (SAM's) on porous silica, titania and zirconia were produced by reacting solutions of anhydrous C<sub>30</sub>-trichlorosilane (nominal C<sub>30</sub>) with a slurry of previously humidified silica, titania or zirconia gels with mean pore sizes of about 30 nm. These materials show significant variations in their ability to separate isomers when functioning as reversed-phase materials in a HPLC column. <sup>13</sup>C and <sup>1</sup>H NMR methods, applied to samples in the absence of solvent, allow us to obtain information on a) the distribution of average conformations characterizing the methylene groups on the C<sub>30</sub> chains, b) the fraction of methyl groups at the layer surface, and c) the uniformity of the density within the SAM layer. It is shown that large amplitude motions characterize all methylene carbons and a restriction to mainly an all-trans conformation typifies many such carbons; hence, characteristics of the alkane rotator phase are compared with those of the SAM layers. Substantial upfield chemical shifts are associated with methyl groups at an air interface. Finally, using spin diffusion methods, the SAM's are seen to exhibit substantial heterogeneity of layer density.

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- 237.** MORPHOLOGICAL INVESTIGATION OF POLY (STYRENE-B-ISOBUTYLENE-B-STYRENE) POLYMERS USING SOLID-STATE NMR SPECTROSCOPY AND TRANSMISSION ELECTRON MICROSCOPY. David Mountz, Kenneth A. Mauritz, and W. L. Jarrett, University of Southern Mississippi, School of Polymers and High-Performance Materials, Hattiesburg, MS 39406-0076

One key area of investigation the Mauritz research group is the synthesis and characterization of ionomeric materials and their possible application as chemical-resistant clothing for the Army. In order to obtain the desired properties, i.e. permeability for water yet effective blockage of toxic chemicals, knowledge of the material morphology is extremely important. One method of probing morphology is spin-diffusion.<sup>1,3</sup> In cases where it is possible to selectively obliterate <sup>1</sup>H magnetization, the domain size can be determined by observing its recovery in one region via transfer of magnetization from the unaffected regions. This paper will present results using this method as well as TEM on a series of poly(styrene-b-isobutylene-b-styrene) polymers with varying styrene content and degrees of sulfonation.

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- 238.** INVESTIGATING THE HYDROLYTIC DEGRADATION OF POLY(ESTER URETHANE) ELASTOMERS USING <sup>1</sup>H AND <sup>13</sup>C NMR. David P. Lang and Roger A. Assink, Sandia National Laboratories, P.O. Box 8500, Albuquerque, NM 87185-1407

Hydrolytic degradation has been shown to be a significant problem for poly(ester urethane) elastomers exposed to high humidity environments. The ester group in the soft segment is particularly susceptible to hydrolysis. The resulting reduction in molecular weight leads to deterioration of the elastomer's mechanical properties. In this study, <sup>13</sup>C and <sup>1</sup>H NMR spectroscopies were used to characterize the hydrolytic degradation of a poly(ester urethane) elastomer. Formation of carboxylic acid and alcohols are related to a marked increase in segmental mobility of the polymer.



Using  $^1\text{H}$  NMR we measured the spin-spin relaxation time of the soft phase and followed the increase in mobility of these segments. The induction time for increased mobility implies an autocatalytic degradation mechanism. Both measurements were performed on the solid polymer. These measurements provide an excellent monitoring tool of the chemical and physical state of polymer during the aging process. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-4AL85000.

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- 239.** APPLICATION OF SOLID-STATE NMR TO NYLON6/CLAY NANOCOMPOSITES. A. Asano and D.L. VanderHart, National Institute of Standards and Technology, Polymers Division, Gaithersburg, MD 20899; J.W. Gilman; National Institute of Standards and Technology, Fire Science Division, Gaithersburg, MD 20899;

Solid-state  $^{13}\text{C}$  and  $^1\text{H}$  NMR techniques, including cross-polarization (CP), magic-angle-spinning (MAS) and multiple-pulse, have been applied to various nylon6/clay nanocomposites, made by both blending and in-situ polymerization, to elucidate its morphology. Two clays were used, one is a synthesized diamagnetic laponite, the other is a naturally occurring,  $\text{Fe}^{3+}$  containing paramagnetic montmorillonite (mmt).  $^{13}\text{C}$  CPMAS spectra reveal that the presence of the clay promotes the growth of the  $\gamma$ -crystalline phase over the usual  $\alpha$  phase, but annealing results in some conversion of the  $\gamma$  to the  $\alpha$  phase. Uniformity of clay dispersion in the nylon6/mmt-clay nanocomposites is examined by indirectly measuring, via  $^1\text{H}$ - $^{13}\text{C}$  CP, the  $^1\text{H}$  spin-lattice relaxation time,  $T_1\rho$ , and extracting the paramagnetic contribution. This contribution propagates, via spin-diffusion, from the clay surfaces. Morphological information (ratio of the  $\alpha$ - and  $\gamma$ -crystalline phases of nylon6, relative proximity of each kind of crystal phase to the clay surface, crystal domain size and crystallinity) is also deduced using both  $^{13}\text{C}$  detection and multiple-pulse  $^1\text{H}$  measurements. The average repeat distance (crystalline plus non-crystalline dimensions) is found to be 14nm for nylon6 and the nanocomposites.

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- 240.** CARBON-13 NMR INVESTIGATION OF DYNAMIC COUPLING OF GUEST MOLECULES IN HOST-GUEST COMPLEXES OF CRYPTOPHANE-E. Melanie Gile, Rebecca Sanders, Shawn McCleskey, Phillip Smith, and James J. Dechter, Department of Chemistry, University of Central Oklahoma, Edmond, OK, 73034

Cryptophane-E is a good host molecule for small tetrahedral-shaped guest molecules. We have assigned the  $^{13}\text{C}$  NMR spectrum for Cryptophane-E and for four bound guest molecules:  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CHBr}_3$ . Significant  $^{13}\text{C}$  NMR complexation shifts have been observed for these guests which are all in the slow exchange limit at room temperature. We have measured the  $^{13}\text{C}$  NMR relaxation parameters for the hydrogen bearing carbons of the host cage as well as for the four bound guest molecules. We have found that  $\text{CH}_3\text{I}$  and  $\text{CH}_2\text{Cl}_2$  guests show little dynamic coupling to the host molecule even though they are incarcerated by the host, while  $\text{CHCl}_3$ , and  $\text{CHBr}_3$  are strongly coupled. The presence of dynamic coupling appears to be related to the steric size of the guest molecules. Future work will involve relaxation studies as a function of temperature and efforts to model the motional behavior of the guests inside the host in an effort to establish controlling factors for dynamic coupling.

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- 241.** SOLID-STATE  $^{13}\text{C}$  NMR STUDY OF DYNAMICS IN METHANE HYDRATE. Mark F. Davis, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO, 80401; Steven F. Dec, Colorado School of Mines, Department of Chemistry and Geochemistry, Golden, CO, 80401.

There has been recent substantial interest in the properties of gas clathrate hydrates or simply, gas hydrates. In particular, methane hydrate has received increased attention because of the existence of plentiful natural gas hydrate deposits in the earth that may be an abundant future energy source. While extensive studies of methane hydrate have been performed from a macroscopic point of view, very few investigators have directly probed the structure and dynamics of the methane hydrate phase. In this work we report on a detailed investigation of the chemical exchange of methane between the two hydrate cages present in methane hydrate at temperatures near 273 K as determined using high-resolution, solid-state  $^{13}\text{C}$  NMR. Using a classical 2D exchange experiment,<sup>1</sup> we have observed this chemical exchange. Additional 1D NMR experiments provide for further analysis of the exchange process. In particular, rates of exchange and activation energies for this two-site exchange process will be discussed. The relation of these results to the stability of methane hydrate will be presented.

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- 242.** STRUCTURE AND DYNAMICS OF BIFUNCTIONAL SELF ASSEMBLED MONOLAYERS. Shane Pawsey, Linda Reven, McGill University, Department of Chemistry, 801 Sherbrooke St. West, Montreal, Quebec, Canada H3A 2K6; S. DePaul, Max Planck Institute für Polymerforschung, Postfach 3148 D-55021 Mainz, Germany

Self-assembled monolayers (SAMs) on planar substrates have been extensively studied. We have shown that SAMs can be deposited on metal oxide powders and colloidal particles, allowing NMR techniques to be applied to these systems. A major goal in this field concerns the introduction of specific surface functionalities. However, in the case of metal oxides, the introduction of terminal polar functional groups can be problematic due to interaction with the surface, resulting in looping structures. Solid-state  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  1D and 2D NMR studies of the self-assembly of  $\text{HO}_2(\text{CH}_2)_n\text{PO}_3\text{H}_2$  ( $n=2, 4, 11$ , and  $15$ ) on metal oxides have been undertaken. These bifunctional surfactants were chosen since long chain carboxylic and phosphonic acids both form ordered SAMs on metal oxide powders. The  $^{31}\text{P}$  NMR spectra, as well as the average chain conformation and mobility as determined from  $^{13}\text{C}$  NMR data, indicate that only the phosphonic acid group is chemisorbed, producing a carboxylic acid functionalized surface.  $^1\text{H}$  fast MAS and double quantum NMR data indicate the degree of hydrogen bonding.

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- 243.** QUANTITATION OF THE SOLID-STATE NMR OF SILICA GEL AT VARIOUS DEGREES OF DEHYDRATION AND DEHYDROXYLATION. I-Ssuer Chuang and Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO, 80523.

Quantitation in the solid-state  $^1\text{H}$  and  $^{29}\text{Si}$  NMR of silica gel under various treatments with different degrees of dehydration and dehydroxylation was examined in detail. Results with three external intensity references are described. Experiments to establish a valid sample volume for reliable quantitation by  $^1\text{H}$  CRAMPS are presented. A detailed analysis of  $^1\text{H} \rightarrow ^{29}\text{Si}$  cross-polarization (CP) spin dynamics was performed on variable CP contact time experiments of silica gel with various degrees of dehydration and dehydroxylation. The quantitative results are interpreted by our previously reported, generalized silica surface model based on the surface structure of beta-cristobalite.

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- 244.** AN INVESTIGATION OF SODIUM METASILICATE BY MULTI-NUCLEAR NMR SPECTROSCOPY AND AB INITIO CALCULATIONS: IMPLICATIONS FOR THE DETERMINATION OF LOCAL STRUCTURE AT OXYGEN SITES IN SILICATES. T. Clark, P. Grandinetti, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210-1173

Sodium metasilicate,  $\text{Na}_2\text{SiO}_3$ , has been investigated by  $^{29}\text{Si}$ ,  $^{23}\text{Na}$ , and  $^{17}\text{O}$  MAS NMR spectroscopy. The  $^{17}\text{O}$  quadrupolar coupling parameters have been measured for the bridging oxygen (BO) and non-bridging oxygen (NBO) sites. Ab initio calculations performed for the oxygen sites in  $\text{Na}_2\text{SiO}_3$ ,  $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ ,  $\text{Li}_2\text{Si}_2\text{O}_5$ , and  $\text{K}_2\text{Si}_4\text{O}_9$  suggest that quadrupolar coupling parameters are calculable for BO and NBO in alkali silicates and that relatively simple model clusters may be used to depict these environments. The presence of alkali cations is shown to systematically shift the magnitude of the quadrupolar coupling constant and the quadrupolar asymmetry parameter for a given Si-O-Si angle, with this shift being influenced by the cation's field strength. A parametrized equation describing the relationships between structural features and quadrupolar coupling parameters for BO sites is also discussed. Having established several trends between structure and NMR parameters in crystalline alkali silicates, it is now possible to more effectively probe the oxygen environment in silicate materials lacking long-range order, such as alkali silicate glasses. In this respect, the utility of  $^{17}\text{O}$  solid-state NMR has been significantly expanded.

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- 245.** TWO-DIMENSIONAL ISOTROPIC/ANISOTROPIC  $^{29}\text{Si}$  NMR ON  $^{29}\text{SiO}_2$  ENRICHED BINARY SILICATE GLASSES. Eila Ebrecht and Berthold Thomas, Freiberg University of Mining and Technology, Institute of Analytical Chemistry, Leipziger Str. 29, 09599 Freiberg, Germany; Michaela Zeyer and Christian Jäger, Friedrich-Schiller-Universität Jena, PATF, IOQ, Max-Wien-Platz 1, 07743 Jena, Germany
- $^{29}\text{Si}$  magic angle spinning (MAS) nuclear magnetic resonance (NMR) is a common approach for quantifying  $Q^n$  groups in alkali silicate glasses. However, it is not possible to derive information about the connectivities of these  $Q^n$  units, enabling improved studies of the medium range order, by one-dimensional (1D)  $^{29}\text{Si}$  MAS NMR. In previously published works<sup>1,2</sup> 2D double quantum (DQ) NMR had been applied for measuring the connectivities of the  $Q^n$  units. In this work we have confirmed these isotropic chemical shift data for the various  $Q^{3,jkl}$  and  $Q^{4,jklm}$  units using 2D isotropic/anisotropic  $^{29}\text{Si}$  NMR. The anisotropy and chemical shift tensor data for the  $Q^{3,jkl}$  and  $Q^{4,jklm}$  units have been obtained applying the PHORMAT (phase corrected magic angle turning) experiment. The chemical shift tensor data of the  $Q^{3,jk}$  units differ by about 2 ppm. This corresponds with the difference between the isotropic chemical shifts of the  $Q^{3,jkl}$  units, which are about 2 ppm.

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- 246.** PHOTO-INDUCED DECOMPOSITION OF TRICHLOROETHYLENE ON SILICA GEL. Jianhua Li and Gary Maciel; Department of Chemistry, Colorado State University, Fort Collins, Co 80523-1872

The photo-induced decomposition of trichloroethylene adsorbed on silica gel has been studied by  $^{13}\text{C}$  solid state NMR<sup>1</sup>. The sample has been irradiated with long-wavelength UV light while exposed to air. The products of the photodecomposition were studied under various reaction environments and the relationship between the reaction and the substrate has been studied as function of different types of silica gel. The results show that similar photo-induced decomposition occurs on a variety of silicas and under a variety of conditions.

Ting Tao, Jane J. Yang, Gary E. Maciel, *Environ. Sci. Technol.* 1999, 33, 74-80.

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- 247.** INVESTIGATION OF MOLECULAR ASSEMBLY IN ORDERED NANOPOROSITIES USING SOLID-STATE NMR. L.-Q. Wang, Jun Liu, Y. Shin, W. D. Samuels, G. J. Exarhos, Material Science Department, Pacific Northwest National Laboratory, Richland, WA 99352

Assembly of organized molecular structures in ordered nanoporosity has shown to be a very useful approach to synthesize novel functional nanoscale materials. This approach allows rational design of wide range of materials properties, such as pore dimension, surface chemistry, stereochemistry, spatial distribution of the functionality, etc. The molecular conformation and the mechanisms of the assembly in the nanoporosity have been investigated using variable-temperature solid-state  $^{13}\text{C}$  NMR,  $^{29}\text{Si}$  NMR and two-dimensional proton wide line separation (2D WISE)  $^1\text{H}$ - $^{13}\text{C}$  NMR spectroscopy in combination with BET and TEM measurements. The chain length of silanes and pore size of nanoporous silica are varied systematically. Information on silane organization and relaxation in nanopores was obtained using a combination of NMR line-shape,  $T_{\text{CH}}$  (cross-polarization time constant), and 2D WISE analyses. It was found that molecular conformations are related to the chain lengths, and pore sizes. The pore size, as well as the uniformity of the porosity, can affect how the long chain molecules are assembled. Homogeneous molecular layers can be formed in 10 nm pores. Smaller pore sizes cause pore clogging and chain entanglement. Larger pore sizes increase the degree of pore irregularity, and produce disordered multilayer coating. Molecules with intermediate chain lengths form better molecular layer structures.

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- 248.** NMR-SPECTROSCOPIC INVESTIGATION OF THE PREPARATION AND HYDROLYSIS OF HYPERCOORDINATED SILICON COMPOUNDS. Jana Peters, Institute of Analytical Chemistry; B. Schluttig, Institute of Inorganic Chemistry and B. Thomas, Institute of Analytical Chemistry, Freiberg University of Mining and Technology, Leipziger Str. 29, D-09596 Freiberg, Germany

Hydrolyses of alkoxyxilanes by sol-gel-processes usually results in amorphous or partly crystallized  $\text{SiO}_2$ . By variation of the reaction conditions and using hypercoordinated silicon intermediates it should be possible to synthesize crystalline  $\text{SiO}_2$  at low temperatures. Solid-state NMR spectroscopy is a suitable method to distinguish between amorphous, pre-crystalline, partially crystalline and crystalline products formed during reaction. Synthesis of the hypercoordinated silicon complexes based on reaction of alkoxyxilanes or silica gel with different structure directing agents. The synthesized silicon species were principal investigated by  $^{29}\text{Si}$ -NMR spectroscopy and additional methods like IR-spectroscopy or powder x-ray diffraction measurements. Using these techniques numerous non-crystalline silicon compounds can be detected. Their order in comparison with amorphous solids is increased but less than in crystalline materials. Following hydrolyses of the hypercoordinated silicon complexes should prefer the formation of crystalline  $\text{SiO}_2$ .

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- 249.**  $^{13}\text{C}$  NMR LINE SHAPES OF ACETONE ADSORBED ON SILICA. Ting Tao, Vicky H. Pan; Jian-Wei Zhou and Gary E. Maciel. Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872

$^{13}\text{C}$  cross polarization (CP) or direct polarization (DP) NMR data were obtained with MAS on samples of acetone (with  $^{13}\text{C}$  labels at C-1 and/or C-2) adsorbed on dry silica gel, as a function of temperature with magic-angle spinning. Various contributions to the observed linewidths and  $T_2^*$  values are considered in terms of a previously postulated model of the acetone/ $\text{SiO}_2$  system; in that model, acetone species are in equilibrium between a physisorbed-acetone state and a state consisting of acetone units that are hydrogen bonded to silanol moieties on the silica surface.<sup>1</sup> Spin dynamics simulations (using ANTIOPE software) are useful in interpreting the effects of variations of experimental parameters. It is concluded that the main linewidth contributions, which increase at low temperatures, are: a) a dispersion of chemical shift in the hydrogen-bonded state, associated with the inhomogeneous character of the silica surface; b) the interference between MAS averaging of the chemical shift anisotropy and molecular motion; and c) chemical exchange broadening. Prominence of the last of these contributions is most consistent with data obtained as a function of magnetic field strength, MAS speed and temperature.

1. Vicky H. Pan, Ting Tao, Jian-Wei Zhou and Gary E. Maciel, *J. Phys. Chem. B*, 1999, 103, 6930-6943.

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- 250.** CHARACTERIZATION OF SITE III SODIUM CATIONS IN LiNaX INVESTIGATED USING  $^{23}\text{Na}$  MAS NMR AND  $^{23}\text{Na}$  MQMAS NMR. Robyn J. Accardi, Department of Chemical Engineering, University of Delaware, Newark, DE 19716; Hubert Koller, Institute of Physical Chemistry, University of Münster, D-48149 Münster, Germany; Raul F. Lobo, Department of Chemical Engineering, University of Delaware, Newark, DE 19716

The characterization of sodium cations in site III of LiNaX was investigated using variable temperature  $^{23}\text{Na}$  MAS NMR and  $^{23}\text{Na}$  MQMAS NMR. Samples were investigated in vacuum and in the presence of oxygen. The paramagnetic shift effect of oxygen was used to determine the accessibility of sodium cations in site III. The room temperature  $^{23}\text{Na}$  MAS NMR spectrum of the oxygen-containing sample shows a significant downfield paramagnetic shift of the site III cation resonance indicating the accessibility of these sodium cations to the oxygen molecules. However, this shift decreases substantially at lower temperatures. To better understand the various contributions to these observed shifts,  $^{23}\text{Na}$  MQMAS NMR was used to calculate both the isotropic chemical shift and the quadrupolar shift. Results show that the quadrupolar interactions shift the resonance upfield in the opposite direction of the observed paramagnetic shift. Variable temperature  $^{23}\text{Na}$  MQMAS NMR spectra indicate that these quadrupolar shifts increase at lower temperatures thus explaining the sharp decrease in the observed paramagnetic shift.

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- 251.** DEVELOPMENT OF AN ISOLATED FLOW VARIABLE TEMPERATURE (VT) MAS NMR PROBE FOR IN SITU STUDIES OF HETEROGENEOUS CATALYSIS. Lauren K. Carlson, Paul K. Isbester and Eric J. Munson, University of Minnesota, Department of Chemistry, Minneapolis, MN 55455

We are developing an isolated flow variable temperature (VT) MAS NMR probe that can simultaneously monitor reactions occurring on the catalyst bed with the characterization of the product gas stream using an online gas chromatograph. With our original design we can spin the catalyst bed at speeds greater than 2 kHz and reach temperatures in excess of 300°C. We have studied the conversion of methanol to gasoline (MTG) range hydrocarbons on zeolite catalyst HZSM-5 with this probe. We have performed both batch and flow studies of the MTG reaction using the probe and have found that the equilibria between the two operating conditions differ. In batch studies an equilibrium between  $^{13}\text{C}$ -labeled methanol and dimethyl ether at 250°C exists while under flow conditions at temperatures greater than 200°C, no such equilibrium exists. These differences illustrate the utility of our probe for obtaining a more complete understanding of reactions as they occur under typical operating conditions. Recently, we have made several changes to our isolated flow VT MAS system. These changes include reducing the rotor diameter to increase spinning speed, exploring alternate rotor materials to improve spinning stability, modifying the sample chamber to increase gas/catalyst interactions, and installing a projection tube at the product gas end of the rotor to obtain better isolation. With these modifications, we have increased the maximum spinning speed to > 5 kHz with greatly improved reliability. We are currently evaluating the flow and temperature characteristics of this improved design. Future work includes extending the temperature range, incorporating external analysis using a GC/MS, and additional applications to heterogeneous catalysis.

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- 252.**  $^{27}\text{Al}$  MAS, QPASS AND MQMAS NMR OF ZEOLITES: EXPERIMENTAL STUDY AND QUANTIFICATION OF THE SPECTRA. Valérie Montouillout, Anne-Agathe Quoineaud and Christian Fernandez; Laboratoire de Catalyse et Spectrochimie, University of Caen Basse-Normandie, 14050 Caen (France)

Various zeolites have been studied using  $^{27}\text{Al}$  MAS, QPASS and MQMAS NMR in order to get access to the different types of sites, especially following a dehydration or a dealumination. For instance, in dealuminated zeolites, it is clearly seen the presence of four Al species, among them two are in tetrahedral coordination. A simultaneous simulation of the MAS and MQMAS spectra leads to a correct evaluation of the relative intensities and to the distribution of chemical shifts and quadrupolar parameters.

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- 253.** MULTINUCLEAR SOLID-STATE NMR STUDIES OF SEMICONDUCTOR AND ZEOLITE PHOTOCATALYSTS. Sarah J. Pilkenton, Megan A. MacNaughtan, Ajit R. Pradhan, Weizong Xu, Sarah Klosek, and Daniel Raftery, Purdue University, 1393 Brown Laboratories, West Lafayette, IN 47907

Solid-state NMR methods are applied to study the surface chemistry of a number of promising semiconductor and zeolite photocatalysts. Absorption studies of acetone, ethanol, and 2-propanol on  $\text{TiO}_2$  powder and  $\text{TiO}_2$  supported on porous Vycor glass show the formation of strongly surface bound species. The identity of the surface bound species allows us to predict the photocatalytic reactivity of the system. By mixing  $\text{V}_2\text{O}_5$  and  $\text{TiO}_2$  we are able to extend the range of light absorbed by the catalyst to include visible light.  $^{51}\text{V}$  NMR is used to determine the oxidation state of vanadium and the reactivity of the mixed catalyst.  $\text{SnO}_2/\text{TiO}_2$  is another mixed oxide system where  $^{119}\text{Sn}$  NMR is used to probe the tin sites. For zeolite and zeolite-silica composite catalysts, solid-state NMR can be used to identify the reactivity of the catalyst using probe molecules such as chloroform. Intermediates and surface bound products are identified with  $^{13}\text{C}$  and  $^1\text{H}$  NMR during the reactions on the catalysts.

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- 254. SOLID STATE NMR STUDIES OF ENVIRONMENTAL CATALYSTS.** Jianjun Wu, Alexander Panov, Alexander Saladino, 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, Cu-ZSM-5 and Fe-ZSM-5, are active for the thermal SCR (selective catalytic reduction) of NO<sub>x</sub> with hydrocarbons in the presence of excess oxygen. Solid state <sup>15</sup>N and <sup>13</sup>C MAS NMR have been used to investigate the role of potential reaction intermediates, such as acetone and acetone oxime, in the SCR of NO<sub>x</sub> over H-ZSM-5, CuZSM-5 and Fe-ZSM-5. In another example of environmental catalysis, the photo and thermal oxidation of cyclohexane, with molecular oxygen, on cation-exchanged zeolites has also been studied using natural abundance <sup>13</sup>C solid state NMR. The photo and thermal oxidation of cyclohexane yields cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide as the major products. This process exhibits potential as an environmentally benign method for the selective oxidation of hydrocarbons. In the final example, the photodegradation of toluene on TiO<sub>2</sub> and titanium-exchanged zeolites has been investigated using <sup>13</sup>C solid state NMR. The results of complementary gas chromatography (GC) studies will also be presented.

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- 255. MAS NMR STUDIES OF STRUCTURAL DAMAGE IN LiMn<sub>2</sub>O<sub>4</sub>-BASED SPINELS FOR LITHIUM RECHARGEABLE BATTERIES.** Michael C. Tucker, Elton J. Cairns, and Jeffrey A. Reimer; Ernest Orlando Lawrence Berkeley National Laboratory and Department of Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720

The lithium manganese oxide spinel system is a promising alternative to commercially-available positive electrode materials owing to its low cost, low toxicity, and environmental friendliness. These spinels are high-voltage battery materials; starting at LiMn<sub>2</sub>O<sub>4</sub> composition, for instance, lithium ions can be extracted at 4 volts or inserted at 3 volts vs. lithium metal. However, commercialization of this material has been slowed by the rapid fade of rechargeable capacity upon multiple charge/discharge cycles. The present work utilizes MAS NMR to observe structural damage caused by electrochemical and chemical processes that occur during repeated cycling. An attempt is made to uncouple the simultaneous processes that occur during electrochemical cycling by subjecting the spinel to certain exaggerated model processes. The types of damage introduced by the model processes are used to explain the changes observed with NMR after many electrochemical cycles. Spinel LiMn<sub>2</sub>O<sub>4</sub> shows a large 7Li MAS NMR peak at ~510 ppm (vs. 1M LiCl), assigned to lithium in the tetrahedral spinel site, and two smaller peaks in the range 550-590 ppm assigned to tetrahedral lithium in spatial proximity to spinel lattice defects.<sup>1</sup> It is observed that both water damage and overdischarge lead to new peaks at much lower shifts, due to electrolyte byproducts and a new tetragonally-distorted spinel phase, respectively. No new peaks are observed for LiMn<sub>2</sub>O<sub>4</sub> cycled many times, ruling out these processes as contributors to the capacity fade. Long-term cycling does, however, lead to a reduction in the lithium intensity, and a broadening of the residual MAS linewidth. Similar effects are seen for LiMn<sub>2</sub>O<sub>4</sub> held at high potentials, suggesting electrolyte oxidation at the spinel surface may play a large role in the damage occurring during cycling.

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- 256. INVESTIGATIONS OF BISMUTH VANADATES BY USING <sup>51</sup>V AND <sup>17</sup>O SOLID STATE NMR.** Namjun Kim; Clare P. Grey, SUNY at Stony Brook, Department of Chemistry, Stony Brook, NY 11794-3400

Oxide ion conductors are of great technological importance due to their use in various solid state ionic devices such as solid-oxide fuel cells and oxygen separation membranes. Among these materials, bismuth vanadium oxide (Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>) and related phases have recently attracted considerable interest, because of their high oxide-ion conductivities at relatively low temperatures.<sup>1</sup> For example, these materials show much higher conductivities than the fuel-cell material, stabilized-zirconia, which requires operating temperature near 1,000°C in the fuel cell. Both <sup>51</sup>V and <sup>17</sup>O MAS NMR variable temperature experiments have been used to study the local environments in pure and doped forms of Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub>. Both experiments reveal considerable ionic motion even at moderate temperatures (less than 250°C). The <sup>17</sup>O/<sup>51</sup>V and <sup>51</sup>V/<sup>17</sup>O TRAPDOR NMR experiments have been exploited to determine the connectivities between the two sets of atoms, and to assign the <sup>17</sup>O resonances. The use of <sup>51</sup>V/<sup>17</sup>O TRAPDOR to indirectly monitor oxygen mobility is explored. Finally, results from the application of these double resonance experiments to study V-O connectivity in a variety of vanadate model systems will be presented.

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**NMR Symposium Poster Session—Namjun Kim, SUNY at Stony Brook, Department of Chemistry, Stony Brook, NY 11794-3400**

- 257. ANALYSIS OF SOLID-STATE <sup>207</sup>Pb POWDER PATTERNS.** Alicia Glatfelter, University of Delaware, Department of Chemistry and Biochemistry, Newark, DE 19716; Scott Van Bramer, Widener University, Department of Chemistry, Chester, PA 19013; Guenther Neue, University of Dortmund, 4600 Dortmund-Eichlinghofen, August-Schmidt-Strasse, Dortmund, Germany; Jeff Smith, University of Delaware, Department of Chemistry and Biochemistry, Newark, DE 19716; Cecil R. Dybowski, University of Delaware, Department of Chemistry and Biochemistry, Newark, DE 19716

<sup>207</sup>Pb NMR spectroscopy is a useful, but somewhat difficult, technique for the study of solid lead inorganic and organometallic complexes. The

resonance lines of most solids tend to be very broad due to large chemical shift anisotropy. Uniform excitation of such broad lines is difficult. Because of the need to detect at times immediately after the end of the pulse in this technique, acoustic ringing of the probe is another problem. There are three ways to deal with these problems: (1) detect the spectrum in a single experiment that compensates for acoustic ringing, accounting for nonuniform excitation in the analysis; (2) detect in a point-by-point fashion in a series of experiments; or (3) detect with low-level tailored excitation over a broad band with subsequent analysis of the response to extract the spectrum. Each method has strengths in certain applications. We discuss the first method, based on a sequence involving a spin echo and spin-temperature inversion to suppress acoustic ringing. The analysis of the response involves the evaluation of a transfer function, which may be generated theoretically or measured. We compare theoretically and experimentally determined transfer functions for this sequence.

Supported by Grant No. 33633 of the Petroleum Research Fund of the American Chemical Society.

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- 258.** A COMBINED MULTINUCLEAR SOLID-STATE MAGNETIC RESONANCE AND AB INITIO STUDY OF HEXAMETHYLBORAZINE. Michelle A. M. Forgeron, David L. Bryce, Roland Rösler, Klaus Eichele, and Roderick E. Wasylshen, Department of Chemistry, Dalhousie University, Halifax, NS, Canada B3H 4J3

Results of a comprehensive multinuclear magnetic resonance study of hexamethylborazine (HMB) are reported. Borazines are in some ways the inorganic analogs of benzenes; HMB is the simplest air-stable member of the borazine family. It is therefore of interest to compare the NMR properties of benzenes with those of the corresponding borazines. Boron-11 NMR spectra of MAS powdered samples of solid HMB were acquired at two different applied magnetic fields and analyzed to yield the quadrupolar coupling constant,  $2.97 \pm 0.03$  MHz, asymmetry parameter,  $0.01 \pm 0.01$ , and isotropic chemical shift,  $78.3 \pm 0.4$  ppm. Our experimental results indicate that the effects of the neighbouring  $^{14}\text{N}$  nuclei ( $I = 1$ ) on the  $^{11}\text{B}$  MAS lineshapes are negligible. The lack of  $^{11}\text{B}$ - $^{14}\text{N}$  residual dipolar coupling implies rapid jumps of HMB about its principal rotation axis; this has been confirmed by carrying out variable-temperature experiments on a deuterated sample. The rate of in-plane jumps of the borazine ring becomes comparable to the deuterium quadrupolar coupling constant at approximately -120°C. In addition, the analysis of the  $^{15}\text{N}$  NMR spectra of stationary and MAS samples of  $^{15}\text{N}$  labelled HMB will be reported. Finally, restricted Hartree-Fock calculations have been employed to propose the orientations of the  $^{11}\text{B}$  electric field gradient tensor and boron and nitrogen chemical shielding tensors in the molecular frame; the largest component of each of these tensors for is found to be perpendicular to the molecular plane.

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- 259.** STRUCTURE AND DYNAMICS OF DI-SODIUM PHOSPHOTUNGSTATE USING SOLID-STATE  $^1\text{H}$ ,  $^{23}\text{Na}$  AND  $^{31}\text{P}$  NMR, X-RAY DIFFRACTION AND IR. Andrew M. Herring, Colorado School of Mines, Department of Chemical Engineering and Petroleum Refining, Golden, CO, 80401; Steven F. Dec, Colorado School of Mines, Department of Chemistry and Geochemistry, Golden, CO, 80401

The proton conductivity of heteropoly acids such as di-sodium phosphotungstate has long been of interest because of the potential to use these compounds as the proton conducting medium in devices such as fuel cells, either as thin films or in composite materials. The objective of the present study is to develop an understanding of the proton conductivity or mobility based on the structural and dynamic properties of these Keggin anion systems.  $^1\text{H}$  MAS NMR spectra of the limited hydrated form of di-sodium phosphotungstate indicate that there are two chemically distinct proton sites. One of these  $^1\text{H}$  sites exhibits a Pake pattern, at sufficiently low temperatures, from which an inter-proton distance of 0.36 nm can be calculated. This Pake pattern begins to narrow near room temperature and the temperature dependence of this effect will be discussed in terms of the relative diffusion of the protons in this site. The powder X-ray diffraction pattern is cubic and the DRIFTS shows well defined O-H bending bands which will be used to further elucidate structural details. Additional structural details determined from  $^{23}\text{Na}$ ,  $^{31}\text{P}$  NMR, and  $^1\text{H}$ - $^{31}\text{P}$  REDOR will be presented. Supported by NSF CTS-9512228.

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- 260.** SOLID-STATE  $^{25}\text{Mg}$  STUDIES ON MODEL MAGNESIUM OXYGEN SYSTEMS. Herman Lock and Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO 80523; J.J. Fitzgerald, J. Huang and J. Shore, Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007.

Solid-state  $^{25}\text{Mg}$  NMR investigations are reported on a range of model magnesium oxygen systems.  $^{25}\text{Mg}$  MAS and static NMR measurements were performed on  $\text{MgO}$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{MgTiO}_3$ ,  $\text{MgZrO}_3$ ,  $\text{Mg}_2\text{SiO}_4$ ,  $\text{MgNb}_2\text{O}_6$ ,  $\text{MgWO}_4$  and  $\text{MgTa}_2\text{O}_6$  at 9.4 and 14.1 Tesla. Chemical shift and quadrupole parameters were obtained from simulations. Similar techniques are currently employed to observe  $^{25}\text{Mg}$  NMR on the Mg-containing clay montmorillonite.

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- 261.** <sup>27</sup>Al, <sup>31</sup>P, AND <sup>13</sup>C MAS NMR STUDY OF VX, GD, AND HD REACTIONS WITH NANOSIZE Al<sub>2</sub>O<sub>3</sub>. George Wagner, Lawrence Procell, and Richard O'Connor, Research and Technology Directorate, US Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD 21010; Olga Koper and Kenneth Klabunde, Department of Chemistry, Kansas State University and Nantek, Inc., Manhattan, KS 66506; Shekar Munavalli, Geo-Centers, Inc., Gunpowder Branch Box 68, Aberdeen Proving Ground, MD 21010
- Reactions of VX, GD, and HD with nanosize Al<sub>2</sub>O<sub>3</sub> have been studied by <sup>31</sup>P and <sup>13</sup>C MAS NMR. All three agents hydrolyze to form non-toxic surface-bound phosphonates (VX and GD) and alkoxides (HD). HD also undergoes minor dehydrohalogenation to yield volatile vinyl products. <sup>27</sup>Al MAS NMR was used to assess changes in various surface sites of the high-surface area nanosize particles, and to characterize the surface alkoxides and aluminophosphonates. Results for the latter species are compared to aluminophosphonate model compounds.
- NMR Symposium Poster Session—George Wagner, Research and Technology Directorate, US Army ECBC, Attn: AMSSB-RRT-CA, APG, MD 21010-5424. Tel: (410) 436-8468, Fax: (410) 436-7317, E-mail: george.wagner@sbccom.apgea.army.mil**
- 262.** DIVALENT ION DISTRIBUTIONS IN [Pb,Sr]TiO<sub>3</sub> SOLID SOLUTIONS. Xin-Gang Zhao, David Bussian and Gerard S. Harbison, Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304.
- <sup>207</sup>Pb MAS NMR, X-ray powder diffraction and Monte Carlo metropolis calculations have been used to study cation ordering and nearest neighbor chemical shifts in [Pb,Sr]TiO<sub>3</sub> solid solutions. <sup>207</sup>Pb MAS NMR spectra of solid solutions with X<sub>Sr</sub> > 0.8 show a series of resolved signals from lead atoms with 4, 5 or 6 strontium nearest neighbors along the unit cell axes. The signals are further split, apparently by next-nearest neighbor (along face diagonal) effects. The magnitude and sign of the shift, approximately -70 ppm per strontium nearest neighbor, can be explained by dispersion contributions to the shielding hyperpolarizability. Analysis of the intensities of the lead resonances using a Monte-Carlo/Metropolis program indicates substantial cation ordering, with unlike nearest neighbor pairs and next-nearest neighbor pairs being energetically favored over like pairs by 1 – 3 kJ/mol. A concave deviation from the Vegard law is observed in this solid solution, and the conventional interpretation of this deviation is consistent with the NMR/Monte Carlo analysis. At higher lead concentrations, Monte-Carlo calculations predict alternate ordering of the divalent cations in three dimensions; the range of concentrations at which this ordering is predicted coincides with the appearance of a broad hump in the NMR spectrum, and of discrete domains in electron micrographs, but precedes that of the ferroelectric phase transition at X<sub>Sr</sub> ~ 0.5.
- NMR Symposium Poster Session—Gerard S. Harbison, 508 Hamilton Hall, Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304. Tel: (402) 472-9346, Fax: (402) 472-9402, Email: harbison@unlserve.unl.edu**
- 263.** OXYGEN LINKAGES IN TITANOSILICATE GLASSES EXAMINED BY OPTIMISED <sup>17</sup>O SOLID-STATE MQ-MAS EXPERIMENTS. Flemming H. Larsen, Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, UK; Stéphanie Rossano, Laboratoire de Mineralogie-Cristallographie, Université Paris 6, 75252 Paris cedex 05, France; Ian Farnan, Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, UK
- The structure of titanosilicate glasses are of interest both technologically and geochemically. The addition of Ti to a silicate melt or glass results in remarkable changes to the density, compressibility and thermal expansion. Moreover, there are anomalous changes in the heat capacity (C<sub>p</sub>) just above T<sub>g</sub> when compared with binary silicate melts. These changes in thermodynamic properties must be associated with profound structural changes in the liquid although there is considerable disagreement about the nature of these changes from work using scattering and vibrational techniques. <sup>17</sup>O NMR should be able to resolve these questions of local structural changes providing an accurate description of the local environments for the oxygens can be found. In order to describe the distinct oxygen sites and their distributions MQ-QCPMG-MAS NMR experiments using FAM-II pulses for the 3Q to 1Q transfer have been utilized. These methods have been tested for I=5/2 nuclei by <sup>27</sup>Al experiments on kyanite (Al<sub>2</sub>SiO<sub>5</sub>) and thereafter applied for <sup>17</sup>O. In both cases the FAM-II pulses have been optimised numerically. Various sites in <sup>17</sup>O-enriched K<sub>2</sub>O-TiO<sub>2</sub>-(SiO<sub>2</sub>)<sub>2</sub> (KTS<sub>2</sub>) glass are observed and the distinct sites have been assigned to a certain kind of oxygen by comparison with known <sup>17</sup>O chemical shifts (eg. Si-O-Si, Si-O-Ti, Si-O-K, Ti-O-Ti). Determination of the effect on the quantitative nature of MQ-MAS by the FAM-II 3Q-1Q conversion will be discussed as this is essential for constraining the local structure of titanosilicate glasses by the oxygen site abundances.
- NMR Symposium Poster Session—Flemming H. Larsen, University of Cambridge, Dept. of Earth Sciences, Downing Street, Cambridge CB2 3EQ, United Kingdom. Tel: +44 1223 333 373, Fax: : +44 1223 333 450, E-mail : flar00@esc.cam.ac.uk**
- 264.** STRUCTURAL INVESTIGATIONS OF SILVER BOROPHOSPHATE GLASSES. C. Jäger, M. Zeyer, Friedrich Schiller University Jena, IOQ, Max-Wien-Platz 1, D-07743 Jena, Germany; B. Cherry, J.W. Zwanziger, Indiana University, Dept. of Chemistry, Bloomington, IN 47405, USA
- Silver borophosphate glasses with multiple phosphate and borate resonances have been investigated both by 1D and 2D NMR techniques. <sup>31</sup>P and <sup>11</sup>B MAS NMR spectra provide useful information on the coordination numbers and the Q<sub>n</sub> units. However, line assignments in terms of the structural units are particularly difficult for the <sup>31</sup>P NMR spectra. Also, the bonding scenarios of the next nearest units cannot be obtained from the spectra. For obtaining a more complete picture of the glass structure 2D NMR techniques have been used such as <sup>11</sup>B MQMAS for identifying the number of different borate units and <sup>11</sup>B-<sup>31</sup>P HETCOR NMR using cross-polarization and REDOR for probing borate and phosphate units connectivities. First results will be discussed.
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- 265.** SOLID-STATE  $^{31}\text{P}/^{27}\text{Al}$  AND  $^{31}\text{P}/^{23}\text{Na}$  MAS NMR DIPOLAR DEPHASING INVESTIGATIONS OF CONNECTIVITY IN SODIUM ALUMINOPHOSPHATE GLASSES. David P. Lang and Todd M. Alam, Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185-1407.

Solid state  $^{31}\text{P}/^{27}\text{Al}$  and  $^{31}\text{P}/^{23}\text{Na}$  MAS NMR dipolar dephasing experiments have been used to investigate the spatial distribution of aluminum and sodium cations with respect to the phosphate backbone for a series of NAP glasses,  $x\text{Al}_2\text{O}_3 \cdot 50\text{Na}_2\text{O} \cdot (50-x)\text{P}_2\text{O}_5$  ( $0 \leq x \leq 17.5$ ). From the  $^{31}\text{P}/^{27}\text{Al}$  and  $^{31}\text{P}/^{23}\text{Na}$  connectivity data gathered, information about the medium range order in these glasses is obtained. The expanded connectivity data allows for better identification and interpretation of the new resonances observed in the 1D  $^{31}\text{P}$  MAS NMR spectra with the addition of alumina. The results of the dipolar dephasing experiments show that the sodium-phosphate distribution remains relatively unchanged for the glass series, and that the addition of aluminum occurs primarily through the depolymerization of the phosphate tetrahedral backbone. Dipolar dephasing experiments also provide insight about the degradation of these glasses in an aqueous environment. Using  $^{31}\text{P}/^1\text{H}$  CP as a filter, the proximity of hydrated phosphorus environments to P-O-Na or P-O-Al environments can be established using triple resonance  $^{31}\text{P}/^1\text{H}$  CPMAS select  $^{31}\text{P}/^{23}\text{Na}$  and  $^{31}\text{P}/^{27}\text{Al}$  dipolar dephasing techniques, respectively. Replacement of  $^{23}\text{Na}$  (or  $^{27}\text{Al}$ ) by  $^1\text{H}$  as a modifier ion is seen as one dominant pathway for water incorporation into the phosphate backbone. 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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- 266.** QUANTIFICATION OF THE PHOSPHORUS-SULFUR BONDING PREFERENCE AND PHASE-SEGREGATION PHENOMENA IN AMORPHOUS P-S-SE MATERIALS BY MULTIPLE-PHASE  $^{31}\text{P}$  AND  $^{77}\text{Se}$  NMR. Paul F. Mutolo, Department of Chemistry, University of California, Santa Barbara, CA 93106; Hellmut Eckert, Institut für Physikalische Chemie, WWU Münster, 48149 Münster, Germany.

Comprehensive structural investigations of five series of melt-quenched samples in the P-S-Se glass-forming system by multiple-phase (solution, solid, melt)  $^{31}\text{P}$  NMR and melt-phase  $^{77}\text{Se}$  NMR have uncovered a marked preference for P-S bond formation over P-Se bonding throughout the system. Results of extensive variable high-temperature (VT)  $^{77}\text{Se}$  NMR measurements of samples containing 10 atom% P are accurately described by a distribution of four possible selenium species. This selenium speciation distribution is nearly statistical with the exception that P-bonded species are suppressed by the preference for P-S bonding; however, a significant fraction of P-Se bonding still remains in sulfur-rich samples. In samples with phosphorus contents of 20 atom% and greater, segregation phenomena result from the propagation of the disparate structural characteristics of the two binary glass systems (P-S and P-Se) in these ternary samples which is clearly driven by the P-S bonding preference.  $^{31}\text{P}$  MAS-NMR results reveal the presence of increasing fractions of  $\text{P}_2\text{S}_n$  molecular units with increasing sulfur content in these series; the clusters segregate from the remaining covalent network P-Se glass, resulting in heterogeneous materials. Some homogeneous materials are found at the lowest sulfur contents, whereas the sequestration of phosphorus by sulfur leads to some sulfur-rich samples that are devoid of P-Se bonding. In samples of 40- and 50 atom% P, selenium incorporates into the molecular species resulting in the four, mixed-chalcogen molecules,  $\text{P}_2\text{Se}_{3-x}\text{S}_x$  ( $x=0-3$ ). The identity of these molecular units are confirmed by solution-state  $^{31}\text{P}$  NMR of  $\text{CS}_2$  solutions extracted from the solid glasses. Extensive  $^{31}\text{P}$  VT-NMR data of these higher phosphorus-content materials show that the  $\text{P}_2\text{S}_n$  and  $\text{P}_2\text{Se}_{3-x}\text{S}_x$  molecular species also exist in the glass-forming melts. The speciations determined in the solid glass arise as a consequence of the thermodynamic equilibria of the melt which are arrested at the glass transition temperature. Thus, for generating polymeric glass networks devoid of molecular cluster units in this composition region, the development of synthesis methods alternative to melt-quenching will be necessary.

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- 267.** CHARACTERIZATION OF LOW-DIMENSIONAL III-V SEMICONDUCTORS AND DEVELOPMENT OF OPNMR METHODS. Sophia E. Hayes, Lawrence Livermore National Laboratory & U.C. Berkeley, Department of Chemical Engineering, 201 Gilman Hall, Berkeley, CA 94720; Anant K. Paravastu and Jeffrey A. Reimer, U.C. Berkeley, Department of Chemical Engineering, 201 Gilman Hall, Berkeley, CA 94720.

Low-dimensional semiconductor structures of GaAs such as quantum wells and nanoclusters have been prepared and characterized by various techniques, including x-ray diffraction, x-ray photoelectron spectroscopy, photoluminescence, and solid-state NMR. We have also applied optically polarized NMR (OPNMR) techniques to the study of these materials, to gain a better understanding of their structure and electronic properties. Optical pumping of semiconductor materials has been utilized to achieve NMR sensitivity enhancements in a variety of III-V and II-VI semiconductors. The technique has been applied to both bulk materials, as well as semiconductor heterostructures. We will present some of the hardware requirements for these experiments, as well as conditions for optical pumping including pumping at or above the bandgap, laser polarization, and laser power.

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- 268.** APPLICATIONS OF HYPERPOLARIZED  $^{129}\text{Xe}$  NMR TO THE STUDY OF POROUS MATERIALS. Igor Moudrakovski, NRC, Ottawa, Ontario, Canada K1A 0R6; Andrej Noso and Stephen Lang, Carleton University, Ottawa, Ontario, Canada K1S 5B6; Christopher Ratcliffe and John Ripmeester, NRC, Ottawa, Ontario, Canada K1A 0R6.

$^{129}\text{Xe}$  NMR spectroscopy is a popular method for the study of microporous solids. Information can be obtained on the structure and statistics of filling of the void space, intersite and interparticle exchange, diffusion of molecules in the porous space, etc. For a long time the applicability of  $^{129}\text{Xe}$  NMR spectroscopy to materials has been hampered by a relatively low sensitivity, especially on materials with low surface areas. The development of optical pumping methods for the generation of hyperpolarized (HP) xenon has resulted in a tremendous increase in scope for  $^{129}\text{Xe}$  spectroscopy. Recent developments in Continuous Flow (CF) production of hyperpolarized xenon<sup>1</sup> and HP Xe delivery into MAS probes<sup>2,3</sup> are particularly useful for material sciences applications. By directing the output of a flow system for the continuous production of HP Xe directly into NMR probes (static, MAS or imaging), a particularly useful set of experiments becomes possible. Even at low concentration of Xe in the gas mixture (~ 1%) used for optical pumping gives single-scan sensitivity for many materials. The fact that the other gas components do not interfere significantly means that the spectra are taken essentially at zero xenon pressure, and that they are characteristic of the framework itself. Further it is possible to monitor changes in void space in real time during processes such as catalyst activation and adsorption and desorption. Examples of applications of the technique to the microporous and mesoporous materials of different chemical nature will be given, including the time-dependent behavior of a programmable sorbent and the study of surface reactions of organic films proposed for sensor applications. With a continuous flow, micro-imaging applications also are possible, with full chemical shift images becoming available in a reasonable length of time. Applicability of the method for zeolites and porous glass will be demonstrated.

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- 269.** TRENDS IN INDIRECT SPIN-SPIN COUPLING TENSORS: RECENT RESULTS FROM FIRST-PRINCIPLES CALCULATIONS. David L. Bryce and Roderick E. Wasylshen, Dalhousie University, Department of Chemistry, Halifax, Nova Scotia, B3H 4J3

The indirect spin-spin coupling (*J*) interaction is of fundamental importance in magnetic resonance spectroscopy. The *J* coupling between nuclei across hydrogen bonds, particularly in polypeptides, lately has been the focus of a great deal of attention from both experimentalists and theoreticians. Recent work has firmly established the reliability of multiconfigurational self-consistent field (MCSCF) calculations with large basis sets in the prediction of both the isotropic and anisotropic portion of the *J* tensor for small molecules containing first- and second-row elements (Bryce, D. L.; Wasylshen, R. E. J. Am. Chem. Soc. 2000, 122, 3197). In the present work, the results of MCSCF calculations of *J* tensors for a selection of small molecules will be discussed. In particular, three issues will be addressed. First, by examining molecules with relatively low symmetry, we will investigate variations of the asymmetry and orientation of the symmetric *J* tensor with respect to molecular geometry. Second, we will explore the relative importance of the antisymmetric portion of the *J* tensor as a function of molecular symmetry. Finally, although many researchers assume that the Fermi contact mechanism dominates *J* couplings for light atoms, recent work has shown that this is not always the case. To afford further insight into recent experimental results, we will examine the relative importance of the various *J* coupling mechanisms for  $^2\text{J}(\text{N}, \text{N})$  couplings in model systems.

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- 270.** THEORETICAL AND EXPERIMENTAL NMR STUDIES OF PEPTIDE-T. Devin N. Sears, Department of Chemistry MC(111), University of Illinois at Chicago, Chicago, IL. 60607; Angel C. de Dios, Joyia Rich, Department of Chemistry, Georgetown University, Washington, D.C. 20057-2222

Peptide-T, primary structure ASTTTNYT, and its D-Ala analog (D-ASTTTNYT) are known to bind to CD4 receptors on human T cells blocking the HIV virus from binding. Previous NMR studies of this peptide have been carried out in DMSO.<sup>1,2</sup> In this study the results of NMR experiments, carried out in a %50 H<sub>2</sub>O in D<sub>2</sub>O solvent system, are reported. This choice of solvent prevents complete exchange of the amide backbone protons such that nearly all proton resonance assignments could be made through the use of DQ-COSY, TOCSY, 1H-13C HMQC, and 1H-15N HMBC experiments. Using NOESY and ROESY cross peak volumes and three bond J(NH-Ha) coupling constants to generate restraints, molecular dynamics calculations resulted in an ensemble of 3-D structures of Peptide-T and its analog. Ab initio calculations of geometries and chemical shifts of Peptide-T done at the density functional theory (DFT) level, using the hybrid B3LYP functional with a 6-31G\*\* basis allows for the comparisons of the ab initio geometry calculations with the molecular dynamics structures obtained via the NMR restraints. The preliminary results of this work indicate Peptide-T adopts a bent conformation in aqueous solutions, which is in agreement with the previously reported studies.

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- 271.** AB INITIO ELECTRIC FIELD GRADIENT CALCULATIONS IN AMINO ACID AND PEPTIDE HYDROHALIDES. Chunlei Guo and Gerard S. Harbison, Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304.

In the gas phase or in environments of high symmetry, the quadrupolar coupling constants of chlorine, bromine and iodine nuclei in halide ions are zero. In the halide salts of amines, amino acids and peptides, however,  $^{35}\text{Cl}$  quadrupole coupling constants of up to 10 MHz, and  $^{79}\text{Br}$  couplings of up to 60 MHz have been measured, reflecting the substantial asymmetry of the coordination site in these compounds. Using the X-ray or (where available) the neutron diffraction structures of several amino acid hydrohalides, we have used *ab initio* methods to calculate the electric field gradients at the halide sites. We employ the commercial program Gaussian-98, using the MP2 method with 6-311+G(2d,p) and 6-311++G(3df,2pd) basis sets in the calculations. A dramatically simplified model for the halide ion coordination, using ammonium ions to replace  $-\text{NH}_3^+$  and waters to replace  $-\text{O}-\text{H}$  groups, is sufficient to achieve good agreement with experiment, and accurately reproduces both quadrupolar coupling constants and asymmetry parameters. Calculated chemical shielding anisotropies, while comparatively small, are in agreement with our limited experimental data. The success of the calculations demonstrates that the electric quadrupole coupling tensor of these ions is governed almost exclusively by the effects of local hydrogen bonding, and is therefore a useful probe of halide ion coordination.

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- 272.** HOMONUCLEAR PROTON DECOUPLING IN MAS SPECTROSCOPY AT HIGH SPINNING FREQUENCY. Elena Vinogradov<sup>1</sup>, P. K. Madhu<sup>2</sup>, and Shimon Vega<sup>1</sup>; <sup>1</sup>Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel; <sup>2</sup>Institut für Chemie, Johannes Kepler Universität, Altenbergerstrasse 69, A-4040 Linz, Austria

The application of combination of Magic Angle Spinning (MAS) and frequency switched Lee-Goldburg homonuclear decoupling (FSLG)<sup>1,2,3</sup> on a coupled proton system is investigated theoretically and experimentally. Phase modulated versions of the FSLG experiments<sup>4</sup> are considered and their performance at high spinning frequencies evaluated. The combination of sample spinning with periodic RF irradiation creates a Hamiltonian with two principal frequencies, the spinning frequency and inverse of the RF cycle time, that can be incommensurate. Average Hamiltonian Theory (AHT) is a feasible tool for describing the proton response for rotor periods that are integer multiples (N) of the RF cycle times. When this condition is not satisfied Floquet theory can be used to describe the proton evolution.

In this presentation both theoretical approaches will be explored. For high spinning frequencies, broadenings of the proton lines are compared with simulations and resonance conditions for N=3,4 are defined in terms of two-mode Floquet energy level crossings. Homonuclear correlation two-dimensional experiments as a function of the spinning frequency are compared with numerical simulations. In particular, short RF cycles and high spinning frequencies are considered.

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- 273.** HOMONUCLEAR DIPOLAR INTERACTIONS BETWEEN QUADRUPOLEAR NUCLEI UNDER MAGIC-ANGLE-SPINNING CONDITIONS. Mattias Edén and Lucio Frydman; Department of Chemistry (M/C 111), University of Illinois at Chicago, 845 W. Taylor St, Rm 4500, Chicago, IL 60607

The quadrupolar and dipolar interactions do not commute with each other when dealing with homonuclear pairs of coupled quadrupolar nuclei. This can result in a significant broadening of the central transition peaks in either conventional or MQ MAS spectra. Such broadenings depend on the magnitudes and relative orientations of the dipolar and quadrupolar interactions, as well as on the sample spinning frequency. We present numerical simulations and experiments for systems where these effects may appear, and explain them in terms of average Hamiltonian theories developed in conventional and in quadrupole-driven interaction frames.

**NMR Symposium Poster Session—Mattias Eden; Department of Chemistry (M/C 111), University of Illinois at Chicago, Chicago, IL 60607-7061, E-mail: mattias@hermes.chem.uic.edu**

- 274.** OPTIMIZED MULTIPLE-QUANTUM NMR OF SPECIES WITH STRONG QUADRUPOLEAR INTERACTION USING A COMPOSITE CONVERSION PULSE. Christian Fernandez, Valérie Montouillout and Anne-Agathe Quoineaud; Laboratoire de Catalyse et Spectrochimie, University of Caen Basse-Normandie, 14050 Caen (France)

We describe a pulse sequence leading to better conversion from the multiple quantum (MQC) to single-quantum (SQC) coherence in MQMAS experiments of spin 3/2 and spin-5/2 nuclei. The proposed sequence consists in a customized series of pulses with phase alternation and variable lengths. The pulse lengths have been calculated and optimized numerically. The experimental results corroborate the calculated signal enhancement. A particularly useful result for applications derives from the better detection of very strong quadrupolar couplings as demonstrated on the MQMAS spectrum of the AlO6 site in andalusite (CQ: 15.3 MHz). Application of the method to some catalysts will be shown.

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- 275.** SENSITIVITY ENHANCEMENT OF THE CENTRAL TRANSITION NMR SIGNAL OF QUADRUPOLEAR NUCLEI UNDER MAGIC-ANGLE SPINNING. Zhi Yao; Hyung Tae Kwak; Philip J. Grandinetti, The Ohio State University, Department of Chemistry, 120 W. 18th Avenue, Columbus, Ohio 43210-1173; Dimitris Sakellariou, Lyndon Emsley; Laboratoire de Stéréochimie et des Interactions Moléculaires, UMR 5532 ENS-Lyon/CNRS, Ecole Normale Supérieure de Lyon, 69364 Lyon, France
- A new approach for enhancing the sensitivity of the NMR of the central transition of a spin 3/2 quadrupolar nuclei is presented. The enhancement is a result of a selective saturation of the satellite transitions during a fast 180° phase alternation pulse train with magic-angle spinning. In this selectively saturated state, the population  $s$  of all eigenstates  $\sim m$  with the same sign of  $m$  become equal and lead to an enhanced central  $m = -1/2 \rightarrow 1/2$  transition polarization. Enhancements up to a factor of 2 are predicted by numerical simulations, and values of 1.7 and 1.9 have been obtained experimentally for the central transitions of  $^{23}\text{Na}$  in polycrystalline  $\text{Na}_2\text{C}_2\text{O}_4$  and  $^{87}\text{Rb}$  in polycrystalline  $\text{RbClO}_4$ , respectively. Most importantly, we find no significant anisotropic lineshape distortion using this approach. Reductions in the enhancement appear to arise from homonuclear dipolar couplings which reduce the degree of selective saturation. The enhancement as a function of pulse train evolution time, modulation frequency rf field strength, and sample spinning speed has also been investigated, and the conditions for optimum enhancement are discussed. Extension of these ideas to higher spin quadrupolar nuclei with greater enhancements is possible, and in general, a theoretical maximum enhancement factor of  $S+1/2$  can be obtained with selective saturation of the all satellite transitions.

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- 276.** ANGLE AND DISTANCE DETERMINATION BY SOLID-STATE NMR: ROTATIONAL-ECHO DOUBLE RESONANCE OF THREE-SPIN SYSTEMS. Sue M. Mattingly, Frederick G. Vogt, James M. Gibson and Karl T. Mueller; Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA, 16802-6300
- One of the most successful techniques for measuring internuclear distances between hetero-atoms is the rotational-echo double-resonance (REDOR) experiment.<sup>1,2</sup> This technique is shown here to be applicable for both distance determination and for precise measurement of the angle between the internuclear vectors in triply-labeled spin systems. Simulations utilizing the REDOR three-spin signal combined with the REDOR transform<sup>3</sup> and related techniques<sup>4</sup> lead to a precise method for determining the angle. The REDOR measurement is performed using each of the heteronuclei in the triad as a detection point, and the results are explained using density matrix arguments. It is shown that, as long as the scalar coupling is taken into account, the two distances and the angle can be measured from two separate 2-D-REDOR experiments, one on each of the heteronuclei. These experiments are applied to labeled samples of uracil and glycine. Methods are explained and demonstrated for determining the angle in addition to the two internuclear distances for the three-spin system. Simulations are also used to examine the three-spin REDOR signal in detail. The methodology demonstrated here is not limited to crystalline materials, and could be employed for geometry measurements in systems where X-ray diffraction is not applicable. To investigate this possibility, we are applying this technique to bound bio-molecules.

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- 277.** RADIO FREQUENCY FIELD STRENGTH MAPPING AND SIMULATIONS FOR SELECTED COIL CONFIGURATIONS OF LARGE-VOLUME MAS SYSTEMS. C. Keeler, H. Lock and G. E. Maciel, Colorado State University, Department of Chemistry, Fort Collins, CO 80523
- Radio Field (RF) strengths for selected coil conformations were mapped for 9.5 and 14 mm Chemagnetics-style MAS systems at 100 MHz. The results for each configuration were compared to RF field strengths calculated from the Biot-Savart law. RF fields were determined as a function of both radial and axial dimensions within the sample area through the use of carefully designed inserts containing  $^{13}\text{C}$ -carbonyl labeled glycine. The signal area of the carbonyl peak, determined through direct polarization and cross polarization, were also compared as a function of sample position. These results are used to discuss the merits and/or drawbacks of particular coil properties and their relationships to signal-to-noise and absolute quantitation by spin-counting.

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- 278.** PULSED DYNAMIC NUCLEAR POLARIZATION AT 140 GHz/5 TESLA. V. Weis, M. Bennati, E. MacNamara, V. Ladizhansky, R. G. Griffin, MIT/Harvard Center for Magnetic Resonance, 170 Albany Street, Cambridge MA, 02139, USA
- Dynamic Nuclear Polarization (DNP) represents a magnetic resonance technique to increase the sensitivity of NMR experiments by transferring the much larger electron spin polarization from unpaired electron spins to magnetic nuclei (usually protons). The typical DNP experiment consists of a two step process which includes the initial polarization of nuclei with non zero hyperfine coupling to the nearby electron spin and subsequent 1H-1H spin diffusion to disperse the nuclear polarization throughout the solid state matrix.

In this contribution we introduce a new polarization mechanism based on an electron-nuclear double resonance experiment which generates nuclear polarization along the Zeeman quantization axis. Two descriptions of the experiment are presented. The first interpretation, describing

a solid effect in the electron dressed state, is in close analogy to the well known 'solid state effect' being used to polarize nuclei at low Zeeman fields. The second interpretation analyzes the experiment in terms of electron-nuclear cross polarization.

Room temperature DNP experiments were carried out in a custom-designed 140 GHz/5 Tesla pulsed EPR/ENDOR spectrometer on a powder sample of bis-diphenylene-phenyl-allyl (BDPA) radical dispersed at a level of ~ 1% by weight in a protonated polystyrene matrix. We demonstrate the polarization transfer by monitoring both the loss of electron spin polarization and the increase of nuclear polarization on a timescale of a few microseconds.

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- 279.** NON-DESTRUCTIVE EVALUATION OF COMPOSITES VIA NQR STRAIN MEASUREMENTS. Stephanie A. Vierkötter and David Gregory, Quantum Magnetics, Inc., 7740 Kenamar Court, San Diego, CA 92121-2425.

It has been known for several decades that NQR frequencies shift as a function of stress, and hence, stress induced strain. However, engineers and test analysts still cannot purchase a NQR strain gauge that could help them to evaluate fiber-reinforced polymeric composite structures non-destructively. The need for such a tool exists since current strain gauges have significant drawbacks, especially for non-destructive Evaluation (NDE) on structures and parts that are already in service. Applications span many industries, including aerospace, space and missile, civil infrastructure, automobile and sporting goods. Quantum Magnetics, Inc., has taken on the challenge to fill the need for such NDE tool via development of a practical NQR strain gauge. A carefully selected NQR active additive is homogeneously blended into the composite. The structure is interrogated by a NQR coil, and the frequency response is measured. This response is strain dependent and can be used to assess the structural health of the examined composite. The measurement can be performed anywhere on the structure and at any time during the structure's lifetime. The measurement is non-intrusive and non-contacting; in contrast to many other strain sensing techniques, no wires or cables need to be attached and no external stress needs to be applied. The presentation will discuss the results of two programs that are aimed at developing such NQR strain gauges. We have studied the NQR responses of fiberglass/epoxy samples under tensile loads as well as fiberglass/epoxy and hybrid composite samples with residual strains that result from manufacturing via compression molding. Both in-service NDE and quality control applications will be addressed. Supported by BMDO grant F29601-98-0170 and NSF grant DMI-9960693.

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- 280.** DISCLOSURE OF THE ROTATIONAL EXCHANGE GRADIENT IMAGER. Rex E. Gerald II, Robert J Klingler, and Jerome W. Rathke, Argonne National Laboratory, Chemical Technology Division, Argonne, Illinois 60439

In the rotating frame, the radiofrequency (rf) magnetic field at every point around a straight wire inductor has an angular-dependent direction with respect to the laboratory frame, and a magnitude that is inversely proportional to the distance from the wire. Nuclear spin magnetization initially directed to the y-axis by an x-phase rf pulse in one local rotating frame will exhibit a phase and frequency shift when detected in other local rotating frames whose axes are not coincident but rotationally disposed with respect to the initial rotating frame. In effect, the magnetization will experience a Doppler shift when mechanically translated from one local rotating frame to another. Mechanical translation of a sample about a straight wire inclined at the magic angle produces averaging of spin interactions described by second-rank tensors as well as a frequency shift equal to the rate of rotation.

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## Perspectives in Analytical Chemistry Oral Sessions

- 281.** IS WHAT WE ARE REALLY BETTER THAN WHAT WE WERE? R. K. Skogerboe, Department of Chemistry, Colorado State University, Ft. Collins, CO 80523

*Analytical spectroscopy has remained the tour de force in elemental analysis because it offers an impressive array of possibilities. A large segment of the current emphases have focused on Atomic absorption, emission, and mass spectrometry. These techniques have been brought to the forefront by extensive research efforts involving new methodologies. But, are they really new or simply rediscoveries of old approaches or concepts? This report will delineate a number of recent developments that are actually expressions or elaborations of old technologies.*

**Perspectives in Analytical Chemistry Oral Session—Rod Skogerboe, 1229 Forest Hills Lane, Ft. Collins, CO 80524. Tel: 970-224-5949, Fax: 970-474-0357, E-mail: skog@lamar.colostate.edu**

- 282.** PLASMA SPECTROCHEMICAL INSTRUMENTATION: CONSTRAINTS AND OPPORTUNITIES. Gary M. Hieftje, Department of Chemistry, Indiana University, Bloomington, IN 47405

*There are three main ways by which advances in science or technology occur. The first is incremental and involves a refinement or extension of current knowledge, practices, instrumentation, and techniques. Predicting which of these current trends becomes dominant is then a matter of evaluating each of the competing methods and weighing the strengths and weaknesses of each against the anticipated needs of science, technology, and society. Thus, both the capabilities of a present technology and the drivers that dictate its use are critical. The second way by which advances arise is through technology transfer. Quite often, these developments are more important than those that occur by extension of current knowledge, and are more unanticipated. Sometimes these advances are the result of collaboration but more frequently happen because of familiarity of a single person with more than one field. An example in another discipline is the invention of the scanning tunneling microscope; the existence and spatial dependence of electron tunneling had long been known, and the piezoelectric means by which probes could be moved on an angstrom scale were well established. Yet it took clever insight and knowledge of these facts for the STM to be developed. The third path to new advances is via true discovery or invention: the "Eureka" process. These occurrences are less frequent than either of the others above, and can seldom be foreseen. Occasionally, they arise from close and clever observation, such as in the discovery of fullerenes or "Buckyballs". Sometimes they are the result of unexpected insight of a physical, chemical, or instrumental problem. Either way, by their inherently unpredictable nature, they cannot realistically be part of a framework for guessing future developments.*

*In this presentation, the first two approaches will be employed in order to project some developments likely to occur in plasma spectrochemical analysis.*

**Perspectives in Analytical Chemistry Oral Session—Gary M. Hieftje, Department of Chemistry, Indiana University, Bloomington, IN 47405**

- 283.** MICRO MIRRORS IN ATOMIC SPECTROSCOPY. William G. Fateley, Bob Hammaker, Richard DeVerse, Threë LC; Dave McCurdy, Truman State University

- 284.** HIGHLY MULTIPLEXED CAPILLARY ELECTROPHORESIS. Edward S. Yeung, Xiaoyi Gong, Gang Xue, Lianjia Ma, Seong Ho Kang, Yonghua Zhang, Ho-ming Pang, Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, IA 50011
- Capillary electrophoresis (CE) is now a mature technique for analytical separations. In its various modes, impressive performance has been demonstrated for ionic as well as for neutral compounds. The Human Genome Project provided the impetus for developing multiple capillary systems. However, capillary arrays are not just for DNA analysis. Every CE protocol can be similarly multiplexed to achieve higher throughput and reduced reagent consumption without sacrificing its good resolving power and full automation. We have solved the two major problems associated with highly-multiplexed CE. To account for variations in migration times and injected amounts among the many capillaries, we used two internal standards and a straightforward algorithm to normalize all peak areas and migration times. This correction works for both zone electrophoresis and micellar electrokinetic chromatography. To extend the applicability to non-fluorescing compounds, we constructed a simultaneous multiplexed absorption detector for 96 capillaries. Entire sample trays in the 96-well microtiter plate format can be analyzed in one operation. This high-throughput capability gives CE a unique advantage over column liquid chromatography in most applications. Examples from DNA analysis, enzyme assay, peptide mapping and combinatorial synthesis will be presented.*

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- 285.** ANALYTICAL CHEMISTRY: THE MULTIDISCIPLINARY AND ESSENTIAL SCIENCE. Henry N. Blount, III, National Science Foundation

- 286.** PANEL DISCUSSION—ANALYTICAL CHEMISTRY: FROM WHERE WE HAVE BEEN, TO WHERE WE ARE GOING. E. S. Yeung, G. M. Hieftje, H. N. Blount, W. G. Fateley, R. K. Skogerboe.

## Supercritical Fluids — Theory & Applications Oral Sessions

- 287.** SUPERCRITICAL AND SUBCRITICAL GASES AS SOLVENT SUBSTITUTES FOR HOMOGENEOUS HYDROGENATION. Philip G. Jessop, Jason Bonilla, Richard Brown, Erin McKoon, Colin Thomas, Department of Chemistry, University of California, Davis, CA 95616  
*Compressed CO<sub>2</sub> and other gases with critical points near room temperature can serve as solvent substitutes in a number of different ways. The gas can be:*

- used as a supercritical fluid (SCF),<sup>1</sup>*
- combined with water to make a SCF/aqueous biphasic medium,<sup>2</sup>*
- used as a swelling agent for organic liquids,<sup>3,4</sup> or*
- used as a gaseous (subcritical) accelerant for solventless reactions of solids.<sup>5</sup>*

*Examples of each of these possibilities will be described, with an emphasis on applications to homogeneous catalytic hydrogenation of arenes, olefins, and carbon dioxide.*

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**Supercritical Fluids Oral Session—Philip G. Jessop, Department of Chemistry, University of California, Davis, CA 95616. Tel: (530) 754-9426, Fax: (530) 752-8995, E-mail: jessop@chem.ucdavis.edu**

- 288.** BIPHASIC CATALYSIS IN WATER/CARBON DIOXIDE MICELLAR SYSTEMS: TOWARDS ENHANCED REACTIVITY AND SEPARATION. Gunilla B. Jacobson, William Tumas, Los Alamos National Laboratory, Los Alamos, NM, 87545; Keith P. Johnston, Dept. of Chem. Eng., University of Texas, Austin, TX, 78712

*We will report on biphasic catalysis in water/carbon dioxide micellar systems for several important reactions, including hydroformylations and hydrogenations.<sup>1</sup> The recent development of surfactants capable of forming emulsions and microemulsions of H<sub>2</sub>O and CO<sub>2</sub> has led to micellar systems that are good solvents for both hydrophilic and hydrophobic species.<sup>2</sup> We have been examining catalytic reactions using water-soluble catalysts and lipophilic substrates in two-phase systems where the catalyst and product are obtained in separate phases after completing the reaction. The use of micellar systems, either emulsions or microemulsions, results in increased reaction rates due to the large surface area and low surface tension between water and carbon dioxide, as compared to a biphasic water/organic solvent system. Also, by using supercritical carbon dioxide, instead of an organic solvent, the micellar system can easily be broken after completing the reaction, simply by decreasing the pressure. This allows for simple separation of the products, which is obtained in the CO<sub>2</sub> phase, and no solvent separation step is necessary as the CO<sub>2</sub> is simply evaporated. The aqueous phase, now containing the catalyst and surfactant, can be recycled. For example, we have found that the rates and conversions of the hydrogenation and hydroformylation of long chain alkenes using water soluble rhodium-phosphine complexes are significantly higher in CO<sub>2</sub>/water emulsions than in two-phase CO<sub>2</sub>/water or toluene/water mixtures.*

1. G. B. Jacobson, C. T. Lee, Jr., K. P. Johnston, W. Tumas, *Biphasic Catalysis in Water/Carbon Dioxide Emulsions*, *Journal of the American Chemical Society*; 1999; 121(50); 11902.
2. a) Johnston, K. P. et al. *Science*, 1996, 271, 624-626. b) G. B. Jacobson, C. T. Lee, Jr., K. P. Johnston, *Organic synthesis in water/carbon dioxide microemulsions*. *J. Org. Chem.*, 1999, 64, 1201. c) G. B. Jacobson, C. T. Lee, Jr., S. R. P. daRocha, K. P. Johnston, *Organic synthesis in water/carbon dioxide emulsions*. *J. Org. Chem.*, 1999, 64, 1207.

**Supercritical Fluids Oral Session—Gunilla B. Jacobson, Los Alamos National Laboratory, CST-12 MS E537, Los Alamos, NM, 875 45. Tel: 505-665-7626, Fax: 505-667-6561, E-mail: jacobson@lanl.gov**

- 289.** POLYMERIZATIONS IN SUPERCRITICAL CARBON DIOXIDE. Reddy Venumbaka; Rodney L. Welsch; Xiaochuan Hu; Joseph H. Koo; Patrick E. Cassidy; John W. Fitch and Michael T. Blanda, Waste Minimization and Management Research Center, Southwest Texas State University, San Marcos, TX 78666

- 290.** METAL EXTRACTIONS USING WATER IN CARBON DIOXIDE MICROEMULSIONS. Matthew Z. Yates, Mary L. Cambell, Deborah L. Apodaca, T. Mark McCleskey, Los Alamos National Laboratory, CST-18, Mail Stop J514, Los Alamos, NM 87545; Eva R. Birnbaum, Los Alamos National Laboratory, CST-9, Mail Stop E518, Los Alamos, NM 87545

*Water in supercritical carbon dioxide microemulsions are examined as a new medium for the extraction of metal ions from contaminated surfaces. Microemulsions were used to extract both Cu<sup>2+</sup> ions as copper nitrate on filter paper and Eu<sup>3+</sup> as EuCl<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub> powders. In two extraction steps, >99% of the copper was removed from a copper nitrate spiked filter paper using 60 µL of water and 200 mg of surfactant in 10 g of CO<sub>2</sub>. Up to 18 mM copper can be extracted into the microemulsion, corresponding to 3 M copper inside the aqueous phase. The kinetics of copper extraction from filter paper was monitored by in situ UV-Vis spectroscopy; extraction was complete in less than 90 minutes. The versatility of the microemulsion was demonstrated by changing the environment within the microemulsion to facilitate the extraction of the*



metal oxide  $\text{Eu}_2\text{O}_3$ . Microemulsions were formed with a 20 wt% nitric acid solution rather than pure water and shown to solubilize  $\text{Eu}_2\text{O}_3$  via formation of  $\text{Eu}(\text{NO}_3)_3$ . Fluorescence spectroscopy was used to monitor the europium ion in the microemulsion and provide evidence that the europium ion interacts with the carboxylate head group of the surfactant.

**Supercritical Fluids Oral Session—Matthew Z. Yates, Los Alamos National Laboratory, CST-18, Mail Stop J514, Los Alamos, NM 87545. Tel: (505) 667-2658, E-mail: myates@lanl.gov**

- 291.** SOLUBILITIES AND EXTRACTION OF IRON(III), CERIUM(IV) AND TERBIUM(III)  $\beta$ -DIKETONATES IN SUPERCRITICAL CARBON DIOXIDE. Wendy C. Andersen, Robert E. Sievers, University of Colorado at Boulder, Department of Chemistry and Biochemistry, Boulder, CO 80309-0215; Anthony Lagalante and Thomas J. Bruno, Chemical Sciences and Technology Laboratory, National Institute of Standards and Technology, Boulder, CO 80303

$\beta$ -diketonates have been widely studied as chelating agents for metal ion removal in supercritical fluid extraction (SFE) with carbon dioxide. The extraction efficiency in SFE is limited by the solubility of the metal chelate in supercritical  $\text{CO}_2$  as well as properties of the chelating agent. We have measured the solubility of several  $\beta$ -diketonates of iron(III), cerium(IV), and terbium(III) by near infrared spectroscopy to determine which chelating agents provide the greatest potential for supercritical fluid extraction of metal compounds from hazardous and radioactive wastes. 2,2,7-Trimethyl-3,5-octanedionate, (tod), chelates are an order of magnitude more soluble than similar  $\beta$ -diketonates. The crystal structures of these compounds support these findings, showing that the tod ligand better shields the charged central metal atom from non-polar solvent molecules. An SFE method was developed to extract  $\text{Fe}^{3+}$  from aqueous samples using supercritical  $\text{CO}_2$  and H(tod). Solubility results and extraction data will be presented.

**Supercritical Fluids Oral Session—Wendy C. Andersen, University of Colorado at Boulder, Department of Chemistry and Biochemistry, Boulder, CO 80309-0215. Tel: 303-492-8624, Fax: 303-492-1414, E-mail: anderswa@ucsub.colorado.edu**

- 292.** REMOVAL OF POLYMER COATINGS WITH SUPERCRITICAL FLUIDS. Laurie Williams, Los Alamos National Laboratory, CST-12, P.O. Box 1663, Mail Stop E537, Los Alamos, NM 87545; James B. Rubin, Los Alamos National Laboratory, NMT-16, P.O. Box 1663, Mail Stop E537, Los Alamos, NM 87545.

Numerous environmental regulations, and the wide range of concerns pertaining to environmental release paths, is leading industries to seek non-hazardous, low-discharge coatings removal technologies. Supercritical fluids are used as solvent in many commercial applications, including the extraction of caffeine from coffee and essential oil and spices from plants for use in perfumes and foods. Supercritical fluids, especially carbon dioxide, as an alternative coatings removal technology has tremendous potential as they offer many advantages over conventional organic solvents and are non-harmful to most substrate surfaces. To exploit the use of supercritical fluids in the removal of coatings and in extraction technologies, it is important to understand their properties and how supercritical fluids interact with materials. This paper will discuss the interactions between a supercritical fluid, carbon dioxide in particular, and polymers and then focus attention on the specific interactions which are brought to bear when a polymeric coating is to be removed or involved in an extraction operation.

**Supercritical Fluids Oral Session—Laurie Williams, Los Alamos National Laboratory, CST-12, P.O. Box 1663, Mail Stop E537, Los Alamos, NM 87545. tel: 505 667-3706, Fax: 505 667-6561, E-mail: williams1@lanl.gov**

- 293.** SUPERCRITICAL FLUID PRODUCTION OF MICROPARTICLES FOR MEDICAL APPLICATIONS. Theodore W. Randolph, Dept. of Chemical Engineering, University of Colorado at Boulder, Boulder, CO 80309

Precipitation with a compressed antisolvent, a process used to produce polymeric microspheres, is combined with a polarity-reversing solubilization technique (hydrophobic ion-pairing) to generate controlled drug delivery from microspheres. A charged pharmaceutical agent is solubilized in a solvent compatible with the particular polymer by stoichiometric replacement of the polar counter ions of the drug with more hydrophobic surfactants. A solution of polymer and ion-paired drug is co-precipitated into microspheres using compressed carbon dioxide as an antisolvent. In vitro evaluation of several formulations (gentamycin, DNA etc.) indicates nearly complete encapsulation of the drug within the polymer and controlled drug release kinetics for several months. Further release work suggests that the ion-paired drug is released from the polymer matrix as a complex, rather than by diffusing from the matrix as a charged molecule. A brief summary of in vivo (murine and ovine models) and in vitro cell culture (rat alveolar macrophage cell line NR8383) drug release studies will be presented.

The time scale of surface tension evolution in jets of miscible fluids injected into near- and supercritical fluids was investigated computationally. These results, combined with experimental results using high speed photography and linear jet breakup theory, show that the mechanism of formation of polymer microparticles is not controlled by atomization of the liquid solvent jet. Rather, the rapid decrease in surface tension caused by the high mass-transfer rates in supercritical fluids results in homogeneous nucleation and growth under gas-like mixing conditions.

Process conditions may be adjusted to modify crystallinities of the polymer within the microparticles. This in turn influences the ease with which residual solvent can be extracted, as well as the response of alveolar macrophages (as oxidative burst and tumor-necrosis factor- $\alpha$  production) to the particles.

**Supercritical Fluids Oral Session—Ted Randolph, Professor of Chemical Engineering, Co-Director, Center for Pharmaceutical Biotechnology, University of Colorado, Boulder, CO. Tel: (303) 492-4776, E-mail: randolph@pressure3.colorado.edu**

- 294.** STABILIZATION OF TRYPSINOGEN DURING FINE PARTICLE FORMATION FOR PULMONARY DRUG DELIVERY USING CO<sub>2</sub>-ASSISTED AEROSOLIZATION AND BUBBLE DRYING. Joseph A. Villa, Robert E. Sievers, Scott P. Sellars, Graham S. Clark, Boris Mioskowski, and Kyle D. Kusek, University of Colorado, CIRES and Department of Chemistry and Biochemistry, Campus Box 216, Boulder, CO 80303; John Carpenter, School of Pharmacy, University of Colorado Health Sciences Center, 4200 E. 9th Ave., Denver, CO 80262; James Matsuura, Alza Corporation, 1501 California Ave., Palo Alto, CA 94304

*Fine pharmaceutical particles (0.5 – 5 micrometers) can be produced using a recently invented supercritical or near supercritical CO<sub>2</sub>-assisted aerosolization and bubble drying process. Bubble drying rapidly occurs at temperatures between 25 and 70°C, which is much lower than conventional spray drying usually requires. This technique utilizes the high solubility of carbon dioxide in water, coupled with expansion of the solution through a restrictor, as a means to aerosolize aqueous solutions of drugs. When the micro-bubbles formed are dried, solid or hollow spherical particles are formed. The dried aerosol particles can be collected for subsequent use in dry powder inhalers or in metered dose inhalers. Trypsinogen has been used as a model protein and has been stabilized through the use of sugars added to the solutions before bubble drying. Trehalose-trypsinogen mixtures showed complete retention of enzyme activity at a ratio of 98:2 and 92% activity at a 50:50 weight ratio.*

**Supercritical Fluids Oral Session—Joseph Villa, University of Colorado, CIRES and Department of Chemistry and Biochemistry, Campus Box 216, Boulder, CO 80303. Tel: 303-492-8624, Fax: 303-492-1414, E-mail: villaj@colorado.edu**

- 295.** COMPRESSIBLE MOBILE PHASES IN PACKED CAPILLARY COLUMN CHROMATOGRAPHY. Naijun Wu, Milton L. Lee. Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602-5700, USA

*Supercritical or enhanced fluid mobile phases inherently provide low viscosity, high diffusivity, and solvating power. Low viscosity and high diffusivity allow the use of relatively long packed columns to produce high column efficiency in relatively short time. In LC, heated or CO<sub>2</sub>-modified liquids have been used as mobile phases, and in typical supercritical fluid chromatography (SFC), neat CO<sub>2</sub> or CO<sub>2</sub> with modifiers have been used.*

*In such situations, a restrictor must be used to maintain the mobile phase as a uniform fluid throughout the whole column length. When the restrictor is removed, a large difference in density of mobile phase occurs between the two ends of the column. Most of the pressure drop occurs near the outlet of the column when a packed capillary is utilized. The mobile phase can be introduced into the column as a liquid and removed as a gaseous vapor at the column outlet when temperatures are higher than the boiling point of the liquid. When a supercritical fluid is introduced, the mobile phase exits as a gas at the column outlet. Solvating gas chromatography (SGC) has been used to describe these situations. In this presentation, fundamental and practical aspects of SGC and SFC will be discussed, and various separations will be demonstrated.*

**Supercritical Fluids Oral Session—Naijun Wu, Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602-5700. Tel: (801) 378-4466, Fax: (801)378-5474, E-mail: NWU@chemdept.byu.edu**

- 296.** HYDROTHERMAL PROCESSING OF TRANSURANIC CONTAMINATED COMBUSTIBLE WASTE. S. J. Buelow,<sup>1</sup> L. Worl<sup>2</sup>, D. Harradine<sup>1</sup>, D. Padilla<sup>2</sup>, R. McNroy<sup>1</sup>, <sup>1</sup>Chemistry Division, <sup>2</sup>Nuclear Materials Technology Division, Los Alamos National Laboratory Los Alamos, NM 87545

*Experiments at Los Alamos National Laboratory have demonstrated the usefulness of hydrothermal processing for the disposal of a wide variety of transuranic contaminated combustible wastes. This paper provides an overview of the implementation and performance of hydrothermal treatment for concentrated salt solutions, explosives, propellants, organic solvents, halogenated solvents, and laboratory trash, such as paper and plastics. Reaction conditions vary from near ambient temperatures and pressure to over 1000 °C and 100 MPa pressure. Studies involving both radioactive and non-radioactive waste simulants are discussed.*

**Supercritical Fluids Oral Session—Steven J. Buelow, Chemistry Division, Los Alamos National Laboratory Los Alamos NM 87545. Tel: (505) 667-1178, E-mail: buelow@lanl.gov**

- 297.** <sup>1</sup>H DYNAMIC NUCLEAR POLARIZATION IN SUPERCRITICAL ETHYLENE AT 1.4 T. Jian Z. Hu; Shi Bai; Mark S. Solum; Paul D. Ellis; David M. Grant, Department of Chemistry, Ronald J. Pugmire, Department of Chemical and Fuels Engineering, University of Utah, Salt Lake City, Utah 84112, Robert A. Wind; Clement R. Yonker, Pacific Northwest National Laboratory, P.O. Box 999, Richmond, Washington 99352, Craig M. V. Taylor, Los Alamos National Laboratory, CST-12 MS J964, Los Alamos, NM 874 45.

*H dynamic nuclear polarization (DNP) has been measured in supercritical ethylene in the pressure range 60-300 bar and in an external field of 1.4 T. A single-cell sapphire tube was used as a high pressure cell, and powdered 1,3-bisdiphenylene-2-phenyl allyl (BDPA) free radicals were added and distributed at the wall of the cell. At all pressures the dominant DNP effect was a positive Overhauser enhancement, caused by proton-electron contact interaction at the fluid/solid radical interface. The observed enhancements varied from 12 at 60 bar to 17 at 300 bar. Besides the Overhauser enhancement, also a small solid state and thermal mixing enhancement were observed, indicating that part of the ethylene is adsorbed at the radical surface for a prolonged time. The effects of the experimental conditions on the Overhauser enhancement factors are discussed, and enhancements of at least 40-60 are estimated when EPR saturation factors and the leakage factor become maximal. These data indicate that DNP-enhanced NMR has the potential of extending the impact of NMR in research areas involving supercritical fluids. Also, the application of supercritical fluid ethylene on C1-chemistry will be discussed briefly.*

**Supercritical Fluids Oral Session—Jian Z. Hu, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Tel: (801) 585-3419, Fax: (801) 581-8433**

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# ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

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