Rocky Mountain Conference on Magnetic Resonance

Volume 21 *21st Rocky Mountain Conference on Analytical Chemistry*

Article 1

7-30-1979

21st Rocky Mountain Conference on Analytical Chemistry

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(1979) "21st Rocky Mountain Conference on Analytical Chemistry," *Rocky Mountain Conference on Magnetic Resonance*: Vol. 21, Article 1.

DOI

https://doi.org/10.56902/RMCMR.1979.21.1

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21st Rocky Mountain Conference on Analytical Chemistry

Abstract

Abstracts and meeting program from the 21st annual meeting of the Rocky Mountain Conference on Analytical Chemistry, co-sponsored by the Rocky Mountain Section of the Society for Applied Spectroscopy and the Rocky Mountain Chromatography Discussion Group. Held in Denver, Colorado, July 30 - August 1, 1979.

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21ST
ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

ABSTRACTS & MEETING PROGRAM

Sponsored jointly by

Rocky Mountain Society
For Applied Spectroscopy

and

cky Mountain Chromatography Discussion Group

DENVER CONVENTION COMPLEX
Denver, *Colorado*

July 30 — August 1, 1979

WELCOME!

I am very pleased to welcome you to the 21st Annual Rocky Mountain Conference on Analytical Chemistry. Over the past few years, the Conference has grown into one of the most prominent summer analytical meetings in the United States. I am pleased to report that last year nearly 500 scientists presented and listened to 120 technical papers in fields ranging from magnetic resonance spectroscopy to environmental chemistry.

This year, with nearly 200 invited and submitted papers as well as an extensive equipment exhibition and short course/seminars on ion selective electrodes, inductively-coupled plasma spectroscopy, and gas chrometography/mass spectrometry. We anticipate another substantial growth in attendance. In addition, I am pleased to announce that this year we have an outstanding guest speaker for the Conference Banquet. Mr. Vance Brand, National Aeronautics and Space Administration, will speak about some of his experiences as the Apollo command module pilot on the Apollo-Soyez Test Project Mission.

I wish to thank you as well as all of the people who participated in planning the Conference for your support in making this year's meeting a productive and successful one.

Sincerely,

H. E. Taylor

H. E. Taylor
Conference Chairman

REGISTRATION HOURS AND LOCATION

Sunday, July 29, Executive Tower Inn	4:00 p.m. - 8:00 p.m.
Monday, July 30, Denver Convention Complex	7:30 a.m. - 3:30 p.m.
Tuesday, July 31, Denver Convention Complex	7:30 a.m. - 3:30 p.m.
Wednesday, August 1, Denver Convention Complex	7:30 a.m. - 11:30 a.m.

Registration at the Executive Tower Inn is located in the main lobby.

Registration at the Denver Convention Complex is located on the first floor in the lobby on the Champa St. entrance (doorway under the bridge).

Plan to register early and avoid the lines.

REGISTRATION FEE

Registration fee for the three-day conference is $20.00 and $10.00 for students. There is no fee for unemployed or retired chemists.

Badges are required to attend all technical programs and the exhibit area. Those not wishing to attend technical meetings can obtain "exhibit area only" badges.

SOCIAL FUNCTIONS

All conference attendees are invited to a free mixer on Monday, July 30, from 5:30 p.m. to 8:00 p.m. at the Executive Tower Inn. Please plan to attend as this is an opportunity to meet and talk with other conferees.

CONFERENCE BANQUET

A conference banquet will be held on Tuesday, July 31, at the Executive Tower Inn. The. activities will begin promptly at 7:00 p.m. Tickets will be on sale until 12:00 p.m., Monday, July 30, at the registration desk. The cost per person is $8.00

Mr. Vance Brand, from the National Aeronautic and Space Administration, will be the guest speaker at the banquet. He will discuss his experiences as an astronaut on the Apollo-Soyez Test Project and his current responsibilities as a commander on the Space Shuttle orbital test flights.

Seminars — Continued

A basic description of plasmas, how they work and what their advantages and disadvantages compared with other techniques. A discussion of specific applications will also be presented.

9:00 a.m., Wednesday, August 1, Second Floor, Room 2G

"Analytical Techniques for Specific Ion Electrodes," presented by Mr. J. Osmun, Orion.

A discussion of the principle of operation of several types of electrodes including: Gas sensing, solid state, plastic, liquid, and glass. Techniques for handling, standardizing and the analysis of solutions will be presented.

ORGANIZERS OF THE 21st ANNUAL CONFERENCE ON ANALYTICAL CHEMISTRY

Howard E. Taylor, Conference Chairman

Committee Chairmen

F. E. Lichte - Publicity
M. J. Fishman - Registration - Treasurer
J. Turbett - Exhibition (22nd Annual Conference Chairman)
D. Hunter - Printing
W. Wigington - Banquet/Mixer
W. McCarty - Banquet/Mixer
E. Huffman - Visitors information
R. Heidel - Seminars

Program/Symposium Chairmen

H. E. Taylor - General
D. A. Netzel - Nuclear Magnetic Resonance
G. R. Eaton - Electron paramagnetic Resonance
S. R. Koirtyohann - Environmental Chemistry
R. K. Skogerboe - Atomic Spectroscopy
D. Lawlor - Chromatography
D. Carpenter - Surface Analysis
J. Gurnsey - Poster

PROGRAM

GENERAL SESSIONS

H. E. Taylor, Chairman

Monday Morning, July 30 — Second Floor, Room A-F
L. D. Frederickson, Presiding

8:30	Introductory Remarks, H.E. Taylor	
8:35	1 -	"Selenium Determination by Neutron Activation and Inorganic Ion Exchange," *D. Knab* and E.S. Gladney
9:00	2 -	"Diode Array Holographic and Interference Filter Spectrometer Techniques for the Rapid Determination of Gallium and Iron," *R.J. Sironen* and D.F. Carpenter
9:25	3 -	"Analytical Applications of Metal Film Electrodes in Electrochemical Stripping Analysis," *J.E. Bonelli,* H.E. Taylor and R.K. Skogerboe
9:50	Break	
10:30	4 -	"Precision Abrasion Mass Spectroscopy," *C.J. Wolf* and M.A. Grayson
10:55	5 -	"Gases in Chromatography: As Carrier and as Standard," *E.R. Kebbekus*
11:20	6 -	"Direct Determination of Fluoride in Brines with an Ion Selective Electrode by a Modified Standard Addition Method," *R.R. Spencer* and V.C. Marti

Monday Afternoon, July 30 — Second Floor, Room A-F
R. Lehman, Presiding

1:30	7 -	"Determination of Selected Anions in Water by Ion Chromatography," *G. Pyen* and M.J. Fishman
1:55	8 -	"The Stabilization of PPB HG(II) Solutions Stored in Polyolefin Bottles by Humic Acid," *R.W. Heiden* and D.A. Aikens
2:20	9 -	"An Intra-Laboratory Quality Assurance Program," *M.J. Maurits* and E.W. Sarver
2:45	Break	
3:15	10 -	"Carbon-13 Spin Lattice Relaxation in Model Aromatic Compounds," W.D. Hammill Jr., R.J. Pugmire and D.M. Grant.
3:40	11 -	"A Mercury Vapor Generation System for Mercury Analysis by Inductively Coupled Plasma Spectroscopy," *R.F. Suddendorf* and K.W. Boyer
4:05	12 -	"Increasing the Capabilities of an Automated A.A. System," J. *Crock*, L.R. Layman and F.E. Lichte

Tuesday Morning, July 31 — Second Floor, Room A-F
F. E. Lichte, Presiding

8:30 13 - "Determination of Trace Elements by Direct Furnace Atomization from Metal Samples," *B. Wysocki,* G.G. Welcher and J.Y. Marks

8:55 14 - "Evaluation of an ICP-Echelle Spectrometer System for Multielement Analysis," *D.L. Dick,* W. Hanagan, M.M. Miller and R.K. Skogerboe

9:20 15 - "Preconcentration of Trace Elements by Reduction and Precipitation using $NaBH_4$," *W. Hanagan* and R.K. Skogerboe

9:45 Break

10:30 16 - "The Role of Oxidizing Gases in Signal Depressions in Flameless Atomic Absorption Spectroscopy," *S.G. Salmon* and J.A. Holcombe

10:55 17 - "A Two Channel Atomic Absorption Spectrophotometer with Cathode Ray Tube Readout and Its Applications," *A. Rattonetti* and G.P. Thomas

11:20 18 - "A Multi-Element Sequential Plasma Spectrometer," *G.P. Thomas,* S.B. Smith Jr. and H.L. Kahn

Tuesday Afternoon, July 31 — Second Floor, Room A-F
T.R. Steinheimer, Presiding

1:30 19 - "Selective Electron Capture Sensitization," *M.P. Phillips,* R.E. Sievers, R.M. Barkley, M.A. Wizner, M.J. Bollinger, R.S. Hutte, P.D. Goldan and F.C. Fehsenfeld

1:55 20 - "Application of Capillary Column GC/MS to Water Pollutant Analysis," *E.M. Chait* and T.A. Blazer

2:20 21 - "High Pressure Ion-Pair Liquid Chromatography Study of Coal Derived Liquids," *W.D. Reynolds* and J.K. Olson

2:45 22 - "An ASTM Method for Testing Fixed-Wavelength Photometric Detectors used in Liquid Chromatography," T. Wolf, *G.T. Fritz* and L.R. Palmer

3:10 Break

3:40 23 - "High Performance Liquid Chromatographic Assay of N-Oxide Metabolites from Tertiary Amines," *J.A. Thompson*

4:05 24 - "Correct Mobile Phase Preparation for Reversed Phase LC Separations," *F.M. Rabel*

4:30 25 - "Automated Qualitative and Quantitative Analysis of GC/MS Data of Complex Mixtures for Environmental Pollutant Analysis," *G.I. Ouchi* and D. Smith

Wednesday Morning, August 1 — Second Floor, Room A-F
J. R. Garbarino, Presiding

9:00 26 - "Laser Induced Fluorescence Spectra of CFCD," *S.E. Bialkowski*
9:25 27 - "^{13}C and ^{1}H NMR Analysis of High Boiling Petroleum Fractions," K.D. Berlin, *D.J. O'Donnell*, G.P. Sturm and J.W. Vogh
9:50 Break
10:20 28 - "Analysis of Gases and Oils Released by Microwave Power from Colorado Oil Shale," *D.G. Soucy*, W.T. Lutz and E.T. Wall
10:45 29 - "Heavy Metals and Their Relationship to Solids in Storm Runoff," *D.R. Bourcier* and R.P. Sharma
11:10 30 - "A Cost Effective Approach to the Analysis of Organics in Water," *D.E. Smith* and R.E. Finnigan
11:35 31 - "Wide Range Calibration for Direct, Accurate Analysis of Solid Samples in Furnace Atomic Absorption," *J.A. Nichols* and R. Woodriff

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

S. R. Koirtyohann, Chairman

Tuesday Morning, July 31 — Second Floor, Room B-E

9:00 Introductory Remarks — S.R. Koirtyohann

Inorganic

9:05 32 - "An Overview of Inorganic Speciation," *R.S. Braman*
9:50 33 - "Comparison of Acid Leaching Properties of Coal Waste Products before and after Neutron Irradiation," *W.D. James*
10:15 Break
10:45 34 - "On the Chemical Speciation of Fly Ash: Some Studies of Matrix Composition and Structure and the Distribution of Trace Elements," *L.D. Hulett* and A.J. Weinberger
11:10 35 - Geothermal Development and Environmental Analytical Chemistry in the Pacific Northwest," J. *Baldwin* and C.A. Allen
11:35 36 - "Anionic Speciation of Environmental Waters by Ion Chromatography," *T.B. Hoover*

Tuesday Afternoon, July 31 — Second Floor, Room B-E

Organic

1:30	37 -	"A Master Analytical Scheme for Organics in Water," *A.W. Garrison,* J.F. Ryan and E.D. Pellizzari
2:15	38 -	"Sampling and Analysis of Haloethers in Water and Wastewater," *J.M. Kyne,* J.E. Longbottom and P.L. Sherman
2:45	39 -	"Determination of Selected Volatile Organic Priority Pollutants in Water by Computerized Gas Chromatography-Quadrupole Mass Spectrometry," *B. Hughes* and W. Pereira
3:10	Break	
3:40	40 -	"Fractionation and Gas Chromatographic/Mass Spectrometric Characterization of Organic Compounds Extracted from Diesel Engine Exhaust Particulates," *C.F. Rodriguez,* J.B. Fischer and H.G. Wheeler
4:05	41 -	"Validation of Analytical Data in Pesticide Residue Analysis Using Multiple Detection Systems," *R.C. Hanisch,* G.W. Sovocool and R.G. Lewis
4:30	42 -	"Environmental Monitoring at an In Situ Oil Shale Site," *F.R. McDonald,* T. Owens and U. Sharum

SYMPOSIUM ON CHROMATOGRAPHIC TECHNIQUES

D. Lawlor, Chairman

Wednesday Morning, August 1 — Second Floor, Room E-D

8:30	Introductory Remarks — D. Lawlor	
8:35	43 -	"Macroporous Resins in Liquid Chromatography," *H.F, Walton* and K. Aramaki
9:05	44 -	"Industrial Hygiene Air Sample Analyses Improved Results through Automation using Glass Capillary Columns and a Multi-Channel Data System," *U.A. Sikorski* R.C. Domingo and D.R. Brezinski
9:30	45 -	"Reversed-Phase Liquid Chromatography of Catecholamines and their Congeners with Electrochemical Detection," *P.A.Asmus* and C.R. Freed
9:55	Break	
10:30	46 -	"Rapid Semiquantitative Analysis of Selected Pesticides in Natural Water by High-Pressure Liquid Chromatography," *T.R. Steinheimer* and D.M. Walker

10:55 47 - "Multiplex Gas Chromatography," J.B. *Phillips*

11:20 48 - "Pyrolysis GC - Mass Spectrometric Identification of Intractable Materials," J. *Wuepper*

Wednesday Afternoon, August 1 — Second Floor, Room C-D

1:30 49 - "Measuring Diols in Oxyethylene — Oxy Propylene Copolymers," *S.L. Wellons*
1:55 50 - "Quantitative Analysis of Hydrochlorothrazide in Equine Urine and Plasma by High Pressure Liquid Chromatography," *G.A. Maylin* and J.D. Henion
2:20 51 - "HPLC Peak Identification using UV Spectra obtained from a Millisecond-scan Vidicon Detector," *R.M. Smith, KM.* Aldous, D. Choudhury and B. Bush
2:45 Break
3:15 52 - "Application of Specific Gas Chromatographic Detectors to the Identification of Organic Vapors in Ambient Atmospheres," *B.B. Kebbekus,* J. Kemp and J.W. Bozzelli
3:40 53 - "Determination of Nitrosoamines by Liquid Chromatography Using a Photoconductivity Detector," *R.H. Bennett* and E.S. Peterson
4:05 54 - "A Selective Detector Suitable for Gas Chromatography," D.G. Sutton, K.R. Westberg and *J.E. Melzer*

SYMPOSIUM ON ATOMIC SPECTROSCOPY

R. K. Skogerboe, Chairman

Monday Morning, July 30 — Second Floor, Room B-E

9:00 Introductory Remarks, R.K. Skogerboe

SESSION ON AEROSOL PRODUCTION, CONDITIONING AND TRANSPORT FOR ATOMIC ANALYSIS

9:05 55 - "Experimental Evaluation of Principles Applicable to Aerosol Production, Conditioning and Transport," *R.K. Skogerboe,* S.J. Freeland, K. Kronholm and G. Butcher
9:40 56 - "Production and Atomization of Homogenate Aerosols," *R.C. Fry* and N. Mohamed
10:00 Break

10:30 57 - "Ultrasonic Nebulization - Pros & Cons," *V.A. Fassel,* R. Winge, W. Haas, F. Grabau, B. Bear and M. Floyd

10:55 58 - "Analytical Consequences of Nebulizer Performance," *J.A. Holcombe*

11:20 59 - "Characterization of a One-Piece All Glass Cross Flow Nebulizer used with an ICP/Spectrometer," *D. Yates,* D. Fraley, S. Manahan and F. Lichte

11:40 60 - "A Critical Evaluation of Noise Contributions in Flame Atomic Absorption Spectrophotometry," *M.W. Routh* and P.R. Liddell

Monday Afternoon, July 30 — Second Floor, Room B-E

SESSION ON APPLICATIONS OF ATOMIC SPECTROSCOPY

1:30 61 - "Characterization of Sources of Turquoise by X-Ray Spectrometry," M.L. *Parsons*

1:55 62 - "Application of the Inductively Coupled Plasma to Elemental Analysis of Foods and Related Material," *R.F. Suddendorf,* and K.W. Boyer

2:20 63 - "Use of ICP-MAES for Simultaneous Determination of Macro and Micro Nutrients in Ammonium Bicarbonate-DTPA Extracts of Soils," *P.N. Soltanpour,* S. Workman and A.P. Schwav

2:45 Break

3:15 64 - "Solvent Extraction Studies for the Recovery of Metals from Electroplating Wastes Using An Inductively Coupled Argon Plasma," *T. Clevenger* and D. Yates

3:40 65 - "Silicon Determination in Groundwater Samples by Flameless Atomic Absorption Spectroscopy," *N.J. Kelly,* J.P. Erspamer, T.M. Niemczyk and E.A. Walters

4:05 66 - "Spectrochemical Determination of Iridium and Yttrium in Plutonium," J.V. *Pena,* M.W. Meyers and D. Steinhaus

4:30 67 - "Multielement Detection of Trace Impurities in Silicon by Metastable Transfer Emission Spectrometry," *D.G. Sutton,* L. Galvan and N. Cohen

SYMPOSIUM ON THE NMR OF MACROMOLECULES

D. A. Netzel, Chairman

Monday Morning, July 30 — Third Floor, Room A-F
G. E. Maciel, Presiding

8:30 Introductory Remarks, D.A. Netzel

SESSION I. SOLID STATE NMR

8:35	68 -	"Expectations for Resolution in High Resolution ^{13}C NMR of Solids - Particularly Polymers," *D.L. VanderHart*, W.L. Earl and A.N. Garroway
9:00	69 -	"^{23}Na Solid-State NMR of Beta-Aluminas," *R.W. Vaughan*, M. Polak and A. Highe
9:30	70 -	"High Resolution Solid State NMR of Hydrogen on Catalytically Active Surfaces," *B.C. Gerstein*, P. Dubois Murphy, L.M. Ryan, R.E. Taylor and M. Silva-Crawford
10:00	Break	
10:30	71 -	"13 Spectroscopy of Small Organic Molecules at Cryogenic Temperatures," *K. Zilm*, D.M. Grant, R.T. Conlin and J. Michl
11:00	72 -	"Recent Developments in High Resolution Deuterium NMR in Solids-Double Quantum NMR and Magic Angle Spinning," M. Alla, D. Eckman and *A. Pines*
11:30	73 -	"Dynamic Frequency Shifts in Spectrally Degenerate Spin Systems," *L.G. Werbelow*

Monday Afternoon, July 30 — Third Floor, Room A-F
V. Bartuska, Presiding

1:30	74 -	"Relaxation in Polymeric Blends," M.D. *Sefcik*, J. Schaefer, E.O. Stejskal and R.A. McKay
2:00	75 -	"High Resolution ^{13}C NMR Investigation of Solid Phenolic Resins and Related Compounds," *C.A. Fyfe*, A. Rudin and W.J. Tchir
2:30	76 -	"^{13}C NMR Solids Techniques for Characterizing Blends of Elastomers and Polyolefins," *C.J. Carmen*, J.B. Pausch and A.N. Garroway
3:00	Break	
3:30	77 -	"C-F Double Resonance Studies of Bulk Fluoropolymers," *J. Lyerla* and C.S. Yannoni

4:00	78-	**"Solid State NMR of Elastomer; Low and High Resolution," J.** *Ackerman* **and J.E. Mark**
4:30	79-	**"Macromolecular Dynamics of Fluorocarbon Polymers Studied by Multiple Pulsed NMR,"** *A.J. Vega* **and A.D. English**

Tuesday Morning, July 31 — Third Floor, Room A-F
D. A. Netzel, Presiding

9:00	80 -	**"^{13}C NMR Studies of Coals," V.J. Bartuska,** *G.E. Maciel* **and F.P. Miknis**
9:30	81 -	**"^{13}C NMR Studies of Oil Shales by Cross Polarization and Magic Angle Spinning,"** *F.P. Miknis,* **V.J. Bartuska and G.E. Maciel**
10:00	Break	
10:30	82-	**"CP/MAS Studies of Methylated Hydroaromatic Species: Changes of Symmetry in the Solid State as compared to The Liquid State,"** *R.J. Pugmire,* **K.W. Zilm, D.K. Dalling and D.M. Grant**
11:00	83 -	**"^{13}C NMR Studies of Solid Plant Materials," G.E. Maciel and** *V.J. Bartuska* **and D.W. Sindorf**
11:30	84-	**"Solid State High Resolution ^{13}C NMR Studies of Cellulose,"** *W.L. Earl* **and D.L. VanderHart**

Tuesday Afternoon, July 31 — Third Floor, Room A-F
F.P. Miknis, Presiding

SESSION II. FUELS

1:30	85 -	**"Carbon-13 Spectra-Structure Correlations for Hydrocarbons,"** *N.F. Chamberlain*
2:00	86 -	**"Application of Relaxation Resolution to Carbon-13 FT NMR of Fossil Fuel Fractions,"** *M. Melchoir*
2:30	87 -	**"High Temperature Carbon-13 NMR Studies of Polycyclic Aromatic Compounds and Coal Products,"** *H.C. Dorn,* **L.T. Taylor and T. Glass**
3:00	Break	
3:30	88 -	**"Characterization of Heteroatom Content in Coal Product Fractions by ^{19}F NMR,"** *L.T. Taylor,* **H.C. Dorn, P. Sleevi and T. Glass**
4:00	89 -	**"NMR Examination of Fuels and Fractions from Oil Shale,"** *R.N. Hazlett* **and J. Solash**
4:30	90 -	**"Average Molecular Structure Analysis of Coal Derived Liquids by NMR Spectrometry,"** *D. Cantor*

Tuesday Morning, July 31 — Third Floor, Room B-E
M.P. Schweizer, Presiding

SESSION MI. BIOPOLYMERS

9:00	91 -	**"High Field NMR Studies of Biological Systems,"** *E. Oldfield*
9:30	92 -	**"Motility in Biopolymers Investigated by NMR Relaxation,"** *T.L. James*
10:00	Break	
10:30	93 -	**"Oligonucleotide Conformation. Phosphorus-Proton and Proton-Proton Nuclear Overhauser Effects,"** *P.A. Hart*
11:00	94 -	**"^{13}C and ^{2}H NMR Studies of Labeled Collagen in the Solid State and in Solution,"** *D.A. Torchia,* **L.W. Jelinski and C.E. Sullivan**
11:30	95 -	**"NMR Studies of Model Biomembranes: Structure and Metal Ion Binding,"** *C.S. Springer*

Tuesday Afternoon, July 31 — Third Floor, Room B-E
N. Matwiyoff, Presiding

1:30	96 -	**"Proton NMR Studies of Metal Bleomycin Complexes,"** *E. Mooberry,* **J. Greene and R. Lenkinski**
2:00	97 -	**"NMR Studies of Bleomycin Complexes with Nucleic Acids and Metals,"** *H.D. Glickson,* **T.T. Sakai, J.M. Riordan, J.M. Geckle, R.F. Lenkinski and N.R. Kirshna**
2:30	98 -	**"^{23}Na and ^{31}P NMR Studies of Metal Ion Binding to Phosphatidylserine Vesicles,"** *R.J. Kurland* **D. Papahadjopoulos, M. Hammoudah, S. Nir and J. Benz**
3:00	Break	
3:30	99 -	**"Solvent Proton Magnetic Relaxation Studies of Concanavalin A: Relation of Conformation to Metal and Saccharide Binding,"** *R.D. Brown III,* **S.H. Koenig and C.F. Brewer**
4:00	100 -	**"2,5-Dichloro-4-Nitroanisole, Studies of Concentration Versus Observed Nuclear Overhauser Effect,"** *E. Mazzola* **and S.W. Page**
4:30	101 -	**"15-Nitrogen NMR Spectra of NO$_x$ Complexes," R.D. Feltham, J.** *V. Dubrawski* **and J.D. Gust**

Wednesday Morning, August 1 — Third Floor, Room B-E
J.D. Glickson, Presiding

9:00	102-	**"Carbon-13 NMR Studies of Dihydrofolate Reductase Enriched with ^{13}C Labeled Amino Acids,"** *N. Matwiyoff,* **R.L. Blakeley, L. Cocco, J.P. Groff and R.E. London**
9:30	103-	**"Carbon-13 NMR Studies of Transfer RNA,"** *M.P. Schweizer,* **W.D. Hammil Jr. and D.M. Grant**
10:00	Break	
10:30	104 -	**"The Structure and Conformation of Dideoxyribonucleoside Methyl Phosphonates, a NMR Study,"** *L.S. Kan,* **D. Cheng, K. Jayaraman, P.O.P TS'O, E. Yano, J. Yano and P.S. Miller**
11:00	105 -	**"NMR Studies of Peptide Conformation through Amide Hydogen Exchange Measurements,"** *N.R. Krishna,* **J.D. Glickson, D.H. Huang and G. Goldstein**

Wednesday Afternoon, August 1 — Third Floor, Room B-E
W. Canghey, Presiding

1:30	106-	**"^{1}H NMR Investigation of Phosphopeptides,"** *D. Ziessow,*
2:00	107 -	**"High Resolution PMR Studies of Phospholipid Sterol Interactions,"** *G.G. McDonald*
2:30	108 -	**"^{1}H, ^{2}H and ^{17}O Relaxation Study of Muscle Water,"** *B.M. Fung* **and T.W. McGaughy**
3:00	Break	
3:30	109-	**"^{1}H NMR Studies of Antibiotics in Perdeuterated Lipid Bilayers,"** *G.W. Feigenson* **and P.E. Meers**
4:00	110-	**"Structure of Satratoxins F and G, Metabolites of Stachybotrys Atra: Application of Proton and Carbon-13 NMR Spectroscopy,** *E. Mazzola,* **M.E. Stack and R.M. Eppley**

Wednesday Morning, August 1 — Third Floor, Room A-F
S. Kaplan, Presiding

SESSION IV. POLYMERS

9:00	111 -	**"Oxygen-17 NMR Studies of Macromolecules,** *D. Fiat*
9:30	112-	**"NMR Relaxation Measurements on Macromolecules,"** *N. Wade-Jardetzky* **and 0. Jardetsky**
10:00	Break	

10:30 **113 - "Internal Motions in Copolyesters Containing Terephthalic Acid, Butanediol, Azelaic Acid, and Ethylene Glycol as Studied by Relaxation Times,"** *J.M. Hewitt,* **P.M. Henrichs, G.A. Russell and M.A. Sandhu**

11:00 **114- "Quantitative Determination of Residual Polyvinyl Acetate and Sodium Acetate in PVA: PMR Integration,** J.R. DeMember

11:30 **115 - "Quantitative Analysis of the Microstructure of Polybutadiene using 20 MHZ Carbon-13 NMR and 300 MHZ Hydrogen-1 NMR Spectroscopy," D.H. Beebe and R.C. Hirst**

Wednesday Afternoon, August 1 — Third Floor, Room A-F
D. Fiat, Presiding

1:30 **116- "Application of ^{13}C NMR to Urea Formaldehyde Polymers and to Acetamide Formaldehyde Model Compounds of UF Polymers,** *L.K. Woods* **and S.F. Lange**

2:00 **117- "Pulse NMR Relaxation of a Polystyrene-Polyethylene Oxide Diblock Copolymer,"** *S. Kaplan* **and J.J. O'Malley**

2:30 **118 - "An NMR Study of the Polymerization of Norborene Endcapped Polyimides,"** *A Wong* **and W. Ritchey**

3:00 **Break**

3:30 **119 - "Internal Motion in Perdeurated Polymers by ^{2}H NMR," K. Seidman, J. McKenna, G.B. Savitsky and** *A.L. Beverlein*

4:00 **120- "Investigation of the Assignment of the 2190cm^{-1} Infrared Band in Polyfumaronitrile,"** *K.L. Gallaher,* **J.G. Grasselli and D. Berlec**

SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

G. R. Eaton, Chairman

Monday Morning, July 30 — Third Floor, Room B-E
J. E. Wertz, Presiding

SESSION I

9:00 **Introductory Remarks, G. R. Eaton**

9:05 **121 - "ESR Studies of Trapped Electrons,"** *H.C. Box*

9:35 122- "Spin-Label Probes of Antibody Function," *P. Gettins,* R.A. Dwek, A.T. Morris, B.J. Sutton and K.J. Willan

10:00 Break

10:30 123 - "ESR Detection of Radicals Produced in the Reaction of Thiols with NO Containing Compounds," *G.C. Yang* and A. Joshi

10:45 124 - "Investigations on the Mutagenicity and Electron Spin Resonance Spectra of Nitrosofluorene-Lipid Adducts," *R. Sridhar,* M.J. Hampton, J.E. Steward and R.A. Floyd

11:05 125 - "Carcinogen and Paramagnetism of Hepatic Cell Organella," Y. Sakagishi, M. Sonoda and *T. Komoda*

11:25 126 - "EPR Studies on Human Serum," *E. Kimoto*,T. Kakuda, T. Yamaguchi, M. Kohno and F. Morishige

11:45 127- "ESR Detection of Electrolytically Generated Unstable Radicals," *R.D. Allendoerfer* and J.B. Carroll

Monday Morning, July 30 — Third Floor, Room C-D
S. S. Eaton, Presiding

SESSION II

10:30 128 - "EPR Studies of Deuterated Nitroxide Spin Labels," A. Mathew, W.R. Hedrick and *J.D. Zimbrick*

10:45 129- "Spin Echo and CW Measurements of Electron Spin Relaxation of Nitroxides in Solution," *R.N. Schwartz* and M.K. Bowman

11:05 130 - "Study of the Products of Coal Hydrogenation and Deuteration by EPR," *I.B. Goldberg,* H.R. Crowe, J.J. Ratto, L. Heredy and R. Skowronski

11:25 131 - "EPR Studies of Oil Shale, Shale Oil, and Spent Shale," B.L. Sidwell, L.E. McKinney, M.F. Bozeman, P.C. Egbujor, *G.R. Eaton,* S.S. Eaton and D.A. Netzel

11:40 132- "ESR Studies of Heavy Metal Environmental Pollutants," *J.K.S. Wan*

Monday Afternoon, July 30 — Third Floor, Room A-F
J. C. Seidel, Presiding

SESSION III

1:30 133- Society for Applied Spectroscopy - Student Award Address. "Proton Hyperfine Splitting and Conformation in Nitroxyl Radicals, *M.J. Heinig,* G.R. Eaton and S.S. Eaton.

1:50 134 - **"EPR Spectra of the Livers in Diseased States,"** *F. Morishige*, **H. Tanaka, E. Kimoto, and H. Kawasaki**

2:10 135 - **"Spin-Trapping and Liquid Chromatographic Separation and Identification of Unstable Radicals of Amino Acids, Peptides, and Nucleotides,"** *H. Hatano*, **K. Makino, N. Suzuki, A. Moriya, and S. Rokushika.**

2:30 Break

3:00 136 - **"Heme-Spin-Labeling of Hemoproteins,"** *T. Asakura* **and P.W. Lau**

3:30 137 - **"Quantitative Determination of Nitrosyl-Hemoglobin in the Blood by EPR,"** *T. Nakajima*

3:50 138 - **"ESR and Visible Absorption Spectroscopy of Horseradish Peroxidase, Free and Bound to Donor Substrate at Cryogenic Temperatures,"** *MM. Maltempo*

4:10 139 - **"The 02-Binding Site of Cytochrome COxidase as Revealed by EPR Spectroscopy,"** *G.W. Brudvig*, **J.H. Stevens, D.F. Bocian, and S.I. Chan**

4:25 140 - **"Effect of Polymer Matrix on the Rotational Motion of Spin-Labeled Protohemin Coordinated to Polymer-Chain,"** *S. Hata* **and E. Tsuchida**

4:40 141 - **"ESR Studies of Ion Pair Formation with the Triphenylene Anion Radical,"** *M.T. Jones* **and R.H. Ahmed**

Monday Afternoon, July 30 — Third Floor, Room C-D
H. Kashiwabara, Presiding

SESSION IV

1:30 142 - **"Hole Centers in the Alkaline Earth Oxides,"** *J.E. Wertz*, **D.A. Dixon and F. Dravnieks**

1:50 143 - **"Host Lattice Effects in the EPR Spectra of Gd3+ Ion in Some Lanthanide Hydroxides,"** *H.A. Buckmaster*, **V.M. Malhotra and W.J. Chang**

2:10 144 - **"EPR of Organic Compounds in Ambient Temperature Molten Salts,"** *J.S. Wilkes* **and L.P. Davis**

2:25 145 - **"ESR Investigations of the Thermal Decomposition of Energetic Materials,"** *H.L. Pugh Jr.*, **L.P. Davis and J.S. Wilkes**

2:40 146 - **"Relaxation Spectra of Polymers Obtained from ESR and NMR Studies," T. Tanigawa, T. Kitahara, S. Shimada and** *H. Kashiwabara*

3:00 Break

3:30 147 - **"ESR of F-Center in BaTi03," M.** *Tsukioka*

3:45 148 - "EPR of E' Centers in Ultrapure Fused Silica," M. Schwab and *M.J. Moran*

4:00 149- "EPR in the Study of Radiation Damage in Silicate Glasses," M. Schwab and *M.J. Moran*

4:15 150 - "Trapping Regions for Allyl Radicals in Irradiate Polyethylene," *T. Fujimura*, N. Hayakawa and I. Kuriyama

4:30 151 - "EPR and Endor Evidence for Polarized Clusters in the Paraelectric Phase of Ferroelectrics," *N.S. Dalai*

4:45 152 - "ESR Studies of Diffusion in Liquids," *M-K Ahn*

Tuesday Morning, July 31 — Third Floor, Room C-D
M. T. Jones, Presiding

SESSION V

9:00 153 - "Solvent Polarity Effects on Correlation Times for Nitroxide Spin Probes," *J.J. Windle*

9:15 154- "Bifunctional Spin Labels Designed for Saturation Transfer EPR Studies of Anisotropic Motion in Membranes," *B.J. Gaffney,* G.L. Willingham, M-W Tse and A. Mahon

9:35 155 - "Spin-Labeling Studies of Lignins," *P. Tormala* and J.J. Lindberg

10:00 Break

10:30 156 - "Diagnostic Applications for Spin Assay Techniques," *C.J.C Hsia*

10:50 157 - "A Study of Ribosomes Using the Spin Label Method," *H. Dugas*, A. Rodriguez and N. Brisson

11:10 158 - "Rotational Motions of Muscle Proteins Studied by Saturation Transfer EPR," *J.C. Seidel*

11:40 159 - "Saturation Transfer EPR of Viruses," *M.A. Hemminga*

Tuesday Afternoon, July 31 — Third Floor, Room C-D
M. Maltempo, Presiding

SESSION VI

1:30 160 - "Photoassisted Electrolysis and the EPR Connection," *J.F. Houliban* and D.P. Madacsi

1:45 161 - "Electron Spin Polarization in Photosynthesis," *O. Adrianowycz*, K.W. Kinnally and J.T. Warden

2:05 162 - "The Use of a New Spin Broadening Agent in Thylakoid Suspensions to Mask External Spin Label Signal," *DM. Nesbitt* and S.P. Berg

2:20	163 -	**"Application of EPR to the Analysis of Spatial Organization of Redox Components in Mitochondrial Membranes,"** *T. Ohnishi*, **J.C. Salerno and H. Blum**
2:40	164-	**"Electron Spin Relaxation in Bacterial Photosynthetic Systems,"** *M.K. Bowman,* **J.R. Norris and C.A. Wraight**
3:00	Break	
3:30	165 -	**"The Primary Events in Green Plant Photosynthesis — Studied by Time-Resolved Electron Spin Echo Spectroscopy,"** *M.C. Thurnauer* **and J.R. Norris**
3:50	166 -	**"Intercellular Viscosity of Lymphocytes Determined by an ^{15}N Spin Label Probe,"** *W.R. Hedrick,* **A. Mathew and J.D. Zimbrick**
4:05	167 -	**"Translational Motion of the Spin Label Tempamine in the Internal Aqueous Compartment of Spinach Thylakoids and Red Blood Cells,"** *P. Morse*
4:20	168 -	**"Metal-Nitroxyl Interactions," P.M. Boymel, D.L. DuBois, K. More, G.R. Eaton,** *S.S. Eaton* **and D.J. Greenslade.**
4:40	169 -	**"ESR Studies of Dimeric Copper Complexes of Adenine," D. Sonnenfroh and** *R. Kreilick*

Wednesday Morning, August 1 — Third Floor, Room C-D
C. E. Klopfenstein, Presiding

SESSION VII

9:00	170 -	**"EPR Possibilities at S-Band (2-4 GHz),"** *J.R. Pilbrow*
9:40	171 -	**"ENDOR Investigations in the Nematic and Smetic Phase of Liquid Crystals," H. Kurreck and** *B. Kirste*
9:55	172 -	**"ENDOR Studies of Radicals Adsorbed on Metal Oxide Powders,"** *R.B. Clarkson*
10:10	Break	
10:35	173 -	**"Field Theoretical Treatment of the Proton HFA in the Aromatic Ion Radicals,"** *S. Aono*
10:50	174 -	**"ENDOR on Vanadyl Complexes in Frozen Solution,"** *H. Van Willigen*
11:05	175 -	**"Two-Way EPR Cavity and Stark Effect in NO,"** *I. Suzuki* **and Y. Kaneko**
11:20	176-	**"Nanosecond Time-Resolved EPR Spectroscopy,"** *A.D. Trifunac*

Wednesday Afternoon, August 1 — Third Floor, Room C-D
G. R. Eaton, Presiding

SESSION VIII

1:30 177- **"Computer Graphics and the Interpretation of EPR Data,"** *C.E. Klopfenstein*

2:10 178 - **"A Digital Acquisition System for an ESR Spectrometer: Application to the Generation of Dispersion Absorption Plots," F.G. Herring and** *P.S. Phillips*

2:30 179 - **"Computer Simulation of EPR Powder Spectra,"** *R.L. Belford* **and M.J. Nilges**

3:00 **Break**

3:30 180 - **"Analysis of Electronic Rearrangements by EPR,"** *J.H. Ammeter*

4:10 181 - **"Digitized EPR and ST-EPR Systems,"** *T. Watanabe*, **T. Sasaki, K. Sawatari and S. Fujiwara**

4:25 182 - **"An efficient Approach to Simulation of EPR Spectra of High Spin Fe^{3+} in Rhombic Ligand Field,"** *M.J. Scullane*, **L.K. White and N.D. Chasteen**

4:40 183 - **"Calculation of Powder ESR Spectra with Hyperfine and Quadrupolar Interactions,"** *A. Lund*

SYMPOSIUM ON SURFACE ANALYSIS

D. Carpenter, Chairman

Wednesday Morning, August 1

9:00 **INTRODUCTORY REMARKS —Davis Carpenter**

9:05 184 - **"Environmental Aspects of Surface Analysis,"** *D. Natusch*

9:45 **Break**

10:15 185- **"Introduction to Auger, ESCA and SIMS,"** *C. Evans*

11:00 186 - **"Computerized Quadrapole Secondary Ion Mass Spectroscopy for Surface Analysis,"** *B. Phillips* **and N.E. Lares**

Wednesday Afternoon, August 1

1:30 187 - **"Catalytic Properties of Metals for Carbon Oxidation,"** *A.O. Wist*

2:00 188 - **"Mean Free Path of 1.2 Kev Photoelectrons in Thin Poly(methyl methacrylate) Films,"** *R.F. Roberts*, **D.L. Allara, C.A. Pryde and D.N. Buchanon**

2:30 189 - **"Near Surface Analysis by Electron** Microprobe," . *Doyle*

2:55 190 - **"Ion Scattering Profiles of Polypropylene Coatings on** CuO^{18} **Films Before and After Oxidative Degradation of the Polymer,"** *A.W. Czanderna* **and** A.C. **Miller**

POSTER SESSION

Open Monday — Wednesday 9 **a.m. -** 5 **p.m.**
Authors will be present on Tuesday 1-3 **p.m.**

191 — **"Analytical Laboratories' Environmental Analyses at Rocky Flats,"** *C.E. Gies* **and** *J.R. Cobb*

192 - **"Plutonium Metal Analysis at Rocky Flats,"** *D.I. Hunter* **and P.A. Hymen and H.L. Wells**

193 - **"Isotopic Fractionation of** $^{15}NH_3$ **in All-Glass Still,"** *W.A. O'Deen* **and** *L.K. Porter*

194 — **"Synthesis of Oxazolidine Radicals with a Functional Group for Protein Modification,"** *J.L. Jones,* **T.M. Harris and D. Puett**

195 — **"A Versatile Low Cost Laboratory Instrument** Calibrator/Test Set," *J. Salsgiver*

196 — **"Electron Spin Resonance Study of the Copper** (II) **Complexes of Human and Dog Serum Albumin and Some Model Peptides."** G. *Rakbit* **and B. Sarkar**

1

SELENIUM DETERMINATION BY NEUTRON ACTIVATION AND INORGANIC ION EXCHANGE, *D. Knab* and E.S. Gladney, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545.

Gamma spectroscopy of neutron activiated ^{75}Se is the preferred method of quantizing selenium in environmental samples. Low concentrations of selenium (1 ppm) in many matrices preclude instrumental determinations due to interferences from matrix activation products. Consequently, it is often necessary to chemically separate selenium for accurate determinations.

Absorption of selenium (IV) on Al_2O_3 or SnO_2 inorganic ion exchange columns from HCl is quantitative while excluding most matrix activation products. Reduction of selenium (IV) to selenium (IV) is *fast* and complete in boiling 6 M HCl; used as the exchange solution. Detection limits for biological samples are approximately 10 ppb for 1 g samples irradiated at 10^{13} n/cm2/sec for seven hours and counted for 500 min. Detection limits for geological samples are about 50 ppb because of interference from ^{182}Ta decay. The absorbed ^{75}Se decay gammas at 265 and 280 keV are readily resolvable from the major contaminant, 233p, by Ge(Li) spectroscopy. Determinations of selenium in NBS SRM give good agreement with certified values in beef liver, orchard leaves, and fly ash.

Selenium is absorbed on Al2O3 from 6 M HCl . l M H3PO4. The phosphate is necessary to elute ^{32}P a major activation product, which absorbs from HCl only. It is necessary to ash and sieve SnO_2 to obtain an ion exchanger with suitable absorption and flow characteristics.

2

DIODE ARRAY HOLOGRAPHIC AND INTERFERENCE FILTER SPECTROMETER TECHNIQUES FOR THE RAPID DETERMINATION OF GALLIUM AND IRON, D.F. Carpenter and *R.J. Sironen*, Rockwell International, Golden, Colorado 80401

The spectrophotometer has long been a standard laboratory instrument used for the quantitative determination of gallium and iron in plutonium. The spectrophotometer, although automated, is too slow to handle the sample load. A faster, and if possible, more accurate method was required. This paper reports results concerning the relative merits of the two techniques to the standard spectrophotometric method.

3

ANALYTICAL APPLICATIONS OF METAL FILM ELECTRODES IN ELECTROCHEMICAL STRIPPING ANALYSIS

J.E. Bonelli and H.E. Taylor
U.S. Geological Survey
Box 25046, Denver Federal Center
Denver, CO 80225

and

R.K. Skogerboe
Colorado State University
Ft. Collins, CO 80526

Thin metal films electrodeposited on conducting substrates have recently found widespread use in electrochemical-stripping analysis. Mercury films on carbon, platinum, or gold have been favored because of their relatively wide working potential range, ease of preparation, and multielement analysis capabilities. Their use is in general limited, however, to determinations of elements that form mercury amalgams and have redox potentials greater than that of hydrogen reduction on mercury and less than that of mercury oxidation. Many elements of analytical interest do not meet one or both of these criteria.

Continuing interest in stripping methods is due largely to the extraordinary detection limits attainable with relatively simple and inexpensive instrumentation. A significant advance would be realized if, in addition to this advantage, the present limited scope of stripping-analysis methods could be expanded. One potentially productive approach to expanding the scope of these methods is to utilize electrode materials other than mercury.

Relative performance features of three thin metal film electrodes (Hg, Au, Ga) are compared in the context of ultratrace elemental analyses in natural water matrices. Comparative evaluations are based on scope, analysis sensitivity, selectivity, and multielement-analysis capability. Specific circumstances exist in which Au and Ga electrodes may be expected to provide superior analytical performance to the conventional Hg electrode.

4

PRECISION ABRASION MASS SPECTROSCOPY*, *C.J. Wolf,* and M.A. Grayson, McDonnell Douglas Corporation, St. Louis, Missouri 63166.

A new technique called Precision Abrasion Mass Spectroscopy (PAMS) is described. PAMS is used to quantitatively characterize the distribution of indigenous volatile compounds trapped within a solid matrix. Intractable samples, such as thermoset resins or fiber-matrix composites, are abraded directly in the ion-source housing of a mass spectrometer. Precision abrasion accurately and reproducibly removes a known volume of sample as a function of time. Volatile compounds are released during mechanical abrasion, and they are identified and quantitated mass spectrometrically. The instrument to perform PAMS, the experimental technique, and applications with epoxy resins and fiber glass-epoxy composites are presented and discussed.

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*This research was conducted under the McDonnell Douglas Independent Research and Development Program.

5

GASES IN CHROMATOGRAPHY: AS CARRIER AND AS STANDARD, *E.R. Kebbekus,* Matheson, East Rutherford, New Jersey 07073.

As gas chromatography has developed the need for more specialized or more highly purified gases to serve as carrier has arisen. Developments in both columns and detector systems have been the reasons for such increased demands on the carrier gas. Most recently with the ever widening use of capillary columns there has developed a need for carrier gases with very low levels of such impurities as oxygen. This paper will discuss this need for specialized, or highly pure, carrier gases to help eliminate either column or detector related problems. In addition, specific attention will be given to the system needed to maintain the purity of the carrier gas when in use. Such considerations are mandatory when considering capillary gas chromatographs employing very low flow rates since extremely small atmospheric leaks will contaminate the carrier gas and rapidly destroy the capillary column.

The second half of this paper will discuss the availability of some specialized gas mixtures that can be used to serve as calibration mixtures in various types of environmental monitoring. Consideration will be given to mixtures containing benzene and other solvent vapors either separately or as multicomponent mixtures, sulfur hexafluoride, nickel carbonyl, ethylene oxide and multi-component sulfur containing mixtures. Also a technique for obtaining mixtures at ambient air levels will be discussed.

6

DIRECT DETERMINATION OF FLUORIDE IN BRINES WITH AN ION SELECTIVE ELECTRODE BY A MODIFIED STANDARD ADDITION METHOD, *R.R. Spencer,* V.C. Marti, U.S. Geological Survey, Lakewood, Colorado.

Determination of fluoride in brines by colorimetric or ion specific electrode methods which require prior distillation of the sample is costly and time consuming. Large amounts of expensive silver sulfate must be added to complex chloride ion and multiple distillations of the same sample must be performed to insure full recovery of fluoride. A standard addition method as adapted to analyze these brines without complicated sample pretreatment. Brine samples are buffered to pH 5.0-5.5 and interfering ions such as aluminum, iron and silica are masked by addition of an acetate-(1,2-cyclohexylenedinitrilo) tetraacetic acid (CDTA) solution. Aliquots of a standard fluoride solution are then added and potential differences recorded after each addition. Data obtained are fitted by a computerized program to an equation previously reported for the determination of fluoride in sea water. Brines analyzed by this method ranged in concentrations from 0.1 to 70 mg/L fluoride with specific conductances of 20,000 to 225,000 umho/cm with the majority over 100,000 umho/cm. Percent relative deviations were less than 15 percent for concentrations above 1.0 mg/L fluoride and averaged 36 percent below 1.0 mg/L fluoride. The method compared well with other standard fluoride procedures.

7

DETERMINATION OF SELECTED ANIONS IN WATER BY ION CHROMATOGRAPHY, *G. Pyen* and M. Fishman, U.S. Geological Survey, Lakewood, Colorado.

Atmospheric precipitation and natural waters have been analyzed for bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate, using ion chromatography. Simultaneous analyses for these seven anions require approximately 20 minutes.

Replicate analyses were performed on both standard reference water samples and precipitation samples. Percent relative standard deviations were less than nine percent for all anions except nitrite in the reference samples. Similar precision was found for chloride, nitrate, and sulfate at concentrations less than 5 milligrams per liter (mg/L) in the precipitation samples.

To determine reliability of results, several samples were spiked with known concentrations of fluoride, chloride, nitrate, and sulfate; recoeries ranged from 96 to 103 percent. Known amounts of bromide and phosphate were added, separately, to several other waters, which contained bromide or phosphate. Recovery of added bromide and phosphate ranged from approximately 95 to 104 percent. No recovery data were obtained for nitrite.

Chloride, nitrate, nitrite, orthophosphate, and sulfate, in several samples, were also determined independently by automated colorimetric procedures. An automated ion-selective electrode method was used to determine fluoride. Results are in good agreement with results obtained by ion chromatography.

The study indicates that ion chromatography is as sensitive, accurate, and precise as other standard methods.

8

THE STABILIZATION OF PPB HG(II) SOLUTIONS STORED IN POLYOLEFIN BOTTLES BY HUMIC ACID, *R.W. Heiden*, Owens-Corning Fiberglas Technical Center, Granville, Ohio 43023 and D.A. Aikens, Rennselaer Polytechnic Institute, Troy, New York 12181.

For the prevention of losses of mercury from ppb water samples stored in polyolefin bottles, routine monitoring programs require reliable methods which are also simple. Widely used methods of preservation are not always fully effective in preventing losses of mercury and often require the addition of large amounts of oxidants or complexing agens which can alter the sample components seriously. To minimize the impact of added chemicals we have purified, commercially available humic acid (HA) added in small quantities as a solution to stored water samples. The HA, which is a ubiquitous component of surface waters can strongly complex Hg(II), thereby providing a basis for stabilizing action.

To evaluate the HA as a prospective preservative for routine applications we have examined the impact of several variables on the stability of ppb (Hg(II). Among the variables studies are pH, the compositions of the water samples and polyolefin bottles, and the levels of HA. Comparisons will be made to common methods for stabilizing Hg(II).

9

AN INTRA-LABORATORY QUALITY ASSURANCE PROGRAM, *W.J. Maurits* and E.W. Sarver, Aberdeen Proving Ground, Maryland 21010.

A quality assurance program has been developed to control all aspects of analyses conducted in support of the US Army Installation Restoration Program. Currently, a Central-Field Laboratory concept is utilized. The field laboratories maintain responsibility for the quality of data and are served by the central laboratory which provides standard analytical reference materials, training in quality control techniques, evaluation of proposed methods, assistance in setting up methods, and an overall review of the program. Controls are imposed at many points on each analytical system. These controls include rigid definition of sampling and subsampling techniques, acceptance of reagents, exclusive use of approved reference materials, certification of each analyst, calibration of all equipment, maintenance of control charts, and a full prior test and evaluation of analytical techniques. A QA coordinator at each laboratory is responsible to ensure that local operation is in control.

10

CARBON-13 SPIN LATTICE RELAXATION IN MODEL AROMATIC COMPOUNDS, *T.D. Alger,* W.D. Hamill, Jr., R.J. Pugmire, D.M. Grant, Utah State University and University of Utah, Salt Lake City, Utah 84112.

Several model aromatic compounds—naphthalene, phenanthrene, pyrene, etc., were studied at 25.1 and 75.3 MHz, and 33°C. The ^{13}C spin-lattice relaxation times, T_1's, were measured at the two frequencies along with the nuclear Overhauser effects (NOE's). Estimations of the various relaxation contributions were also made for the dipolar mechanism $(T^{D}{}_1)$, the chemical shift anisotrophy mechanism $(T_1{}^{CSA}$ and the spin rotation mechanism $(T_1{}^{SR})$. For the carbon-13 nuclei with attached protons, the NOE measurements approached the maximum value of 3.0 (dipolar relaxation domination), and the values of the $T_1 \sim T$ ~ 1 to 11 seconds range. These values were relatively unaffected by field variations. In contrast, the values of the NOE parameter for non-protonated carbons varied from as low as 1.13 (little or no enhancement) to a maximum of about 2.7. Generally, the value of NOE in such cases was about 2 at 25.1 MHz and 1.5 at 75.3 MHz. For these non-protonated carbons, the relative contributions of T^{D}_{1}, CSA , AND SR were a aboutequal nd relatively large at 25.1 MHz (greater than 100 seconds and as large as 300-1000 seconds). At 75.3 MHz, the T_1^{CSA} contribution is dominant in these non-protonated carbons; the chemical shift anisotrophy contribution to

T ranges from 33 to 330 seconds at this field strength. Future measurements of T1 for aromatic compounds with non-protonated carbons should be measured at the higher field strengths to decrease the T values. Chemical shift anisotropies similar to those measured in simple aromatic compound (200 to 250 ppm) are adequate to account for the observed values of T_1^{CSA}

11

A MERCURY VAPOR GENERATION SYSTEM FOR MERCURY ANALYSIS BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY, *R.F. Suddendorf* and K.W. Boyer, Department of Health, Education, and Welfare, Food and Drug Administration, Washington, D.C. 20204.

A new apparatus and procedure for determination of mercury using the ICP is described. The technique uses a reducing solution to generate mercury vapor, which is then swept to the plasma for determination. The method is rapid, does not require any specialized equipment in addition to the ICP, and is simple to perform. The mercury vapor generation described has the advantage of leaving other potentially interfering elements behind in the reducing solution.

Included in the discussion will be a description of the experimental apparatus, optimum experimental conditions, detection limits and working curves obtained with this technique. In addition, data showing its applicability for analysis of total mercury in fish will be presented.

12

INCREASING THE CAPABILITIES OF AN AUTOMATED ATOMIC ABSORPTION SYSTEM, *J.G. Crock,* L.R. Layman, and F.E. Lichte, U.S. Geological Survey, Lakewood, Colorado.

Atomic absorption spectrophotometry (AAS) has proven itself in the determination of numerous elements in diverse matrices. Recently, one manufacturer has offered an automated sequential multielemental analysis instrument.

With the multielement capability, a situation often rises in which both trace and major elements must be determined using the same solution from a given sample preparation. Frequently the concentration of one or more of the elements in solution is outside the optimum analytical range of the instrument. This situation usually necessitates several manual dilutions and repeat analyses. Another way to accomplish the dilutions is with a multichannel peristaltic pump. By interfacing the peristaltic pump with a Perkin-Elmer 5000 A.A. spectrophotometer, a system is attained which is very useful when diverse elements or concentration ranges are required. For example, in an agricultural study, major and minor elements, e.g., Na, Ca, K, and Mg are determined by on-line dilution with the addition of appropriate buffers, while Fe and Mn are simply diluted. In addition, there is enough sample in the autosampler tube to run several elements which require no dilution, e.g., Zn and Cu. The interface and required instrumental modifications are described.

13

DETERMINATION OF TRACE ELEMENTS BY DIRECT FURNACE ATOMIZATION FROM METAL SAMPLES,

B. Wysocki, G.G. Welcher, and J.Y. Marks, Materials Engineering and Research Laboratory, Pratt & Whitney Aircraft Group, Middletown, CT 06457.

Preliminary work demonstrated the feasibility of the determination of lead, bismuth, selenium, tellurium, thallium and tin in nickel-base alloys by direct atomization from metal chips. One of the major limitations in the use of the technique was the lack of suitable solid reference materials containing the trace elements of interest. In the present work, studies are presented which show that standards may not have to be of exactly the same composition as the samples to effect an accurate analysis. Accurate determinations of some trace elements may be made in completely different alloy matrices than that of the standards. Guidelines for selection of standards will be discussed. In addition, other factors such as selection of optimum heating parameters, advantages of reduced background and segregation of trace elements in the sample are considered.

[1] J.Y. Marks, G.G. Welcher and R.J. Spellman, Appl. Spectrosc. 31,9 (1977)

14

EVALUATION OF AN ICP-ECHELLE SPECTROMETER SYSTEM FOR MULTI-ELEMENT ANALYSES,

D.L. Dick, W. Hanagan, M.M. Miller, and R.K. Skogerboe, Colorado State University, Ft. Collins, Colorado 80523.

An inductively coupled plasma has been combined with an echelle spectrometer to evaluate the capabilities for multielement analyses. The analytical features of this combination will be discussed in relation to those representative of other types of spectrometers and excitation sources.

15

PRECONCENTRATION OF TRACE ELEMENTS BY REDUCTION AND PRECIPITATION USING $NaBH_4$, *W. Hanagan* and R.K. Skogerboe, Colorado State University, Ft. Collins, Colorado 80523.

The development and evaluation of a new multielement preconcentration technique involving reduction and precipitation of trace elements using $NaBH_4$ will be discussed.

16

THE ROLE OF OXIDIZING GASES IN SIGNAL DEPRESSIONS IN FLAMELESS ATOMIC ABSORPTION SPECTROSCOPY, *S.G. Salmon,* and J.A. Holcombe, The University of Texas at Austin, Austin, Texas 78712.

Gas phase reactions are known to be the source of some of the interference effects exhibited by flameless atomic absorption spectroscopy. Oxidation of the analyte after atomization would account for depression of the analytical signal. By using an optical system which is capable of obtaining time and spatially resolved absorption profiles above a carbon filament atomizer, the effect of oxidizing gases on the absorbance signal of various metals was determined. The rate of decay of the absorbance signal for some metals is not consistent with a thermodynamically controlled reaction scheme predicted by the metal oxide bond strengths. The possibility of kinetically controlled reaction schemes has been investigated. In addition to the question of thermodynamic or kinetic control of the gas phase reaction it has been observed that the presence of excess oxidizing gas causes the atomization of certain metals to commence at higher temperatures. The significance of the gas phase reactions to the interference problem encountered in flameless atomic absorption will be discussed.

17

A TWO CHANNEL ATOMIC ABSORPTION SPECTROPHOTOMETER WITH CATHODE RAY TUBE READOUT AND ITS APPLICATIONS, *A. Rattonetti* and G.P. Thomas, Instrumentation Laboratory, Inc., 115 Constitution Drive, Menlo Park, CA 94025.

Two channel atomic absorption has many advantages: increased analytical speed, dual wavelength calibration of the same element to increase concentration range, background correction from 180—900 nm, and internal standardization.

When combined with a microcomputer and CRT readout, the capabilities are greatly enhanced: display of the shape and storage of working curves, display of the nature and magnitude of the background signal compared to the corrected signal, and presentation of concentration and ratio of the two elements being determined.

The value of these features in flame and graphite atomizer applications will be shown with examples drawn from geochemical and biological samples.

18

A MULTI-ELEMENT SEQUENTIAL PLASMA SPECTROMETER, S.B. Smith, Jr., H.L. Kahn, and *G.P. Thomas,* Instrumentation Laboratory Inc., 115 Constitution Drive, Menlo Park, CA 94025.

An inductively-coupled plasma (ICP) spectrometer has been developed with the intention of taking advantage of all the promising possibilities of ICP emission spectroscopy, while avoiding some of the problems that have arisen. The optical design is based on a very rapidly scanning double monochromator of approximately 0.02 nm resolution, controlled by a microcomputer. Wavelength calibration is continuous — at least once per scan — and is performed against the known line spectrum of a low-pressure mercury source.

This system can determine 10–20 elements per minute in a single sample. The elements to be determined and their emission lines are selected by the operator; once the program is found effective it is stored on a cassette for future use. The rigidity sometimes associated with fixed element multi-element equipment is thus avoided. The use of double monochromators minimizes stray light, thereby reducing spectral interferences.

Analytical information as well as spectral data and curves are read out on a built-in CRT. Data can also appear on a rapid external line printer.

19

SELECTIVE ELECTRON CAPTURE SENSITIZATION, *M.P. Phillips,* R.E. Sievers, R.M. Barkley, M.A. Wizner, M.J. Bollinger, and R.S. Hutte, University of Colorado, Boulder, Colorado 80309 and P.D. Goldan and F.C. Fehsenfeld, Aeronomy Laboratory, NONA/ERL, Boulder, Colorado 80303.

The response of the electron capture detector (ECD) to compounds such as N_2O depends not only on the initial attachment process but to the subsequent negative ion chemistry as well. This can be understood from the low pressure negative ion chemistry of N_2O Any compound compound that reacts with O^-or NO can increase the effective rate of attachment of electrons to N_2O. Because of this, the sensitivity of the

The purpose of this method is to effect standardization of detector specifications. The procedures provide a means for verifying the performance of any fixed-wavelength photometric, detector, for monitoring the changes in a specific detector's performance, and for comparing the performance of different photometric detectors.

23

HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC ASSAY OF N–OXIDE METABOLITES FROM TERTIARY AMINES, *J.A. Thompson,* University of Colorado, Boulder, Colorado 80309.

N-Oxides are important metabolites of many drugs which contain tertiary amino groups. These include antihistamines (e.g., chlorpheniramine), tricyclic anti-depressants (e.g., imipramine), phenothiazine neuroleptic (e.g., chlorpromazine) and analgesics (e.g., methadone). Investigations of the metabolic disposition of specific drugs which undergo such biotransormations, and studies which are designed to answer basic biochemical questions about the activity of the enzymes involved, require reliable assay procedures which are easy to perform. Few procedures are presently available to analyze these very polar compounds. The most common method has been thin-layer chromatography, but if radioactive compounds are not used, quantification is very difficult. Gas chromatography has not been successful, because these hydrophilic metabolites are not readily extractable from aqueous media and are not sufficiently volatile for gas phase analysis. In fact, conversion back to the parent tertiary amine is often observed in the GC. Analysis by HPLC eliminates the need for a preliminary extraction and is well suited to separations of polar compounds. We have investigated the HPLC analyses of several N-oxide metabolites, including chlorphenirmaine, N-oxide, nicotine N-oxide and cotinine N-oxide. A C–18 reverse phase column did not yield satisfactory results with regard to peak shapes or retention times, despite the use of a wide variety of mobile phase conditions. Polar bonded phase columns, however, can be successfully applied to this work. We have found conditions for the simultaneous analyses of nicotine and its major metabolites, nicotine N-oxide and cotinine on a u-Bondapak-NH2 column. A bonded alkylnitrile column has also been employed in these studies. N-oxide metabolites have been analyzed from urine samples and from *in vitro* incubations with rat liver homogenates.

24

CORRECT MOBILE PHASE PREPARATION FOR REVERSED PHASE LC SEPARATORS, *F.M. Rabel*, Whatman, Inc., Clifton, New Jersey 07014.

A considerable amount of LC in the reversed phase mode is being done today. Although many of the separations done in this mode require only organic/water mobile phases, many need addition of salts, acids or bases to give the correct selectivity and peak symmetry. Although many papers report the pH of the solution being made, it is generally unclear how the pH was measured. In fact, pH is only applicable to aqueous solutions and other "apparent" pH measurements made with glass electrodes in the organic/water mobile phase combinations may be very much misleading.

The correct use of the glass electrode pH meter will be discussed as well as how to measure apparent pH's in mixed solvent systems. Why incorrect pH readings can affect column stability and life will also be mentioned.

25

AUTOMATED QUALITATIVE AND QUANTITATIVE ANALYSIS OF GC/MS DATA OF COMPLEX MIXTURES FOR ENVIRONMENTAL POLLUTANT ANALYSIS, *Glenn I. Ouchi*, David Smith, Finnigan Instruments, 845 W. Maude Avenue, Sunnyvale, CA 94086.

A minicomputer-based method has been developed for the qualitative and quantitative analysis of the GC/MS data required from complex organic mixtures. The method utilizes reverse library search using spectra of expected target compounds from a "user" library. The "user" library is built from spectra of standard compounds. Unknown compound spectra from GC/MS profiles can also be built into the "user" library for quantitative profile comparisons.

Target compound identification is based on relative retention data and mass spectral pattern matching. Quantitation is achieved by performing the appropriate calculations on the peak areas of a selected ion for each component and a selected ion of an internal standard. Multiple internal standards can also be used. Components not identified by reverse search are forward library searched.

This method has been uilized for environmental pollutant analysis.

26

LASER INDUCED FLUORESCENCE SPECTRA OF CFCI, *S.E. Bialkowski*, National Bureau of Standards, Washington, D.C. 20234.

Present interest in the chemistry resulting from fluorocarbon diffusion into the atmosphere has generated a need for spectral information on fluorocarbon species. The CFCI radical has been produced by both i.r. photolysis and He metastable reaction of C2F3CI. Laser induced fluorescence and excitation spectra taken at subambient temperatures has yielded sufficient information to determine certain rovibronic constants. Medium resolution excitation spectra of single vibronic levels has shown CFCI to be a nearly symmetric oblate top. The 1, , transitions are analyzed and yield a change in the A rotational constant of ~ 1.84 cm^{-1} for the 2^0_0, 2^1_0, and 2 vibronic bands. Vibrational analysis has yielded upper state values of w$_2$'= 394 cm^{-1} and w$_3$' = 739 cm-1 along with their associates anharmonicities. Ground state vibrational analysis gives w1" = 1168 cm^{-1}, w$_2$"= 448 cm^{-1} and W3" = 750 cm^{-1}. The vibronic origin, being T$_0$= 25283 cm"1, is shifted 300 cm"1 to the blue of the previously reported matrix origin. Finally, the rotational bandwidth as compared to the vibronic spacing is discussed in terms of the feasibility for identification by spectral analysis.

27

^{13}C and ^{1}H NMR ANALYSIS OF HIGH BOILING PETROLEUM FRACTIONS, K.D. Berlin, *D.J. O'Donnell,* Oklahoma State University, Stillwater, Oklahoma 74074, G.P. Sturm and J.W. Vogh, Bartlesville Energy Technology Center, Barlesville, Oklahoma 74003.

In order to improve refinery techniques and recovery processes of crude petroleum, it has been highly desirable to analyze the higher boiling petroleum distillates. In this study, selecyed gel permeation chromatographic (GPC) fractions of high boiling (535–675°C) distillates from two crude oil sources were analyzed using ^{13}C and ^{1}H NMR spectroscopy. Although several alternative techniques have been employed previously to obtain parameters descriptive of the average composition of a given fraction, ^{13}C NMR analysis afforded a unique method of directly assessing the aromatic carbon content. For a particular series of GPC fractions, the percentage of aromatic carbon varied from 13.2% to 29.2% of the total carbon integral. Measurement of the specific signal intensities in the aliphatic region of the ^{13}C NMR spectra was used to estimate average side chain lengths (C9-C20) within a particular GPC series. Comparison of the ^{13}C NMR spectra with the ^{1}H NMR spectra made possible the characterization of certain structural variables (e.g., degree of branching, degree of substitution on arenes, etc.) in the fractions of the petroleum distillates. This permitted an estimate of the level of contribution of each variable in the overall composition of the sample. Comparisons between GPC fractions obtained from a single crude source revealed distinct trends in almost every structural variable. Interestingly, it was observed that degree of branching, aromatic-H/aliphatic-H, etc., from one source varied in a manner similar to a corresponding GPC series of fractions obtained from a different source. These trends and the spectra will be discussed.

28

ANALYSIS OF GASES AND OILS RELEASED BY MICROWAVE POWER FROM COLORADO OIL SHALE, *D.G. Soucy,* W.T. Lutz, E.T. Wall, University of Colorado at Denver, Denver, Colorado 80202.

The gases and oils released from Colorado oil shale using a high intensity microwave field were compared to those obtained by a standard thermal process. Hydrogen, hydrocarbon, and inert gases of interest were determined by using a non-dedicated, inexpensive modified gas chromatograph. Both flame ionization and thermal conductivity detectors were used to permit a sensitive single injection analysis. Released oil was chemically profiled using a short capillary column and high sensitivity, sulfur, nitrogen, carbon and hydrogen analyzers. Chemical differences in the products relating to grade of shale and time of power application may suggest an altered mechanism of pyrolysis.

29

HEAVY METALS AND THEIR RELATIONSHIP TO SOLIDS IN STORM RUNOFF, *D.R. Bourcier* and R.P. Sharma, Utah State University, Logan, Utah 84322.

Although a considerable amount of work has been done in order to develop models for estimating metal loadings in urban runoff, some basic information on the relationships between various storm water parameters is still lacking. In a previous study at a viaduct road runoff site in Pullman, WA, metal input from sources other than motor vehicles was excluded and a definite relationship was observed between total solids and metal concentrations. This study was undertaken to determine if the same models can be used for *storm* events occurring at a different geographical location where the input of solids and metals from sources other than motor vehicles was not controlled. Storm runoff was collected at 20 different roadside sites during each of two separate storm events at the non-industrialized area of Logan, UT. The samples were analyzed for total solids and metals (lead, copper, zinc, iron, chromium, and cadmium). Since several methods of digestion of runoff samples are given in the literature, the two most common procedures were compared. After pre-digestion with HNO3, the 40 samples were each separated into two aliquots. One aliquot was further digested with $HCl-HNO_3$ while the other was digested with $HF-HNO_3$. The two digestion procedures did not provide significant differences in metal levels suggesting that the time consuming $HF-HNO_3$ digestion procedure is not required. Significant correlations were observed between metals vs. total solids and regression equations were developed for the two parameters. The models were compared to those designed from data obtained from the earlier study. It was observed that the regression models are not identical when utilized for two separate geographical areas where the source of input of metals and solids to the road surface differs. This information is considered valuable in understanding the role of the various parameters in the development of models for estimating metal loadings in road runoff.

30

A COST EFFECTIVE APPROACH TO THE ANALYSIS OF ORGANICS IN WATER,

David E. Smith, Robert E. Finnigan, Finnigan Instruments, 845 W. Maude Avenue, Sunnyvale, California 94086.

With the advent of minicomputers, data systems for mass spectrometers have evolved into an integral part of mass spectroscopy systems. Rapid development of chromatographic techniques, particularly capillary chromatography, has placed great demands on the speed of data acquisition and processing. Increased utilization of mass spectroscopy in response to government regulations has added further requirements for verification of data quality. Economic pressures have forced major consideration of the cost effectiveness of the mass spectrometer-data system combination.

This presentation will examine a cost comparison of GC vs. GC/MS for organics in water analysis. The comparison includes analysis time, capital costs for equipment, and data reliability. The data for the comparison was gathered from interviews of over 100 scientists in government, industry, and commerical laboratories.

31

WIDE RANGE CALIBRATION FOR DIRECT, ACCURATE ANALYSIS OF SOLID SAMPLES IN FURNACE ATOMIC ABSORPTION, *John A. Nichols* and Ray Woodriff, Montana State University, Bozeman, Montana 59717.

A constant temperature furnace is used which has a long enough tube length so that the kinetics of analyte loss from the heater tube are essentially constant and unaffected by large variations in types of sample matrices. Simple application of the diffusion laws predicts a linear relationship between the peak width, measured at a chosen fixed height, and the logarithm of analyte quantity (or concentration, in a fixed sample volume). Woodriff and Marinkovic, *Anal Chem 49,* 2008, have confirmed this relationship for standards of 3 elements, but report deviations from linearity for elements which interact with graphite.

This work explores the use of several calibration parameters, especially peak-width-at-fixed-height (PWAFH), for solid samples with complex matrices. Precise and accurate results are readily obtained for Pb, Zn and other elements which do not interact with graphite. Elements which react with graphite, such as Cu or K, are not as readily determined, although these do escape from a porous graphite crucible which is tightly closed with a screw-in graphite cover.

32

AN OVERVIEW OF INORGANIC SPECIATION, R.S. Braman, University of South Florida, Tampa, Florida 33620.

Environmental analyses for molecular forms of inorganic elements are difficult because of low concentrations generally encountered. Organometallic compounds present in natural waters can be as low as 1 ppt as was found for tin. Trace amounts of mercury forms or sulfur compounds in air can be in the several nonogram percubic meter concentration range. Air analyses are complicated by the presence of reactive compounds such as ozone and nitrogen dioxide are also present.

Because of the low concentrations encountered direct analyses are rarely possible although attempts to use long path spectroscopy have been successful.

Analytical methods developed for speciation are a combination of preconcentration sampling, separation and selective detection with analyte sizes in the 0.01 to 100 ng range. Preconcentration has been done by physical absorption onto high surface area solids and by reversible chemisorption (air analyses) and by degassing water samples after chemical pretreatment such as the hydriding procedure for arsenic compounds.

Gas chromatography and HPLC have been used in separations. Use of latter is on the increase and is showing good promise for future applications.

Selective and specific detection is best achieved by emission spectroscopic techniques because of low detection limits. Atomic absorption spectroscopy is gaining use.

Current problems include interfacing of preconcentration — separation schemes with detectors and development of methods for analysis of sediment and biological materials.

33

COMPARISONS OF ACID LEACHING PROPERTIES OF COAL WASTE PRODUCTS BEFORE AND AFTER NEUTRON IRRADIATION, W.D. James, University of Missouri, Columbia, Missouri 65211.

Trace element contamination entering ground and waste water systems has come under close scrutiny in recent months. Specifically, concentration limits for several elements in leachates from fossil fuel wastes have been suggested by EPA. Efforts to ensure compliance with these guidelines will require development and use of routine analytical procedures.

A tracer technique involving pre-irradiation of fly ash with reactor neutrons and counting of leachates of that fly ash for radioactive species has been proposed by this laboratory. This technique would allow rapid simultaneous determination of many elements of interest. Preliminary data indicate that neutron irradiation did not significantly alter leaching properties under the experimental conditions.

The evaluation of this technique is now being extended to its use in leaching studies of coal and some residues produced in coal conversion processes. In particular, the following materials are currently being studied: NBS Fly Ash (SRM 1633), NBS Bituminous Coal (SRM 1623a), in situ coal gasification process ash (from laboratory experimental system), tar residue centrifuged from the product oil of a liquification process, and the ash of that tar. Leaches have been performed on both irradiated and un-irradiated fractions of these materials to determine whether radiation damage causes significant changes in leaching behavior. Results of these experiments will be discussed.

34

ON THE CHEMICAL SPECIATION OF FLY ASH: SOME STUDIES OF MATRIX COMPOSITION AND STRUCTURE AND THE DISTRIBUTIONS OF TRACE ELEMENTS, *L.D. Hulett* and A.J. Weinberger, Oak Ridge National Laboratory*, Oak Ridge, Tennessee 37830.

There is reason to speculate that trace elements may exist, at least in part, as solid solutions in fly ash matrix materials. Their chemical species may be determined primarily by the matrix in which they are dissolved. Preliminary work has shown that elements such as V, Mn, Cr, and Mo, which would be expected to be soluble in Fe_3O_4, are indeed more concentrated in the magnetic fractions of fly ashes. Alkali, alkaline earths, are earths, and certain other elements, which would be expected to be soluble in aluninosilicates, are more concentrated in the non-magnetic phases. An etching method has been developed to remove glass phases and leave crystalline mullite and silica residues. Qualitative analysis of the crystal phases by scanning electron microscopy and x-ray fluorescence shows that Na, Mg, K, Ca, Rb, Sr, and Y are completely removed and are therefore primarily associated with the glass phases. Large percentages of As and Pb appear to also be associated with the glass matrix. Cr, Ti, Fe, and Zr remain in the mullite phase but not exclusively. Work is in progress to measure accurate distributions of the trace elements and determine more about the properties of the glass matrix.

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*Operated for the U.S. Department of Energy by Union Carbide Corp. under Contract W-7405-eng-26.

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GEOTHERMAL DEVELOPMENT AND ENVIRONMENTAL ANALYTICAL CHEMISTRY IN THE PACIFIC NORTHWEST, *J.M. Baldwin,* Allied Chemical Corporation, 550 Second Street, Idaho Falls, SD 83401 and C.A. Allen, EG&G Idaho, Incorporated, P.O. Box 1625, Idaho Falls, ID 83401.

The development of the geothermal resources of the Pacific Northwest appears to raise some questions about environmental effects that may be unique even within the geothermal development field. Accurate estimation of environmental effects is complicated by the geographically ubiquitous nature of the resource and the multitude of possible beneficial uses. Typically, geothermal manifestations in the Pacific Northwestern region of this country produce large quantities of relatively low temperature water that does not contain an extraordinarily high concentration of dissolved solids. Thus the resource may be better suited to small-scale, direct thermal applications than to electrical power production. Typical uses may include industrial process heating, domestic heating, and agricultural applications, as well as electrical power generation.

This range of potential applications raises a wider variety of environmental concerns that may be encountered in other geographical areas and places a correspondingly greater demand on the skills of the analytical chemist. In this paper, we will present an account of some typical environmentall-related analytical problems from geothermal energy development, and their solutions.

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ANIONIC SPECIATION OF ENVIRONMENTAL WATERS BY ION CHROMATOGRAPHY, T.B. Hoover, Environmental Protection Agency, Athens, Georgia 30605.

Ion chromatography (IC) is an effective instrumental technique for the measurement of anionic species in water. Different oxidation states of an element are separated but the sample species are in hydrolytic equilibrium with the eluent. Fundamental operating parameters for IC will be reviewed, including the effects of eluent characteristics (buffer system, concentration, and pH) on the retention times of common anions. Detection limits for direct injection and preconcentrator column techniques will be compared for different sample volumes. Methods were developed or improved for the separation and measurement of arsenite, arsenate, selenite, and selenate. Some factors in the analysis of industrial effluents for both nitrite and nitrate will be discussed.

37

A MASTER ANALYTICAL SCHEME FOR ORGANICS IN WATER, *A.W. Garrison,* US-EPA, Athens Georgia 30605, J.F. Ryan, Gulf South Research Institute, New Orleans, Louisiana 70186, and E.D. Pellizzari, Research Triangle Institute, Research Triangle park, NC 27709.

Any water sample, regardless of its source, contains complex mixtures of synthetic and natural organic compounds. Analytical chemists are very frustrated by questions such as "What organics does this river water contain?" or "What are the levels of chlorinated phenols in this effluent?" If given enough time, the chemist can provide answers, but available methods are usually incomplete and a protocol must be assembled to fit each situation. Without experienced consideration, the chosen methodology will likely not be comprehensive, and entire classes of organics may be missed. Quantitative results are unsatisfactory unless the chemist goes to great pains to analyze standards of each compound with the same analytical protocol used for samples.

A Master Analytical Scheme for organics in water, currently being developed under an EPA contract, will help alleviate these difficulties for volatile (gas chromtographable) organics in water. This general protocol will be based on capillary column GC/MS. Preferred extraction, concentration, and clean-up methods will be specified by the Scheme to allow maximum separation and recovery of a compound or class of compounds of interest to the user, or to allow the survey analysis of almost all volatile organics. Scheme development will include measurement of recoveries and response factors for several hundred model compounds that represent all classes of volatile compounds in all major types of water. This computerized data base will allow the user to obtain an estimate of concentration without using individual standards. The Master Analytical Scheme will provide the first unified protocol for broad-spectrum qualitative and semi-quantitative analysis of organics in water; although not perfect, it should help solve many of the frustrated chemist's problems.

38

SAMPLING AND ANALYSIS OF HALOETHERS IN WATER AND WASTEWATER, *J.M. Kyne,* P.L. Sherman, Monsanto Research Corporation, and J.E. Longbottom, Environmental Protection Agency.

A method has been successfully developed for the analysis of five halothers in water or wastewater by non-gas chromatographic/mass spectrometric techniques. The five haloethers analyzed by this procedure are: bis(2-chloroisopropyl) ether, bis(2-chloroethyl) ether, bis(2-chloroethoxy) methane, 4-chlorodiphenyl ether and 4-bromodiphenyl ether. The method utilizes a liquid-liquid extraction with methylene chloride, a solvent exchange to hexane and an optional column chromatographic cleanup procedure to remove potential interferences. The analysis is accomplished by gas chromatography with an electrolytic conductivity detector. The work upon which this publication is based was performed pursuant to Contract No. 68-02-2633 with the Environmental Monitoring and Support Laboratory of the Environmental Protection Agency.

DETERMINATION OF SELECTED VOLATILE ORGANIC PRIORITY POLLUTANTS IN WATER BY COMPUTERIZED GAS CHROMATOGRAPHY–QUADRUPOLE MASS SPECTROMETRY,

W.E. Pereira and *B.A. Hughes,* U.S. Geological Survey, Lakewood, Colorado.

This method describes the determination of 19 selected volatile, purgeable, Priority Pollutants in water. The procedure is based on the purge-and-trap technique and is applicable to the analysis of purgeable organic compounds in raw and treated surface waters, ground water, and industrial effluents. The method generates semiquantitative data for the 19 selected compounds as well as qualitative GC-MS characterization of any purgeable organic compounds that may be present in the sample. The method was evaluated at the 5-50 microgram per liter (ug/1) level; lower detection levels are possible.

The technique involves purging a 5-milliliter (ml) sample of water with an inert gas. The purged organic compounds are trapped on a porous polymer adsorbent, and then thermally desorbed onto a gas chromatography column and analyzed using GC-MS computer techniques. The volatile compounds are tentatively identified using relative retention time data, and their mass spectra are characterized with the aid of a computerized "Reverse—Library Search" procedure. Quantitative measurement of identified compounds is based on the Internal Standardization Method, using a purgeable internal standard labeled with deuterium.

The precision and accuracy of the method were evaluated by spiking organic-free water with standards. Two internal standards were used in the procedure, 1,2-Dibromoethane-d_4 and Bromochloromethane. 1,2-Dibromoethane-d_4 was used as the internal standard for quantitation. A standard amount of Bromochloromethane was added to each sample to ascertain if the GC-MS was operating within the limits set by the method.

Examples of qualitative GC-MS characterization of other purgeable organics are presented in the analysis of tap water, chlorinated sewage effluent, and indstrial effluent.

40

FRACTIONATION AND GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC CHARACTERIZATION OF ORGANIC COMPOUNDS EXTRACTED FROM DIESEL ENGINE EXHAUST PARTICULATES, *C.F. Rodriguez,* J.B. Fischer, H.G. Wheeler, Southwest Research Institute, P.O. Drawer 28510, San Antonio, Texas 78284.

Use of the diesel engine has been continuously increasing recently, and although it burns cleaner with respect to some pollutants, concern has been raised regarding potentially toxic organic compounds contained in the large amounts of particulate matter present in diesel exhaust. The objective of this program was development of preparative methods for analytical characterization of the organic constituents of diesel exhaust. Particulates were collected onto large glass fiber filter papers which were exhaustively extracted with dirst dichloromethane and then acetonitrile. Only the dichloromethane extracts were used for the analytical study. The extracts were concentrated and separated by liquid partitioning into acidic, basic and neutral fractions. The neutral fraction was further separated into four groups by column liquid chromatography on silica gel. Fractions having biotoxicity activity were characterized by determination of carbon, hydrogen, and nitrogen by elemental analysis; functional groups by infrared spectroscopy; sulfur by flame photometric gas chromatography; and structure by gas chromatography/mass spectrometry. Some tentative identifications were made of compounds not previously reported in diesel engine exhaust.

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VALIDATION OF ANALYTICAL DATA IN PESTICIDE RESIDUE ANALYSIS USING MULTIPLE DETECTION SYSTEMS, *Robert C. Hanisch*, G. Wayne Sovocool, and Robert G. Lewis, Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

Quantitative measurements of levels of several organochlorine pesticides and toxic substances, including chlordane related compounds, in human tissue samples were cross compared by several chromatographic detector systems. These detectors included electron capture, a mass spectrometer operated in the selected ion monitoring mode, the Hall electrolytic conductivity detector, and a photoionixation detector. Errors in measurement were evaluated in terms of origin and magnitude. The influence of common interferences such as polychlorinated biphenyls on the analytical results will be discussed.

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ABSTRACT NOT SUBMITTED.

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MACROPOROUS RESINS IN LIQUID CHROMATOGRAPHY, *Harold F. Walton,* and Kazuko Aramaki, University of Colorado, Boulder.

As stationary phases for liquid chromatography, ion-exchange resins combine hydrophobic and pi-bonding interactions with ionic forces. The ions may act electrostatically through hydration, ion exchange or Donnan exclusion of co-ions, or they may interact with solute molecules in a specific manner.

Our research concerns the role of ion-exchange resins in liquid chromatography of organic compounds. Conventional resins with 4% crosslinking, packed in short columns, give very good resolution of xanthines and analgesic drugs. They permit detection of 5 nanograms of theophylline in blood serum. Macroporous ion-exchange resins give poorer plate heights but allow much faster flow rates, so that more plates can be generated in unit time.

The uses of macroporous resins in liquid chromatography will be discussed. Examples include ligand-exchange chromatography, the chromatography of alkaloids and drugs and size-exclusion chromatography of humic substances.

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INDUSTRIAL HYGIENE AIR SAMPLE ANALYSES IMPROVED RESULTS THROUGH AUTOMATION USING GLASS CAPILLARY COLUMNS AND A MULTI-CHANNEL DATA SYSTEM, *U.A. Sikorski,* R.C. Domingo, and D.R. Brezinski, DeSoto, Incorporated, Des Plaines, Illinois 60018.

The problems related to the analysis of the air sampled in our immediate environment using charcoal tubes were identified and their possible solutions presented in this paper. The NIOSH procedure is well established and generally accepted but can be greatly enhanced with a few modifications.

The objectives of this paper are to improve qualitative identification through better resolution using glass capillary columns and obtain more accurate quantitative results via an autosampler and an external calibration method.

Oftentimes, an internal standard cannot be used because there is no room in the chromatogram for the internal standard. Additionally, adding a trace amount of an internal standard in the desorbed sample is a difficult task. The analyst is then left with no alternative but to use an external calibration method. The reproducibility of injection, the major source of error in manual injection, is eliminated using a Varian Series 8000 autosampler installed on a Varian 3700 gas chromatograph.

A multi-channel Spectra-Physics SP—4000 chromatography data system facilitates peak identification by matching the retention time of the unknown components to known laboratory standards using two or more glass capillary columns. Quantitative results are obtained using an "internal graphing" external calibration method available in the data system.

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REVERSED-PHASE LIQUID CHROMATOGRAPHY OF CATECHOLAMINES AND THEIR CONGENERS WITH ELECTROCHEMICAL DETECTION, *P.A. Asmus* and C.R. Freed, University of Colorado Medical Center, Denver, Colorado 80262.

Using reversed-phase ion-pairing liquid chromatography and electrochemical detection with mobile phases composed of simple acids, we have developed assay techniques to measure catecholamines and their congeners in plasma, urine and tissue samples with sensitivity to the subpicomole level. Ion-pairing chromatography with trichloroacetic acid in phosphate buffer as the mobile phase provides a good retention, peak symmetry and high efficiency. The solute capacity ratios were dependent on the hydrophobicity and concentration of the ion-pairing reagent and the pH of the mobile phase. Chromatography was compared to that seen using sodium octylsulfate as the ion-pairing reagent. Trichloroacetic acid gave retention and efficiency similar to sodium octylsulfate. These experiments show that simple acids can replace alkylsulfates as ion-pairing reagents for the separation of the catecholamines and their metabolites. The assay methods have been applied to measurement of L-dopa metabolites in urine and plasma of patients with Parkinson's disease with L-dopa and carbi-dopa and to catecholamines and their metabolites in rat hypothalamus, brain stem and heart tissue in the course of studies on L-lopa and a-methyldopa metabolism.

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RAPID SEMI-QUANTITATIVE ANALYSIS OF SELECTED PESTICIDES IN NATURAL WATER BY HIGH-PRESSURE LIQUID CHROMATOGRAPHY, *T.R. Steinheimer* and D.M. Walker, U.S. Geological Survey, Lakewood, Colorado.

Analytical methods are needed to carry out surveillance and monitoring programs for combinations of pesticide compounds occurring in natural water samples. New procedures must demonstrate sensitivity, compound selectivity, speed, and amenability to continuous multiple sample processing. High-pressure liquid chromatography (HPLC) seems ideally suited to carbamate and triazine pesticide separations because of its speed and generally mild conditions. In addition, the increasing use of mixed pesticide formulations coupled with the presence of metabolic and/or degradation products requires high efficiency separations offered by liquid chromatography columns. The most satisfactory separation of complex mixtures has been achieved using reverse-phase columns and conditions.

This report describes a rapid semi-quantitative procedure for the analysis of residues of 5 triazine herbicides and 5 carbamate pesticides in raw water using high-pressure liquid chromatography. With the exception of two very polar carbamates each pesticide is extracted and concentrated using a commercially available pre-concentration device. All compounds are separated by gradient elution HPLC employing untra-violet detectors. Identifications are made by comparisons of sample against reference standards using multiple wavelength absorbance ratios and relative retention data. Recoveries from natural water samples spiked at the 5—20 ug/1 level averaged 80—90% for the 10 compounds examined.

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MULTIPLEX GAS CHROMATOGRAPHY, J.B. Phillips, Southern Illinois University, Carbondale, Illinois 62901

The purpose of any analytical chromatography procedure is the production of information. Using chemical separation as the means is only incidental to the purpose but does have important consequences for the efficiency and rate of information production. Gas chromatography is commonly thought of as a separation method and is commonly employed for analysis. But, these two features are not indivisibly linked, nor are they fundamental to the definition. Gas chromatography may be employed as an analysis technique without physically separating anything. By considering a chromatographic system in terms of information carried by chemical signals, its limits when operated in a separations mode are made apparent and new nonseparation modes of operation which go beyond these limits are suggested.

Modulation of the column input chemical signal by a pseudorandom series multiplexes information from all retention times into each output signal point. Information may be recovered from the multiplexed signal through a variety of computational methods. Multiplex and throughput advantages analogous to those of FT–IR and FT–NMR exist for such nonseparation chromatographic techniques and may eventually be as important for new applications of chromatography as they are for the spectroscopic techniques.

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PYROLYSIS GAS CHROMATOGRAPHIC MASS SPECTROMETRIC IDENTIFICATION OF THE INTRACTABLE MATERIALS, *J.L. Wuepper,* Whirlpool Corporation, Benton Harbor, Michigan 49022

While considerable work has been reported on various aspects of pyrolysis gas chromatography of polymers in general, the identification of various kinds of intractable samples is usually based on pyrogram fingerprinting techniques without the benefit of the unequivocal nature of mass spectra of the peaks and without the benefit of data system manipulation of data. The pyrolysis gas chromatographic mass spectrometric-data system (PGCMSDS) procedure described here was initially used for fast characterization of unknown carbon filled cured rubbers, but the ease of pyrogram peak identification with the quadrupole data system immediately suggested that the method be extended to other intractables such as paint, fibers, epithelial tissue, gum, and possibly others such as polymers. PGCMSDS seems to offer considerable potential where pyrogram profile matching is not sufficient for the intended result of the analysis such as might exist in other problem solving laboratories or in the forensic sciences and when independent data is needed to support other results.

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ABSTRACT NOT SUBMITTED

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QUANTITATIVE ANALYSIS OF HYDROCHLOROTHIAZIDE IN EQUINE URINE AND PLASMA BY HIGH PRESSURE LIQUID CHROMATOGRAPHY, *G.A.Maylin,* and J.D. Henion, Cornell University, Ithaca, New York 14853

Biological fluids are so chemically complex that detection, isolation and quantitation of administered drugs and their metabolites can be very challenging. Thin layer chromatography (TLC) provides a sensitive, inexpensive means of screening large numbers of samples for drugs, but has some limitations with respect to accurate quantitative analysis. High pressure liquid chromatography (HPLC) utilizing variable wavelength UV detection or fluoroescence detection can provide optimum separation and detection capabilites for organic molecules not amenable to gas chromatographic (GC) analysis. In particular, reliable quantitation of the components of interest can be achieved which enables one to monitor important pharmacological processes.

We have utilized the unique capabilities of HPLC to perform qualitative and quantitative analysis of hydrochlorothiazide (HCT) in horses. A normal phase Porasil column and an eluant consisting of 95/5 chloroform/EtOH provides efficient separation of HCT from an internal standard, trichlormethiazide (TCM), and endogenous materials of equine urine and plasma. Optimum performance of the chromatographic system can be obtained by efficient clean up of the biological extract. Details of the procedures used and detection limits down to 5 ng/ml urine will be described.

51

HPLC PEAK IDENTIFICATION USING UV SPECTRA OBTAINED FROM A MILLISECOND-SCAN VIDICON DETECTOR, *R.M. Smith, KM.* Aldous, D. Choudhury and B. Bush, New York State Department of Health, Albany, NY 12201.

Most HPLC detection systems monitor one or two UV absorbing wavelengths and therefore retention time is the only wualitative information obtained. However, in most chromatographic systems, the analysis of complex mixtures are encountered and retention time alone is entirely inadequate for substance identification.

The presentation will describe the interfacing of a scanning vidicon UV detector with ixisting HPLC equipment to provide an instantaneous complete UV spectrum for every peak in a chromatogram. This UV "fingerprint" can be used to identify unknown compounds by searching

UV spectral libraries or by comparison with spectra generated from known standards in the laboratory.

Chromatograms and spectra to be shown include those obtained from the analysis of 250-ng of decachloro 5,5′-bicyclopentadienyl in an industrial effluent component. UV spectra and detection limits of more than 20 polynuclear aromatic hydrocarbons which are found in air samples will also be shown and compared with spectra obtained with a conventional spectrophotometer.

52

APPLICATION OF SPECIFIC GAS CHROMATOGRAPHIC DETECTORS TO THE IDENTIFICATION OF ORGANIC VAPORS IN AMBIENT ATMOSPHERES, *B.B. Kebbekus*, J. Kemp and J.W. Bozzelli, New Jersey Institute of Technology, Air Pollution Research Laboratory, 323 High Street, Newark, New Jersey 07102.

As the effects of long term exposure to low levels of organic vapors in air become of increasing interest, methods for determining the concentrations of specific compounds must be developed. High resolution glass capillary gas chromatography has proved to be capable of separating the complex mixture of organics found, but the identification of the individual peaks remains a problem. This paper will present a method of identification for target compounds based on both their chromatographic retention times and their response on more than one detector. The flame ionization detector is used as a general detector for all organic substances. The electron capture detector provides high sensitivity and specificity for such electrophilic compounds as chlorinated hydrocarbon solvents. The photoionization detector senses all substances with ionization potentials below 10.2 eV. This eliminates a large number of peaks due to the relatively uninteresting saturated hydrocarbons which commonly arise from gasoline.

Chromatographic effluent streams are split to the detectors using low dead volume splitting tees where the sensitivity will allow, or samples are sequentially analyzed using a combination of detectors.

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DETERMINATION OF NITROSOAMINES BY LIQUID CHROMATOGRAPHY USING A PHOTOCONDUCTIVITY DETECTOR,

R.H. Bennett and **E.S. Peterson, Jefferson Chemical Company, Austin, Texas 78765.**

Widespread interest now exists in the level of nitrosoamines in various consumer products due to the potential carcinogenic effect of some nitrosoamines. The Thermal Energy Analyzer (TEA) Detector, developed by Thermoelectron Corporation, has been widely publicized as the preferred liquid (LC) or gas (GC) chromatographic detector for identification and quantitation of ppb levels of nitrosoamines. However, a need exists for a less expensive and less sophisticated detector, especially as applied to nonvolatile nitrosoamines in routine quality control situations.

An analytical scheme and data will be presented for the quantitation of low ppb levels of N-nitrosodiethanolamine **and** N-nitroso-morpholine **in the parent amines with** preconcentration. **The system uses liquid chromatography for analytical separation and the recently introduced Tracor Model 965 Photoconductivity LC Detector. Relative molar response data of various nitrogen species will be presented and results will be** compared **to data obtained with the Thermal Energy Analyzer.**

The system also promises to be of general utility for nitrosoamines if combined with various collection, separation and preconcentration steps.

54

A SELECTIVE DETECTOR SUITABLE FOR GAS CHROMATOGRAPHY,

D.G. Sutton, K.R. **Estberg, and** *J.E. Melzer,* **The Aerospace Corporation,** El **Segundo, CA.**

A sensitive new detector for hydrocarbons has been demonstrated on the basis of the spectrophotometric **determination of the intensity of the** $CN(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ **emission that results from the introduction of the sample into active nitrogen. The most intense spectroscopic feature of the CN flame is the Av = 0 sequence at 383 to 388** nm. **Both saturated and unsaturated samples, with or without halogen constituents, are detectable by monitoring the same feature. A minimum detectable limit of 100 pg. and a linear response over four orders of magnitude in sample size has been demonstrated for vinyl fluoride.**

Selectivity to simple alkanes is established by the addition of HCl **to the active nitrogen flow. Selectivity to oxygen containing species is possible by monitoring the intensity of** $OH(A^{2-}\Sigma^+ \rightarrow X^2)$ **or**

$NO(A^{2}\Sigma^{+}X^{2}\Pi)$ emission. In addition, the system may be made selective to organo-metallic compounds by monitoring the fluorescence from the metal atom and the CN fluorescence simultaneously. Examples will be shown of general and selective chromatograms.

55

EXPERIMENTAL EVALUATION OF PRINCIPLES APPLICABLE TO AEROSOL PRODUCTION, CONDITIONING AND TRANSPORT *R.K. Skogerboe,* S.J. Freeland, K. Kronholm, and G. Butcher, Department of Chemistry, Colorado State University, Ft. Collins, Colorado 80523.

Flame and plasma atomic emission and absorption analysis systems rely on the production of an aqueous aerosol and its subsequent delivery to the atomization medium. Aerosol production, its transport, and its spatial distribution within the flame/plasma are aerodynamically controlled processes. The size characteristics of the aerosol, the effects that size has on the vaporization and atomization processes, and the occurrence and extent of interference effects are also prominently influenced by aerodynamic conditions. For these reasons, the analytical sensitivity and accuracy are largely determined by the aerodynamic characteristics of the system used. Thus, the importance of these fluid mechanical factors cannot be overemphasized.

The present discussion will examine the fundamental principles which apply to the processes of nebulization, aerosol conditioning, transport, and vaporization. Data supporting the applicability of the principles will be presented.

56

THE PRODUCTION AND ATOMIZATION OF HOMOGENATE AEROSOLS, *R.C. Fry* and N. Mohamed, Kansas State University, Manhattan, KS. 66506.

The discipline of analytical atomic spectrometry has long needed a nebulizer based of dealing directly with solid animal and plant tissues. The prospects for achieving such a method that is relatively free from lengthy sample preparation steps will be examined in this presentation.

The method under consideration involves the Willems rapid homogenizing principle followed by direct nebulization of a homogenate aliquot. When the resultant aerosol is introduced into premixed combustion flames or electrical plasmas, we are naming the overall process "Slurry Atomization".

The sonic/cavitation homogenizer is used to make suspended sample particles sufficiently small that they can be nebulized, transported through the spray chamber and burner head or torch head, and atomized. An additional benefit for the procedure is that a more representative sub-sample can often be obtained following the homogenization treatment. This is espcially important in dealing with large-size solid samples such as foods from which a smaller sub-sample must be taken prior to the analytical measurement step. The homogenizing time is $\leq$ 2 minutes. The effect of homogenizer and Babington type nebulizer conditions on aerosol transport and particle atomization will be discussed.

57

ULTRASONIC NEBULIZATION - PROS AND CONS V.A. Fassel, R. Winge, W. Haas, F. Grabau, B. Bear, and M. Floyd, Iowa State University, Ames, Iowa 50011.

Ultrasonic nebulization techniques have been utilized in the Ames Laboratory for the past 15 years for generating aerosols of liquid samples prior to their introduction into plasmas. In this presentation, the speaker will review experiences to data with ultrasonic nebulization systems and indicate directions of research that should lead to further improvements in their performances.

58

ANALYTICAL CONSEQUENCES OF NEBULIZER PERFORMANCE, J.A. Holcombe, University of Texas, Austin, Texas 78712.

The droplet size distribution entering the thermal source can have significant analytical consequences. In addition to governing delivery efficiencies of the sample to the source, particle trajectory based on the inertial forces can influence the spatial location of the sample in the source and, ultimately, vaporization/atomization characteristics. Examples will be cited using monodispersed droplets to demonstrate the "matrix problems" which can be directly related to nebulizer performance. Discussion will focus on preferential location of the analyte within the source as a function of particle inertial forces and the effect on the analytical signal. The analytical implications of these results to samples with high desolved salt concentrations will be presented. A discussion of high salt content samples which can cause nebulizer clogging in ICP nebulization systems also will be included. Possible mechanisms for this "salting out" will be presented.

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CHARACTERIZATION OF A ONE-PIECE ALL GLASS CROSS FLOW NEBULIZER USED WITH AN ICP/SPECTROMETER,

D. Yates, D. Fraley, S. Manahan, and F. Lichte, The Environmental Trace Substances Research Center and Department of Chemistry of the University of Missouri, Columbia, MO.

The nebulizer continues to be a major problem area with ICP instrumentation. Nebulizer are, in general, prone to misalign, clog and break. They are also a potential source of blank problems due to metal components. In addition, the capital investment is generally several hundred dollars.

As part of an ongoing research program involving improvement in ICP instrumentation, we have developed a cross-flow nebulizer which is fabricated from glass parts. The resulting product is rigid, one piece, all-glass cross-flow nebulizer.

This new nebulizer has operated successfully for two years. Due to its construction, no alignment or breakage problems have occurred. It is no more prone to clog than conventional cross-flow nebulizers.

In this paper, a description of the construction and performance of this nebulizer will be presented. Performance data, comparing commercial cross-flow and concentric nebulizers with the all glass nebulizer will be presented.

60

A CRITICAL EVALUATION OF NOISE CONTRIBUTIONS IN FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY,

M.W. Routh and P.R. Liddell, Varian Instrument Group, Palo Alto, California 94303.

Noise in atomic absorption instruments can come from several different sources. The dominant noise source can vary according to the instrument (e.g., single beam or double beam), the element being measured and the measurement conditions. In addition, the dominant noise source at low absorbance may be quite different from that at high absorbance. Noise levels have been measured under a variety of conditions using comparable single and double beam instruments. The dominant noise sources for each condition and the differences between the double and single beam instruments were determined. At low absorbance, in the vicinity of the detection limit, the major types of noise are photon noise, flame noise and, for a single beam instrument, lamp flicker noise. For a double beam instrument, lamp flicer noise is eliminated but the photon noise is higher than that for a comparable single beam instrument. With increasing absorbance, sample absorption noise becomes more important and is nearly always the main contribution in the normal working range. Sample absorption noise depends on the noise produced by the atomization system (nebulizer, spray chamber, burner). The absorbance signal depends on the efficiency of the atomization system. Therefore it is the nebulizer/spray chamber/burner system which determines the signal-to-noise ratio or precision.

61

CHARACTERIZATION OF SOURCES OF TURQUOISE BY X-RAY SPECTROMETRY, *M.L. Parsons,* Arizona State University, Tempe, Arizona 85281.

Turquoise is a semi-precious mineral which has been used as an ornament since the time of the pharaohs. Since most turquoise is not of gem-grade quality, low-grade ore has often been treated in various ways to improve its color and durability. In times of high demand many types of imitation materials have been represented as gem-grade turquoise.

Unfortunately, the need for determining fake or treated turquoise rarely occurs until a stone has been incorporated into a piece of jewelry. This necessitates an analytical procedure which is non-destructive. Thanks to current technology it is possible to produce fake turquoise and commercially treated low-grade turquoise which are not capable of detection with current gemnological methods.

We have developed a procedure incorporating optical microscopy, scanning electron microscopy, and X-ray fluorescene spectroscopy, in which turquoise can be successfully tested. This process will be discussed and the overall problem amplified.

62

APPLICATION OF THE INDUCTIVELY COUPLED PLASMA TO ELEMENTAL ANALYSIS OF FOODS AND RELATED MATERIAL, *R.F. Suddendorf* and K.W. Boyer.

The Food and Drug Administration administers both periodic and continuing programs to monitor the elemental composition of foods. These programs analyze a wide variety of foods in various regions of the country for elements of both toxic and nutritional interest. As a consequence of this wide ranging activity, the agency spends a significant amount of time and effort to support these programs.

In an attempt to reduce the time and manpower spent on these programs in the past few years the agency has increasingly emphasized the use of multielement methods of analysis wherever possible. Emission spectrosopic analysis, specifically using the Inductively Coupled Plasma, has demonstrated the potential for decreasing the amount of time required per analysis while increasing the level of analytical support for these programs.

Applications of the Inductively Coupled Plasma for analysis of samples encountered in our laboratory will be presented. Sample preparation procedures employed in conjunction with ICP analysis will be discussed, including sample homogenization and digestion methods. Specialized analysis techniques for elements such as mercury will be illustrated and compared with more traditional methods. Finally, problems that have been encountered utilizing ICP analysis with respect to sample preparation and introduction to the plasma will be included.

63

USE OF INDUCTIVELY–COUPLED PLASMA SPECTROMETRY FOR THE SIMULTANEOUS DETERMINATION OF MACRO AND MICRO-NUTRIENTS IN NH_4HCO_3–DTPA EXTRACTS OF SOILS,

P.N. Soltanpour, S.M. Workman, A.P. Schwab, Colorado State University, Ft. Collins, Colorado 80251.

Twenty-six soils were extracted with 1M NH_4HCO_3 - 0.005 M DTPA solution (Soltanpour and Schwab, 1977). Inductively-coupled plasma optical emission spectrometry (ICP–OES) was used to simultaneously determine P, K, Zn, Fe, Cu, and Mn in the extracts. These analytical results were compared with those obtained with a colorimetric method for P and flame atomic absorption spectrometry (AAS) for the cations. It was necessary to change the carbonate-bicarbonate matrix (1M) to a more soluble matrix in order to prevent formation of crystals and clogging at the capillary tip. This was achieved by a 1:5 dilution with 0.5N HNO_3 followed by shaking for 10 minutes. Results from the ICP–OES and the flame AAS methods were comparable. Analysis of P by ICP–OES gave larger values than analysis by a colorimetric method due to presence of organic P in the extracts.

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SOLVENT EXTRACTION STUDIES FOR THE RECOVERY OF METALS FROM ELECTROPLATING WASTES USING AN INDUCTIVELY COUPLED ARGON PLASMA,

T. Clevenger and D. Yates. Environmental Trace Substances Research Center, University of Missouri, Columbia, MO.

There currently exists over 15,000 metal finishing operations in the

United States. It is estimated that these facilities dispose of sludges containing metals valued at $150,000 to $200,000 as well as spending $50,000 to haul the sludges to disposal sites.

Several recovery processes have been investigated to recover these metals. All of these processes have one common problem, the inability to recovery metals from wastes containing several metals with varying concentrations.

In this paper, the applicability of solvent extraction using chelating agents as a separation method is discussed. In particular, emphasis is given to a discussion of the inductively coupled argon plasma (ICAP) as a sensitive real time monitor of the metals in solution.

The ICP provides several important assets to this study. These include: sufficient sensitivity for all elements, response linearity of 5 orders of magnitude, good precision and accuracy, simultaneous analysis of all elements of interest, and the use of small samples.

65

SILICON DETERMINATION IN GROUNDWATER SAMPLES BY FLAMELESS ATOMIC ABSORPTION SPECTROSCOPY,

M.J. Kelly, J.P. Erspamer, T.M. Niemczyk, and E.A. Walters, Department of Chemistry, The University of New Mexico, Albuquerque, NM 87131.

Flameless atomic absorption techniques can be very sensitive for trace metal analysis. In some cases, however, the full potential of the technique is not realized. The formation of carbides on the furnace wall has been proposed for some of the more refractory elements such as Si. This gives rise to incomplete atomization and memory effects. Furthermore, the high temperature required for the atomization of these species causes the premature degradation of the graphite tube. Foil lined tubes (1) and other noncarbon surfaces (2,3) have been employed to alleviate some of these problems.

We have investigated the use of foil lined tubes and graphite tubes with modified surfaces to enhance the atomization efficiency of Si. The absorption vs. time profiles are utilized for the interpretation of the data. The results obtained by flameless techniques will be compared to those obtained when a flame is used.

(1) B.V. L'vov and L.A. Pelieva, Can. J. Spectrosc, 23, 1 (1978).
(2) H.M. Ortner and E. Kantusher, Talanta, 22, 581 (1975).
(3) J.H. Runnels, R. Merryfield and H.B. Fisher, Anal. Chem., 47, 1258 (1975).

66

SPECTROCHEMICAL DETERMINATION OF IRIDIUM AND YTTRIUM IN PLUTONIUM, *J.V. Pena,* W.M. Myers and D. Steinhaus, University of California, Los Alamos Scientific Laboratory, Los Alamos, NM 87545.

A method was developed for analyzing plutonium materials for iridium in the concentration range 100 ug/g to 2000 ug/g and yttrium in the 15 ug/g to 1000 ug/g range. In this method the samples are ignited to PuO_2 and partially dissolved in 15.6$\underline{M}$ HNO_3 and 0.1M HF. The undissolved portion containing about 30% of the iridium is filtered, mixed with NaC1-graphite mixture, and analyzed by a dc arc excitation technqiue in an argon-oxygen atmosphere. The sample spectra, as well as spectra of standards which provide calibration data, are recorded on the same photographic film.

The dissolved plutonium is separated from the remaining iridium and yttrium by absorption on an anion exchange resin from 12M HCl. The effluent is dried by evaporation, dissolved in 1M HCl, and mixed with the appropriate amount of NaCl-graphite prior to dc arc excitation. The sum of the values obtained on the two portions is reported for each element. The relative standard deviation and bias of the method are less than 10%.

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MULTIELEMENT DETECTION OF TRACE IMPURITIES IN SILICON BY METASTABLE TRANSFER EMISSION SPECTROMETRY, *D.G. Sutton,* L. Galvan, and N. Cohen, The Aerospace Corporation, El Segundo, Calif.

Trace metal impurities in solar grade silicon have highly detrimental effects on the energy conversion efficiency of manufactured cells. It is, therefore, desirable to continuously monitor the level of impurities in the host material at several stages of the manufacturing process. A rapid, inexpensive, sensitive technique for quantitative multielement detection is thus required. We will discuss the application of Metastable Transfer Emission Spectrometry (MTES) to these ends.

The technique involves mixing active nitrogen with a flow of argon carrier gas containing the vapor from a heated silicon sample. Energy transfer from the active nitrogen species to the trace constituents entrained in the argon flow results in atomic fluorescence. The spectrum reveals the identity of the impurities and the intensity of the atomic emission lines can be directly related to concentration of the impurities in the gas flow. The active nitrogen is produced in an electronically quiet microwave discharge and does not radiate in the near ultraviolet or visible part of the spectrum. In addition, the observation zone is downstream from the discharge. Thus, little or no electronic or spectral background is encountered and sensitivities are potentially high. Rapid scan or multichannel techniques give multielement detection capability. Data will be presented to show that the vaporization process is congruent. Therefore, the composition of the vapor is representative of the solid sample. The detection of Na, Ca, Mg, Al, Fe, and Cr in a silicon matrix will be documented, and the extension of MTES to the detection of additional impurities will be discussed.

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EXPECTATIONS FOR RESOLUTION IN HIGH RESOLUTION ^{13}C NMR OF SOLIDS: PARTICULARLY POLYMERS,

D.L. VanderHart, W.L. Earl, and A.N. Garroway. National Bureau of Standards, Washington, D.C. 20234.

The combined techniques of high-power proton decoupling and rapid magic-angle sample spinning yield ^{13}C spectra whose resonances occur at their isotropic chemical shift positions, just as in liquids. However, the lines observed in solids are often one to two orders of magnitude broader than for corresponding liquid resonances. Molecular packing heterogeneities, frozen conformational differences, molecular motion, off-resonance proton irradiation, insufficient decoupling power, magic-missetting, and rotor instabilities all contribute to the linewidth, but their relative importance will vary depending on the particular system. For example, crystalline materials consistently yield sharper resonances than glassy materials.

The relative importance of these linebroadening effects will be discussed for polyethylene, a system containing both crystalline and glassy components, and for a cured epoxy which is a glass. The dependence of each broadening mechanism on the static field will be noted. It is not clear at this point that higher magnetic fields imply improved resolution in solids.

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^{23}NA SOLID STATE NMR IN BETA–ALUMINAS, *R.W. Vaughan,* **M. Polak, and A. Highe, California Institute of Technology, Pasadena, California 91125.**

The first-order quadrupolar spectrum of non-integer nuclei can be obtained using a recently developed double resonance technique) in both single crystal and polycrystalline solids. This interferometric scheme provides a sensitive, indirect means of obtaining first-order quadrupolar spectra, and it will be demonstrated with ^{23}Na spectra of beta-alumina, a fast ion conductor. The experimentally determined electric field gradients will be compared with point charge calculations to aid in identification of the sodium sites, and temperature-dependent changes in the first-order satellite spectrum of 23Na will be used to characterize the multiple-site sodium exchange processes present.

1. M. Polak and R.W. Vaughan, J. Chem. Phys., 69, 3232 (1978).

70

HIGH RESOLUTION SOLID STATE NMR OF HYDROGEN ON CATALYTICALLY ACTIVE SURFACES, *B.C. Gerstein,* **P.D. Murphy, L.M. Ryan and R.E. Taylor, Iowa State University, Ames, Iowa 50011.**

High resolution solid state techniques in nuclear magnetic resonance have been used to identify the environments of protons in catalytically active zirconim halohydrides, single crystal quartz, hydrogen molybdenum bronze, and gamma alumina. Comparison with the solid state spectrum of hydrogen in water indicates that one identification of hydrogen in quartz is on a hydroxyl group. On the other hand, measurements on other compounds such as the two dimensional conductor ZrClH, and the metallic H1.6MoO3 indicate clearly the non-hydroxyl nature of protons in these compounds, and are strongly suggestive of hydrogen nuclei being in contact with electrons in the conduction bands.

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^{13}C SPECTROSCOPY OF SMALL ORGANIC MOLECULES AT CRYOGENIC TEMPERATURES,

K.W. Zilm, DM. Grant, R.T. Conlin, and J. Michl, University of Utah, Salt Lake City, Utah 84112.

Isolation of reactive species in noble gas matrices at cryogenic temperatures has become an important method of preparation and characgerization of such species. To augment the spectroscopic techniques now being used to study such matrices we have developed the ^{13}C (and ^{29}Si) NMR spectroscopy of these matrices. An apparatus for obtaining cross polarization spectra with a receiver coil at 15°K will be described and results of its use presented. Besides matrix isolated species, several series of small organic molecules have been studied in order to better understand trends in chemical shift tensor components and our preliminary data will be presented.

Another feature of matrix isolation is the magnetic dilution effected by the low concentration. Techniques for assigning the shift tensor to the molecular axes will be discussed which take advantage of this dilution.

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ABSTRACT NOT SUBMITTED

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DYNAMIC FREQUENCY SHIFTS IN SPECTRALLY DEGENERATE SPIN SYSTEMS,

L.G. Werbelow, Montana State University, Bozeman, Montana 59717.

Whenever motional narrowing obtains, the perturbation-response characteristics of nuclear paramagnetism are quantitatively described by rate constants of the functional form,

$$\text{Rate} \sim 2' \underbrace{\sum_{n}\sum_{n'}}_{\substack{\text{interaction}\\ \text{strengths}}} \xi_{n}\,\xi_{n'} \sum \overbrace{<|T^{k}_{n}|><|T^{-k}_{n'}|>}^{\substack{\text{spin matrix elements}\\ \text{"selection rules"}}} \int_{0}^{\infty} \underbrace{<V^{k}_{n'}(t)V^{-k}_{n}(0)>}_{\substack{\text{lattice correlation}\\ \text{of fluctuation}}} \overbrace{(\cos w_{k}t - i\sin w_{k}t)}^{\text{spectral density of fluctuation}}\,dt.$$

The indicated summation extends over all interaction (n) and projection of interaction (k). For certain coherence rates, a summation over eigenbasis is also implied.

Although various time inversion and time reversal arguments suggest that the correlation function is an even function of time, this function is introduced into magnetic relaxation theory in a causal manner and hence the odd (purely imaginery) component survives the one-sided Fourier transformation. Whereas the real component of this spectral represenation is identified with the randomization of phase coherence and the establishment of Boltzmann distributions, the imaginary component must be identified with an ultrafine second order shift in the various single and multiple quantum coherences.

If extreme narrowing arguments obtain, it can be rationalized that this ultrafine shift is negligible. Likewise, if nonextreme narrowing obtains, the adiabatic contribution to the linewidth renders the ultrafine shift negligible in a relative sense. However, for certain spin systems characterized by coincident Lorentzians, it is conceivable that the width of at least one spectral component will be insensitive to this adiabatic term. The necessity to consider the ultrafine frequency shift has recently been illustrated for multiply degenerate spin one-half systems relaxed by dipolar interactions (L.G. Werbelow, A. Thevan and G. Pouzard, J. Chem. Soc. Faraday II, July 1979; L.G. Werbelow, J. Magn. Resn., May, 1979) and for multipolar spin systems relaxed by quadrupolar interactions (L.G. Werbelow, J. Chem. Phys., June 1979).

74

RELAXATION IN POLYMERIC BLENDS, *M.D. Sefcik,* J. Schaefer, E.O. Stejskal, and R.A. McKay, Monstanto Company, St. Louis, Missouri 63166.

Magic-angle cross polarization ^{13} nmr of monimally homogeneous glassy polymers provides information about both structure and dynamics. These techniques are also applicable to more complicated polymeric solids such as poly(phenylene oxide)/-polystyrene (PPO/PS) blends. Changes in isotropic shifts (line-shapes) of the blends (relative to the component homopolymers) are observed so that mixing in PPO/PS blends must be on an individual chain-for-chain basis. Despite the intimacy of the PPO/PS 75/25 blend (which actually produces a densified material), the spin-lattice T1p (C) for both PPO and PS are slightly decreased in the blend. This suggests that the thermodynamically good mixing of the two chains produces extended local conformations with reduced net steric interactions, resulting in modes increases in either the frequency or amplitude of mid-kHz torsional oscillations within these conformations. An increase in the PS < T_{1S}(ADRF) > is observed reflecting the weak static ^1H-^1H interchain interaction between PS protons and the relatively few protons of surrounding PPO chains; the fact that < T_{1p}(C) > T1s(ADRF) move in opposite directions confirms the motional character of the former. All T1s(ADRF)'s >> T1p(C)'s.

The PPO/PS blends are not spatially homogeneous. As indicated by the dispersion of PS main-chain proton T_{1p}' (Figure 4), segregation is determined not by molecular weight or polydispersity, but rather by stereo configuration.

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HIGH RESOLUTION ^{13}C NMR INVESTIGATION OF SOLID PHENOLIC RESINS AND RELATED COMPOUNDS, *C.A. Fyfe,* A. Rudin and W.J. Tchir, Geulph Waterloo Centre for Graduate Wirk in Chemistry, Ontario, Canada.

High resolution ^{13}C nmr spectra of solid phenol-formaldehyde polymers have been obtained using C.P. and magic-angle spinning techniques on samples directly moulded into the spinner shape. The signals due to methylene and methylene ether links and to free paraformaldehyde have been identified by comparison with high resolution ^{13}C nmr spectra of the resins in solution and by incorporation of ^{13}C enriched formaldehyde into the solid polymer. Quantitative determinations of relative amounts of the identified functional groups have been made and studies as a function of the curing process. These measurements have been extended to other related polymer systems.

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^{13}C NMR SOLIDS TECHNIQUES FOR CHARACTERIZING BLENDS OF ELASTOMERS AND POLYOLEFINS, *C.J. Carman,* J.B. Pausch. The BF Goodrich Research & Development Center, Brecksville, OH 44141, and A.N. Garroway, Naval Research Laboratory, Washington, DC 20375.

Comparable high resolution ^{13}C nmr spectra can be obtained from solid elastomers by using either standard free induction decays obtained at a high temperature or by using magic angle spinning at room temperature. These spectra are suitable for material identification or molecular structure determination. However, the advantages of enhanced spectra from cross polarization techniques are not realized for elastomers as contrasted to plastics. A series of experiments using different decoupling field strengths or no decoupling reveals that dipolar coupling is averaged out due to the molecular motion in elastomers. Thus, cross polarization does not produce a spectrum even for the cross-linked rubber. However we show that an EPDM elastomer having a low level of crystallinity will produce a cross polarization spectrum. Combining magic angle spinning and cross polarization for the pure rubber and for blends with polyolefins yields structural information on both the rubber and the plastic, as well as molecular dynamic information. The results suggest crystallinity imparts enough restriction in mobility so that the phenomenon of cross polarization occurs. Analytical applications are suggested for related systems.

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ABSTRACT NOT SUBMITTED

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SOLID STATE NMR OF ELASTOMERS: LOW AND HIGH RESOLUTION,

J.L. Ackerman and J.E. Mark, University of Cincinnati, Cincinnati, Ohio 45221.

The molecular theory of rubberlike elasticity is based on the statistical mechanics of polymer chains and networks. Although established in the 1940's, the theory contains a key assumption, namely that of affine deformation, which has not been subject to direct experimental investigation, except for very recent work using small angle neutron scattering[1], which requires highly sophisticated (and not widely available) experimental facilities. We present here a wideline solid state NMR experiment which might provide a test of the affine assumption.

Also to be discussed is the application of high resolution cross polarization techniques to the study of phosphazene polymers[2] ("inorganic rubber"), elastomers whose backbone consists of alternating phosphorus and nitrogen atoms.

1. C. Picot, et al., Macromolecules, 10, 436 (1977).
2. H.R. Allcock, Phosphorus-Nitrogen Compounds: Cyclic, Linear and High Polymeric Systems, Academic press, New York, N.Y., 1972.

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MACROMOLECULAR DYNAMICS OF FLUOROCARBON POLYMERS STUDIED BY MULTIPLE PULSE NMR, *A.J. Vega* and A.D. English, E.I. du Pont de Nemours and Company, Wilmington, Delaware 19898.

^{19}F multiple pulse spectra are shown to be useful in determining crystallinity and detecting macromolecular motion in polytetrafluoroethylene (OTFE). The spectra were obtained between -150^{o} and $+340^{o}$C with a REV-8 sequence. The spectra can unambiguously be decomposed into crystalline and amorphous fractions. The 6 relaxation is observed in the crystalline regions and is in agreement with previous anelastic and dielectric measurements. The T relaxation is also observed can be shown to be due to reorientation about a local chain axis in the amorphous regions. Further evidence of these motional models has been obtained from relaxation measurements under REV-8 multiple pulse conditions. The motion in the amorphous regions at high temperatures involves reorientation of the chain axis and increase in amplitude with temperature. This behavior can quantitatively be described in terms of a local order parameter. Applications of these concepts to other polymer systems will be discussed.

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^{13}C NMR STUDIES OF COAL, *G.E. Maciel* and V.J. Bartuska, Colorado University, Fort Collins, CO 80523, and F.P. Miknis, Laramie Energy Technology Center, Laramie, WY 82071.

^{13}C nmr studies, using magic-angle spinning and cross polarization, have been carried out on a variety of solid coal and coal derived samples. Apparent aromatic carbon fractions, f , have been derived. Fine structure beyond the aromatic/aliphatic separation was found for some samples. Coals heated to various temperatures were examined, showing a preferential depletion of aliphatic carbons. Various aspects of the analytical reliability of the method have been explored.

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CARBON–13 NMR STUDIES OF OIL SHALES BY CROSS POLARIZATION AND MAGIC ANGLE SPINNING, *F.P. Miknis,* Laramie Energy Technology Center, Laramie, WY 82071, V.J. Bartuska and G.E. Maciel, Colorado State Univerity, Fort Collins, CO 80523.

^{13}C nmr spectra have been obtained on several oil shales and oil shale kerogens from around the world. High-power ^{1}H decoupling (to remove H-^{13}C dipolar broadening), cross polarization (to circumvent the bottleneck of long relaxation times), and magic-angle spinning (to remove broadening due to chemical shift anisotropy) have been employed. Spectra were obtained at 15.1 MHz, using a ^{13}C rf field of about 40 gauss. Pulse Fourier transform experiments in the absence of cross polarization give spectra which indicate the analytical validity in the cross polarization spectra. The samples studied represent a variety of geological ages, origins, depositional environments and source locations. The spectra show variations in the aliphatic and aromatic carbon distributions of the oil shales and reveal correlations between aliphatic arbon contents and potential oil fields. Hints of additional fine structure are present in the spectra of some samples. The influence of sample pretreatment is explored.

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CP/MAS STUDIES OF METHYLATED HYDROAROMATIC SPECIES: CHANGES OF SYMMETRY IN THE SOLID STATE AS COMPARED TO THE LIQUID STATE, *R.J. Pugmire,* K.W. Zilm, D.K. Dalling, and D.M. Grant, University of Utah, Salt Lake City, Utah 84112

Data has been obtained on a series of methylated hydroaromatic species that exhibit a break in the molecular symmetry in the solid state as compared to the solution spectra. Anomolous chemical shifts in certain carbons but close correlation at other positions are noted in the solids data as compared to the solution spectra of several species in the series 9,10-dihydroanthracene, and its methylated derivatives 9-methyl-,9,9-dimethyl-,9,10-dimethyl-(cis and trans),9,9,10-trimethyl-, and 9,9,10,10-tetrameth -9,10-dihydroanthracene. In some cases the integrated line intensities also exhibit anomolous behavior. The nature of these anomolies and their possible explanation will be discussed.

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^{13}C NMR STUDIES OF SOLID PLANT MATERIALS, *V.J. Bartuska,* D.W. Sindorf and G.E. Maciel, Colorado State University, Fort Collins, CO 80523.

The ^{13}C NMR approach, using matic-angle spinning and cross polarization, has been applied to the study of seeds, wood samples and wood-derived materials. Special emphasis has been devoted to lignin samples obtained from various sources and from a particular source by different separation techniques and to cellulose samples believed to belong to different crystalline forms. Attempts have been made to correlate the lignin spectra with likely structural components and the cellulose spectra with current views of cellulose structures.

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SOLID STATE HIGH RESOLUTION ^{13}C NMR STUDIES OF CELLULOSE, *W.L. Earl* and D.L. VanderHart, National Bureau of Standards, Washington, DC 20234.

High power proton decoupling in combination with magic angle spinning can produce ^{13}C spectra of solids with quite high resolution whose resonances usually occur at the isotropic chemical shift positions. However, molecular motion and chemical exchange in liquids averages shift effects due to conformational differences and due to hydrogen bonding which are present in the solid state NMR spectra.

Cellulose is relatively crystalline natural polymer and consequently gives narrow ^{13}C NMR lines in the solid. The peak positions for native cellulose (Lattice 1) and for regenerated cellulose (Lattice II) are shifted relative to each other. These differences and differences due to chemical modification of the glucose units of cellulose will be discussed in terms of the chemical and structural changes in the polymers.

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CARBON—13 SPECTRA-STRUCTURE CORRELATIONS FOR HYDROCARBONS, *N.F. Chamberlain,* Exxon Research and Engineering Company, Baytown, Texas 77520.

Although the fuels and other fractions derived from petroleum and coal are much too complex for practical multicomponent analysis, determination of the distribution of hydrocarbon types in such materials has been of considerable help in processing and utilization studies. The combination of hydrogen NMR and mass spectrometry has been especially useful for hydrocarbon type characterization of suitable chromatographic fractions and carbon-13 NMR promises to add more accuracy and detail. Realization of the full potential of carbon-13 NMR requires detailed correlations of spectral parameters and molecular structure like those which have been published for the paraffins but not for other hydrocarbon types. This paper will present such correlations for aromatics, olefins, and cycloparaffins insofar as the current literature data will permit.

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APPLICATIONS OF RELAXATION RESOLUTION IN THE ^{13}C FTNMR SPECTRA OF FOSSIL FUEL FRACTIONS, M.T. Melchior, Exxon Research and Engineering Company, Linden, NJ 07036.

The ^{13}C NMR spectra of heavy liquids such as petroleum residua must be viewed with special attention paid to the wide range of molecular type and size in such materials. Foremost among the consequences of this chemical diversity are limited chemical shift resolution and a broad distribution of relaxation times and line widths. A number of approaches to extracting maximum information from complex overlapping spectra have been developed, some of the more interesting of which involve relaxation time, rather than chemical shift discrimination. Application of pulse sequences aimed at relaxation resolution of carbon types will be discussed.

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ABSTRACT NOT SUBMITTED

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ABSTRACT NOT SUBMITTED

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NMR EXAMINATION OF FUELS AND FRACTIONS FROM SHALE OIL, *R.N. Hazlett* and J. Solash, Naval Research Laboratory, Washington, DC 20375.

The U.S. Navy has programs to evaluate the production of distillate fuels from shale oil. Useful information on these fuels can be obtained with PMR and Carbon-13 NMR. Data on recent products will be presented.

n-Alkanes, major components in all shale-derived jet fuels, exert significant control over the freezing point. Examination of fractions of crude shale oil by ^{13}C NMR indicates that some of the n-alkanes can form by pyrolysis of large polar molecules.

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AVERAGE MOLECULAR STRUCTURE ANALYSIS OF COAL-DERIVED LIQUID BY NMR SPECTROMETRY, *DM. Cantor,* Phillips Petroleum Company, Bartlesville, Oklahoma.

Characterization of samples in terms of selected average properties is an attractive approach to the analysis of complex mixtures like coal-derived liquids. Using NMR and other data, a series of parameters can be calculated that quantitate structural features, and provide a description of a sample's average molecular structure. This technique has the advantage of yielding readily interpretable results, expressed in terms that are familiar to chemists.

Derivation of the equations used to calculate average molecular structure parameters is straightforward, but requires that several assumptions about the sample's composition be made. This talk will examine these assumptions in some detail. To ensure precise and accurate measurements, considerable care must be taken in the choice of experimental conditions. Some aspects of these choices will also be discussed. Finally, possible ways in which average molecular structure parameters can be used will be discussed.

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HIGH-FIELD NMR STUDIES OF BIOLOGICAL SYSTEMS*, *E. Oldfield,*† University of Illinois at Urbana, Urbana, IL 61801.

Using a combination of ^{2}H and ^{31}P NMR we have investigated the interactions between a variety of proteins and lipids in model and biological membranes. The results suggest that polar group interactions are important in causing lipid "immobilization" (long correlation times), but that protein surfaces cause a disordering hydrocarbon chain organization of protein-associated lipids. Exchange between free bilayer and boundary lipid occurs faster than 10^{3} sec^{-1} implying that a given set of lipid molecules do not remain with the enzymes studies during their catalytic cycle. The effects of proteins on lipid ^{2}H and ^{31}P NMR spectra are quite different to those generated by the sterol cholesterol.

We have recently begun a program aimed at elucidating the conformations of glyco lipid polar headgroups (sugars) in cell surfaces, and preliminary ^{2}H NMR results will be presented.

*Supported in part by grants from the National Science Foundation (PCM 78-23021), the National Institutes of Health (HL-19481), The American and Illinois Heart Associations (77-1004, N2) and the Alfred P. Sloan Foundation.

†Alfred P. Sloan Research Fellow, 1978-1980.

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MOTILITY IN BIOPOLYMERS INVESTIGATED BY NMR RELAXATION, *T.L. James,* Department of Pharmaceutical chemistry, University of California, San Francisco, Calif. 94143.

The magnitude and rates of conformational fluctuations of nucleic acids may pertain to their interaction with other molecules such as proteins, drugs, or methylating agents. The conformational flexibility of proteins may be important in catalysis, allosteric control, and energy transfer. Although the static picture of nucleic acids and some proteins has been fairly well characterized by x-ray cystallography and NMR work, very little is known of the dynamics in biopolymers.

NMR appears to be especially suited for investigating internal motions as well as the overall rotational reorientation of biopolymers. Although we have been developing and emphasizing a technique involving rotating frame spin-lattice relaxation in an off-resonance rf field ($T_{1p}{}^{ff}$), measurements of the spin-lattice relaxation time (T_1) and the nuclear Overhauser effect (NOE) have also been quite useful. ^{13}C, ^{1}H, and ^{31}p relaxation experiments have been carried out with proteins and nucleic acids. Studies of backbone nuclei have yielded quick, reliable values for the overall rotational correlation time of proteins using the T_{1p} method. T_{1p} experiments with histidine C–2 protons of ribonuclease have revealed differences in the internal motion of the four histidines. Sequential unfolding of ribonuclease by addition of guanidinium chloride has revealed differential changes in the mobility of the histidines, including some not observable by T measurements.

Investigation of nucleic acids has revealed a subnonosecond motion associated with the rotational wobbling about the bonds in the ester link P–O–C, which is not temperature- or salt-dependent. Another motion which is on the microsecond time scale and may be due to the flexing motions defining the persistance length of the nucleic acid, has been found to be dependent on temperature and the presence of magnesium ion.

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OLIGONUCLEOTIDE CONFORMATION. PHOSPHORUS–PROTON AND PROTON-PROTON NUCLEAR OVERHAUSER EFFECTS,

P.A. Hart, **University of Wisconsin, Madison, Wisconsin 53706.**

Changes in the circular dichroism of adenylic acid oligomers have been interpreted to indicate a regular decrease in base stacking in the temperature range 0 to 50°C. In order to understand the conformational changes that accompany this loss of stacking, I have initiated conformational analyses of the dimer, trimer and tetramer using the proton-proton nuclear Overhauser effect (NOE) to study changes of the glycosyl bonds and the phosphorus-proton NOE to study changes in the phospodiester backbone. The proton-proton studies completed so far indicate a shift to smaller probabilities of finding the syn glycosyl conformer at lower temperatures in the range 8 to 30°C. Phosphorus chemical shifts indicate changes in the backbone conformation as well and phosphorus-proton NOE's will be reported that will allow the backbone conformations to be specified.

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^{13}C AND ^{2}H NMR STUDIES OF LABELED COLLAGEN IN SOLUTION AND THE SOLID STATE,

D.A. Torchia, **L.W. Jelinski and C.E. Sullivan, National Institute of Dental Research, Bethesda, Maryland 20205.**

Collagen is the major protein component in many tissues. The molecular dynamics and interactions of native collagen in solution and as fibrils were investigated using ^{13}C — ^{1}H magnetic double resonance spectroscopy at 1.4 Tesla. Specific regions of the molecule were studied by incorporating ^{13}C enriched amino acids into chick calvaria collagen via tissue culture. ^{13}C spectra (scalar decoupled, dipolar decoupled and proton-enhanced) provided linewidths, lineshapes, T and NOE values of the labeled carbons. Analysis of these parameters showed that rapid anisotropic motion of protein backbone carbons ($T < 10'$s) and sidechain carbons ($T <$ s) takes place in the fibrils. These results indicate that interactions between the amino acid sidechains (which are presumed to stabilize fibril structure) occur in fluid-like domains.

Collagen motion and structure is currently being characterized by pulsed ^{2}H NMR at 5.2 Tesla. The results of these experiments will also be described.

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NMR STUDIES OF MODEL BIOMEMBRANES: STRUCTURE AND METAL ION BINDING, *C.S. Springer, Jr.,* SUNY at Stony Brook.

Aqueous solutions of small monolamellar phospholipid vesicles have been studied. When Pr^{+3} ions are introduced only into the external aqueous phase of such a solution, certain ^{1}H, ^{31}P, and ^{13}C NMR lines of the lipid headgroups are split into two peaks, representing the outside and inside surfaces. The Pr^{+l3} ions cannot penetrate into the interior aqueous cavity of the vesicles. Using the relative areas and chemical shifts of such a pair of peaks, and the relative areas and chemical shifts of a similarly split pair of peaks corresponding to a polar solute equally distributed between the two aqueous phases, along with a hydrodynamic measurement, we have been able to ascertain phospholipid structural packing parameters and Pr^{+l3} ion surface binding parameters. We find that the phospholipid molecules in the outer monolayer of this highly curved membrane are constrained to be in a much more "rigid" environment than thos in the inner monolayer. This gives rise to a significant difference in melting behavior between the two monolayers. The binding of the Pr^{+3} ions to the lipid phosphate groups on the outer surface can best be fit with a cooperative model involving two types of interacting binding sites. The tense (T) sites, with low affinity for Pr^{+l3}, present in the absence of metal ions, quickly give way to relaxed (R) sites, involving two phospholipid molecules and with three orders of magnitude greater affinity, as the metal ions bind to the surface. This positive cooperativity partly counteracts the deleterious effects of the positive charge accumulation. We picture the binding site conversion as a headgroup onformational change mostly involving the choline moiety. The results for binding on the inside vesicle surface, although more sparse, indicate that the overall affinity for Pr^{+3} is significantly greater and that the site stoichiometry may be different.

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PROTON NUCLEAR MAGNETIC RESONANCE STUDIES OF METAL BLEOMYCIN A_2 COMPLEXES, *E. Mooberry* and J. Greene, North Carolina Agricultural and Technical State University, and R.F. Lenkinski, University of Alabama, Birmingham, Alabama.

Bleomycin A_2 is a glycopeptide antibiotic employed in cancer chemotherapy. We have investigated the interaction of several metals with bleomycin A_2 by proton NMR at a frequency of 360 MHz. In order to determine the structure of the metal-bleomycin complex manganese was added to a bleomycin solution and proton spectra obtained. Unfortunately at 360 MHz, no differential broadening of the spectral lines was observed; however, at 80 MHz, one of the imidazole proton lines broadened selectively. We attribute these observations to frequency effects of the relaxation times and unfavorable exchange times.

Proton NMR spectra were obtained for other metal complexes such as Co^{2+}, Yb^{2+}, and Cu^{2+}. The Co^{2+} interaction of bleomycin A_2 is interpreted in terms of oxidation to Co^{2+} to Co^{3+} thereby giving a diamagnetic complex with only small shifts of the proton lines. This observation agrees with previous UV results from other laboratories. Little effect was observed from the interaction of Yb^{2+} and bleomycin A_2 while large line broadenings were observed for the Cu^{2+} complex.

Finally preliminary synthetic studies have indicated the existence of a platinum bleomycin A_2 complex. These complexes are potentially double acting anti-cancer drugs because of the inclusion of platinum.

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NMR STUDIES OF BLEOMYCIN COMPLEXES WITH NUCLEIC ACIDS AND METALS,

J.D. Glickson, R.F. Lenkinski, N.R. Kirshna, T.T. Sakai, J.M. Riordan, J.M. Geckle and D.J. Patel, The University of Alabama in Birmingham, Birmingham, Alabama 35294.

The glycopeptide antibiotic bleomycin is employed in cancer chemotherapy and in the scintigraphic detection of a broad range of solid tumors and malignant lymphomas. Complexes of cleomycin with polyvalent metals play an important role in both its clinical functions. The structure and dynamics of binary complexes of bleomycin with nucleic acids and polyvalent metals has been investigated by multinuclear NMR spectroscopy. The frequency dependence of ^{13}C, T_1 and NOE measurements has been interpreted in terms of the microdynamics of this antibiotic. Binding of this agent to poly (dA-dT) and various self-complementary dG-dC tetranucleotides has been examined by ^1H NMR spectroscopy. Proton NMR, potentiometric titrations, and fluorescene experiments have been employed to define the structure and stability of bleomycin complexes with Zn(II), Cu(II), Ca(II), Ga(III), Tb(III), and Gd(III). The kinetics of dissociation of the Zn(II) and Ga(III) complexes was determined by transfer of magnetization experiments.

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SODIUM–23 AND PHOSPHORUS–31 NMR STUDIES OF METAL ION BINDING TO PHOSPHATIDYLSERINE VISICLES, *R.J. Kurland,* M. Hammoudah, S. Nir, J. Benz and D. Papahadjopoulos, State University of New York at Buffalo, Buffao, New York 14214.

Metal ions play a key role in many processes involving model and biological membranes, particularly those containing acidic lipids such as phosphatidylserine (PS), with net negative charge at the membrane-water interface. For example, the effects of $Ca2+$ on the permeability of PS model membranes and the fusion of PS vesicles is much stronger than that of $Mg2+$. We have studied the binding of metal ions to sonicated (unilamellar) PS vesicles by two NMR techniques: competition effects on Na-23 spin-lattice relaxation; direct effects on P-31 NMR shifts and relaxation. The latter results show that $Ca2+$ binds more strongly to the PS headgroup than does $Mg2+$ and that the headgroup mobility decreases substantially on Ca^{2+} binding, but not on Mg^{2+}. The binding of metal ions can be treated quantitatively in terms of a modified Gouy-Chapman type model, as shown by an analysis of the Na-23 relaxation rate data [R. Kurland, C. Newton, S. Nir and D. Papahadjopoulos, Biochim. Biophys. Acta, 551, 137 (1979)]. This model considers not only non-specific binding of a cation due to the potential of the negatively charged PS surface, but also specific ligation by PS headgroup moeities. A comparison of our P-31 results with those for another acidic lipid, phosphatidylglycerol (PG) [P.R. Cullis and B. DeKryff, Biochim. Biophys. Act, 436, 523 (1976)], suggets that the carboxylate moiety, present in PS but not in PG, plays an important part in the binding of Ca^{2+}.

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SOLVENT PROTON MAGNETIC RELAXATION STUDIES OF CONCANAVALIN A: RELATION OF CONFORMATION TO METAL AND SACCHARIDE BINDING, *R.D. Brown, III,* S.H. Koenig, IBM Thomas J. Watson Research Center, Yorktown Heights, NY, and C.F. Brewer, Albert Einstein College of Medicine, Bronx, NY.

Our recent studies of conformational changes in the lectin Concanavalin A (Con A) and their relation to metal and saccharide binding are reviewed. The experimental technique involves observations of solvent proton spin-lattice relaxation rates over a wide range of magnetic fields and as a function of time, using an automated field-cycling method which will be described briefly. Con A has two proximate metal binding sites on each monomer: a "transition metal" site (S1|) and a "calcium" site (S_2), which bind sequentially; S1 must be occupied before S_2 can bind. Introduction of metals into these sites induces a change in the protein from an initial, "unlocked" conformation, characterized by weak binding and low saccharide affinity, to a final "locked" conformation, characterized by greatly enhanced metal binding and full saccharide binding activity. By observing the effects of a variety of metals either in combination or singly, e.g., Ca-Mn-Con A, Mn-Mn-Con A, Ca-Ca-Con A, in the presence and absence of saccharide, we have been able to show: (1) the conformation change corresponds to a cis-trans isomerization of an amide bond in the vicinity of the metal sites; (2) the "locked" conformation is metastable on removal of the metals; (3) conformation is the primary determinant of saccharide binding; (4) saccharides alone can induce the "locked" conformation in apo-Con A; and (5) saccharide binding to the "locked" metallo-protein induces an additional, incremental, conformation change.

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2,5-DICHLORO-4-NITRONAISOLE, STUDIES OF CONCENTRATION VERSUS OBSERVED NUCLEAR OVERHAUSER EFFECT, *E.P. Mazzola* and S.W. Page, Food and Drug Administration, Washington, DC 20204.

The dependence of observed nuclear Overhauser effect has been studied for solutions of 2,5-dichloro-4-nitroanisole over the concentration range 0.04–0.5 M. Solutions were degassed and prepared in deuterochloroform by the Wilmad Company. One group contained 1% TMS while a second did not. The methoxyl protons were irradiated, and the resulting nuclear Overhauser effect upon H-6 measured. The results are discussed in terms of contributing relaxation mechanisms.

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THE NITROGEN-15 NMR SPECTRA OF NO COMPLEXES, *J.V. Dubrawski* and R.D. Feltham, University of Arizona, Tuscon, Arizona and J.D. Gust, Arizona State University, Tempe, Arizona.

The use of 15N NMR to probe the solution structure of nitrogen containing organic compounds has been rather limited due to the insensitivity of the ^{15} nucleus, and to the difficulties encountered in synthesizing enriched organo-nitrogen compounds. In contrast single-step high yield syntheses of a variety of transition metal complexes of NO ligands are frequently possible. Complexes containing 95% enriched NO ligands including *cis*-[Fe^{15}NO(S$_2$CNMe$_2$)$_2$1], and [Ru^{15}NO)-(S$_2$CNMe$_2$)$_2$X] (X NO$_2$, Br, I, and OH) were prepared in good yields by the direct reaction of ^{15}NO. The labelled nitro complexes, *cis*-[Ru(NO)-(S$_2$CNMe$_2$)$_2$-(^{15}NO$_2$)] and *trans*-[Pd(^{15}NO$_2$)$_2$(PR′R″$_2$)$_2$] (R′ = Me, R" = Ph; R′ = Ph, R" = Me; R′ = R″ = Et) were obtained from the reaction between Ag^{15}NO$_2$ and the corresponding metal halide. The The positional substitution was confirmed by the shifts of the fundamental vibrations of the NO ligands observed in their infrared spectra. The NMR spectra of these complexes were obtained at 9.12 MHz. The effects which metal, coordination geometry, and other ligands in the coordination sphere have on the NMR spectra of these complexes will be discussed. The possible use of NMR spectroscopy to probe the solution dtructures of metal-NO$_x$ complexes will also be described.

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^{13}C NMR STUDIES OF DIHYDROFOLATE REDUCTASE ENRICHED WITH [^{13}C] LABELED AMINO ACIDS, R.L. Blakeley, L. Cocco, and J.P. Groff, The University of Iowa, Iowa City, Iowa 52240 and R.E. London and *N.A. Matwiyoff,* Los Alamos Scientific Laboratory, Los Alamos, NM 87545.

An intensive ^{13} NMR program of the study of the structure and dynamics of [methyl-^{13}C] methionine, [guanido-13C] arginine, and [^{13}C$_\gamma$]trypotophan labeled dihydrofolate reductase has been undertaken.

The immediate goal of our studies of the methionine labeled enzyme has been assignment of the resonances to each of the seven methionine residues in the *S. faecium* enzyme. Two strategies have been followed: 1) carboxymethylation of the enzyme which has been found to be specific for Met-28 and Met-50; 2) studies with spin labeled analogs of both the co-factor, NADPH, and the inhibitor, methotrexate. Use of the latter derivatives which contain covalently linked TEMPO (tetramethylpiperidinooxy free radical) groups, enable us to distinguish methionine residues close to the binding site. The series of methotrexate spin labels synthesized represents the most systematic study of its kind undetaken. The most interesting data yet obtained in our investigations correspond to the tryptophan labeled enzyme. In this case, the presence of only four tryptophan residues, spread over a chemical shift range of 5.2 ppm, lead to highly favorable conditions for assigning the resonances. We have made these assignments based on the sensitivity of the resonances to substrates/inhibitors, spin labeld NADPH analogs, and structural data recently derived from crystallographic analysis of a related dihydrofolate reductase derived from L casei. Of greatest interest is the unusual dynamic behavior manifested by two of the tryptophan residues. In one case (Trp-21) a slow exchange between two conformations (most probably rotational isomers) has been deduced based on the presence of a split resonance. In another case (Trp-5), the Trp residue shows evidence of slow chemical exchange between conformations characterized by very different chemical shifts. We believe that this behavior is indicative of "breathing" of the protein, i.e., a relaxation of the tertiary enzyme structure. These studies are of interest both from the standpoint of providing general information on the structure and dynamics of proteins, and, more specifically, because dihydrofolate reductase is a key target of cancer chemotherapy. Thus, the drugs methotrexate and aminopterin act as inhibitors of this enzyme. A deeper understanding of the characteristics of the enzyme binding site can, in principle, lead to the design of more specific inhibitors.

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CARBON–13 NMR STUDIES OF –LABELLED TRANSER RNA,

M.P. Schweizer, W.D. Hamill, Jr. and D.M. Grant, University of Utah.

We will report on some recent carbon-13 nmr studies on the structure and interaction of several individual isoaccepting transfer RNAs selectively labelled with carbon-13. For example, ^{13}C-uracil labelled tRNAS were produced from a uracil requiring strain of E. coli designated SO-187. The genotype is his, leu,metB, lac, mtl, malA, xyl, str^r, paxAl, cdd-50, tpp-75, pyrE-50, pyrG-l5, thyA102 and the strain requires histidine, leucine, methionine, cytidine, thymidine, and uracil for growth. The strain was grown in a minimal medium of glucose, salts, and the required nutrients including 90% C-4 carbon-13 labelled uracil. The cells were harvested in the late log phase. The bulk tRNA's were extracted by treating the cells with phenol and salt water, precipitation with ethanol, extraction with 2M LiC1, dialysis and reprecipitation, and purification with DEAE-Sephacel. A total of 4.7 grams of unfractionated tRNA's were recovered from 2.2 kilograms of E. coli cell paste. Purified isoaccepting tRNA's were obtained by sequential chromatography of the bulk tRNA on columns of benzoylated DEAE cellulose, DEAE-Sephadex A-50 and Sepharose 4B.

Coupled and decoupled carbon-13 NMR data were taken at 23.5 kilogauss on a Varian XL-100 Fourier transorm equipped spectrometer and at 70 kilogauss on a Varian SC-300 superconducting spectrometer. Line assignments of the C-4 carbons in the modified nucleotides 4-thiouridine (s^4U), dihydrouridine (UH_2), ribothymidine (rT), pseudouridine (   ), and others were made based on comparison with model compounds and via long range coupling constants and single frequency decoupling. The effects of termal perturbation, magnesium ion concentration and synthetase enzymes on the chemical shifts and relaxation properties of the C-4 carbons have been explored.

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THE STRUCTURE AND CONFORMATION OF DIDEOXYRIBONUCLEOSIDE METHYL PHOSPHONATES, A NMR STUDY,

L.S. Kan, D. Cheng, K. Jayaraman, P.S. Miller, E. Yano, J. Yano, and P.O.P. Ts'o. Johns Hopkins University.

A series of dideoxyribonucleoside methyl phosphonate analogs, d-NpN and dNpNp, which contain a nonionic 3′-5′ methyl phosphonyl internucleoside linkage were prepared. The synthetic procedure employed was similar to the phosphotriester approach used to synthesize deoxyribooligonucleotides. The dimers were obtained as mixture of two diastereoisomers differing in configuration at the internucleoside methyl phosphonyl group and were separated by column chromatography. The diastereoisomers of each dimer have different conformations in solution as shown by ultraviolet hypochromicity data, circular dichroism spectra, ^{1}H and ^{13} NMR spectroscopy. For dApA, isomer 1 is more highly stacked than isomer 2, although both isomers are less stacked than the dinucleoside monophosphate, dApA. The circular dichroism spectrum of isomer 2 is very similar to that of dApA while the spectrum of isomer 2 shows loss of rotation at 270 nm and greatly diminished rotation at 250 nm. The results indicate that the stacked bases in dApA isomer 1 are oriented in an oblique manner, while those in isomer 2 are oriented in a parallel manner. The ^{1}H NMR spectra of the diastereoisomers of each of these dimers were analyzed by spectrum simulation techniques. Thus, all the coupling constants and chemical shifts of the proton resonances of the deoxyribofuranose ring, the phosphonate methyl group and the bases of these dimers, as wll as the corresponding monomer components, could be accurately determined. For each dimer analog, the base stacking mode of isomer 1 is similar to its parent diester while the extent of base overlap in isomer 2 is less than that in isomer 1. The conformations of the sugar-phosphate backbones of each isomer are very similar and these in turn are very similar to the conformations of the parent dinucleoside monophosphate. The configuration of the phosphonate methyl groups of dApA)$_{1\&2}$ were assigned using nuclear Overhauser enhancement (NOE) techniques. The carbon-13-enriched (at P—CH$_3$) dApdA)$_{1\&2}$ AND THE corresponding monomer dAp are investigated by ^{13}C NMR. The chemical shifts and coupling constants of ^{13}C atoms are measured at various temperatures. From the chemical shift data of these diastereoisomers, a similar conclusion to that obtained by ^1H NMR studies is drawn, i.e., the extent of stacking in isomer 2 is less than that in isomer 1, and the stacking pattern in both isomers is similar to dApdA. The sugar and backbone conformation of dApdA)$_{1\&2}$ as defined by the sugar puckering and the rotation about Ψ , Φ , ω' , and to is quite similar between these two isomers except the conformer about Φ' in isomer 1 is 89% in the gt′ population, which is 16% larger than that in isomer 2. This may account for the difference observed in the base stacking mode.

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NMR STUDIES OF PEPTIDE CONFORMATIONS THROUGH AMIDE HYDROGEN EXCHANGE MEASUREMENTS,

N.R. Krishna, J.D. Glickson, D.H. Huang and G. Goldstein, The University of Alabama in Birmingham, Birmingham, Alabama 35294.

Differential exhange rates of NH hydrogens of peptides and proteins are of considerable interest since these rates provide information about the secondary and tertiary structure of molecules. Our laboratory has been measuring the amide hydrogen exchange rates of oligopeptides in H_2O through a combination of two separate experiments: (i) the transfer of solvent saturation and (ii) saturation recovery experiments. The saturation recovery rates could be measured in a straightforward manner using Redfield's 2-1-4 pulse method. The problems associated in interpreting the data from the above two experiments, when a peptide exists in a dynamic equilibrium among different conformations, will be discussed. Some typical experimental results obtained on two cell-differentiating pentapeptide fragments will be presented.

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ABSTRACT NOT SUBMITTED

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ABSTRACT NOT SUBMITTED

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^1H, ^2H, AND ^{17}O RELAXATION STUDY OF MUSCLE WATER, *B.M. Fung* and T.W. McGaughy, University of Oklahoma, Norman, Oklahoma 73019.

T_1,$T_2$and T_{1p} of proton, deuteron, and oxygen-17 in muscle water were studied at 9.21 mHz as functions of temperature. Over the temperature range of 0° to 37°C, the relaxation times of all three nuclei in muscle water exhibit Arrhenius behavior with the following apparent activation energies (kJ/mol):

	T0	T_2	T_{1p}
^1H	9.1	-1.3	6.7
^2H	19	4.3	7.2
17	18	14	9.1

In addition, they have the following interesting features:

(1) The ratio *T1* (pure water)/T1 (muscle water) for 2H and ^{1} is similar and has very little temperature dependence. This ratio is larger for ^1H, and decreases with decreasing temperature. Its value at 25°C and 9.21 MHz is 9.0 for ^1H, and 3.6 for ^2H and 17O.

(2) At 25°C and 9.2 MHz, the ratio T_1/T_2 for muscle water is 8.5 for both H and ^2H. It decreases with decreasing temperature. This ratio is only 1.8 for ^{17}O, and has a much smaller temperature dependence.

These data can be explained in the following way: T of water in muscle water is determined by cross relaxation between protons in macromolecules and protons in water in the hydration layer. T1's of deuteron and oxygen-17 are determined by the rotational motion of water molecules in both the hydration layer and in the bulk. The factors of reduction for these two nuclei are therefore the same and smaller than that for proton. T_2's of ^1H and ^2H are affected by a hydrogen exchange process between water and the amino and hydroxyl groups in the proteins, which does not affect T_2 of ^{17}O.

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^1H NMR STUDIES OF ANTIBIOTICS IN PERDEUTERATED LIPID BILAYERS, *G.W. Feigenson* and P.R. Meers, Cornell University, Ithaca, NY 14853.

We have used 1HNMR spectroscopy of study valinomycin incorporated into sonicated aqueous bilayer vesicles. The observation of proton resonances from the valinomycin is made possible by reducing the background proton signals from the lipid through the use of perdeuterated dimyristoyl phosphatidylcholine (DMPC-d$_{72}$). The chemical shifts of the CαH and the L-Lac CH3 peaks correspond to the shifts observed in nonpolar solvents for uncomplexed valinomycin. These chemical shifts titrate upon addition of Rb$^+$ or K$^+$, but not Na$^+$, to limiting values similar to the shifts observed in various solvents for the fully ion-complexed form. These chemical shift data imply that uncomplexed valinomycin in a phospholipid bilayer has the same "bracelet" conformation as has been observed in nonpolar solvents, and that ion-complexed valinomycin in the bilayer has the same conformation in the bilayer as has been observed in various solvents. The ion binding behavior, as followed by HNMR, does not correspond to simple 1:1 binding.

110

STRUCTURE OF SATRATOXINS F AND G, METABOLITES OF STACHYBOTRYS ATRA. APPLICATION OF PROTON AND CARBON-13 NUCLEAR MAGNETIC RESONANCE,

E.P. Mazzola M.E. Stack, and R.M. Eppley, Food and Drug Administration, Washington, DC 20204.

Stachybotrys atra occurs in foods and feeds and has been implicated as the causative agent in several large-scale instances of animal illness and death. This mold produces metabolites of the general trichothecene class and, more specifically, of the macrocyclic ring-containing roridin and verrucarin group. In addition to roridin E, verrucarin J, and another roridin, satratoxin H, two more S. atra metabolites, designated satratoxins F and G, have been found by proton and carbon-13 nmr to have the following structures:

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ABSTRACT NOT SUBMITTED

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NMR RELAXATION MEASUREMENTS ON MACROMOLECULES, *N. Wade–Jardetzky*; O. Jardetzky, **Stanford Magnetic Resonance Laboratory, Stanford University, Stanford, California 94305.**

Relaxation time measurements on the NMR spectra of flexible macromolecules — ranging from simple random coil homopolymers to highly structured polymers with complicated monomer sequences, such as proteins — in principle provide information not only on the overall motion of the polymer, but also on the individual motions of the monomer units within it. The nature of the derived information, however, critically depends on the theoretical model used for the analysis of the data. A comparison of several theoretical models has therefore been made in the analysis of data on several polymers. The results show that the analysis of a single relaxation measurement — e.g., a T1 - permits a range of interpretations that is too wide to be useful. Simultaneous measurement and analysis of several relaxation parameters — T1, T_2 and NOE — at several frequencies is required to narrow down the choice of interpretations and establish confidence limits for each interpretation. The rate parameters (correlation times) are generally less sensitive to the assumptions of each model than are the amplitude parameters. A systematic comparison of different motional models and a phenomenological analysis implying no model at all can be made using the formalism of King and Jardetzky (1). The conclusion is that the rates of individual motions can be identified with reasonable accuracy, treating the analysis as an eigen-value problem, as defined in reference (1). Precise information on the nature and amplitude of each motion is not contained in an NMR relaxation measurement. The method is therefore most useful for comparative studies of relative degrees of mobility in different parts of the macromolecule.

1. Chem. Phys. Letters, 1978.

113

INTERNAL MOTIONS IN COPOLYESTERS CONTAINING TEREPHTHALIC ACID, AZELAIC ACID, BUTANEDIOL AND ETHYLENE GLYCOL AS STUDIED BY ^{13}C RELAXATION TIMES, *J.M. Hewitt,* P.M. Henrichs, G.A. Russell and M.A. Sandhu, Eastman Kodak Company, Rochester, NY 14650.

This study has utilized both spin-lattice relaxation times and nuclear Overhauser enhancements to give information about internal motions in a series of four-component copolyesters containing various amounts of terephthalic acid, azelaic acid, butanediol and ethylene glycol. The T1 values at 63KG varied from 0.2 to 1.0 sec and were markedly dependent on chemical sequencing. The NOE's are nearly complete for the backbone methylenes. These polymers are apparently rather mobile, probably because rotation about the $-CH_2-O-$ bonds in the ester group is facile. The barrier to rotation about the carbon-carbon bond next to the carbonyl in the $-CH_2-\overset{O}{\overset{\|}{C}}-$ group is also low. As azelaic acid is replaced by terephthalic acid in the polymer chain, reductions in the T1 values occur, particularly for the $-CH_2-$ group attached to oxygen. The reduction is due to the substitution of the relatively freely rotating $CH_2-\overset{O}{\overset{\|}{C}}-O-$ group in azelaic acid by the more restricted $\overset{\|}{C}-O-$ group in terephthalic acid. Reduction in T1 values for carbons a number of bonds removed from the acids occur since the alkyl chains are effectively almost rigid rods rotating about the pivot points formed by the ester groups.

114

QUANTITATIVE DETERMINATION OF RESIDUAL POLYVINYL ACETATE AND SODIUM ACETATE IN PVA: PMR INTEGRATION, J.R. DeMember, Polaroid Corporation, Cambridge, MA 02139.

We have succeeded in getting more detailed and more accurate information in the analysis of commercial polyvinyl alcohol (PVA) than has been possible previously. We have found that the mole percent of residual polyvinyl acetate (PVAc) in commercial PVA is a variable at less than 1% (M/M). Both the experimental and reproducible error of this determination of residual PVAc is a very low +.05% as shown in Table 1. The mole percent of sodium acetate (NaAc) was found to be a variable within 1.5% to 3.2% (M/M) for the lots studied. The error in this case is also a very low +0.1%. Because of the nature of other methods used previously in determining these parameters for PVA, and even though a low reproducibility error has been observed, a relatively high experimental error has always been resultant. The much higher experimental accuracy of PVA analysis by proton magnetic resonance (PMR) spectroscopy is a result of:

a.) observing the undisturbed solution of PVA. (This is, no titrants and no kinetic process are introduced to change the system.)

b.) the combined accuracy of PMR integration with novel resolution enhancement computer programs which we have developed.

In addition and most importantly, the analysis — after overnight dissolution — for both PVAc and NaAc takes one hour.

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QUANTITATIVE ANALYSIS OF THE MICROSTRUCTURE OF POLYBUTADIENE USING 20 MHZ ^{13}C AND 300 MHZ ^{1}H NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY, *D.H. Beebe* and R.C. Hirst,

The Goodyear Tire & Rubber Company, Akron, Ohio 44316.

In polybutadiene there are three distinct structural units possible: 1,2-Bd, cis-1,4-Bd and trans-1,4-Bd. With ^{1}H NMR the 1,2-Bd content can be measured easily. However the cis-1,4- and trans-1,4-Bd units are usually poorly resolved even at 220 MHZ and 300 MHZ. ^{1}H spectra recorded at 300 MHZ required the use of elevated temperature, homonuclear spin decoupling, and low 1,2-Bd content in order to resolve the olefinic cis-1,4- and trans-1,4-Bd units. In this case the distribution of 1,4-Bd triads was also determined.

A number of authors have shown ^{13}C NMR spectra to be quite sensitive to the distribution of the three types of Bd units regardless of the 1,2-Bd content. However a large number of lines appear in the spectrum when the 1,2-Bd content becomes large, and thus there are a number of different choices possible for lines used for a quantitative method. None of the previous studies described an explicit method for the determination of the content of the 1,2-, cis-1,4- and trans-1,4-Bd units.

This work has developed a fast, quantitative ^{13}C NMR method for the determination of the three Bd structural units and applied the method to polybutadienes with 1,2-Bd contents varying from 8 to 90%. In addition the disagreement in the literature on a number of ^{13}C NMR assignments has been resolved. For high 1,2-Bd contents the distribution of 1,2-Bd triads are discussed.

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ABSTRACT NOT SUBMITTED

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PULSED NMR RELAXATION OF A POLYSTYRENE/POLY(ETHYLENE OXIDE) DIBLOCK COPOLYMER, *S. Kaplan* and J.J. O'Malley, Xerox, Webster Research Center, Rochester, NY 14644.

Temperature dependent Nuclear Magnetic relaxation times were measured for a polystyrene/poly (ethylene oxide) (PS/PEO) diblock copolymer as well as for the individual homopolymers in order to study the effect of block copolymerization on molecular motions. Copolymer T_2 results show a two component decay in the temperature range between the PEO and PS glass transitions. A sharp transition is also seen at the PEO crystalline melting point. T1 data display a single exponential recovery, attributed to spin diffusion from the PS to the PEO domain. Detection of individual transitions of homopolymer components in the copolymer reveal phase incompatability in the diblock system. Evidence is presented consistent with some degree of component interaction. At low temperatures, the PEO Free Induction Decay shows resolved dipolar structure not present in the copolymer, and the T_1 minimum at the PEO glass transition is lower in the copolymer than in the homopolymer. This behavior is interpreted in terms of increased molecular motion from localized disorder in the PEO crystalline region induced by the PS.

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AN NMR STUDY OF THE POLYMERIZATION OF NORBORNENE ENDCAPPED POLYMIDES, *A.C. Wong* and W.M. Ritchey, Case Western Reserve University, Cleveland, Ohio 44106.

Using the techniques of C–13 and H–1 NMR, monomers and prepolymers of three norbornene endcapped polymides were characterized and their thermally induced polymerization processes were studied. In the case of the lower molecular weight compound N-phenyl nadimide, the polymerization was studied using "solution state" NMR. At least two mechanisms were found to be present in the process and their occurrence was temperature dependent.

Due to the insolubility of the higher molecular weight polymers, resulting from extensive cross-linking, only partially polymerized Bis nadic ester/methylene dianiline and PMR resins (designated for polymerization of monomer reactants) were studied with "solution state" NMR.

Mechanisms similar to that of N-phenyl nadimide were found in the early stage of polymerization. Preliminary results of the more highly cross-linked samples were obtained with "solid state" C—13 NMR.

119

INTERNAL MOTION IN PERDEUTERATED POLYMERS BY 2H NMR,

K. Seidman, J. McKenna, G.B. Savitsky and A.L. Beyerlein.

The decay of the broad deuterium band obtained in the ^{2}H spectrum of perdeuterated tetracosane has been studied. If each deuteron in tetracosane would have the same relaxation time, the decay of the envelope would be exponential. However because of internal rotation each deuteron has a different relaxation time which depends on the number of internal motions contributing to its relaxation. Because of the variation in the deuteron relaxation rates, along the tetracosane chain, a nonexponential decay is observed for the broad ^{2}H band in perdeuterated tetracosane. This observation is utilized to analyze the internal motions and overall rotation of tetracosane in terms of exact correlation time formulae (R.E. London and J. Avitabile, J. Chem. Phys., 65 2443 (1976)) and asymptotic formulae (Wen—Sheng Kuo, O.J. Jacobus, G.G. Savitsky, and A.L. Beyerlein, J. Chem. Phys., 70, 1193 (1979)). The results show that ^{2}H spectra of perdeuterated polymers at intermediate resolution (13.82 MHz) is a useful way of studying internal motions in polymers.

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INVESTIGATION OF THE ASSIGNMENT OF THE 2190 cm^{-1} IR BAND IN POLYFUMARONITRILE,

K.L. Gallaher, J.G. Grasselli, and D. Berlec, The Standard Oil Company (Ohio), Cleveland, Ohio 44128.

Polyfumaronitrile exhibits a band at 2190 cm^{-1} which has variously been associated with a β— aminonitrile, an iminonitrile, or with C=N in an a pyrrolenine rings. This band is of particular interest because it sometimes appears in degraded polyacrylonitrile and nitrile containing resins. The previous conflicting assignments were made on the basis of IR, UV, ^{1}H NMR, and chemical results. We attempt to shed new light on the problem by application of newer techniques including ^{13}C, ^{14}N and ^{15}N NMR as well as Raman spectroscopy.

A number of model systems were examined including polyfumaronitrile, a cyano-guanadine/formaldehyde copolymer, maleonitrile dimer (2-amino propene 1,1,3 tricarbonitrile) and acetonitrile dimer (3-amino crotonitrile).

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ESR STUDIES OF TRAPPED ELECTRONS, *H.C. Box,* **Roswell Park Memorial Institute, Buffalo, New York 14263.**

Electron trapping and electron hydration are well known and related phenomena in irradiated glasses and irradiated aqueous solutions respectively. Electron trapping in irradiated single crystals, on the other hand, had not been demonstrated until recently. Electrons stabilized at intermolecular sites has been observed in single crystals of polyhydroxy and a carbohydrate compounds X-irradiated at 4.2°K. The geometries of the traps can be inferred from ESR–ENDOR measurements of proton hyperfine couplings arising from the polar hydroxyl groups dispose about the electron. Typical electron-proton distances are in the range 1.59 to 1.74Å.

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SPIN-LABEL PROBES OF ANTIBODY FUNCTION, *P. Gettins,* **R.A. Dwek, A.T. Morris, B.J. Sutton and K.J. Willan, Dartment of Biochemistry, University of Oxford, South Parks Road, Oxford, 0X1 3QU.**

The antibody molecule performs two distinct functions — antigen recognition and elimination. To carry out these dual functions the antibody molecule has evolved discrete globular domains. One domain binds antigen and the others mediate effector mechanisms.

Antigen antibody recognition results from the complementarity of the antigen in the antibody combining site. We have developed a general approach to examine antibody combining sites by exploiting the idea of a common three dimensional structure in immunoglobulins. A trial structure, based on the sequence is thus obtained and refined by magnetic resonance techniques. E.S.R. studies give information on the depth, rigidity, polarity and asymmetry of the site. Proton n.m.r. paramagnetic difference spectra give information on the nature and relative orientation of the amino acid residues in the site. This is illustrated for the Dnp binding antibody M315, using a series of Dnp nitroxide spin-labels. This method is shown to be applicable to all Dnp binding antibodies.

Many of the secondary immunological functions are controlled by the complement cascade system of proteins which is activated by immune complexes. Introduction of a nitroxide spin-label on carbohydrate in the complement-binding region provides a probe of these processes. The results suggest that the trigger for the cascade system does not occur by transference of information from conformational changes initiated at the antigen binding site.

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ESR DETECTION OF RADICALS PRODUCED IN THE REACTION OF THIOLS WITH -NO CONTAINING COMPOUNDS, *G.C. Young* **and A. Joshi, Food and Drug Administration, Washington, DC 20204.**

Reactions of thiophenol, p-bromothiophenol and p-chlorothiophenol with N-nitroso-dibutylamine, N-nitrosodiethylamine, N-nitrosopiperidine and N-nitrosopyrrolidine yielded almost identical ESR spectra containing five broad lines at a high "g" value (2.027-2.030). Waters (J.C.S. Chem. Comm., 741, 1978) observed similar ESR spectra in the reactions of N-nitrosopiperidine and N-nitrosodiethylamine with thiophenol and thiocresol and attributed them to the $R_2NN(O.)SR$ radical. We observed that p-bromothiophenol, when reacting with t-nitrosobutane (tNB) or $NaNO_2$ or N_2O_4 in methanol also generates a five line ESR spectrum. Thiols are known to produce thionitrites (RSNO) when treated with $NaNO_2$ or N_2O_4 (J. Kanner, J.A. Oil Chem. Soc, 56, 74, 1979). The possible role of RSNO as an intermediate in the reactions of thiols with —NO containing compounds will be discussed.

124

INVESTIGATIONS ON THE MUTAGENICITY AND ELECTRON SPIN RESONANCE SPECTRA OF NITROSOFLUORENE—LIPID ADDUCTS, *R. Sridhar,* **M.J. Hampton, J.E. Steward and R.A. Floyd, Oklahoma Medical Research Foundation, Oklahoma City, Oklahoma 73104.**

The procarcinogen 2-acetylaminofluorene undegoes metabolic activation to 2-nitrosofluorene (NOF). NOF is a powerful mutagen in the Ames assay conducted with TA 98 strain of Salmonella typhimurium in the absence of microsomal activation system. We have shown (Arch. Biochem. Biophys., 185, 450, 1978) that NOF adds to unsaturated liquids in microsomes and liposomes to yield free radicals. NOF-lipid adducts in rat liver microsomes begin to tumble at 45°C but similar adducts in L-α-phosphatidylcholine (type V—E) liposomes tumble at 25°C. Membrane alterations due to NOF-lipid adduct may be a factor in carcinogenesis. NOF adds to methyl oleate or 2,3-dimethylbut-2-ene in an Alderene fashion to yield a hydroxylamine derivative which undergoes oxidation to furnish a fairly stable nitroxyl free radical. The second derivative ESR spectrum of the NOF-methyl oleate adduct is a triplet of a quartet with a 1:3:3:1 pattern. This suggests that the free electron interacts with one nitrogen ($a_N = 11.5$ gauss) and three approximately equivalent protons ($a^H \approx a^H \approx \quad \approx 3.5$ gauss). The second derivative spectrum of the NOF- 2,3-dimethylbut-2-ene adduct is more complex involving a triplet of 14 lines each. Both adducts were less mutagenic than NOF in the Ames assay conducted in the absence of microsomal activation system. (Supported by NIH grants CA21542 and CA18591.)

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CARCINOGEN AND PARMAGNETISM OF HEPATIC CELL ORGANELLA,

Y. Sakagishi, M. Sonoda, and *T. Komoda,* Saitama Medical School, Saitama 350-04, Japan.

Development of a cancer cell seems to be described with changes in its paramagnetism. We have observed EPR signals in rat hepatoma cells of different ages. There is a three-line spectrum which might be due to mitochondria[1].

In this paper we examined the generation of EPR spectra upon mixing the chemical carcinogen di-isopropanol-nitrosamine (DHPN) with albumin and with mitochondria or microsomes. EPR spectra were obtained at -196°C with a JEOL JES-FE-IX spectrometer. When DHPN was mixed with albumin a free radical was detected at $g = 2.00$. However, when DHPN and mitochondria were mixed and incubated at 37°C for 30 minutes a characteristic three-line pattern appeared, with g-values = 2.027, 2.011, and 1.999. No signal was observed in the mixture of microsomes and DHPN.

Based on these results we postulate that metabolism of chemical carcinogens occur in at least two ways: (1) general hydroxylation of drugs in liver cell microsomes[2], and (2) chemical modification by mitochondria.

1. Y. Sakagishi, Bull. of Tokyo Med. & Dent. Univ., 15, 33-57 (1968).
2. H.S. Mason et. al., Oxidases and related redox systems (ed. T.E. King et. al.) Vol. II, pp. 879-889 (1964) John Wiley & Sons, New York.

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EPR STUDIES ON HUMAN SERUM,

E. Kumoto, T. Kakuda, T. Yamaguchi, M. Kohno, and F. Morishige, Fukuoka University and Fukuoka Torikai Hospital.

Difference in EPR spectra in a liquid nitrogen between human blood plasma (heparinized) and serum was recognized in a shape of Cu(II), ceruloplasmin, signal (g=2.05) and in a height of g-2.00 signal. The chemical components of serum, responsible to the latter signal, were not free radicals of low molecular-weight compounds but the complex of Cu(II)—S groups of proteins. With either acidification, reduction or denaturation, Cu(II) signal of serum disappeared and changed to very sharp lines just similar to those of Cu(II)-diethyldithiocarbamate complex in toluene-chloroform. Such sharp lines appeared only from human serum but not from sera of other animals. Blood plasma did not exhibit such sharp lines. Variations in these serum EPR lines in various diseased conditions were investigated.

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ESR DETECTION OF ELECTROLYTICALLY GENERATED UNSTABLE RADICALS, *R.D. Allendoerfer* and J.B. Carroll, Jr., State University of New York, Buffalo, NY 14214.

A novel coaxial microwave cavity design will be presented which enables us to use one of the cavity walls as the working electrode for in situ electrochemical generation of free radicals. Flowing the electrolyte over this cavity wall provides the mass transfer necessary for detectable steady state radical concentrations. A spectrum of the nitromethane radical anion with a half-life of a few milliseconds will be presented to demonstrate the signal to noise ratio achievable. We calculate that radicals with lifetimes as short as 10 usec. can be observed by this method. Using square wave voltammetry and a boxcar integrator, time resolved esr of the electrolysis process is also possible and preliminary results will be presented.

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EPR STUDIES OF DEUTERATED NITROXIDE SPIN LABELS, Abraham Mathew, Wayne R. Hedrick and *John D. Zimbrick*, The University of Kansas, Lawrence, Kansas 66045.

The EPR spectral lines of deuterated nitroxides are narrower than those of undeuterated nitroxides. This makes the measurement of relative amplitude of hyperfine lines more accurate when low spin label concentrations must be detected. Another advantage is that the error arising from the asymmetric line shapes obtained from spin labels with lower tumbling frequencies can be minimized. Deuterated 4-oxo-2,2,6,6-tetramethyl-piperidin-N-oxyl (4-oxo-TMPN) was synthesized starting from deuterated acetone and ammonia. The EPR spectrum of the deuterated nitroxide in water showed three sharp lines, the line widths of which were found to be smaller compared with those of undeuterated 4-oxo-TMPN. The spectral characteristics such as line width, coupling constant, and microwave power saturation of deuterated 4-oxo- TMPN will be compared with those of undeuterated 4-oxo- TMPN. EPR spectral characteristics of other deuterated nitroxides will also be discussed.

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SPIN ECHO AND CW MEASUREMENTS OF ELECTRON SPIN RELAXATION OF NITROXIDES IN SOLUTION*,

R.N. Schwartz, University of Illinois, Chicago, Illinois and M.K. Bowman, Argonne National Laboratory, Argonne, Illinois 60439.

Electron spin echo and continuous wave measurements of electron spin relaxation rates have been carried out for two nitroxide free radicals in toluene over a range of temperatures and concentrations. Reorientational correlation times and the Heisenberg exchange rate for these radicals from the two techniques have been compared. The radicals differ significantly in size and shape. One is perdeuterated tempone (PDT) which is roughly spherical in shape and the other is N-(p-methoxybenzylidene)-4-amino-2,2,6,6,-tetramethylpiperidino-l-oxyl (MBATPO) which is rod shaped. The Heisenberg exchange rates appears to be roughly equal for the two radicals whereas the reorientational correlation times are quite different. The inhomogeneous broadening from unresolved proton hyperfine in these radicals must be considered when extracting information about Heisenberg exchange phenomena and rotational diffusion from the CW spectra. The electron spin echo measurements are unaffected by unresolved hyperfine. The electron spin lattice relaxation rates for these two radicals were measured and are far less sensitive to motion of the radicals than is the electron spin relaxation rate.

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*Work performed under the auspices of the Office of Basic Energy Sciences of the Department of Energy.

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STUDY OF THE PRODUCTS OF COAL HYDROGENATION AND DEUTERATION BY EPR, *I.B. Goldberg,* **H.R. Crowe, J.J. Ratto, L. Heredy, and R. Skowronski, Rockwell International Science Center, Thousand Oaks, Calif., 91360.**

The products of bituminous coal hydrogenated by H_2, D_2, tetralin and tetralin-d_{12} were separated by solvent extractions with hexanes, benzene and benzenemethanol solvents. The g-factors, lineshapes and the microwave magnetic susceptibility were measured for each fraction. The results show that the unpaired electron density decreases in the sequence Insoluble fraction $\gg$ benzene methanol soluble fraction $>$ benzene soluble fraction (asphaltene) $\gg$ hexane soluble fraction. The g-factor decreases in the opposite sequence. The linewidths of spectra of the deuterated products were typically 2/3 of that of the hydrogenated product, and the lineshape was less symmetric. These EPR parameters provided an indication of the sites in which hydrogen is added to coal. It was also found that the total unpaired electron concentration in the products are approximately equal to that of the starting coal, but the reconstructed spectrum is considerably different. Tracer amounts of Mn^{2+} were detected in the insoluble residues and are believed to arise from H^2 reduction of manganese in the silicates present in the coal.

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ELECTRON PARAMAGNETIC RESONANCE STUDIES OF OIL SHALE, SHALE OIL, AND SPENT SHALE, B.L. Sidwell, L.E. McKinney, M.F. Bozeman, P.C. Egbujor, *G.R. Eaton,* **S.S. Eaton, and D.A. Netzel, University of Denver, University of Colorado at Denver and Laramie Energy Technology Center, Laramie, Wyoming 82071.**

Electron paramagnetic resonance (EPR) reveals the presence of free radicals in raw shale, shale oil, and spent shale. Thirty-four samples of raw shale, and the spent shale and shale oil produced in the Fischer assay of these raw shale samples were studied. There is a significant correlation between the gallons per ton oil yield as estimated by Fischer assay and the spin density in the raw oil shale. However, the scatter in the data (due to uncertainties in sample preparation, Fischer assay results, and estimation of spins per gram of sample) limits the analytical utility of this finding. Sample preparation techniques affect the EPR signal.

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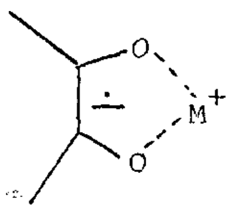
ESP STUDIES OF HEAVY METAL ENVIRONMENTAL POLLUTANTS, *J.K.S. Wan,* **Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6.**

The ability of ortho-quinones such as 9,10-phenanthroquinone (PQ) to form paramagnetic adducts with organometals has recently been emphasized. Among the controversial heavy metal environmental contaminants, Hg, Pb, Sn, and Uranium have been investigated by e.s.r. in our laboratory. The main objective is to explore the use of electron spin resonance method to study the exchange reactions between heavy metal contaminants and the alkali metal—PQ complexed ion-pairs. In many cases the exchange reaction is very specific and highly efficient. The organometallic-PQ adducts have a general structure which is consistent with the e.s.r. analysis:



Two of the metal adducts, RHg—PQ and UO_2—PQ, are further characterized by very low g-factors. In addition to the traditional methods of preparing metal—PQ ion-pairs by metal reduction, we have investigated the photochemical preparations of a series of metal—PQ ion-pairs and triple ions. In many cases time-resolved CIDEP technique can be applied to study the formation of the ion-pair. Some of these results will be discussed.

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SOCIETY OF APPLIED SPECTROSCOPY - STUDENT AWARD ADDRESS, PROTON HYPERFINE SPLITTING AND CONFORMATION IN NITROXYL RADICALS, *M.J. Heinig,* **G.R. Eaton, University of Denver, Colorado 80208 and S.S. Eaton, University of Colorado, Denver, Colorado 80202.**

Long-range proton hyperfine splitting has been observed in a series of 4,4-dimethyloxazolidine-N-oxyl (doxyl) derivaties of medium- and large-ring alicyclic molecules. The splittings have been assigned to protons bonded to ring carbons adjacent to the point of attachment of the doxyl substituent. Temperature dependences of the splittings will be related to conformational barriers which have been measured or calculated for medium and large rings.

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EPR SPECTRA OF THE LIVERS IN DISEASED STATES, *F. Morishige,* H. Tanaka, E. Kimoto and H. Kawasaki, Fukuoka Torikai Hospital, Fukuoka University and Kurume University, Japan.

EPR studies have been made of human and animal livers, in a liquid nitrogen, in various diseased states.

In Vc deficiency of guinea pigs, cyto. p-450 signals at g=2.41, 2.25, and 1.91 decreased. The CCl4-fatty livers exhibited a disappearance of Cyto. p-450 signals, and an increase of both signals of non-heme ferric complex (g=4.2) and high spin heme (g=6.0). Neither normal nor fatty livers showed (Cu(II) signal though they contained much higher amount of copper than the blood. Patient's liver during laparotomy exhibited, in some cases, high Cu(II) signal, may be, due to unwanted oxidation. In DAB hepatoma of rats, cyto. p-450 signals disappeared. The 3-line signal g=2.01, coupling constant 17 — 18 gauss, characteristic to NO-heme iron of denatured protein appeared. Both signals of serum transfer in and celuroplasmin were demonstrable in tumar mass. EPR technique seems to offer a means monitoring the peroxidative conditions of the livers.

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SPIN-TRAPPING AND LIQUID CHROMATOGRAPHIC SEPARATION AND IDENTIFICATION OF UNSTABLE RADICALS OF AMINO ACIDS, PEPTIDES, AND NUCLEOTIDES, *H. Hatano,* K. Makino, N. Suzuki, A. Moriya, and S. Rokushika, Kyoto University, Kyoto 606 Japan.

2-Methyl-2-nitrosopropane is a useful spin-trapping reagent, which enables to convert unstable radicals appeared during gamma-irradiation into stable spin adducts. In the course of the spin-trapping research, radiolysis of the spin-trapping reagent could result in producing self-trapped adducts.

The spin-adducts of gamma-irradiated 2-methyl-2-nitrosopropane in aqueous solution were separated on a column of high performance liquid chromatograph and structures of the separated radicals were determined by electron spin resonance measurements as follows; $(CH_3)_3CN(0.)C(CH_3)$ $(CH_3)CN(0.)CH_2C(CH_3)_2N{=}0$ and $CH_3N(0.)C(CH_3)_3$.

Radical produced in gamma-irradiated aqueous solutions of L-Ala and L-Val were studied by the method of spin-trapping and the high performance liquid chromatography. The unstable radicals were converted into stable spin-adducts by the spin-trapping method, and then separated individually by the chromatography. The separated fractions containing spin-adducts were detected by an ESR spectrometer used as a radical detector, and simultaneously their ESR spectra were observed by the ordinary ESR spectrometer. From the obtained ESR spectra, structures of the spin-adducts of the radicals were identified successfully, as follows; $(CH_3)_3CN\text{-}(0.)CH_2CH(NH_2)COO^-$(I) and $CH_3CH(COO^-)N(0.)C(CH_3)_3$(II) from L-Ala, $(CH_3)_3CN(0.)CH_2CH(CH_3)CH(NH_3^+)COO^-$(III) $(CH_3)_3CN(0.)C(CH_3)_2CH(NH_3^+)COO^-$f IV), $(CH_3)_2CHCH(COO^-)N(0.)C(CH_3)_3$(V) from L-Val. On the spectra of (I) and (III), the selective broadenings of the line shapes were clearly observed.

Aqueous solutions of four dipeptides, Cly-Cly, Cly-Ala, Ala-Cly and Ala-Ala, were gamma-irradiated with 2-methyl-2-nitrosopropane as a spin-trapping reagent. The stable spin-trapped radicals in the irradiated solutions were separated by the chromatography and detected by ESR spectroscopy. From the ESR spectra of fractions giving each peak in the chromatograms, structures of most of the trapped radicals were determined successfully, as follows; $.CH_2CONHCH_2COO^-$, $H_3N^+CH_2CONHCHCOO^-$, $.CH_2CONHCH(CH_3)COO^-$, $H_3N^+CH_2CONHC(CH_3)COO^-$, $CH_3CHCONHCH_2COO^-$, $H_3N^+CH(CH_3)CONHCHCOO^-$, $CH_3CHCONHCH(CH_3)COO^-$, $H_3N^+CH(CH_3)CONHC(CH_3)COO^-$, $H_3N^+CH(CH_2)CONHCH(CH_3)COO^-$ and/or $H_3N^+CH(CH_3)CONHCH(CH_2)COO^-$.

About the similar works on nucleotides, 5′-UMP, 5′-CMP and 5′-TMP, Hatano, Rokushika and Kominami have already reported in Intern. J. Rad. Biol., 30, 525 (1976); Rad. Res., 72, 89 (1977); Bull. Inst. Chem. Res., Kyoto Univ., 55, 23 (1977), and about that on methionine by Makino and Hatano, in Chemistry Letters, 119 (1979).

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HEME–SPIN–LABELING OF HEMOPROTEINS, *T. Asakura* and P.W. Lau, University of Pennsylvania, Philadelphia, PA 19104.

A nitroxide spin label was attached to the propionic acid groups of protoheme IX, which was used to study the structure and function of various hemoproteins after reconstitution. EPR spectrum is sensitive to the spin state of the heme iron as well as the heme environment. Therefore the heme-spin-labeling constitutes an elegant method to probe the conformation in the vicinity of the heme pocket to study changes as the result of ligation, protein association, modification, etc. The results showed the different mode of association of heme with apoproteins in different hemoproteins such as hemoglobin, myoglobin and peroxidases.

Further studies were carried out by preparing various hybrid hemoglobins in which a spin label was attached to either *a* or β subunits. The oxygen binding properties (P_{50} and n-value) were unaffected by the attachment of the spin label. The results showed the structural non-equivalence of the α and the b chains of hemoglobin. By monitoring the fractional changes in EPR and visible spectra during ligand binding of the heme-spin-labeled hybrid hemoglobins, we could determine the sequence of ligand binding by hemoglobin. We found that oxygen and carbonmonoxide bind with hemoglobin in different sequence and the sequence of oxygen binding was strongly affected by the addition of organic phosphate.

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ABSTRACT NOT SUBMITTED

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ESR AND VISIBLE ABSORPTION SPECTROSCOPY OF HORSERADISH PEROXIDASE, FREE AND BOUND TO DONOR SUBSTRATE AT CRYOGENIC TEMPERATURES, M.M. Maltempo,

The spectroscopic properties of ferric horseradish peroxidase (HRP) and its complexes with the donor-substrate aminotriazole (AT) and the fluoride (F) anion have been studied by ESR at 80°K and by visible spectrophotometry at 130°K–170°K. The ESR spectrum of free HRP consists of a superposition of a typical ferric high-spin signal and a signal corresponding to a quantum mechanical mixture of mid-spin (S=3/2) and high-spin (S=5/2) states. The ESR spectrum of HRP–AT showed a single quantum mixed-spin signal ($g_{\perp} = 4.7$, $g_{\|} = 2.0$); the spectrum of HRP–F shows a single, typical, high-spin signal with a small rhombic splitting at $g_{\perp} \sim 6$.

The high-spin to quantum mixed-spin ESR spectral transition observed in HRP at 80°K, upon the addition of excess AT, is correlated with a 10% decrease in the peak absorbance of the 640 nm band as compared with that of the 500 nm band, as monitored by spectrophotometry at 130°K–170°K. The visible spectral transition is similar to that previously correlated with ESR-monitored high-spin to quantum mixed-spin transitions in Chromatium cytochrome The enzyme and substrate used in this study were obtained from commercial sources. The identification of a commercially available quantum mixed-spin heme complex should greatly facilitate cryogenic studies which require large quantities of material, such as far infrared spectroscopy.

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THE OXYGEN BINDING SITE OF CYTOCHROME c OXIDASE AS REVEALED BY EPR SPECTROSCOPY,

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Cytochrome a3 and Cu$_{23}$ comprise the oxygen binding site in cytochrome c oxidase. In the oxidized enzyme neither of these metal ions gives rise to an EPR signal due to strong anti-ferromagnetic coupling of the heme and copper. However, we have shown that both the heme and copper can be made EPR visible upon the binding of nitric oxide. Nitric oxide binds to Cu$_{a3}$ in the oxidized enzyme and results in the appearance of a high-spin heme EPR signal which can be assigned to cytochrome §3. The competition of cyanide and fluoride binding with nitric oxide in the oxidized enzyme—NO complex has been studied and these studies indicate that interacting ligand binding sites are present on both cytochrome $\underline{a}3$. The addition of azide to the oxidized enzyme—NO complex produces a one electron reduction of cytochrome $\underline{a}3$ which results in a triplet EPR signal due to coupling of ferrocytochrome $\underline{a}3$-NO and Cu$_{a_{3+2}}$. The triplet species is probably a nitric oxide bridged ferrocytochrome $\underline{a}3$-NO-Cu$_{a3}$ species.

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EFFECT OF POLYMER MATRIX ON THE ROTATIONAL MOTION OF SPIN-LABELED PROTOHEMIN COORDINATED TO POLYMER-CHAIN,

S. Hata and E. Tsuchida, Waseda University, Tokyo 160, Japan.

The immobilization of heme by globin chain in hemoglobin and myoglobin is interesting aspect in biological and chemical fields. The mode of the interaction will be understood by the model complex system. The spin-labelling study of the polymer-hemin complex has revealed the change of the rotational motion of protohemin by the coordination to polymer-ligand. The rotational correlation time of spin-labeled protohemin(SL—H) increased with the addition of homo- or copolymers containing ligand-units in semidilute solution. While non-coordinate polymers or monomer ligands did not affect so greatly. The difference of the above two cases was different temperature dependences of the rotational motions, but there was not so large difference on the activation energy of the rotation. The rotational motion of SL—H was more decreased by the immobilization into the domain of block copolymer. The discussion will also be made on the motion ligand-unit of polymer.

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"ESR STUDIES OF ION PAIR FORMATION WITH THE TRIPHENYLENE ANION RADICAL." *M. Thomas Jones* and Razia H. Ahmed, Department of Chemistry, University of Missouri—St. Louis, St. Louis, MO. 63121.

Ion pair formation of the triphenylene anion radical with alkali metals has been investigated in a variety of solvents by ESR. The goals of this investigation were several-fold. One, to characterize the electronic and molecular structure of the triphenylene radical anion-metal cation pair. Two, to determine if the structure was dependent upon alkali metal and/or solvent. Three, to demonstrate that combined experimental measurements of the g-value and proton hfs, when interpreted through the use of molecular orbital calculations of the experimental observables for different ion pair models, can be very powerful techniques for the characterization of ion pair structures. The results of the study suggest the metal cation resides above the plane of the triphenylene anion and moves in a parallel plane. Changes in cation, solvent, and/or temperature result in modification of the g-values and/or proton hfs as a result of changes in the magnitude of the motion of the cation in the plane parallel to the plane of or by movement up or down relative to the triphenylene anion.

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HOLE CENTERS IN THE ALKALINE EARTH OXIDES, *John E. Wertz,* David A. Dixon and Fricis Dravnieks, Department of Chemistry, University of Minnesota, Minneapolis 55455.

The V^- center in MgO involves a hole trapped on an oxygen atom adjacent to a positive ion vacancy.[1] After this defect was established in MgO, analogous defects have been found in a variety of hosts. In the related V_{OH} center, an impurity OH^- ion is collinear with the trapped hole and the vacancy, viz., O^- [ ] HO^-. If the hole is lost from the V_{OH} center, the stable V_{OH} center results. Extended ionizing radiation permanently reduces the number of V_{OH} centers which can be induced and increases the number of V^- centers. The fate of the hydrogen which is lost from the V_{OH} center is being studied. It is known that bubbles of high-pressure hydrogen exist in some MgO crystals, presumably the product of the decomposition of impurity OH^- ions. It has been shown that V_{OH} centers can be generated from such hydrogen.[2] However, it has not been possible heretofore to introduce hydrogen externally by diffusion. Present studies use ion bombardment for hydrogen introduction. The result of such bombardment will be reported.

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HOST LATTICE EFFECTS IN THE EPR SPECTRA OF Gd^{3+} ION IN SOME LANTHANIDE HYDROXIDES,

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ABSTRACT

Hydrothermally grown single crystals of lanthanide hydroxides, $Ln(OH)_3$ (Ln=La, Sm, Eu, Tb, Y and Ho) incorporating 1% $Gd(OH)_3$ were studied at 293K using 9.3 and 34.2 GHz spectrometers. Well resolved spectra of Gd^{3+} were observed in La,Eu,Y and Ho hosts, whereas a single broad line was observed in Sm and Tb hosts. The angular variation of Gd^{3+} spectra in ZX- and XY- planes indicated that the lanthanide site experiences a trigonal symmetry crystalline electric field. The spin-Hamiltonian parameters were computed by analyzing simultaneously 10 directions of Zeeman field in ZX- plane for each host. The magnitude of dominant spin-Hamiltonian term B_{20} is found to decrease as a function of the ionic radius and the nearest host ligand, which is in contradiction with the point charge model. Unusual features are observed in the linewidths of Gd^{3+} in Eu and Ho hosts which are attributed to magnetic interactions and inhomogeneous crystalline electric fields.

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EPR OF ORGANIC COMPOUNDS IN AMBIENT TEMPERATURE MOLTEN SALTS,

J.S. Wilkes and L.P. Davis, USAF. Academy, Colorado 80840.

Mixtures of N-alkylpyridinium chlorides and aluminum chloride form salts that are molten at or near room temperature. These molten salts provide anhydrous and aprotic media in which organic compounds may be studied. The Lewis acidity of the melts may be varied over a wide range. Poly nuclear aromatic and heterocyclic compounds form radical cations by electrochemical oxidation or, in some cases, spontaneously. The structures of the radicals were determined by EPR techniques also showed that reduction of the pyridinium cation of the molten salt resulted in the formation of a viologen salt. The effect of Lewis acidity on radical cation formation was investigated.

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ESR INVESTIGATIONS OF THE THERMAL DECOMPOSITION OF ENERGETIC MATERIALS, *H.L. Pugh, Jr.,* L.P. Davis, J.S. Wilkes, United States Air Force Academy, Colorado 80840.

We will discuss on-going research at the Frank J. Seiler Research Laboratory in the area of thermochemical decomposition of energetic materials, including TNT and the important nitramine propellants RDX and HMX. Recently, we have used electron spin resonance (ESR) methods *to* obtain the kinetic parameters for *thermal* decomposition of TNT by directly observing radical species concentrations during the reaction. We are presently using ESR of selectively deuterated samples of TNT, computer simulations of TNT ESR spectra, and MNDO molecular orbital calculations to determine the specific radicals involved and the reaction mechanisms driving the TNT decomposition process. Our ESR studies of RDX and HMX indicate that radical species are involved in the thermal decomposition of these nitramines, and our progress involving these materials will also be reviewed.

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RELAXATION SPECTRA OF POLYMERS OBTAINED FROM ESR AND NMR STUDIES, T. Tanigawa, T. Kitahara, S. Shimada and *H. Kashiwabara,* Nagoya Institute of Technology, Showa–Ku, Nagayo, Japan.

Applications of magnetic resonance methods to the studies of molecular motion in polymers became to be very popular recently. Spin label-technique looks like to be a successful application of ESR method. Broad line NMR method has also been a popular application of NMR to the molecular motion study since the dates of the nineteen-fifties. correlation times are used to be calculated from the parameters of ESR or NMR spectra observed and their temperature dependences give us activation energies of the molecular motion studied. However, activation energy obtained in usual magnetic resonance study looks like to be smaller than that obtained from the other measurements like dielectric or dynamic mechanical studies. This is *caused* by the fact that relaxation times in polymers are widely distributed. Miyake pointed out this phenomenon and he presented a useful equation for deriving the relaxation spectrum from the data of magnetic resonance measurement. According to the equation derived by Miyake, some discussions on the molecular motion in solid polymers were made taking the distributions of the relaxation time into consideration. Coincidence of the relaxation spectrum obtained from line width data in ESR with that obtained from NMR data were found when a certain value of activation energy was assumed. This activation energy should be a real activation energy. A few examples of this kind of approach will be presented. Materials studied were irradiated polyethylene in ureapolyethylene inclusion complex, polyethylene labelled by spin trapping *reagent*,and polytetrafluoroethylene.

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ABSTRACT NOT SUBMITTED

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EPR OF ′ CENTERS IN ULTRA-PURE FUSED SILICA, M. Schwab and *M.J. Moran*. Lawrence Livermore Laboratory, P.O. Box 808, Livermore, California 94550.

We have studied the EPR of radiation-induced E′ centers in Suprasil I and Suprasil WI. The *data consisted* of measurements of EPR spectra, spin densities and power saturation behavior. The samples were exposed to Co^{60} *y* -ray, 14.8MeV neutrons and reactor core radiation.

Because of the long relaxation times and T_2 of the E′ center, the first-derivative spectra and spin densities were recorded with low incident microwave power ($\approx$ 40 H_z). The resulting spectra were in general agreement with previously reported data; but exhibited differences in detail depending on the type of fused silica and radiation used. Many of these differences were previously undetected because the data were frequently recorded under power saturating and passage effect conditions.

The data was also used to study the relaxation times of the E′ centers. Spin density and special broadening measurements showed that the dominant mechanism controlling T_2 was dipole-dipole broadening. Power saturation behavior was used to determine the product $T_1 . T_2$. When these data were combined for a sample with $1.5 . 10^{17}$ spins/c.c., corresponding values of T_1 and T_2 were found to be 62 usec, respectively. For other samples, both T_1 and T_2 varied roughly inversely with the absolute spin density.

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EPR IN THE STUDY OF RADIATION DAMAGE IN SILICATE GLASSES,

M. Schwab and **M.J.** *Moran,* **Lawrence Livermore Laboratory, P.O. Box 808, Livermore, California 94550.**

EPR is a sensitive and versatile tool when applied to the study of radiation damage in silicate glasses. We have used EPR spectra, absolute spin density measurements and power saturation measurements to study corresponding features of radiation damage behavior. We have studied Suprasil I, Suprasil WI and BK7 glass samples exposed to Co^{60} γ -rays, 14.8 MeV neutrons, and reactor core radiation fluxes. Data will be presented.

Absolute spin density measurements provide an excellent basis for measuring the dependence of the extent of radiation damage on the type (e.q., fast neutrons vs. γ -rays) and dose of radiation used. We have found that the extent of radiation damage is a complicated function of the irradiation conditions. For Co^{60} γ -ray irradiation of Suprasil I and Suprasil WI, measured spin densities are nearly equal to the two materials for some dose ranges, but differ by as much as a factor of ten for other doses.

EPR spectra provide a complementary source of data for 14 MeV neutron irradiation, the two ultra-pure fused silicas Suprasil I and Suprasil WI display markedly different spectra, implying the presence of different types of damage centers. For Suprasil WI, the spectra for γ-ray and neutron irradiations show similar differences. But, in both of these glasses, the spectra are nearly independent of radiation dosage. Similar data will also be presented for a borosilicate glass (BK7).

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TRAPPING REGIONS FOR ALLYLRADICALS IN IRRADIATED POLYETHYLENE,

T. Fujimura, **N. Hayakawa, and I. Kuriyama,**

The changes of the anisotropic electron spin resonance spectra due to allylradicals in γ-irradiated polyethylene were examined when sample was annealed at some temperatures. The results indicate that allylradicals are formed in both the crystal core and the crystal surfaces.

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EPR AND ENDOR EVIDENCE FOR POLARIZED CLUSTERS IN THE PARAELECTRIC PHASE OF FERROELECTRICS, *N.S. Dalai*, Department of Chemistry, West Virginia University, Morgantown, WV 26506.

With a view to understanding the microscopic details of samples exhibiting structural phase transitions, we have carried out EPR and ENDOR studies of the model compound KD2PO4. The SeO_4^{3-} radical was used as a paramagnetic probe. Electric field dependence of the lineshapes near the paraelectric-ferroelectric phase transition ($T_c = 221$ K) provides the first direct EPR evidence for the presence of polarized cluster at $T > T_c$. The results provide a means of distinguishing between the various theoretical models of the cooperative phenomenon in the KH_2PO_4--Type ferroelectrics.

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ABSTRACT NOT SUBMITTED

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SOLVENT POLARITY EFFECTS ON CORRELATION TIMES FOR NITROXIDE SPIN PROBES, *J.J. Windle*, United States Department of Agriculture, Berkeley, California 94710.

Correlation times, T_c, for di-t-butylnitroxide and a series of 4-substituted piperidine nitroxide spin probes were measured in two solvents of low viscosity and widely different dielectric constants: benzene and water; and in four solvents of higher viscosity and increasing dielectric constants: olive oil, eugenol, cyclohexanol and glycerol. Correlation times for the probes in water were found to be consistently larger than in benzene. In the four viscose solvents T_c for each probe was found to increase linearly with solvent dielectric constant. In all of the solvents, T_c, for each probe depended upon the R-group substituent dipole moment and size. The increase in T_c with solvent dielectric constant can be understood in terms of a "dielectric friction" between the solvent and solute dipoles.

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BIFUNCTIONAL SPIN LABELS DESIGNED FOR SATURATION TRANSFER EPR STUDIES OF ANISOTROPIC MOTION IN MEMBRANES,

B.J. Gaffney, G.L. Willingham, Man-Wing Tse and A. Mahon, The Johns Hopkins University, Baltimore, Maryland 21218.

Membrane proteins move in a medium which is both viscous and highly anisotropic. Therefore, motion of membrane proteins is expected to be characterized by two or more correlation times which are at least several orders of magnitude larger than the times which correspond to the motions of water soluble proteins. Saturation transfer EPR (STEPR) is sensitive to rates expected for rotational motion of membrane proteins. To a first approximation, the membrane normal may be taken as the axis about which the fastest rotational motion occurs. In addition to this assumption, the orientation of the spin label principal axes relative to the membrane normal must be known in order to evaluate the STEPR spectra.

We have prepared a pair of spin labeled, bifunctional protein modification reagents which have the nitroxide principal z axis (pi-orbital direction) parallel and perpendicular, respectively, to the chain separating the two functional groups of the reagents. The reagents have been used to label proteins in red blood cell membranes and the calcium ATPase of muscle membranes. Conventional (V_1) EPR spectra of oriented membranes provide information about the orientation of the reagents in the membranes before and after reaction. STEPR (V_2') spectra for the pair of labels lead to an estimate of the rates of rotational motions of the proteins in these systems.

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SPIN-LABELING STUDIES OF LIGNINS,

P. Tormala, Tampere University of Technology, P.O. Box 527, 33101 Tampere 10, Finland, and J.J. Lindberg, Helsinki University, Meritullinkatu 1A, 00170 Helsinki, Finland.

Spin-labeling and -probe techniques, which were first applied to studies of lipids and proteins, have been used extensively during last years also in dynamic studies of synthetic and modified polymers.

This report described our studies where nitroxide labels and probes have been used to study dynamic structures of thioglycolic acid lignins (TGL) in solution and in solid state.

TGL was spin-labeled by condensation with pyrroline nitroxide radicals. The EPR spectra indicated that the label radicals experience two major environments in pyridine and DMSO$-H_2O$ solutions. The correlation time data of nitroxide probes tumbling in pyridine, DMSO–H_2O and dioxane solutions of TGL gave also information about the rigidity and tightness of the network structure of lignin. Label and probe radicals which were tumbling in solid TGL were applied to study segmental motions and the glass transition of TGL. The results were compared with those obtained with colorimetric, dielectric and NMR measurements.

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ABSTRACT NOT SUBMITTED

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A STUDY OF RIBOSOMES USING THE SPIN LABEL METHOD, *H. Dugas,* A. Rodriguez, and N. Brisson, University of Montreal, Montreal, Canada.

We have used N-(1-oxyl-2,2,5,5-tetramethyl-4-pyrrolidinyl) maleimide spin labels of different length to label selectively the most reactive sulphydryl groups of 70S ribosomes from E. coli. A large portion of the label is on proteins S1 and S18 and the shape of the EPR signal shows two components with a predominance for the strongly immobilized orientation. As the distance between the spin label and the site of attachment on the ribosome increases, the label becomes more mobile. Temperature and Mg2+ ions affect the shape of the EPR signal and reflect conformational changes at the sites of labeling. In particular, at low Mg^{2+} concentration, the ribosomes are dissociated into subunits and labeling in these conditions allows the incorporation of spin labels at the interface where more sulphydryl groups are accessible. However, if already spin-labeled 70S ribosomes are dissociated into subunits, the spectra show that the motion of the spin labels is not affected.

The addition of t-RNA^{Phe} and poly-U ribosomes before or after spin-labeling results in different spectra. For instance, if t-RNA is added to spin-labeled 70S ribosomes, the labels become more mobile. If the ribosome-t-RNA-poly-U complex is spin-labeled then the intensity of the mobile component of the EPR spectra is reduced. These observations suggest that a conformational change is taking place on the ribosome upon t-RNA binding. Since protein S1 is known to interact with poly-U and t-RNA, it is reasonable to assume that in the complex this protein is protected from being labeled. Therefore, the sulphydryl group of protein S1 is very likely exposed and is responsible for the mobile component in the spectra of spin-labeled 70S ribosomes. Reduction of the EPR signal by ascorbate is also reported.

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ROTATIONAL MOTIONS OF MUSCLE PROTEINS STUDIED BY SATURATION TRANSFER EPR,

John C. Seidel, **Department of Muscle Research, Boston Biomedical Research Institute, Boston, Massachusetts.**

The sensitivity of saturation transfer EPR (ST–EPR) to rotational motion in the microsecond range provides a means of studying rotational motions of the contractile proteins of muscle and segments of these proteins. Estimates of these rotational motions have been made using purified proteins and supramolecular complexes that have been formed by aswembly of purified proteins or isolated as such by partially disrupting the intact muscle cell. These motions are of particular relevance to an understanding of the molecular basis of energy transduction in muscle, where the force generating step is generally believed to involve rotation of the myosin crossbridge about some point on the actin filament. By selectively introducing rigidly bound spin labels into specific muscle proteins and into specific regions of these proteins it has been possible to obtain insights into the molecular motions of myosin and actin, and into the nature of interaction between these proteins.

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ABSTRACT NOT SUBMITTED

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PHOTOASSISTED ELECTROLYSIS AND THE EPR CONNECTION,

J.R *Houlihan,* **Penn State University, and D.P. Madacsi, university of Connecticut, Groton, Conn. 06340.**

The selection of optimal materials for device applications requires an understanding of the relationships between intrinsic properties and composition and structure of the material. Such an understanding requires a description of the outer electrons which are responsible for the magnetic, electric, optical and elastic porperties of materials,*i.e., perspective* of the energy bands in solids.

Electron Paramagnetic Resonance techniques are uniquely qualified to help elucidate the energy levels in many materials of current interest in energy research. We shall consider the use of these techniques in the determination of the energy level schemes for a number of transition metal oxides which are of interest for use as photoelectrochemical anodes for the photoelectrolysis of water.[1,2,3] Using theoretical expressions derived by Shimizu[4], the orbital mixture parameter, the normalized core polarization and the normalized radial average can be obtained from the experimentally determined Spin-Hamiltonian parameters g_x, g_y, g_z; A_x, A_y and A_z. Utilizing these calculated values it is then possible to construct an energy level diagram of the d-orbitals which can in turn be correlated with optical spectroscopy results.

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ELECTRON SPIN POLARIZATION IN PHOTOSYNTHESIS,

O. Adrianowycz, **K.W. Kinnally and J.T. Warden**, Rensselaer Polytechnic Institute, Troy, NY 12181.

Electron spin polarization (Chemically Induced Dynamic Electron Polarization) in photosynthetic reaction centers has been probed in the 0.2–10us time domain by laser flash-photolysis electron spin resonance in the direct detection mode. Scenedesmus obliquus, Photosystem 1 subchloroplast preparations and reaction-center preparations from Rps. sphaeroides (R–26). The principal emissive feature in all systems arises from the reaction-center chlorophyll dimer (P_{700} or P_{870}) and exhibits a linewidth and g-factor indistinguishable from those of the "relaxed" cation. Spin lattice relaxation time (T_1) for the cation chlorophyll dimer are estimated to be 200–300ns at 300K. In chloroplasts the lineshape and linewidth of the emissive Signal 1 is independent of the orientation of the chloroplast with respect to the external magnetic field. Orientation dependences similar to those reported by Dismukes et. al. (Biophys. J.21, 239 (1978)) appear when conventional field-modulation detection techniques are utilized. (Supported by The Research Corporation, American Cancer Society and the U.S. Department of Agriculture).

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THE USE OF A NEW SPIN BROADENING AGENT IN THYLAKOID SUSPENSIONS TO MASK EXTERNAL SPIN LABEL SIGNAL, *DM. Nesbitt* and S.P. Berg, University of Denver, Denver, Colorado.

We have examined the internal aqueous space of spinach thylakoids by measuring the rotational motion of the spin label Tempamine (2,2,6,6-tetramethyl-piperidine-N-oxyl-4-amine) inside the thylakoids. Tempamine is freely permeable to the thylakoid membrane such that spin label signal will arise from both the thylakoid interior and the external space. Previous work of this type utilized the spin broadening agent $K_3Fe(CN)_6$ (ferricyanide) to mask the external Tempamine signal (Berg, S.P., Lusczakoski, D.M., and Morse, P.D., Archives Biochem. Biophys. 1979, in press). We report here the use of $K_3Cr(C_2O_4)_3$ (chromium oxalate) (Yager, T.D., Eaton, G.R., and Eaton, S.S., J.C.S. Chem. Comm., 1978, p. 944–945) as a broadening agent for Tempamine and thylakoid preparations. Chromium oxalate is superior to ferricyanide in the following respects: 1) The Tempamine signal is broadened to the same degree at half the molar concentration, therefore reducing the osmolarity. 2) The thylakoid membrane is less permeable to chromium oxalate. 3) Chromium oxalate does not uncouple electron transport, whereas ferricyanide does. These advantages of chromium oxalate open new areas of study of the thylakoid to better our knowledge of the internal thylakoid environment.

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APPLICATION OF EPR TO THE ANALYSIS OF SPATIAL ORGANIZATION OF REDOX COMPONENTS IN THE MITOCHONDRIAL MEMBRANE, *T. Ohnishi,* J.C. Salerno, and H. Blum, University of Pennsylvania, Philadelphia, PA 19104.

Spatial relationship — distance and angle — of neighboring redox active centers in the mitochondrial membrane has been determined from their spin-spin interactions which were manifested as EPR spectral broadening, splitting, or as relief of microwave power saturation (Salerno *et al.*, J. Biol. Chem. in press). Topology of EPR active redox centers in the mitochondrial inner membrane has also been determined at various levels of structural organization by te hspin-spin interaction with an extrinsic paramagnetic probe (Dysprosium–EDTA complex). The g=15 Dysprosium signal exhibits an extremely rapid relaxation, non-saturated even at 100 mW at 5 K and increases the $P_{½}$ of more slowly relaxing intrinsic EPR active centers in its proximity Ohnishi et al (1978) in

"Biochemistry and Genetics of Yeast" (Bacila et al. ed.) Academic Press, pp. 49–63. Analysis of EPR spectra of redox components in the oriented multilayered prepartions of mitochondrial membrane has also been conducted (Salerno et al, Biochim. Biophys. Acta, in press). Based on these results, spatial organization of electron and hydrogen carriers in the succinate-cyt. c reductase segment of the respiratory chain will be presented. Supported by GM 12202 and NSF grant PCM 78-16779.

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ELECTRON SPIN RELAXATION IN BACTERIAL PHOTOSYNTHETIC SYSTEMS*

M.K. Bowman, J.R. Norris, Argonne National Laboratory, Argonne, Illinois 60439 and C.A. Wraight, University of Illinois, Urbana, Illinois 61801.

Dynamic interactions between paramagnetic intermediates within the photosynthetic reaction center contribute to the relaxation of those paramagnetic centers. The relaxation of the bacteriochlorophyll special pair cation radical remaining after light induced electron transfer is strongly influenced by the Fe^{+2} ion in the initial electron transfer chain. Electron spin echo studies of the special pair cation between 2 and 200 K show a thousandfold change in spin lattice relaxation rate and a smaller change in the phase memory relaxation rate. From these studies, both the temperature dependent spin lattice relaxation rate of the high spin Fe^{+2} ion and its distance from the special pair can be determined. Electron spin relaxation is useful as a probe of many other aspects of the photosynthetic reaction center structure.

*Work performed under the auspices of the Office of Basic Energy Sciences of the Department of Energy.

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THE PRIMARY EVENTS IN GREEN PLANT PHOTOSYNTHESIS - STUDIED BY TIME-RESOLVED ELECTRON SPIN ECHO SPECTROSCOPY*

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We are applying several aspects of electron spin echo (ESE) spectroscopy to the study of photosynthesis. This work includes application of the recently developed time resolved ESE techniques to the study of the primary reactions in photosynthesis. Thus, we are able to avoid many of the problems encountered in previous applications of conventional time resolved EPR. Also a new phenomenon, an echo phase shift (EPS) effect has been discovered in the course of these investigations. We have observed within 40 nsec of laser excitation spin polarized EPR signals in several photosynthetic systems. Because of the unique properties of the spin echo technique combined with its inherently superior time resolution, ESE studies have provided the most direct evidence for the existence of several radicals in the early events of green plant photosynthesis. The lifetime of at least one of the early intermediates is determined by the EPS effect to be ~ 300 nsec, well below the time resolution of previous studies. We will use examples primarily from our studies of the blue-green alga Synechoccus lividis (grown in H_2O and D_2O) to describe our work.

*Work performed under the auspices of the Office of Basic Energy Sciences of the Department of Energy.

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INTRACELLULAR VISCOSITY OF LYMPHOCYTES DETERMINED BY AN 15N SPIN LABEL PROBE, *W.R. Hedrick,* A. Mathew, J.D. Zimbrick, The University of Kansas, and T.W. Whaley, Los Alamos Scientific Laboratory.

It has been suggested that spin labels enriched in ^{15}N instead of the naturally abundant ^{14}N may be advantageous in probing biological systems. An nitroxide spin label has an inherently greater sensitivity than the equivalent ^{14}N molecule, since fewer lines are present in the EPR spectrum of the ^{15}N-labeled molecule. Additionally, for spin label undergoing rapid rotation, longer correlation times can be measured if ^{15}N rather than undegoing rapid rotation, longer correlation times can be measured if rather than ^{14}N is present in the nitroxide moiety. ^{15}N-Tempone was synthesized from $(NH_4)_2SO_4$ and phorone and was used as a spin label probe to study the protoplasmic viscosity of lymphocytes. The lymphocytes were suspended in an isotonic solution of ^{15}N-Tempone and nickel chloride. Since the presence of nickel chloride at low concentrations is not sufficient to broaden the extracellular signal completely, the supernatant contribution was subtracted from the EPR spectrum to yield a net intracellular spectrum. The intracellular viscosity was determined to be approximately two times the viscosity of water.

^{14}N-Tempone yielded a similar result. The value of the hyperfine coupling constant for ^{15}N-Tempone in lymphocytes was slightly less than that in water. The EPR signal of the intracellular spin label was observed to decrease exponentially as a function of time with a decay constant of 0I25 + 0.18 min^{-1}.

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TRANSLATIONAL MOTION OF THE SPIN LABEL TEMPAMINE IN THE INTERNAL AQUEOUS COMPARTMENT OF SPINACH THYLAKOIDS AND RED BLOOD CELLS, *P.D. Morse, II,* Wayne State University.

The movement of organic molecules within cells plays a vital role in cell growth, maintenance, and metabolism. Previous studies by myself and co-workers have been directed toward understanding the rotational motion of a water-soluble spin label (2,2,6,6-tetramethyl piperidine-N-oxyl-4-amine) TEMPAMINE in cell and organelle systems as diverse as spinach thylakoids (a highly organized, complex, energy transducing membrane system) and red blood cells (a moderately organized, simple membrane). We have found that TEMPAMINE rotation is hindered by a factor of 10 in spinach thylakoids, 5 in intact red blood cells, and 2 in resealed hemoglobin-free red blood cells ghosts, relative to TEMPAMINE rotation in bulk water.

Translational movement of molecules within cells is clearly more important to cell biochemistry than is rotational motion. We have measured the translational motion of TEMPAMINE inside red blood cells and spinach thylakoids by comparing the linewidths so obtained with the linewidths of TEMPAMINE in glycerol-water solutions which hinder the rotation of TEMPAMINE to the same extent as the particular intracellular environment. This allows us to remove the rotational contribution to linewidth. This treatment will be discussed in some detail. Our preliminary results with spinach thylakoids suggest that TEMPAMINE translational motion is hindered by about a factor of 3 relative to bulk water. Thus, rotational and translational motion in the thylakoid aqueous interior are quite different. One possible explanation for this would require that TEMPAMINE be at least partially bound (relative to the lifetime of the excited state, around 10^{-6} sec) to some membrane components which are themselves in rapid translational motion. Results for red blood cells will also be presented.

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METAL–NITROXYL INTERACTIONS, P.M. Boymel, D.L. Dubois, K. More, G.R. Eaton, University of Denver, *S.S. Eaton,* University of Colorado, and D.J. Greenslade, University of Essex, Colchester C04 35Q, England.

Electron-electron couplings ranging from 4 to ca. 2600G have been observed in the room temperature solution EPR spectra of a variety of spin-labeled copper complexes. Ligand systems include Schiff bases, porphyrins, and acetylacetonates. Simulated spectra have been obtained based on an $ABMRY_n$ spin system with the off-diagonal elements arising from electron-nuclear coupling treated as a perturbation to second order.

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ESR STUDIES OF DIMERIC COPPER COMPLEXES OF ADENINE, D. Sonnenfroh and *R. Kreilick,* University of Rochester, Rochester, NY 14627.

We have studied the esr spectra of a series of dimeric copper square pyramidal complexes with bridging adenine groups and various axial ligands. The copper atoms in these complexes are coupled via electron-electron dipole-dipole and exchange interactions. The copper atoms are held relatively close to one another in these complexes and large dipolar splitting are observed from solid samples. The exchange interaction splits the energy levels of the complexes into singlet and triplet states. Measurements of the temperature dependence of the areas of the esr signals were conducted to determine the sign and magnitude of the exchange energies. All of the complexes were found to have ground singlet states with thermally accessible triplet states. The exchange energies were found to vary with the nature of the axial ligands in these complexes. This variation in exchange is explained by the effect of the axial ligand on the electronic states of the copper atoms.

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EPR POSSIBILITIES AT S–BAND (2-4 GHz), *J.R. Pilbrow,* The Medical College of Wisconsin, Milwaukee, Wisconsin 53226.

The bulk of EPR *spectra reported* in the literature have been obtained at X-Band frequencies (9-10 GHz) and, to a lesser extent, Q-Bank (~ 35 CHz) partly because of the availability of commercial instruments at those frequencies. Two frequencies are often needed for complete

characterization of spectra due to powders and frozen solutions of chemical complexes and biomolecules. Preliminary observations of spectra at S-Band frequencies in the 2-4 GHz range show the following effects in comparison with those at X-Band: improved resolution of spectra which have field dependent linewidths, e.g., cytochrome oxidase where only a broad line was observed at X-Band; improved resolution of part of a spectrum obscured by other lines at X-Band, e.g., low spin Co^{2+} porphyrin; increased intensities of 'forbidden' transitions particularly for Cu^{2+} and Mn^{2+}. A spectrometer which operates at 2.6 and 3.8 GHz at room temperature as well as low temperatures designed and built by Professor James S. Hyde and R.W. Froncisz at the National Biomedical ESR Center in Milwaukee will be described. The importance of computer simulated spectra in assisting with the analysis will be outlined.

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ENDOR INVESTIGATIONS IN THE NEMATIC AND SMECTIC PHASES OF LIQUID CRYSTALS,

B. Kirste and H. Kurreck, Freie Universitat Berlin, Takustro 3, 1000 Berlin 33, West Germany.

The investigation of organic radicals in liquid crystals yields valuable information about the anisotropic hyperfine interactions. Conventionally, the shifts obtained on passing from the isotropic to the nematic phase are measured, but this procedure may cause serious errors if the isotropic couplings are temperature or solvent dependent. This difficulty can be overcome by using ordered smectic mosophases which offer the possibility of arbitrary control of the direction of orientation and thus allow the determination of the shifts and of the isotropic couplings under the same experimental conditions. The resolution of the EPR spectra taken in these highly viscous mesophases is usually worse than in isotropic phases, hence the application of the ENDOR technique is particularly advantageous. Moreover, ENDOR allows the observation of quadrupole splittings of nuclei with spin $I \geq 1$.

We have studied deuterated and ^{13}C- labeled phenalenyls, galvinoxyls, and bis(biphenylenyl)propenyl radicals in liquid crtystals by means of ENDOR and TRIPLE resonance. The ordering parameters could be deduced from an analysis of the ^{1}H and ^{13}C hyperfine coupling shifts. In the case of substituted phenalenyls, a marked additional alignment induced by the substituent was found and the complete deuterium quadrupole tensor could be derived. Conformational changes of some of the radicals were observed on passing to the nematic or smectic phase.

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ENDOR STUDIES OF RADICALS ADSORBED ON METAL OXIDE POWDERS, *R.B. Clarkson,* Varian Instrument Division, Palo Alto, California 94303.

It has long been known that acidic (electrophilic) sites on certain catalysts such as activated alumina are capable of a charge transfer process with polynuclear aromatic hydrocarbons forming stable, adsorbed cation radicals, which may be mobile, and which are associated with a negatively charged counter-ion. In general, the EPR hyperfine structure of the adsorbed radical, which could yield important information concerning the extent of oxidation, mobility, state lifetime, etc., is broadened by a variety of mechanisms, making accurate EPR measurement of the coupling constants difficult.

Using a computer-interfaced ENDOR spectrometer, we have obtained ENDOR spectra of several aromatic cation radicals formed on a variety of metal oxide surfaces. A comparison of the hyperfine constants of the perylene cation radical, for example, adsorbed on alumina, silica, ZnO, and TiO_2 gives insight into the relative electronegativity of the adsorption sites, the lifetime of an adsorbed "state", and in conjunction with the theory of Lunsford[1], offers further evidence that O_2^- is the negative, counter-ion associated with the charge transfer process.

Precise hyperfine constants for aromatic cation radicals adsorbed on a variety of metal oxide powders will be given, together with interpretation of their variation with solid substrate.

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FIELD THEORETICAL TREATMENT OF THE PROTON HFA IN THE AROMATIC ION RADICALS, *S. Aono,* Kanazawa University, Kanazawa, Ishikawa, Japan.

Field theoretical method to estimate the values of the proton hfs in aromatic radicals is presented, and applied to explain why the proton hfs values of the positive ions are larger than those of the negative ions of same species. Since the Hartree-Fock orbitals for neutral molecule are considered inadequate for the corresponding positive ion, the correlation effect represented by the so-called exclusion principle violating diagram is introduced only to the positive ion, so that the symmetry properties between positive and negative ions are taken off.

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ENDOR ON VANADYL COMPLEXES IN FROZEN SOLUTION, *H. Van Willigen,* University of Massachusetts at Boston.

The application of ENDOR in the study of ligand hyperfine interactions in vanadyl (VO^{2+}) complexes will be discussed. Experimental results show that vanadyl complexes in rigid matrices provide excellent ENDOR spectra well above 77 K that can provide detailed information on the magnitude of hyperfine tensor components of magnetic ligand nuclei. Thus whereas with EPR information on bonding and structure must be deduced from subtle variations in g-factor and vanadium hyperfine splitting, the ENDOR technique gives a more direct and complete insight.

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TWO-WAY EPR CAVITY AND STARK EFFECT IN NITROGEN OXIDE, *Isao Suzuki* and Yoshihisa Kaneko, Utsunomiya University, 350 Mine-Machi, Utsunomiya, Japan 320.

A two-way EPR cavity for magnetic dipole transition (MDT) and electric dipole transition (EDT) was manufactured. There are two openings to fit the sample cell for MDT or EDT in the cylindrical TE_{011} mode. One opening is located on the axis of the cavity and the other is located away from the axis. EPR spectra of the mixture of oxygen and nitrogen oxide obtained when the sample cell was inserted in each of the openings showed the selective transition of the MDT or of the EDT of the species. When d.c. electric field parallel to the steady magnetic field was applied to the nitrogen oxide located away from the axis, each of the EDT peaks was divided into two peaks, one of which was higher than the other. The splitting was proportional to the d.c. electric field strength, in agreement with theory.

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NANOSECOND TIME-RESOLVED EPR SPECTROSCOPY, *A.D. Trifunac,* Argonne National Laboratory, Argonne, Illinois 60439.

Time-resolved EPR via electron spin echo with time resolution of ~ 20-30 nsec in both laser photolysis and pulse radiolysis will be described. Various aspects of the experimental approach and possibilities will be illustrated, including: "FID" spectra, the problem of FID suppression and background subtraction.

The radical concentrations attainable in the radiolytic experiment allow the study of CIDEP, radical kinetics and relaxation time measurements. The laser photolysis experiment is primarily used to study CIDEP and radical relaxation. Examples of both experimental approaches will be illustrated and the detailed kinetic analysis of the acetate radical system in pulse radiolysis will be described. The recent finding on the CIDEP and electron T_1 dependence on radical concentration will be presented.

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COMPUTER GRAPHICS AND INTERPRETATION OF EPR DATA, *C.E. Klopfenstein,* University of Oregon.

Advances in technology over recent years have allowed relatively sophisticated data acquisition devices to be interfaced to chemical instruments. Electron Spin Resonance Spectrometers are no exception, and in fact new meaningful modes of data interpretation are available using these digital methods. Spectral subtraction, integration, double integration, base line correction, and digital smoothing are but a few of the techniques used to enhance and interpret EPR data. Several examples of each method will be presented.

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A DIGITAL ACQUISITION SYSTEM FOR AN ESR SPECTROMETER: APPLICATION TO THE GENERATION OF DISPERSION-ABSORPTION PLOTS, F.G. Herring and *P.S. Phillips,* University of British Columbia, Vancouver, B.C. Canada V6T 1W5.

We have built a low cost stand-alone digital data logging system designed around a Fairchild F–8 microprocessor[1]. The system is interfaced to an ESR spectrometer to collect calibrated spectra on paper-tape.

The data are processed off-line on a central computer so as to make maximum use of standard FORTRAN numerical analysis programs. We have also developed algorithms for double integration (for concentration studies), automatic line-width and line-position analysis (for motional studies) and a fast Hilbert transform for generating dispersion spectra.

Dispersion vs. absorption (DISPA) plots for NMR[2,3] have previously been shown to provide sensitive test for Lorentzian line-shape. This technique is also applicable to ESR[4]. The difficulties of collecting ESR dispersion spectra have been overcome by performing a numerical Hilbert transform on integrated digital derivative spectra. We have shown that dipolar and other homogeneous broadening mechanisms do not distort the DISPA plots. However, overmodulation or a poor choice of amplifier time-constant cause large distortions in these plots, even though little or no distortion is apparent in the original spectra.

1. F. G. Herring, J. Mayo and P. S. Phillips, J. Magn. Res., 34, 0000 (1979).
2. D. C. Roe, A. G. Marshall and S. H. Smallcombe, Anal. Chem., 50, 764 (1978).
3. A. G. Marshall and D. C. Roe, Anal. Chem., 50, 756 (1978).
4. F. G. Herring, A. G. Marshall, P. S. Phillips and D. C. Roe, to be published.

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COMPUTER SIMULATION OF EPR POWDER SPECTRA,

R.L. Belford, and M.J. Nilges, University of Illinois, Urbana, Illinois 61801.

A computer program has been developed to provide simulation of EPR spectra of powders and frozen solutions containing paramagnetic transition metal ion compounds. The program handles systems with $S = \frac{1}{2}$ and several interacting nuclear spins. Nuclear quadrupole coupling, nuclear Zeeman, anisotropic hyperfine, and anisotropic electronic Zeeman terms are allowed for, as are noncoincidences between principal axes of the various interaction matrices. Perturbation expressions are often insufficiently accurate; the program uses diagonalization. Several strategems employed to make the programs efficient and economical will be described. The application of this simulation program to anslyses of several complicated EPR spectra of Mo. Ni, and Cu compounds will be described. In particular, nuclear quadrupole coupling constants are being obtained from simulation-aided analyses of the spectra of several powders and glasses. This work is supported by the National Foundation Quantum Chemistry Program, the National Institutes of Health (Gm–22887), and the University of Illinois Research Board.

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ABSTRACT NOT SUBMITTED

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DIGITALIZED EPR AND ST-EPR SYSTEMS, *T. Watanabe,* T. Sasaki, K. Sawatari and S. Fujiwarea, University of Tokyo, Hongo, Tokyo 113, Japan.

A new system for the detection of ST–EPR signals has been developed with the modification of a conventional EPR machine. A transient recorder is used for the data sampling and processing. The signal of the usual EPR spectrometer, which is modulated at 100 kHz, is analyzed by Fouier Transform technique into the sine and cosine components of the frequency domain. Two components of both 100 kHz and 100 kHz are collected simultaneously at each point of the magnetic fields. In-phase and 90° out-of-phase signals with respect to the 1st and 2nd harmonics of the field modulation are obtained from the cosine and sine components after phase correction respectively.

The system which is reported in this paper allows very accurate adjustment of in-phase and 90° out-of-phase, which makes accurate measurement of the saturation transform experiment possible.

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AN EFFICIENT APPROACH TO SIMULATION OF EPR SPECTRA OF HIGH SPIN IRON(III) IN RHOMBIC LIGAND FIELDS, *Michele I. Scullane,* Lawrence K. White, and N. Dennis Chasteen, University of New Hampshire, Durham, NH 03824.

The EPR spectra of iron transport proteins exhibit a resonance with an effective g value of approximately 4.3 due to the presence of high spin Fe(III) in rhombic ligand fields. The position and shape of the resonance are determined by the xero-field splitting, D, and the asymmetry parameters, λ =E/D and μ =a/D, which are dependent upon the character and symmetry of the ligand field. Usually results of Mössbauer studies and EPR measurements at several temperatures are needed to evaluate these parameters unambiguously. Often the g′=4.3 EPR resonance shows fine structure and values for the parameters can be obtained using computer simulation techniques. Conventional simulation methods are impractical because of the amount of computer time required for the calculations, but satisfactory results can be efficiently obtained by use of programs employing the Eigenfield Perturbation Method of Belford, Davis, Belford, and Lenhardt. The g′=4.3 resonances in the EPR spectra of several iron transport proteins have been simulated and the results compared to those obtained by other techniques.

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ABSTRACT NOT SUBMITTED

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ABSTRACT NOT SUBMITTED

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ABSTRACT NOT SUBMITTED

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COMPUTERIZED QUADRUPOLE SECONDARY ION MASS SPECTROSCOPY FOR SURFACE ANALYSIS,

Bradway F, Phillips and Nancy E. Lares, Perkin-Elmer Corporation, Surface Sciences Division, 6509 Flying Cloud Drive, Eden Prairie, MN 55344.

As the field of Secondary Ion Mass Spectroscopy (SIMS) has expanded over the last ten years, the production of several different commercial quadrupole mass spectrometer instruments have broadened the possibilities of combining several surface analysis techniques in one instrument. By using SIMS in combination with Auger or ESCA (Electron Spectroscopy for Chemical Analysis) analysis, the high sensitivity of SIMS can be better utilized by using the Auger or ESCA data to help standardize the SIMS data.

A totally integrated computer system for Auger, ESCA and SIMS and its capabilities will be described. Several special techniques for sample charge neutralization and sensitivity enhancement during SIMS analysis will also be presented.

Examples of data obtained from several different types of specimens (semiconductor materials, metals, minerals) will be presented along with comparisons of the results obtained by using other surface analysis techniques.

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CATALYTIC PROPERTIES OF METALS FOR CARBON OXIDATION,

Abund O. Wist, VCU, Richmond, Va., 23298, Kenneth E. Daugherty, NTSU, Denton, Texas.

The increasing energy shortage in the United States could probably be lessened if improved catalysts were available in fields such as fossil fuel conversion processes, fossil fuel power plants, and waste conversion. Recently a new method has been proposed to measure the catalytic activity of different materials for fossil or other fuels rapidly and accurately. The method consists basically of heating the fuel with various materials in a special sealed chamber and observing the different reaction temperatures.

Using this approach the effect of different materials on the oxidation rate of carbon and coal was measured. The results indicate that the basic catalytic property which affects the oxidation rate of carbon seem to more correlated with the basic shell configuration then with the actual chemical state the metal is in. This means that metals such as lithium, sodium, potassium, and silver have a similar catalytic effectiveness, which is in this case high. Other metals such as berylium, magnesium, calcium, zinc, cadmium show a very low or non-existing catalytic effectiveness. This simple regularity makes it possible to formulate rules, predicting the effectiveness of different metals and metal compounds to catalyze the oxidation rate of carbon, coal and other fuels.

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ABSTRACT NOT SUBMITTED

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NEAR SURFACE ANALYSIS BY ELECTRON MICROPROBE,.

Doyle, Rockwell International Energy Systems Group, Rocky Flats Plant, P.O. Box 464, Golden, CO 80401.

An electron microprobe analyzer is generally considered a bulk analyzer when compared to some of the other surface analysis techniques such as Auger spectroscopy. The normal size of the spot being analyzed by a microprobe is 1 to 2 cubic microns with a depth of one micron. This spot is primarily caused by the electron beam penetrating and scattering into the sample. Characteristic elemental X-rays will be produced in the volume of material where the primary beam voltage is above the absorption edge of the fluorescing element. Thus, to minimize the spot size and depth of analysis, a low energy X-ray line should be selected and the electron beam voltage set at one and one-half to two times the absorption edge of that line. Elements concentrated at or near the sample surface can be easily determined by qualitatively and/or quantitatively determining the elements in the analysis spot at high and low beam voltages. The elements which increase in concentration at the low voltage are concentrated at or near the sample surface.

Several examples of this analysis method will be discussed.

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ION SCATTERING PROFILES OF POLYPROPYLENE COATINGS ON $CuO^{18}_{0.67}$ FILMS BEFORE AND AFTER OXIDATIVE DEGRADATION OF THE POLYMER,

A.W. Czanderna, Solar Energy Research Institute, Golden, CO, and A.C. Miller, Alcoa Technical Center, Alcoa, PA.

Polymers are known to oxidatively degrade in the presence of copper and its salts. A basic question is to determine the role of the polymer-copper oxide interference in the catalyzed oxidative degradation of polypropylene.

Copper films were deposited on glass substrates and oxidized partially or completely to $CuO_{0.67}$ in oxygen-16 or oxygen-18. The 44 nm thick oxide films were overlaid with 40 to 110 nm of polypropylene (pp) by a dip coating process. The pp/$CuO_{0.67}$/glass samples were heated in oxygen-16 at temperatures of 90, 100, 110, and 120° in the presence and absence of getters for the product gases. ISS depth profiles were obtained for deposited copper films, partially and completely oxidized films (both labeled and unlabeled) and for undegraded and oxidatively degraded polymer/oxide sandwiches.

Analysis of the copper oxides formed in oxygen-16 and oxygen-18 showed the expected separation of the maxima of 0.03 E/E_0 in the energy loss spectrum. For all 16–18 combinations, the sum of the peak intensities is the same as for the intensity of oxygen-16 in $CuO_{0.67}$.

In the presence of getters, the copper oxide films is reduced by the polypropylene but is not reoxidized, leaving the copper oxide film nearly all reduced to copper. The O^{16}/O^{18} ratio in the unreduced oxide remained unchanged from the original ratio. The degraded polypropylene was more difficult to sputter and the profile showed copper was present throughout the polymer thickness.

In the absence of getters, the copper oxide film is reduced but reoxidized by the oxygen ambient used during the oxidative degradation. The O^{16}/O^{18} ratio in the oxide after degradation exhibits a marked increase in oxygen-16. Extensive oxidation of the polypropylene is evident from the O^{16} signal in the polymer and, again, copper ions are found distributed throughout the polypropylene.

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ANALYTICAL LABORATORIES' ENVIRONMENTAL ANALYSES AT ROCKY FLATS, *C.E. Gies* and *J.R. Cobb,* Rockwell International, Golden, Colorado 80401.

A flowchart illustrating environmental analyses at the Rockwell International, Rocky Flats Plant will be presented. Analytical areas involved in the analysis of air, water, and soil samples are described with photographs and parameter lists. These areas include atomic absorption spectroscopy, emission spectroscopy, infrared spectroscopy, liquid chromatography, gas chromatography, radiochemistry, and wet chemistry.

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PLUTONIUM METAL ANALYSIS AT ROCKY FLATS, *D.I. Hunter,* P.A. Hyman, and H.L. Wells, Rockwell International, Golden, Colorado 80401.

A flowchart illustrates various analyses performed on plutonium metal at Rocky Flats. Photos and text illustrate and describe the instrumentation modification necessary to handle plutonium in an analytical laboratory. Examples of Thermal Gravimetric Analysis, Spark Source Mass Spectrometry, Atomic Absorption Spectrometry Emission Spectrometry and others are shown.

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ISOTOPIC FRACTIONATION OF $^{15}NH_3$ IN AN ALL-GLASS STILL, *W.A. O'Deen* and *L.K. Porter,* U.S. Department of Agriculture, Ft. Collins, Colorado 80522.

Fractionation of isotopic nitrogen during steam distillation of $^{15}NH_3$ was detected in an all-glass Kjeldahl distillation apparatus. The pattern was similar to that observed in diffusion-tube collection of $^{15}NH_3$. Atom o/o ^{15}N values of the first and last fractions of distillate were significantly different from each other at the 0.5% probability level. The atom o/o value of the first fraction was 3 parts per thousand lower than the standard, which could prove meaningful in natural isotopic abundance studies. Disparity in atom o/o ^{15}N values can be minimized by collecting the total nitrogen sample rather than subsampling a portion of the distillate.

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SYNTHESIS OF OXAZOLIDINE RADICALS WITH A FUNCTIONAL GROUP FOR PROTEIN MODIFICATION,

J.L. *Jones,* T.M. Harris, and D. Puett, Vanderbilt University, Nashville, Tennessee 37232.

In an effort to develop spin probes with additional functionality to study protein conformation using EPR, 2-amino-2-methyl-1,3-propanediol has been condensed with acetone to give an oxazolidine with a free hydroxy group, I. This condensation is accomplished in ethanol with an acid catalyst and does not require a drying agent. The reaction is applicable to tris(hydroxymethyl)aminomethane to give a dihydroxy oxazolidine II.

Compounds I and II have unusually low pK's of 6.2 and 5.5 respectively, allowing the course of the reaction to be followed by titration. These pK's do not reflect ring opening although this does occur at low pH. These structures are in agreement with ^1H nmr and molecular weight determination by titration.

Oxidation of I and II with H_2O_2/NaW gives radicals as viscous yellow oils with G_O and A_O values of 2.0104 and 14.9, and 2.0110 and 14.7 (in methanol).

This procedure provides spin label precursors which are readily synthesized and purified. Additional functionality may be introduced by the use of other ketones. The free hydroxy group will permit attachment of protein modification agents. Supported by AM 15838 and HD07043.

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A VERSATILE LOW COST LABORATORY INSTRUMENT CALIBRATOR/TEST SET,

John Salsgiver, United Technical Corporation, Concord, Mass. 01742.

There are times, that during the course of an investigation the practicing researcher has serious doubts about whether his research instrumentation is performing as he feels that it should. Without this confidence level, he quickly realizes that his results may be in jeopardy. Or there are those times it is obvious that one component of his instrumentation system is malfunctioning — the question being— "which one?". An excellent low cost way to approach this problem is to have available on the bench a dependable "known". The "known" can be used to inject a test signal at the proper point within the system to either locate the malfunctioning component or to verify performance. Further, if this "known" has acceptable accuracy, it can be also useful as a system or instrument calibrator.

New advances in solid state technology now permit the low cost construction of an instrument which can provide the necessary "knowns" to assist in this approach. The new instrument provides manual digital selection of three decades of constant voltage over the range of 0 — 999 mv dc; constant current over the range of 0 — 9.99 ma dc; and timing(event) markers over the range of 0 — 99.9 seconds. Each function has a resolution of 0.1 unit with an accuracy of 0.1%. Further, a multiply by two circuit is included to double the available ranges. In addition, a unique step function variable rate-of-decay test signal is also made available to permit evaluation of electromechanical and similar systems[1]. This new instrument, then, will find many applications in the laboratory in the test and calibration of typical laboratory instruments and systems.

[1] Salsgiver, J., el at., American Laboratory, June 1977.

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ELECTRON SPIN RESONANCE STUDY OF THE COPPER(II) COMPLEXES OF HUMAN AND DOG SERUM ALBUMIN AND SOME MODEL PEPTIDES,

G. *Rakhit* Food and Drug Administration, Washington, DC and B. Sarkar, The Research Institute Hospital for Sick Children at Toronto, Ontario, Canada.

Electron spin resonance spectra of the first Cu(II) complexes of human serum albumin, dog serum albumin, L-aspartyl-L-alanyl-L-histidine N-methyl-amide and L-glycyl-L-glycyl-L-histidine N-methylamide have been studied using isotopically pure ^{65}Cu in its chloride form.

At 77°K, the ESR spectra of Copper(II) complex of human serum albumin exhibited only one form of ESR signal between pH 6.4 and 9.5 No intermediate forms were detected. The presence of equally spaced nine line superhyperfine structure with spacing ~15 G indicated considerable covalent bonding between copper and most probably four nitrogen atoms derived from the protein. The highly complexed form of Cu(II) bound to human serum albumin detected at neutral pH would be consistent with possible participation of the histidine nitrogen in metal-protein binding.

In contrast, the ESR spectra of Cu(II)-dog serum albumin complex showed a gradual transition from a low pH form to a high pH form as the pH was increased to 9.6. These spectra changes were found to be reversible upon lowering the pH. Ligand superhyperfine splittings in the high pH form of ESR signal of dog albumin were rather poorly resolved, indicating a possible departure from axial symmetry in the metal coordination site.

The distinct pH dependence of the ESR signals observed in human and dog serum albumin complexes could be correlated in their respective optial spectra changes as a function of pH.

At room temperature and in the pH range between 6.4 and 9.8, the ESR spectra of Cu(II) complexes of Asp-Ala-His-$NHCH_3$ and gly-gly-His-$NHCH_3$ exhibited well resolved nine line superhyperfine structure indicating a possible metal coordination with four equivalent nitrogen atoms of peptide. At liquid nitrogen temperature both of these peptide complexes exhibited similar ESR spectra with the exception that gly-gly-His-$NHCH_3$ did not show a well resolved superhyperfine structure.

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