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28th Rocky Mountain Conference

Abstract

Program and abstracts from the 28th annual meeting of the Rocky Mountain Conference, co-sponsored by the Rocky Mountain Section of the Society for Applied Spectroscopy and the Rocky Mountain Chromatography Discussion Group. Held in Denver, Colorado, August 3-7, 1986.

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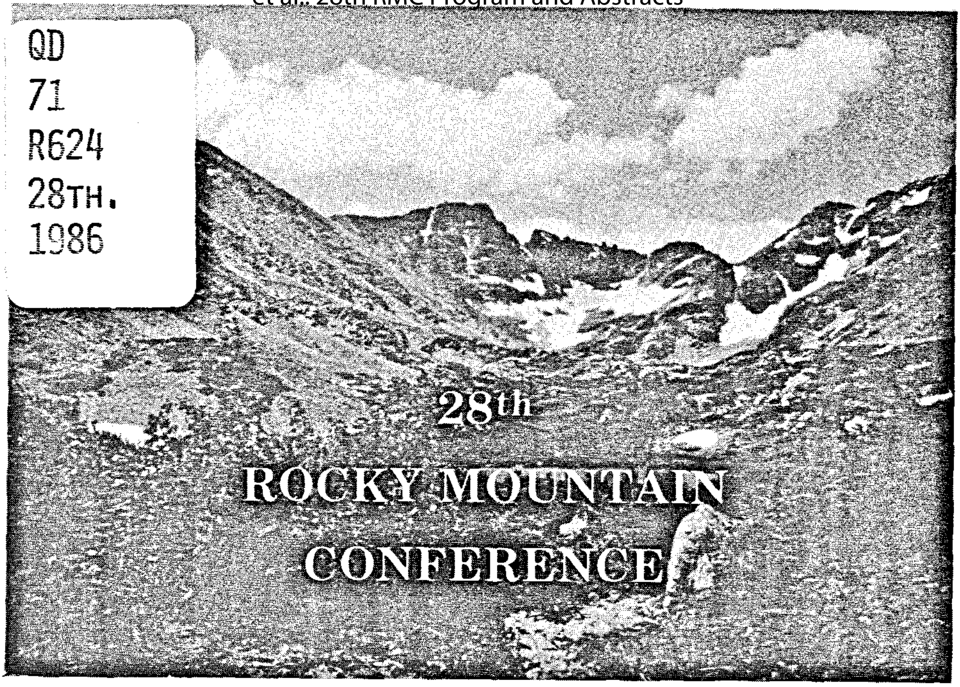

28th
ROCKY MOUNTAIN CONFERENCE

Program
and
Abstracts

August 3-7, 1986

Radisson Hotel Denver
1550 Court Place
Denver, Colorado

Sponsored by

Rocky Mountain Section
Society for
Applied Spectroscopy

Rocky Mountain
Chromatography
Discussion Group

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Symposia Schedule
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WELCOME

We are pleased to present the 28th Rocky Mountain Conference on Analytical Chemistry at the Radisson Hotel Denver. Our hope is that with the scientific program, exhibition and social activities at one location, the conference will better promote and encourage the discussion and exchange of scientific information and ideas among all conferees.

Our graditude extends to the authors of over 280 papers to be presented at the conference and to the exhibitors who support us with one of the largest summer-time exhibitions. These people and companies provide the quality which makes us proud to undertake these annual meetings.

For our out-of-state conferees, we welcome you to Denver and Colorado and hope that during your stay you will take time to enjoy some of the many recreational activities that are available in the area. On behalf of the organizing committee of the conference, the Rocky Mountain Chromatography Discussion Group and the Rocky Mountain Section of the Society for Applied Spectroscopy, I welcome you to the 28th Rocky Mountain Conference.

R. M. Barkley
Conference Chairman

FUTURE CONFERENCES

29th Rocky Mountain Conference - August 2-6, 1987

General Chairperson
Carol Gies
Rockwell International
P.O. Box 464
Golden, CO 80401
(303) 966-7380

Program Chairperson
Michael Reddy
U.S. Geological Survey
5293 Ward Rd.
Arvada, CO 80002
(303) 236-3617

30th Rocky Mountain Conference - July 31-August 5, 1988

31st Rocky Mountain Conference - July 30-August 4, 1989

32nd Rocky Mountain Conference - July 29-August 3, 1990

REGISTRATION

Admission to all technical sessions and the exhibition is by a name badge for the 28th Rocky Mountain Conference. Conference fees are payable by check (dominated in $US. only) made payable to the Rocky Mountain Conference.

Registration Fees - 1986

Registration	45.00
Registration - one specified day	25.00
Student Registration	10.00
Additional Vendor registration	35.00
Unemployed or retired registration	No charge
Film Festival only	No charge
Exhibition only (non-vendor)	No charge

Times

Registration for the 28th Rocky Mountain Conference will be held in the Convention Lobby (on Thursday only, outside of the Columbine room) of the Radisson Hotel Denver during these times:

Sunday, August 3	4:00 pm - 8:00 pm
Monday, August 4	7:30 am - 3:30 pm
Tuesday, August 5	7:30 am - 3:30 pm
Wednesday, August 6	7:30 am - 3:30 pm
Thursday, August 7	8:00 am - 10:00 am

Smoking is not permitted in meeting rooms at the Rocky Mountain Conference.

EXHIBITION

The Rocky Mountain Conference exhibition provides an opportunity to see and discuss the latest in analytical instrumentation, apparatus, supplies and services. The exhibitors support the Rocky Mountain Conference - please support them! The exhibition is held in the Grand Ballroom of the Radisson Hotel Denver.

Hours

Monday, August 4	9:30 am - 5:00 pm
Tuesday, August 5	9:30 am - 5:30 pm
Wednesday, August 6	9:30 am - 3:00 pm

The following exhibitors have reserved space as of June 10, 1986:

Air-Row Enterprises, Inc.
Allied Analytical Systems
Alpkem Corp.
Analect Instruments
Applied Technical Products
Biorad/Digilab Division
Brinkman Instruments Inc.
Brucker Instruments Inc.
Cenref Labs.
Chemical Data Systems
Coors Spectrochemical Labs.
Coulometrics, Inc.
Dionex Corp.
EG&G Princeton Applied Research
Finnigan MAT
GOW-MAC Instrument Co.
Harris Analytical
IBM Instruments
Instruments S.A.
JEOL USA Inc.
Lachat Instruments
MSD Isotopes
Mettler Instruments
Nelson Analytical
Nermag
O.I. Corp.
Oxford Instruments of North America
Perkin-Elmer
Questron
Sadtler Research Laboratories
Sciex
Shimadzu Scientific Instruments Inc.
Sievers Research, Inc.
Spectral Data Services, Inc.
Spectroscopy Magazine
Storage Technology Corp.
Supelco Inc.
Technicon Instruments
U.I.C., Inc.
VG Instruments
Varian Instruments Corp.
Waters Associates
Wilmad Glass
Zymark Corp.

SOCIAL PROGRAM

Registration Night Mixer

A cash bar will be open in the Convention Lobby of the Radisson Hotel Denver on Sunday evening from 7:00 to 9:00 p.m. Plan to meet other conference attendees and beat the Monday rush to pick-up your conference badge and abstract book.

Conference Mixer

All conferees and spouses are invited to attend this lively affair on Monday. August 4. This years mixer will be held in the Grand Ballroom Exhibition area from 5:00 to 7:30 p.m.

Conference Banquet

The 28th Rocky Mountain Conference Banquet is scheduled for Tuesday. August 5. 7:00 p.m. in the Majestic Ballroom. Tickets are $16.00 each for the entree' of Chicken Continental. A limited number of tickets will be available at the registration desk on Monday. A cash bar in the Majestic Lounge will open at 6:00 p.m.

The banquet speaker is Dr. Max Morton. exercise physiologist with the Coors Wellness Center in Golden. Colorado. He holds a doctorate in physical education and has received several professional honors including Outstanding Male Physical Education Professor from Colorado State University. He has been a consultant to the Denver Broncos professional football team since 1970. The title of his presentation is "Fair. Fat and Forty"-or how to keep all the old parts in working order.

Western Supper and Show

On Wednesday. August 6. the Rocky Mountain Conference will sponsor a chuckwagon supper and western entertainment at the Flying W Ranch near Colorado Springs. Dress is western or casual. Alcoholic drinks will not be available. Cost per person is $16.00. including bus transportation. Tickets are available using the preregistration form or at the registration desk till 1:00 p.m. on Tuesday. August 5. The bus will leave the hotel at 5:15 pm.

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ADDITIONAL ACTIVITIES

Visitor Information

Although no specific program is planned for the guests and families of conferees. Denver and the surrounding area boast a large number of activities that are enjoyable for both young and old. For additional information contact the Denver Metro Convention and Visitors Bureau. 225 W. Colfax Ave.. Denver CO 80202. (303) 892-1112 or ask any of the local committee.

Film Festival

The following films will be shown in the Columbine room from 8:30 to 4:00. Monday through Wednesday. Admission to the film festival is by a paid or complimentary conference badge. A schedule will be posted in the registration area.

Astronomy: The Cosmic Quest
Earth Quakes and Technology
Electricity: Electrical Sources
Queue Here for the Wilderness
The Killing Ground
Oil and Its Products
Ecology: The Silent Bomb
Problem Solvers

Employment Clearing House

Space in the Ballroom Foyer will be provided for employees to post job announcements and for conferees to file resumes. The Rocky Mountain Conference assumes no obligation for the confidentiality of information filed with the employment clearing house. the qualifications of job candidates. or the descriptions of jobs offered.

Message Center

Incoming telephone messages for conferees will be posted at the message center in the registration area. The telephone number is (303) 893-3333. ext. 339. Ask for the Rocky Mountain Conference message center. This service will be available from 8:00 a.m. to 4:30 p.m. Monday-Wednesday and from 8:00-10:00 a.m. on Thursday.

Speaker Preparation Room

The Birch room will be open Monday through Wednesday for speakers to organize and preview slides. A 35 mm projector will be available.

ORGANIZERS OF THE 28TH ROCKY MOUNTAIN CONFERENCE

Conference Chairperson - Robert Barkley, CIRES, Univ. of Colorado, Boulder, CO 80309-0449, (303) 492-1158.

Treasurer - Glenda Brown, Rockwell International, P.O. Box 464, Golden, CO 80401, (303) 966-7817.

Registration - Carol Gies, Rockwell International, P.O. Box 464, Golden, CO 80401, (303) 966-7380.

Exhibits - Vanessa Bush, Adolph Coors Co., Mail # BC600, Golden, CO 80401, (303) 277-6078.

Social Events - Greg Johnson, Adolph Coors Co., Mail #288, Golden, CO 80401, (303) 277-5961 and Larry Lockrem, Reservoirs Inc., 1827 Grant St., Denver, CO 80203, (303) 830-1986.

Short Courses/Film Festival - Carlos Arozarena, U.S. Geological Survey, 5293 Ward Rd., Arvada, CO 80002, (303) 236-5345.

Audio-Visual - John Garbarino, U.S. Geological Survey, 5293 Ward Rd., Arvada, CO 80002, (303) 236-3614.

SYMPOSIA CHAIRPERSONS

Atomic Spectroscopy - Thomas Niemczyk, Dept. of Chemistry, University of New Mexico, Albuquerque, NM 87131, (505) 277-5319.

Chromatography - Kenneth Brooks, School of Chem. Sci., 107 Chemistry Annex, University of Illinois, Urbana, IL 61801, (217) 333-6353.

Computer Applications - John Lanning, Dept. of Chemistry, Box 171, Univ. of Colo. at Denver, 1100 14th St., Denver, CO 80202, (303) 556-3203.

EPR - Gareth Eaton, Dept. of Chemistry, Univ. of Denver, Denver, CO 80208, (303) 871-2980 and Sandra Eaton, Dept. of Chemistry, Box 171, Univ. of Colo. at Denver, 1100 14th St., Denver, CO 80202, (303) 556-3204.

Environmental - Michael Reddy, U.S. Geological Survey, 5293 Ward Rd., Arvada, CO 80002, (303) 236-3617.

General Posters - Carlos Arozarena, U.S. Geological Survey, 5293 Ward Rd., Arvada, CO 80002, (303) 236-5345.

ICP/MS - Howard Taylor, U.S. Geological Survey, 5293 Ward Rd., Arvada, CO 80002, (303) 236-1928.

IR - Marvin Goldberg, U.S. Geological Survey, P.O. Box 25046, MS 424, Lakewood, CO 80225, (303) 236-4728.

Ion Chromatography - Frank Williams, Manville Service Corp., R&D Center, P.O. Box 5108, Denver, CO 80217, (303) 978-5595.

Mass Spectrometry - Paul Fennessey, Univ. of Colo. Health Sci. Ctr., 4200 E. 9th Ave., C-232, Denver, CO 80262, (303) 394-7286.

NIRA - Donald Burns, Technicon Instruments Co., 511 Benedict Ave., Tarrytown, NY 10591, (914) 631-8000.

NMR - James Haw, Dept. of Chemistry, Texas A&M University, College Station, TX 77843, (409) 845-1966 and Fran Miknis, Western Research Institute, Box 3395, University Station, Laramie, WY 82071, (307) 721-2307.

SYMPOSIUM ON ATOMIC SPECTROSCOPY

Organized by Thomas M. Niemczyk

Tuesday Morning, August 5

Spruce Room

T. M. Niemczyk, Presiding

8:45 1. **KEYNOTE SPEAKER**

RECENT ADVANCES IN THE USE OF ARRAY DETECTOR TECHNOLOGY FOR ATOMIC SPECTROSCOPY. M. Bonner Denton and Robert B. Bilhorn, University of Arizona, Tucson.

9:30 2. MERCURY DETERMINATION IN MULTI-ELEMENT ICP-AES, ROUTES TO INCREASED SENSITIVITY IN GEOLOGICAL ANALYSIS. T. L. Fries, P. J. Lamothe, K. D. Summerhays and A. Tewari, U.S. Geological Survey.

9:50 3. ANALYTICAL STATUS OF A PRACTICAL INDUCTIVELY COUPLED PLASMA-FOURIER TRANSFORM SPECTROMETER (ICP-FTS). M. W. Tikkanen, and M. W. Routh, Applied Research Laboratories.

10:10 **BREAK**

10:40 4. ANALYSIS OF ORGANIC SOLVENTS BY ICP EMISSION SPECTROMETRY. Danton D. Nygaard, Jack Roberts and David A. Leighty, Allied Analytical Systems.

11:00 5. DETERMINATION OF TRACE METALS IN SEMICONDUCTOR PROCESSING CHEMICALS. K. Fredeen, G. Carnrick, E. Pruszkowski and D. Yates, Perkin-Elmer Corporation.

11:20 6. THE SIMULTANEOUS DETERMINATION OF 19 MAJOR AND TRACE ELEMENTS IN GEOCHEMICAL SAMPLES BY ICP-AES. Liu Zen, Zhu Yong Ping, Ni Tong Wen, Testing Center of Gansu.

11:40 7. AN EVALUATION OF THE INTERFERENCE EFFECTS FOR SLURRY INJECTION OF GEOLOGICAL MATERIALS INTO AN ICP. I. B. Brenner and L. Halicz, Geological Survey of Israel.

Tuesday Afternoon, August 5

Spruce Room

D. Mehs, Presiding

1:30 8. SELENIUM IN BIOLOGICAL MATERIALS BY GFAAS AFTER CLOSED CELL MICROWAVE DIGESTION. Claude Veillon, K. Y.

Patterson and H. M. Kingston. Human Nutrition Research Center. USDA.

1:50 9. DETERMINATION OF MERCURY IN GEOLOGICAL MATERIALS BY CONTINUOUS-FLOW. COLD-VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY. J. G. Crock and K. R. Kennedy. U.S. Geological Survey.

2:10 10. REAL-LIFE ACCURACY OF BACKGROUND CORRECTION IN GRAPHITE FURNACE AAS. Z. Grobenski. R. Lehmann. B. Radziuk. and U. Vollkopf. Perkin-Elmer & Co. GmbH.

2:30 **BREAK**

3:00 11. GRAPHITE FURNACE AA: NEW APPROACHES TO MATRIX MODIFICATION. C. Voth-Beach. Varian Instrument Group. AARC.

3:20 12. FURNACE ATOMIC ABSORPTION SPECTROMETRY WITH DISPOSABLE CHARRING/ATOMIZATION SURFACE. Thomas W. Brueggemeyer. Fred L. Fricke and Carlos A. Bonnin. U.S. Food and Drug Administration.

3:40 13. COMPUTER ENHANCED AUTOMATIC METHODS DEVELOPMENT IN ATOMIC ABSORPTION SPECTROMETRY. F. M. Delles. D. Hoobin. Varian Instrument Group.

4:00 14. OPERATION AND PERFORMANCE OF A NEW COMPUTER-CONTROLLED FURNACE AA SYSTEM. Danton D. Nygaard. Jack Roberts and David A. Leighty. Allied Analytical Systems.

4:20 15. EVALUATION OF A HIGH RESOLUTION SPECTROMETER AND INTERNAL REFERENCES FOR DIRECT TRACE ELEMENT ANALYSIS OF TUNGSTEN POWDERS. S. Erlich and I. B. Brenner. Geological Survey of Israel.

4:40 16. MODERNIZATION OF A SPECTOGRAPHIC DARKROOM. Manuel E. Quintana and Charles T. Apel. Los Alamos National Laboratory.

Wednesday Morning. August 6

Spruce Room

T. M. Niemczyk. Presiding

8:45 17. **KEYNOTE SPEAKER**

SEGREGATED DISCHARGES: A NEW LOOK AT SOME OLD SPECTROSCOPIC TOOLS. David M. Coleman. Wayne State University.

9:30 18. CHARACTERIZATION OF BOUNCE AND EFFICIENCY IN A SINGLE-STAGE INERTIAL IMPACTOR UTILIZING A GRAPHITE FURNACE AS THE COLLECTION SUBSTRATE. K. H.

Dewhurst, D. R. Parker, Y. S. Cheng and T. M. Niemczyk, University of New Mexico.

9:50 19. TWO GEOLOGICAL SAMPLE PREPARATION TECHNIQUES USING LABORATORY ROBOTICS. Paul H. Briggs and S. A. Wilson, U.S. Geological Survey.

10:10 **BREAK**

10:40 20. AUTOMATED DETERMINATION OF TRANSITION METALS IN BRINES AND OTHER IONIC MATRICES. R. B. Rubin and L. Henry, Dionex Corporation.

11:00 21. CHEMICAL AND EXCITATIONAL CHARACTERIZATION OF NITROGEN SOURCES FOR METASTABLE TRANSFER EMISSION SPECTROSCOPY. Hwei-Chen Yang and T. M. Niemczyk, University of New Mexico.

11:20 22. INTERFEROMETRIC/SCHLIEREN OBSERVATION OF MAGNETICALLY-INFLUENCED SPARK DISCHARGES. David M. Coleman, Wu-hwa Hsu, and Vahid Majidi, Wayne State University.

11:40 23. THE CHARACTERISTICS OF A LOW POWER N_2-AR ICP FOR MULTIELEMENT ANALYTICAL EMISSION SPECTROMETRY. S. Erlich and I. B. Brenner, Geological Survey of Israel.

SYMPOSIUM ON CHROMATOGRAPHY

Organized by Kenneth C. Brooks

Tuesday Morning, August 5

Colorado Room

LIQUID CHROMATOGRAPHY

T. J. Wenzel, Presiding

8:10 Opening Remarks

8:15 24. PHOTOCHEMICAL AMPLIFIER FOR DETECTION IN HPLC. Curtis Shellum and John W. Birks, University of Colorado, Boulder.

8:40 25. PHOTOCHEMICAL REACTION - DETECTION OF ANTHRAQUINONES AND NAPHTHOQUINONES IN HPLC. James R. Poulsen and John W. Birks, University of Colorado, Boulder.

9:05 26. THE USE OF TERBIUM(III) AND EUROPIUM(III) AS LUMINESCENT CHROMOPHORES FOR LIQUID CHROMATOGRAPHIC DETECTION. Thomas J. Wenzel and Elsie E. DiBella, Bates College.

9:30 **BREAK**

10:00 27. **PLENARY LECTURE**
A RATIONAL APPROACH TO THE DESIGN OF CHIRAL STATIONARY PHASES FOR ENTANTIOMER SEPARATION. William H. Pirkle, Thomas C. Pochapsky and Daniel S. Reno. University of Illinois, Urbana - Champaign.

11:00 28. LIQUID CHROMATOGRAPHIC SEPARATION OF CR-BETA-DIKETONATES WITH SYSTEMATICALLY MODIFIED LIGANDS. Peter Schultze and Bernd W. Wenclawiak. University of Toledo.

11:25 29. REVERSED PHASE POLYMERS FOR HPLC. James R. Benson, Douglas MacBlane and Naotaka Kitagawa. Interaction Chemicals, Inc.

Tuesday Afternoon, August 5

Colorado Room

GAS AND SUPERCRITICAL FLUID CHROMATOGRAPHY
B. Wenclawiak, Presiding

1:15 30. CHROMATOGRAPHIC DETERMINATION OF TOTAL NITROGEN FOLLOWING KJELDAHL OXIDATION. S. Moldoveanu. Dowell Schlumberger.

1:40 31. SUPERCRITICAL FLUID JET EXPANSIONS USING A SHEATH FLOW NOZZLE. Bruce D. Anderson and Murray V. Johnston. University of Colorado, Boulder.

2:05 32. DIFFERENT MODES OF DENSITY CHANGES IN CAPILLARY SUPERCRITICAL FLUID CHROMATOGRAPHY OF OIL AND GAS SAMPLES. Bernd W. Wenclawiak. University of Toledo.

2:30 **BREAK**

3:00 33. SUPERSONIC JET SPECTROSCOPY WITH A CAPILLARY GAS CHROMATOGRAPHIC INLET. Steven W. Stiller and Murray V. Johnston. University of Colorado, Boulder.

3:25 34. THE REDOX CHEMILUMINESCENCE DETECTOR: HOW DOES IT WORK? S. A. Montzka, R. M. Barkley and R. E. Sievers. University of Colorado, Boulder.

3:50 35. DEVELOPMENTS IN REDOX CHEMILUMINESCENCE DETECTION. R. L. Shearer and R. E. Sievers. University of Colorado, Boulder.

4:15 36. THE ANALYSIS OF OXYGENATES BY THE REDOX CHEMILUMINESCENCE DETECTOR FOR GC. R. S. Hutte and R. E. Sievers. Sievers Research, Inc.

Wednesday Morning, August 6

Colorado Room

APPLICATIONS OF CHROMATOGRAPHY

K. C. Brooks, Presiding

8:15 37. DETERMINATION OF STRYCHNINE IN TISSUE SAMPLES USING REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY. J. N. Gillis, S. R. Kilburn, D. L. Meeker, and C. F. Utter, U.S. Department of Agriculture.

8:40 38. HYDROLYSIS OF SAMPLES FOR AMINO ACID ANALYSIS USING MICROWAVE DIGESTION. E. J. Dorward-King, C. M. Calvert, E. M. Emery, Monsanto Company.

9:05 39. APPLICATION OF AQUEOUS SIZE EXCLUSION CHROMATOGRAPHY TO OIL-FIELD POLYMERS. G. R. McGowan and G. W. Hawkins, Dowell Schlumberger.

9:30 40. ADSORPTION ON THE SURFACE OF ICE. R. A. Sommerfeld and D. Lamb, Rocky Mountain Forest and Range Experimental Station.

9:55 **BREAK**

10:30 CHROMATOGRAPHY POSTERS

Convention Lobby

Authors present 10:30-11:45.

42. CONFIRMATION OF ZERANOL/ZEARALENONE RESIDUES BY GC/MS. W. J. Morris, J. E. Roybal and W. Shimoda, U.S. Food and Drug Administration.

43. DETERMINATION OF DIMETRIDAZOLE/IPRONIDAZOLE METABOLITES IN ANIMAL TISSUE BY GC. M. C. Pullano and C. Andres Geisler, U.S. Food and Drug Administration.

44. CONFIRMATION OF TETRACYCLINE RESIDUES IN ANIMAL FEEDS BY HPLC/UV AND TLC. E. E. Martinez and W. Shimoda, U.S. Food and Drug Administration.

45. A MULTIRESIDUE METHOD FOR BETA-LACTAM ANTIBIOTICS IN MILK AND TISSUE BY HPLC. R. K. Munns and W. Shimoda, U.S. Food and Drug Administration.

47. HIGH PRESSURE LIQUID CHROMATOGRAPHIC-ELECTROCHEMICAL DETERMINATION OF ZERANOL/ZEARALENONE AND THEIR METABOLITES IN EDIBLE ANIMAL TISSUE. J. E. Roybal, R. K. Munns, J. A. Hurlbut, W. J. Morris, and W. Shimoda, U.S. Food and Drug Administration.

48. DETECTION OF SELECTED VETERINARY DRUGS BY HPLC USING ELECTROCHEMICAL DETECTION. J. A. Hurlbut, J. E. Roybal, R. K. Munns, E. E. Martinez, W. J. Morris, and W. Shimoda, U.S. Food and Drug Administration.

SYMPOSIUM ON COMPUTER APPLICATIONS

Organized by John A. Lanning

Wednesday Morning, August 6

Cedar Room

J. A. Lanning, Presiding

8:30 Opening Remarks

8:35 49. FT SPECTRAL DECONVOLUTION IN 1-DIMENSIONAL EPR IMAGING. Martin M. Maltempo, University of Colorado at Denver.

9:05 50. MICROCOMPUTERS APPLIED TO NMR DATA PROCESSING. James W. Cooper, IBM Instruments, Inc.

9:30 51. THE COMPUTER NETWORKING AND WORKSTATION ENVIRONMENT IN NMR. David W. Mehaffy, IBM Instruments, Inc.

9:55 **BREAK**

10:15 52. PHOTOACOUSTIC SPECTROSCOPY APPLIED TO WHOLE COLUMN DETECTION. Kathy Rowlen, James P. Avery, and John W. Birks, University of Colorado.

10:40 53. **PLENARY LECTURE**
ROLE OF COMPUTERS IN THE DESIGN OF ANALYTICAL INSTRUMENTATION. James P. Avery, University of Colorado.

Wednesday Afternoon, August 6

Cedar Room

J. A. Lanning, Presiding

1:30 54. EXPLORATORY CHEMOMETRIC TECHNIQUES APPLIED TO ANALYTICAL DATA. Robert J. Sistko, University of Colorado, Denver.

2:05 55. THE APPLICATION OF PATTERN RECOGNITION IN CHARACTERIZATION OF SOLID PRODUCTS IN AUTOXIDATION OF HYDROCARBON MIXTURES. Kaveh Zarrabi and Stephen R. Daniel, Colorado School of Mines.

2:30 56. APPLICATION OF AN INTEGRATED SOFTWARE SYSTEM FOR PROCESSING OF ANALYTICAL DATA. R. Manabe. M. Borlaug. O. Camia. and J. Sotera. Allied Analytical Systems.

2:55 **BREAK**

3:15 57. LANGUAGE CONSIDERATIONS FOR WRITING A CUSTOM LIMS. Richard Hardenstein. General Government Computer Center.

3:35 58. MICROCOMPUTER BASED LABORATORY INFORMATION MANAGEMENT SYSTEMS (LIMS). Ron Fuller. Core Laboratories.

4:00 59. DESIGNING A CUSTOM LIMS FOR A HIGH VOLUME LABORATORY ON AN IBM PC. Richard Hardenstein. General Government Computer Center.

4:20 60. BARCODE AS A KEY ELEMENT FOR LIMS EFFICIENCY. Richard Hardenstein. General Government Computer Center.

9th INTERNATIONAL SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

Organized by Gareth R. Eaton and Sandra S. Eaton

Monday Morning. August 4

Gold Room

Session I-METAL IONS IN BIOLOGICAL SYSTEMS
G. R. Eaton. Presiding

8:30 61. Opening Remarks

8:35 **PLENARY LECTURE**
ENDOR STUDIES OF METALLOENZYME ACTIVE-SITE STRUCTURE AND FUNCTION. Brian M. Hoffman. Northwestern University.

9:30 62. EPR STUDIES OF THE ROLE OF NON-HEME IRON IN OXYGENASES. Betty Jean Gaffney. D. V. Mavrophilipos. A. S. Yang. and Leslie M. Bloom. The Johns Hopkins University.

10:00 **BREAK**

10:30 63. **PLENARY LECTURE**
EPR SATURATION STUDIES OF METAL ION CENTERS IN PROTEINS AND ENZYMES. Marvin W. Makinen. The University of Chicago.

11:30 64. PULSED ELECTRON PARAMAGNETIC RESONANCE STUDIES OF COPPER BINDING SITES IN AMINE OXIDASES. J.

McCracken. D. Dooley. and J. Peisach. Albert Einstein College of Medicine.

Monday Afternoon. August 4

Gold Room

Session II
L. Kispert. Presiding

1:30 65. SPIN LABEL STUDIES OF THE ACTIVE SITES OF AMINE OXIDASES. Frederick T. Greenaway. Peter Spacciapoli and Coleen M. Young. Clark University.

1:55 66. CW AND PULSED EPR STUDIES OF CYCLIC DIPEPTIDE Cu(II) COMPLEXES. M. Crowder. J. McCracken. J. Peisach. and S. Kubota. IBM Instruments. Inc.

2:25 67. ELECTRON SPIN ECHO AND SATURATION TRANSFER EPR STUDIES OF POLYMER STATE SICKLE HEMOGLOBIN. Michael E. Johnson. Leela Kar. P. Thiyagarajan and Michael K. Bowman. University of Illinois. Chicago.

2:50 **BREAK**

3:20 68. REACTION YIELD DETECTED MAGNETIC RESONANCE (RYDMR) AND MAGNETO-OPTICAL DIFFERENCE SPECTROSCOPY (MODS) OF PHOTOSYNTHETIC REACTION CENTERS. A. J. Hoff. Huygens Laboratory of the State University. The Netherlands.

3:40 69. SPIN-LABELLED 8-HYDROXYQUINOLINE. J. E. Oakdale. C. E. Moore. C. M. Brodbeck. and H. L. Murray. Loyola University of Chicago.

4:00 70. ELECTRON SPIN RESONANCE AND ELECTRON SPIN ECHO STUDIES OF Rh(II) SPECIES IN X AND Y ZEOLITES. Daniella Goldfarb. and Larry Kevan. University of Houston.

4:20 71. CONDUCTING PROPERTIES AND ELECTRON SPIN RESONANCE OF POLYPHENOTHIAZINE AND POLYPHENOXAZINE. M. D. Pace and O.-K. Kim. Naval Research Laboratory.

4:40 72. EPR STUDY OF PHASE TRANSITIONS IN $NH_4Pr(SO_4)_2 \cdot 4H_2O$ MONOCRYSTALS. V. M. Malhotra. R. Chatterjee. H. A. Buckmaster. and W. R. M. Graham. Southern Illinois University.

Tuesday Morning, August 5

Gold Room

Session III-EPR UNDER EXTREME CONDITIONS
I. B. Goldberg, Presiding

8:30 73. USE AND ABUSE OF MICROWAVE EQUIPMENT IN THE NAME OF SCIENCE. Ira B. Goldberg, Rockwell International Science Center.

8:50 74. ELECTRON PARAMAGNETIC RESONANCE AT HIGH PRESSURE USING A DIAMOND ANVIL CELL. Nobuko Sakai and Joe H. Pifer, Rutgers University.

9:30 **BREAK**

10:40 75. QUANTITATIVE STUDIES OF RADICAL DYNAMICS IN LIQUID JETS. David M. Bartels and Alexander D. Trifunac, Argonne National Laboratory.

11:20 76. APPLICATION OF A HIGH-PRESSURE-HIGH TEMPERATURE ESR CAVITY TO THE STUDY OF ENERGETIC REACTIONS. Ted M. McKinney and Ira B. Goldberg, Rockwell International Science Center.

Tuesday Afternoon, August 5

Gold Room

Session IV-SPIN LABELING
G. A. Coulter, Presiding

1:30 77. A SPIN-LABELLED ELECTRODE. K. di Gleria, H. A. O. Hill, D. J. Page, and D. G. Tew, University of Oxford, England.

2:00 78. MEASUREMENT OF ROTATIONAL MOLECULAR MOTION BY SATURATION RECOVERY EPR. P. Fajer, J. Feix, J. Hyde, and D. Thomas, Univ. of Minnesota.

Session V-POSTERS

Convention Lobby

S. S. Eaton, Presiding

Author present 3:00-4:00 for papers labeled A
Author present 4:00-5:00 for papers labeled B

A 79. ESR, ENDOR, AND TRIPLE RESONANCE STUDY OF RADICALS FORMED FROM 9,10-ANTHRAQUINONESULFONATES AND 2-METHYLANTHRAQUINONE IN SOLUTION. R. Makela and M. Vuolle, University of Jyvaskyla, Finland.

A 80. ESR AND ENDOR STUDY OF PHOTO OXIDATION OF PORPHYRINS. S. Stepanovich and H. van Willigen, University of Massachusetts at Boston.

A 81. AN ELECTRON SPIN RESONANCE INVESTIGATION OF RADICAL INTERMEDIATES IN CHOLESTEROL. Cynthia L. Sevilla, David Becker and Michael D. Sevilla, Oakland University, MI.

B 82. EFFECT OF CHOLESTEROL ON THE TRANSPORT OF A COPPER SQUARE PLANAR COMPLEX IN MEMBRANES. W. K. Subczynski, W. E. Antholine, and J. S. Hyde, National Biomedical ESR Center.

A 83. ESR OF CUPRIC HISTIDINE COMPLEXES IN THE LIQUID PHASE. M. Pasenkiewicz, W. Froncisz, R. Basosi, W. E. Antholine, and J. S. Hyde, Medical College of Wisconsin.

B 84. EPR AND SPECTROSCOPIC STUDIES OF CONFIGURATIONAL CHANGES IN COPPER(II) COMPLEXES OF 1,4-DIAZACYCLOHEPTANE. M. S. Hussain and J. S. Hwang, University of Petroleum and Minerals, Saudi Arabia.

A 85. EPR STUDIES ON THE REACTION BETWEEN NITROSYLHEMOGLOBIN AND OXYGEN: A COMPARISON OF IN VITRO AND IN VIVO NO-EXPOSURE. K. Kon, N. Maeda, and T. Shiga, Ehime University, Japan.

B 86. SUPERHYPERFINE COUPLINGS IN VANADYL COMPLEXES WITH S-ADENOSYLMETHIONINE SYNTHETASE. G. D. Markham, The Institute for Cancer Research PA.

A 87. A pH-DEPENDENT EQUILIBRIUM AROUND IRON IN LIPOXYGENASE. D. V. Mavrophilipos and B. J. Gaffney, The Johns Hopkins University, MD.

B 88. BINDING STUDIES OF TRANSITION METALS WITH BISDIOXOPIPERAZINE ANTITUMOR AGENTS AND THEIR HYDROLYSIS PRODUCTS. George C. Yang, Eugene H. Herman, and Antoine N. El-Hage, Food and Drug Administration.

A 89. DETECTION OF ISOLATED AND PAIRED Cu(II) IONS IN NAFION MEMBRANES BY ESR SPECTROSCOPY. S. Schlick and M. G. Alonso-Amigo. University of Detroit.

B 90. EPR OF MEDIUM MOLECULAR WEIGHT CLUSTER COMPOUNDS. G. Kokoszka. D. Palahnuk. and A. Siedle. SUNY. Plattsburgh. NY.

A 91. TEMPERATURE DEPENDENCE OF THE ZERO-FIELD SPLITTING PARAMETERS OF Ni(II) AND Mn(II) IN $ZnSiF_6 \cdot 6H_2O$ AND $ZnSiF_6 \cdot 6D_2O$. John E. Drumheller. Stuart L. Hutton. and R. S. Rubins. Montana State University.

B 92. EPR SPECTRA OF MANGANESE IN MgO POWDERS. S. Eidels-Dubovoi and V. Beltran-Lopez. Instituto Mexicano del Petroleo.

A 93. EPR AND RESONANT CAVITY MEASUREMENTS OF FREE ELECTRONS AND METASTABLE N ATOMS PRODUCED IN $He-N_2$ MICROWAVE DISCHARGE. E. Lopez-Moreno and V. Beltran-Lopez. Universidad Nacional Autonoma de Mexico.

B 94. MAGNETIC RESONANCE STUDIES OF SOLID BARIUM TITANATE. C. E. Forbes. W. B. Hammond. and N. Cipollini. Celanese Research Company.

A 95. MAGNETOHYDRODYNAMICS OF NEMATIC MESOPHASES BY ESR. Michael Eastman. Bassam Freiha. Thomas Mayhew. Minn-Liang Horng. University of Texas at El Paso.

B 96. ESR OF DISCOTIC LIQUID CRYSTALS CONTAINING Cu(II). Michael Eastman. Minn-Liang Horng and Bassam Freiha. University of Texas at El Paso.

A 97. EPR STUDY OF PHOSPHORUS CENTERED RADICALS TRAPPED IN AN X-IRRADIATED SINGLE CRYSTAL OF A PHENOXYPHOSPHORYL XYLOFURANOSE DERIVATIVE. Alice Celalyan-Berthier. Theo Berclaz. and Michel Geoffroy. University of Geneva. Switzerland.

B 98. EPR STUDY OF THE ORIENTED $[C_2Cl_6]^-$ RADICAL IN X-RAY IRRADIATED HEXACHLOROETHANE SINGLE CRYSTALS: AN ON-LINE ANALYSIS. Lowell D. Kispert. Kenneth G. Ezell. Joy Joseph. and Eric Bradford. University of Alabama.

A 99. PROTON COUPLING CONSTANT EXTRACTION: A FAST METHOD FOR ANALYZING ESR SPECTRA BY COMPUTER. A. G. Motten. D. R. Duling. and J. Schreiber. Duke University.

B 100. APPLICATION OF LOOP-GAP RESONATORS TO NUCLEAR MAGNETIC RESONANCE IMAGING AND SPECTROSCOPY. W. Froncisz. Andrzej Jesmanowicz. Thomas M. Grist. J. Bruce Kneeland. and James S. Hyde. Jagiellonian University. Poland.

A 101. FERROMAGNETIC GRADIENT PRODUCING DEVICES. J. P. Hornak. Rochester Institute of Technology.

B 102. SPECTRAL AND SPATIAL COMPONENTS IN ONE DIMENSIONAL EPR IMAGING. Martin M. Maltempo. University of Colorado. Denver.

A 103. APPLICATION OF L-BAND ESR TECHNIQUES TO IN VIVO ANALYSIS. T. Ogata. M. Ono. E. Yoshida. and H. Kamada. Yamagata University. Japan.

B 104. A RADIO FREQUENCY ELECTRON SPIN RESONANCE SPECTROMETER FOR IN VIVO IMAGING. H. J. Halpern. D. Spencer. B. A. Teicher. A. C. Nelson. R. J. Massoth. and M. K. Bowman. University of Chicago Medical Center.

A 105. DEVELOPMENT OF A LOOP-GAP RESONATOR AND A SURFACE COIL WITH AN ELECTRIC SHIELD. M. Ono. T. Ogata. Kou-Chang Hsieh. M. Suzuki. E. Yoshida and H. Kamada. Yamagata University. Japan.

Wednesday Morning. August 6

Gold Room

Session VI-SPIN LABELING AND SPIN TRAPPING
G. A. Coulter. Presiding

8:30 106. **PLENARY LECTURE**
NITROXYL RADICALS AS INTERMEDIATES IN THE ELECTRON TRANSFER BETWEEN CARBON-CENTERED RADICALS AND NITROAROMATICS. S. Steenken. Max-Planck-Institut fur Strahlenchemie.

9:25 107. STIMULATED HUMAN NEUTROPHILS LIMIT HYDROXYL RADICAL FORMATION AS DETECTED BY ESR: INVESTIGATION OF THE ROLE OF NEUTROPHIL LACTOFERRIN. G. M. Rosen. B. E. Britigan. Y. Chai. B. Y. Thompson. and M. S. Cohen. Duke University.

9:50 108. SPIN-TRAPPING METABOLICALLY FORMED FREE RADICAL PRODUCTS FROM HALOGENATED HYDROCARBONS. J. L. Poyer. Walter H. Massion. and Paula Downs. Oklahoma Medical Research Foundation.

10:15 **BREAK**

10:45 109. SPIN-TRAP HPLC AND RESOLUTION-ENHANCED ESR STUDIES ON ORGANIC FREE RADICALS PRODUCED FROM ELECTRODE-SURFACE REACTIONS. H. Hatano. S. Okazaki. A. Naito. T. Nagaoka. and K. Nozaki. Kyoto University.

11:10 110. A DIRECT EVIDENCE FOR THE RADICAL PAIR MODEL IN A MAGNETIC FIELD-DEPENDENT PHOTOREACTION. M. Okazaki, S. Sakata, R. Konaka, and T. Shiga, Ehime University, Japan.

11:35 111. ESR IN MICROBIAL TECHNOLOGY. B. Kalyanaraman, P. J. Kersten, M. Tien, K. E. Hammel and T. K. Kirk, Medical College of Wisconsin.

Wednesday Afternoon, August 6

Convention Lobby

Session VII-POSTERS: SPIN LABELING AND SPIN TRAPPING

S. S. Eaton, Presiding

Author present 2:00-3:00 for papers labeled C.
Author present 3:00-4:00 for papers labeled D.

C 112. MEDIUM EFFECTS ON HYDROGEN BONDING OF SOLVENTS WITH NITROXIDES. I. Bala'a and R. D. Bates, Jr., Georgetown University.

D 113. SPIN LABEL EPR STUDIES OF SICKLE CELL MEMBRANES. Leslie Wo-Mei Fung and David P. Chan, Loyola University of Chicago.

C 114. ACTIVATION AND REVERSIBLE COVALENT MODIFICATION OF BOVINE LIVER FRUCTOSE 1,6 BISPHOSPHATASE BY DISULFIDE-THIOL EXCHANGE: CONFORMATIONAL CHANGES IN THE REGION OF THE ESSENTIAL CYSTEINE RESIDUE OBSERVED BY MEANS OF SPIN LABEL. Henry M. Zeidan, Atlanta University.

D 115. EPR SPECTROSCOPIC EVIDENCE FOR SPATIALLY SEQUENTIAL AMIDE BOND FORMATION IN PLANT POLYGALACTOPYRANURONIDES. Peter I. Irwin and Michael D. Sevilla, Oakland University, MI.

C 116. BINDING OF MANGANESE TO SPIN-LABELED SARCOPLASMIC RETICULUM VESICLES. L. Fielding and C. Coan, University of the Pacific.

D 117. EPR SPECTRA OF SPIN-LABELED PYRIDINES COORDINATED TO CHROMIUM(III) TETRAPHENYLPORPHYRIN CHLORIDE (S=3/2). K. M. More, G. R. Eaton, and S. S. Eaton, University of Denver.

C 118. AN ENDOR STUDY OF MOLECULAR GEOMETRY OF SPIN-LABELED COMPOUNDS IN FROZEN SOLUTION. Gregg B. Wells, and Marvin W. Makinen, University of Chicago.

D 119. STRUCTURE-FUNCTION RELATIONSHIPS IN F_1-ATPase AND DEHYDROGENASES AS STUDIED BY SPIN-LABELED NUCLEOTIDES. I. G. Atchatchloui. S. Fleischer. C. Karim. J. O. *McIntyre. R. Mink. J. H. Park. B. Rudy. R. Vogel. J. Wiese.* and W. E. Trommer. University of Kaiserslautern. West Germany.

C 120. TIME RESOLVED IN SITU RADIOLYSIS ESR STUDIES OF SPIN TRAPPING. Hitoshi Taniguchi. Keith P. Madden. and Richard W. Fessenden. University of Notre Dame.

D 121. PHOTOLYSIS OF PHEOMELANIN PRECURSORS: AN ELECTRON SPIN RESONANCE-SPIN TRAPPING STUDY. Barbara Pilas. Christopher C. Felix. Tadeusz Sarna. and B. Kalyanaraman. Medical College of Wisconsin.

C 122. SPIN TRAPPING WITH α-2.4.6-TRIMETHOXYPHENYL N-TERT-BUTYL NITRONE. Coit M. DuBose and Edward G. Janzen. Oklahoma Medical Research Foundation.

D 123. EPR STUDY OF HYDROGEN PEROXIDE PRODUCING OXIDASES. Y. Sakagishi. T. Hanada. M. Sonoda. and K. Yamanishi. Saitama Medical School. Japan.

C 124.

D 125. THE SPIN TRAPPING CHEMISTRY OF CARBON TETRACHLORIDE IN RAT LIVER MICROSOMES. Rheal A. Towner and Edward G. Janzen. University of Guelph.

C 126. THE LOCATION OF SPIN TRAPS IN MICELLAR SOLUTIONS AS DETERMINED BY HIGH FIELD NMR SPECTROSCOPY. James Hilborn. *D. Larry Haire. Henry J. Stronks. Gregory A. Coulter* and Edward G. Janzen. University of Guelph.

D 127. GC/MS ANALYSIS OF TRIMETHYLSILYLATED SPIN ADDUCTS. Peter Krygsman. D. Larry Haire and Edward G. Janzen. University of Guelph.

C 128. ENDOR SPECTRA OF SPIN ADDUCTS. D. Larry Haire. Yashige Kotaka. Uwe M. Oehler and Edward G. Janzen. University of Guelph.

D 129. ENDOR SPECTRA OF ACYL AMINOXYLS. Uwe M. Oehler and Edward G. Janzen. University of Guelph.

Session VIII-DISCUSSION OF TECHNIQUES IN SPIN LABELING AND SPIN TRAPPING.
G. A. Coulter. presiding

Gold Room

4:00

Wednesday Evening. August 6

Open House at the University of Denver Magnetic Resonance Laboratory.

Thursday Morning. August 7

Columbine Room

Session IX
G. R. Eaton. Presiding

8:30 130. SPECTRAL ROTATION IN PULSED ESR SPECTROSCOPY. J. P. Hornak and J. H. Freed. Rochester Institute of Technology.

9:00 131. FOURIER TRANSFORM ESR: TWO DIMENSIONAL ESR OF NITROXIDES. Jeffrey P. Gorcester and Jack H. Freed. Cornell University.

9:45 **BREAK**

10:05 132. TIME-RESOLVED FOURIER TRANSFORM EPR OF FREE RADICAL REACTIONS. M. K. Bowman. R. J. Massoth. and A. G. Kostka. Argonne National Laboratory.

10:50 133. SENSITIVE EPR OBSERVATION BY USING A COMPUTERIZED SPECTRUM ANALYZER. H. Ohya-Nishiguchi. Kyoto University.

11:10 134. STIMULATED QUANTUM BEATS IN MAGNETIC RESONANCE. R. D. Kendrick and C. S. Yannoni. IBM Almaden Research Center.

Thursday Afternoon. August 7

IBM Instruments EPR User's Group Meeting.

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

Organized by Michael M. Reddy

Tuesday Morning, August 5

Denver Room

V. Janzer, Presiding

8:30 135. DETERMINATION OF ENVIRONMENTAL URANIUM EMISSIONS BY LIQUID SCINTILLATION ALPHA COUNTING. C. R. Beverly, Martin Marietta Energy Systems.

9:00 136. PRECONCENTRATION AND DETERMINATION OF AQUATIC SULFIDE. Dennis DeSalvo, and Kenneth W. Street, Jr., Kent State University.

9:30 137. THE DETERMINATION OF PPB LEVEL SULFIDES IN TURBID WATERS BY GAS DIALYSIS/ION CHROMATOGRAPHY. L. R. Goodwin, D. Francom, and F. P. Dieken, Alberta Environmental Centre.

10:00 **BREAK**

10:45 138. **KEYNOTE SPEAKER**
ENVIRONMENTAL ANALYSES WITH GRADIENT ION CHROMATOGRAPHY - THE NEW DIMENSION. Arthur W. Fitchett, Dionex Corporation.

Tuesday Afternoon, August 5

Denver Room

M. Werner, Presiding

2:00 139. A QUALITY ASSURANCE PROGRAM FOR THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM AND NATIONAL TRENDS NETWORK. Myron H. Brooks, LeRoy J. Schroder, and Timothy C. Willoughby, U.S. Geological Survey.

2:30 140. AN INDIVIDUAL WATER SAMPLE QUALITY ASSURANCE PROGRAM. Richard D. Robinson, Daryl Knab and Daniel R. Perrin, Los Alamos National Laboratory.

3:00 141. STABILITY OF NITRATE IN PRESERVED AND UNPRESERVED NATURAL SURFACE WATERS. F. X. Suarez, D. C. Hillman and E. M. Heithmar, Lockheed Engineering and Management Services Company, Inc.

3:30 **BREAK**

4:00 142. DEVELOPMENT OF NATURAL MATRIX STANDARDS FOR USE IN THE ANALYSIS OF ENVIRONMENTAL MATERIALS. T. E. Gills. National Bureau of Standards.

4:30 143. DETECTION LIMITS FOR ENVIRONMENTAL SAMPLES. James L. Robinson. U.S. Environmental Protection Agency.

Wednesday Morning. August 6

Denver Room

R. See. Presiding

8:00 144. THE DETERMINATION OF AVAILABLE ARSENIC (III) AND ARSENIC (V) IN STREAM SEDIMENTS. Walter H. Ficklin. U.S. Geological Survey.

8:30 145. DETERMINATION OF TRACE TRANSITION METALS AND ORGANICS IN SEAWATER AND BRACKISH ESTUARINE WATER BY MATRIX ELIMINATION - A COMPARISON OF CLOSED AND OPEN MARINE SYSTEMS. M. C. McKay and S. Stone. Dionex Corporation.

9:00 146. INVESTIGATION OF SELENIUM AND OTHER TRACE ELEMENTS IN SOILS FROM THE SAN JOAQUIN VALLEY OF CENTRAL CALIFORNIA. Stephen Wilson. Ron Tidball. D. Brooke Hatfield and Paul Briggs. U.S. Geological Survey.

9:30 **BREAK**

10:15 147. **KEYNOTE SPEAKER**
RECENT ADVANCES IN FURNACE ATOMIC ABSORPTION SPECTROSCOPY. Glen R. Carnick and Walter Slavin. Perkin-Elmer Corporation.

Wednesday Afternoon. August 6

Denver Room

C. Rostad. Presiding

12:30 148. CHANGES IN STRATOSPHERIC OZONE CHEMISTRY RESULTING FROM A NUCLEAR WAR. Sherry L. Stephens. John W. Birks. Michel Rossi. and David Golden. University of Colorado at Boulder.

1:00 149. SOURCES. TRANSPORT. AND PHOTOCHEMICAL PRODUCTION OF ORGANIC COMPOUNDS IN ATMOSPHERIC AEROSOL PARTICLES. P. R. Veltkamp. R. C. Greaves. R. E. Sievers. R. M. Barkley. and R. R. Meglen. University of Colorado at Boulder.

1:30 150. A THEORETICAL ASSESSMENT OF POLLUTANT DEPOSITION TO INDIVIDUAL LAND TYPES DURING A REGIONAL SCALE ACID DEPOSITION EPISODE. Chris J. Walcek. National Center for Atmospheric Research.

2:00 151. A COMPARISON OF TWO MODELS LINKING CHLORINE CHEMISTRY WITH ANTARCTIC OZONE DEPLETIONS. Scott Elliott and F. S. Rowland. University of California. Irvine.

2:30 152. FORMATION OF HUMIC ACID-LIKE SUBSTANCES FROM NON-TRADITIONAL PRECURSORS. Kaveh Zarrabi. Wen-Chia Chen and James A. Rice. Colorado School of Mines. Golden.

3:00 **BREAK**

3:30 153. MULTIRESIDUE DETERMINATION OF CORN PRODUCTION PESTICIDES BY CAPILLARY GLC. T. D. Spittler. J. B. Bourke. D. L. Snook. H. C. Leichtweis. Cornell University.

4:00 154. ACID-NEUTRAL CONTINUOUS LIQUID-LIQUID EXTRACTION OF EPA PRIORITY POLLUTANT AND HAZARDOUS SUBSTANCE LIST COMPOUNDS. Joseph L. Slayton. and E. Ramona Trovato. U.S. Environmental Protection Agency.

GENERAL POSTERS

Organized by Carlos E. Arozarena

Monday Afternoon, August 4

Convention Lobby

C. Arozarena, Presiding

Authors will be present from 2:00-3:00 pm.

155. INFRARED DETERMINATION OF POLYMERIC SEIZING AGENTS ON COTTON YARNS. Nancy M. Morris and Jerry P. Moreau, U.S. Department of Agriculture.

156. EXTENDED CALIBRATION CURVES AND EXCITATION AND EMISSION SPECTRA FOR STUDYING THE LUMINESCENCE OF BENZO(f)QUINOLINE ADSORBED ON SILICA GEL. G. J. Burrell and R. J. Hurtubise, University of Wyoming.

157. STABILITY OF pH AND DIC IN SEALED SYRINGE SAMPLES. E. M. Burke, D. C. Hillman, Lockheed Engineering and Management Services Company, Inc.

158. CHEMICAL AND BIOLOGICAL STUDIES OF DRINKING WATER SOURCES OF WESTERN ILLINOIS RURAL COMMUNITIES. Robert E. Neas, Te-Hsiu Ma, Charlotte Cook and Mary Harris, Western Illinois University.

159. ANALYSIS OF VOLATILE PRIORITY POLLUTANTS BY CAPILLARY GAS CHROMATOGRAPHY. N. H. Mosesman, R. J. Bartram, L. M. Sidisky and J. Brown, Supelco, Inc.

160. NON-DESTRUCTIVE ANALYSIS OF PLUTONIUM BEARING SAMPLES BY CALORIMETRY AND GAMMA SPECTROSCOPY. Barbara M. Hardin and Noralynn J. Caduff, Rockwell International.

161. BEYOND THE ONE HUNDRED PERCENT LINE: A SIMPLE METHOD FOR DETECTING LOW LEVEL ARTIFACTS IN FT-IR SPECTROMETERS. J. J. Raflako and T. Davidson, Celanese Research Company.

162. ANALYTICAL ROOM-TEMPERATURE LUMINESCENCE FROM COMPOUNDS ADSORBED ON A α-CYCLODEXTRIN-NaCl MIXTURE. J. M. Bello and R. J. Hurtubise, Univerity of Wyoming.

163. EFFECT OF TEMPERATURE ON THE LUMINESCENCE PROPERTIES OF p-AMINOBENZOIC ACID ADSORBED ON SODIUM ACETATE. S. M. Ramasamy and R. J. Hurtubise.

University of Wyoming.

164. SULFUR ANALYSIS OF COMPLEX ORGANIC COMPOUNDS USING MICROWAVE OVEN DIGESTION. C. L. Fisher. BASF Corporation.

165. COMPARISON OF ION-TRAP. FLAME-IONIZATION AND NITROGEN-PHOSPHORUS DETECTORS FOR PESTICIDE RESIDUE DETERMINATIONS BY CAPILLARY GAS CHROMATOGRAPHY. Sharon M. Johnson and Thomas R. Steinheimer. U.S. Geological Survey.

166. DEPTH AND TIME PROFILING OF TIN IN ANTIFOULING RUBBERS BY DC ARGON PLASMA ATOMIC EMISSION SPECTROMETRY. Rm. Panayappan. John C. Cooper and Caroline C. Houston. Naval Research Laboratory.

168. ION CHROMATOGRAPHIC ASSAY OF COMBUSTION BOMB AND FUSION PRODUCTS. Raaidah Saari. Ewa Dabek and James Cox. Southern Illinois University.

169. DYNAMIC DEPOLARIZATION MEASUREMENTS ON AQUATIC HUMIC MATERIALS. Marvin C. Goldberg. U.S. Geological Survey.

170. ANALYSIS OF ORGANIC CONTAMINANTS IN PRECISION QUARTZ RESONATOR PACKAGES BY GC/MS. R. M. Sheeley. W. P. Hanson. R. A. Beers. and C. J. Jensik. Dickenson College.

171. ANALYSIS OF ORGANIC CONTAMINANTS IN EXTENDED WEAR CONTACT LENSES WORN BY MILITARY AIRCRAFT PERSONNEL. R. M. Sheeley.W. Halliday. W. M. Yorkgitis and D. D. Click. Dickenson College.

172. STATE OF THE ART CONTINUOUS FLOW ANALYSIS: TO BUBBLE OR NOT TO BUBBLE. C. Hepburn and C. Meuser. Alpkem Corp.

SYMPOSIUM ON INDUCTIVELY COUPLED PLASMA/ MASS SPECTROMETRY

Organized by Howard E. Taylor

Monday Morning, August 4

Spruce Room

H. E. Taylor, Presiding

8:30 173. AN APPROACH TO THE QUANTITATIVE ANALYSIS BY LA-ICP-MS. A. L. Gray, Univ. of Surrey.

9:00 174. ANALYSIS OF SOLID SAMPLES BY LASER ABLATION ICP/MS. R. C. Hutton, J. E. Cantle and D. Hall, VG Isotopes.

9:30 175. ANALYSIS OF HIGH PURITY QUARTZ AND POLYCRYSTALLINE INDIUM PHOSPHIDE BY INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY. Guy A. Laing and John Larkin, Eagle Pitcher Industries.

10:00 176. DETERMINATION OF RARE EARTH ELEMENTS BY ICP/MS. F. E. Lichte and A. L. Meier, U.S. Geological Survey.

10:30 **BREAK**

10:45 177. ANALYTICAL METHODS UTILIZING INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY FOR HYDROLOGIC INVESTIGATIONS. J. R. Garbarino and H. E. Taylor, U.S. Geological Survey.

11:15 178. TRACE METAL ANALYSIS OF WATERS BY ICP/MS. Richard Robinson, Los Alamos National Laboratory.

11:45 179. ANALYSIS OF RESOURCE CONSERVATION AND RECOVERY ACT SAMPLES BY INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY. Daryl Knab and Michael Bell, Los Alamos National Laboratory.

Monday Afternoon, August 4

Spruce Room

F. E. Lichte, Presiding

1:30 180. THE INFLUENCE OF ICP EXCITATION SYSTEMS ON ANALYTICAL PERFORMANCE IN ICP/MS. Alan L. Gray, University of Surrey.

2:00 181. ICP MASS SPECTROMETRY - A DISCUSSION OF THE IMPORTANT SPECTROMETER PARAMETERS. R. C. Hutton, J. E.

Cantle, and T. O. Merren, VG Isotopes.

2:30 182. CURRENT STATUS AND RECENT DEVELOPMENTS IN ICP-MS. G. Gillson, J. Fulford, and D. Douglas, Sciex Inc.

3:00 **BREAK**

3:15 183. RECENT DEVELOPMENTS IN ELECTROTHERMAL VAPORIZATION FOR ICP/MS. P. B. Stockwell, PS Analytical Ltd. and A. C. Grillo, Questron Corp.

3:45 184. HOW TRANSIENT NEED THE SIGNAL BE FOR MULTIELEMENT ICP-MS. R. C. Hutton, J. S. Gordon and P. D. Blair, VG Isotopes.

4:15 185. DETERMINATION OF ULTRA-TRACE PLATINUM IN BIOLOGICAL SAMPLES USING AN ELECTROTHERMAL VAPORIZATION DEVICE FOR SAMPLE INTRODUCTION INTO AN INDUCTIVELY-COUPLED ARGON PLASMA SPECTROMETER. A. Forester Shell Development Company and E. P. Williams, Analytical Consulting Services, Inc.

4:45 186. EQUIVALENCY TESTING OF A COMMERCIAL INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETER AND GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETER IN ENVIRONMENTAL SAMPLES. G. A. Laing, G. K. Ward, and R. E. Perrin, Eagle Pitcher Industries.

5:15 187. THE REDUCTION OF POLYATOMIC ION INTERFERENCES IN ICP-MS ANALYSIS IN THE PRESENCE OF MINERAL ACIDS. A. L. Gray, Univ. of Surrey.

SYMPOSIUM ON INFRARED SPECTROSCOPY

Organized by Marvin C. Goldberg

Monday Morning, August 4

Cedar Room

M. C. Goldberg, Presiding

9:00 Introductory Remarks

9:05 188. LOW FREQUENCY INFRARED AND RAMAN ASSIGNMENTS OF CAMPHOR AND CAMPHOR DERIVATIVES BY DEUTERIUM LABELING. R. D. Freeman, S. B. Kim, W. G. Fateley, R. M. Hammaker, C. E. Meloan, Kansas State University.

9:30 189. FTIR ANALYSIS OF METAL ACETATES IN AQUEOUS SOLUTION. J. E. Tackett and B. D. McCarty. Marathon Oil Company.

9:55 190. FTIR STUDIES OF THE HYDROLYSIS AND CONDENSATION OF ZR(OC$_3$H$_7$). Sivananda S. Jada. Manville R&D Center.

10:20 **BREAK**

10:40 191. FTIR SPECTROSCOPY OF PH$_3$ AND HCN. J.-I. Choe. T. Tipton and S. G. Kukolich. University of Arizona.

11:05 192. QUANTITATIVE DETERMINATION OF DOPANT LEVELS IN PHOSPHOSILICATE AND BOROPHOSPHOSILICATE THIN FILMS BY IR TECHNIQUES. Ronald Carpio and Charla Bertrand. Inmos Corporation.

11:30 193. PHOTOSTABILIZATION AND ATMOSPHERIC SOILING RESISTANCE STUDIES OF SILVER-BACKED POLYMER FILMS FOR SOLAR THERMAL SYSTEMS. C. A. Sergides. A. R. Chughtai and D. M. Smith. University of Denver.

Monday Afternoon. August 4

Cedar Room

M. C. Goldberg. Presiding

1:25 Introductory Remarks

1:30 194. EFFECTS OF PHASE TRANSFORMATIONS ON THE WATER WETTING PROPERTIES OF MONTMORILLONITE. A. A. Ogloza and V. M. Malhotra. Southern Illinois University.

1:55 195. QUANTITATIVE ANALYSIS OF CEMENT. CLAYS AND FLY ASH BY INFRARED SPECTROSCOPY. T. V. Rebagay. D. A. Dodd. and R. H. Guymon. Rockwell International.

2:20 196. TROPOSPHERIC SO$_2$ MEASUREMENTS BY TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY. Elizabeth A. Mishalanie. Michael T. Coffey. and William G. Mankin. National Center for Atmospheric Research.

2:45 **BREAK**

3:15 197. APPLICATIONS OF THE INFRARED MICROSCOPE. W. D. Perkins. The Perkin-Elmer Corporation.

3:40 198. AUTOMATED QUANTITATIVE INFRARED ANALYSIS USING MODERATE-COST FTIR SPECTROMETERS. R. C. Williams. B. F. Goodrich Chemical Group.

4:05 199. HPLC - FTIR. Larry T. Taylor. Virginia Tech.

4:30 200. SOLUBILITY AND DIMERIZATION IN XANTHINES. D. M. Sheeley. R. Gilkey. R. M. Sheeley. G. C. Roper. W. J. Hurst and R. A. Martin. Dickenson College.

SYMPOSIUM ON ION CHROMATOGRAPHY

Organized by F. W. Williams

Monday Morning. August 4

Silver Room

F. W. Williams. Presiding

8:15 Introductory Remarks

8:20 201. **INVITED SPEAKER**

ION EXCHANGE CHROMATOGRAPHY - CAPABILITIES. APPLICATIONS AND FUTURE NEEDS. V. T. Turkelson. Dow Chemical.

9:00 202. MICROLITER SAMPLE INJECTIONS AND EFFECTS OF ELUENT MODIFICATIONS IN ION CHROMATOGRAPHY. Dutt V. Vinjamoori. Monsanto Company.

9:25 203. ANALYSIS OF SUGARS USING PULSED AMPEROMETRIC DETECTION COMBINED WITH ISOCRATIC AND GRADIENT ANION EXCHANGE SEPARATIONS. W. T. Edwards and C. A. Pohl. Dionex Corporation.

9:50 **BREAK**

10:30 204. ELUANT OPTIMIZATION IN ION EXCLUSION CHROMATOGRAPHY. D. T. Gjerde. D. W. Togami and J. H. Nguyen. Wescan Instruments. Inc.

10:55 205. RECENT ADVANCES IN THE ANALYSIS OF ORGANIC ACIDS BY ION CHROMATOGRAPHY. Joseph D. Olechno. D. G. Gillen and R. W. Slingsby. Dionex Corporation.

Monday Afternoon. August 4

Silver room

F. W. Williams. Presiding

1:00 206. TRANSITION METAL CONTAMINATION FROM STAINLESS STEEL AND ITS EFFECTS ON ION CHROMATOGRAPHIC AND HPLC SEPARATIONS. L. Henry. Dionex Corporation.

1:25 207. NEW POLYMER-BASED ION-EXCHANGE COLUMNS. B. G. Sheldon. T. Kitagawa and J. R. Benson. Interaction Chemicals. Inc.

1:50 208. SEPARATION MODES AVAILABLE FOR ION CHROMATOGRAPHY. Petr Jandik. W. R. Jones. D. Cox and J. Oberholtzer. Millipore Corp.

2:15 **BREAK**

2:55 209. THE CARE AND FEEDING OF YOUR COLUMN. Joe Machamer, Ken Rice, and Denise R. Eubanks, Dionex Corporation.

3:20 210. GRADIENT ELUTION IN ION CHROMATOGRAPHY: PREDICTION OF GRADIENT PARAMETERS FROM ISOCRATIC DATA. R. D. Rocklin, J. A. Schibler, and C. A. Pohl, Dionex Corporation.

3:45 211. DETERMINATION OF CATIONS AND AMINES BY INDIRECT PHOTOMETRIC CHROMATOGRAPHY. D. L. McAleese, BASF Corporation.

4:10 212. NEW HIGH PERFORMANCE FIVE MICRON PACKING MATERIALS FOR ION CHROMATOGRAPHY. C. A. Pohl, S. Papanu and M. Taylor, Dionex Corporation.

Tuesday Morning, August 5

Silver Room

J. Blair, Presiding

8:30 Introductory Remarks

8:35 213. ION CHROMATOGRAPHY OF ORGANICS. R. E. Smith, Bendix.

9:00 214. SEPARATION OF ETHANOLAMINES BY SINGLE COLUMN ION CHROMATOGRAPHY. D. T. Gjerde, D. E. Burge, D. W. Togami, Wescan Instruments, Inc.

9:25 215. SELECTIVE AND SENSITIVE DETERMINATION OF TRIVALENT, HEXAVALENT AND TOTAL CHROMIUM IN AIR, WATER AND HAZARDOUS WASTE SAMPLES. S. S. Heberling, M. J. Doyle and R. J. Joyce, Dionex Corporation.

9:50 **BREAK**

10:30 216. EVERYTHING YOU EVER WANTED TO KNOW ABOUT BORIC ACID ANALYSIS BY ION CHROMATOGRAPHY - PART 2. Denise R. Eubanks, Robert J. Joyce and Gary F. Lee, Dionex Corp.

10:55 217. TRACE METAL ANALYSIS VIA CONDUCTIVITY DETECTION. Donald Cox, Millipore Corp.

Tuesday Afternoon, August 5

Silver Room

S. E. Atwood, Presiding

1:00 218. ION CHROMATOGRAPHY OF ALKALINE SULFITE SCRUBBING SOLUTIONS. E. L. Grove, IIT Research Institute.

1:25 219. DETERMINATION OF ORGANICS IN COMPLEX MATRICES: ADDITIVES & BRIGHTENERS IN PLATING BATHS. Mike Doyle and Shawn Heberling, Dionex Corporation.

1:50 220. ANALYSIS OF NICOTINE BY CATION MPIC. J. D. Lamb, D. J. Eatough, B. Sedar and N. L. Eatough, Brigham Young University.

2:15 **BREAK**

2:55 221. QUANTITATIVE ANALYSIS FROM SUB-PPB TO PERCENT LEVELS BY ION CHROMATOGRAPHY. J. A. Schibler and R. D. Rocklin, Dionex Corporation.

3:20 222. INTEGRATED SEPARATION SCHEMES IN ION CHROMATOGRAPHY. W. R. Jones, P. Jandik, A. L. Heckenberg and D. Wong, Millipore Corp.

3:45 223. ION CHROMATOGRAPHIC DETERMINATION OF ALKALINE EARTH METALS WITH POST-COLUMN REACTION AND SPECTROPHOTOMETRIC DETECTION. V. T. Turkelson and S. W. Barr, Dow Chemical.

4:10 224. ENHANCEMENT OF SENSITIVITY AND SELECTIVITY OF CLASSICAL COLORIMETRIC METHODS BY ION CHROMATOGRAPHY. L. Henry, S. Heberling, M. Doyle, B. Joyce, Dionex Corporation.

4:35 225. SELECTIVE DETERMINATION OF CR(III) IN PLATING SOLUTIONS. D. N. Rubel, Armoloy Corporation.

Wednesday Morning, August 6

Silver Room

G. Pickett, Presiding

8:30 Introductory Remarks

8:35 226. THE ION CHROMATOGRAPHIC ANALYSIS OF BORON AND PHOSPHORUS IN CHEMICAL VAPOR DEPOSITED GLASS FILMS. R. M. Merrill and M. T. Kay, Sandia National Laboratories.

9:00 227. ION CHROMATOGRAPHY SEPARATION OF INORGANIC SULFONIC ACIDS. Richard J. Williams, Allied-Signal Corporation.

9:25 228. DETERMINATION OF ARSENITE AND ARSENATE USING INDIRECT PHOTOMETRIC DETECTION. Jennifer G. Burnett and Paul H. McClelland, Hewlett-Packard Company.

9:50 **BREAK**

10:30 229. ANALYSIS OF SOME ELECTROACTIVE ANIONS BY ELECTROCHEMICAL DETECTION IN A FOOD MATRIX. Don Cox and P Jandik, Millipore Corporation.

10:55 230. CONFIRMATION OF THE CHROMOTROPIC ACID DETERMINATION OF FORMALDEHYDE USING ION CHROMATOGRAPHY. J. T. Pierce and R. G. Howard, University of North Alabama.

11:20 231. COMBINING ION CHROMATOGRAPHY AND FLOW INJECTION ANALYSIS FOR ONLINE MONITORING. Gary F. Lee and M. E. Potts, Dionex Corporation.

11:45 232. APPLICATIONS OF ION CHROMATOGRAPHY TO THE ANALYSIS OF NON-CHROMOPHORIC PHARMACEUTICALS AND THEIR METABOLITES. Joseph D. Olechno, Dennis Gillen and William Edwards, Dionex Corporation.

SYMPOSIUM ON MASS SPECTROMETRY

Organized by Paul V. Fennessey

Monday Afternoon, August 4

Colorado Room

P. V. Fennessey, Presiding

1:55 233. PYROLYTIC GAS CHROMATOGRAPHY MASS SPECTROMETRY OF MOLDING COMPOUND FOR THE PLASTIC ENCAPSULATION OF SEMICONDUCTOR DEVICES. Brian J. Starbuck and Elizabeth Cathers, National Semiconductor Corp.

2:20 234. APPLICATIONS OF DIRECT MOLECULAR BEAM MASS SPECTROMETRY TO PYROLYSIS AND CATALYSIS. R. J. Evans, J. Diebold and T. A. Milne, Solar Energy Research Institute.

2:45 236. DEVELOPMENTS IN GLOW DISCHARGE MASS SPECTROMETRY. Neil E. Sanderson, VG Isotopes Ltd.

3:15 **BREAK**

3:40 237. MASS DISCRIMINATION PHENOMENA IN FAST ATOM BOMBARDMENT MASS SPECTROMETRY OF METAL STABLE ISOTOPES. L. V. Miller, P. Peirce, C. Goss, K. M. Hambidge, and P. V. Fennessey, University of Colorado Health Sciences Center.

4:05 238. MEASUREMENT OF PLATELET ACTIVATING FACTOR BY GC/MS. K. L. Clay, Univ. of Colorado Health Sciences Center.

4:30 239. STRUCTURE ELUCIDATION OF THE ANTIGENTIC OLIGOSACCHARIDE ISOLATED FROM CELL WALL OF STREPTOCOCCUS SANGUIS (MITIS) Ss34. A. Bush, P. Fennessey, F. McIntire and S. Tjoa, University of Colorado Health Sciences Center.

SYMPOSIUM ON NEAR INFRARED REFLECTANCE ANALYSIS

Organized by Donald A. Burns

Tuesday Morning, August 5

Cedar Room

GENERAL CONSIDERATIONS

D. A. Burns, Presiding

8:35 Opening Remarks

8:40 240. NIRA: A WELL-KEPT SECRET IN SPECTROSCOPY. Donald A. Burns, Technicon Science Center.

9:05 241. CHEMICAL SENSING WITH NEAR-INFRARED REFLECTANCE ANALYSIS. David L. Wetzel, Kansas State University.

9:45 242. UNDERSTANDING A SAMPLE PROPERTY-TO-NIRA RELATIONSHIP. Joseph G. Montalvo, Steven M. Buco, Devron P. Thibodeaux, and Sherman E. Faught, Southern Regional Research Center.

10:15 **BREAK**

10:45 **IN MEMORIAM**
The late Tomas B. Hirschfeld, Lawrence Livermore National Laboratory, had agreed to deliver the keynote address for this symposium. Excerpts from some of his talks will be presented.

ENHANCEMENTS

11:00 243. SPECTRAL MATCHING IN THE NEAR INFRARED (NIR). P. J. Cooper, T. H. Begley, and K. M. Ronan, Pacific Scientific Co.

11:20 244. QUALITATIVE NIR ANALYSIS USING MULTIDIMENSIONAL DISTANCE MEASURES. H. Mark, Technicon Instrument Corp.

11:40 245. QUANTILE BEAST ATTACKS THE FALSE-SAMPLE PROBLEM IN NIRA. R. Lodder and G. M. Hieftje, Indiana University.

Tuesday *Afternoon*, August 5

Cedar Room

APPLICATIONS

D. A. Burns, Presiding

1:30 246. MONITORING HYDROCARBONS BY NEAR-INFRARED SPECTROSCOPY. B. Buchanan and D. E. Honigs, Univ. of Washington.

1:50 247. NEAR INFRARED REFLECTANCE METHOD FOR WHEAT-FLOUR GLYCOLIPIDS. C. T. Simmons and C. E. McDonald. North Dakota State University.

2:10 248. A STRATEGY FOR THE USE OF NIRA IN LIQUID FORMULA QUALITY CONTROL APPLICATIONS. Tom M. Jones and Lana R. Rademacher. Mead Johnson & Company.

2:30 **BREAK**

ALTERNATIVES

3:00 249. COMPARISON OF THE PERFORMANCE OF INTERFEROMETERS AND DISPERSIVE SPECTROPHOTOMETERS IN THE NEAR INFRARED (NIR). P. J. Cooper, P. J. Clancy, and C. McDonald-Lewis. Pacific Scientific Company.

3:20 250. FOURIER ANALYSIS OF NIR SPECTRA: DERIVATIVE ENHANCEMENTS IN FOURIER SPACE. W. F. McClure. North Carolina State University.

3:50 251. LAPLACE TRANSFORM SPECTROSCOPY. Jonathan H. Perkins and David E. Honigs. University of Washington. Seattle.

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Organized by James F. Haw and Fran P. Miknis

Monday Morning. August 4

Century Room

NMR OF SURFACES
J. F. Haw. Presiding

8:25 Opening Remarks. Welcome to the NMR Symposium

8:30 252. DNP-NMR AS A PROBE OF INTERNAL SURFACES. H. Seidel, R. D. Kendrick and C. S. Yannoni. IBM Almaden Research Center and M. E. Galvin.

9:00 253. SMALL-MOLECULE ^{31}P NMR PROBES OF SURFACES. Laima Baltusis. James Frye. and Gary E. Maciel. Colorado State Univ.

9:30 254. NMR STUDIES OF SUPPORTED BIMETALLIC CATALYSTS. B. C. Gerstein. Xi Wu. and T. L. King. Iowa State University.

10:00 **BREAK**

10:30 255. A STUDY OF CO ADSORBED ON SUPPORTED GROUP 8-10 METALS BY 13-C MAGIC ANGLE SPINNING NMR. R. Shoemaker and T. Apple. University of Nebraska.

11:00 256. MULTINUCLEAR NMR STUDY OF THE VACUUM-CALCINATION AND REHYDRATION OF ZEOLITE NH_4-RHO. Alexander J. Vega and Zeev Luz, E.I. du Pont de Nemours & Co.

11:30 257. DEUTERIUM RELAXATION AND LINESHAPES IN CLATHRATES. Alan D. Ronemus, Michael S. Greenfield, Robert L. Vold, and Regitze R. Vold, University of California, San Diego.

Monday Afternoon, August 4

Century Room

SOLID STATE NMR IN INORGANIC AND ORGANOMETALLIC CHEMISTRY
H. Retcofsky, Presiding

1:30 258. CROSS POLARIZATION DYNAMICS IN AMORPHOUS HYDROGENATED SILICON. Nicholas Zumbulyadis, Eastman Kodak Co.

2:00 259. **PLENARY LECTURE**
NMR OF INORGANIC SOLIDS. Eric Oldfield, University of Illinois, Urbana-Champaign.

3:00 **BREAK**

3:30 260. VARIABLE TEMPERATURE CP/MAS NMR STUDIES OF PARAMAGNETIC AND ANTIFERROMAGNETIC SOLIDS. Gordon C. Campbell and James F. Haw, Texas A&M University.

4:00 261. SOLID-STATE NMR SPECTRA OF METAL NUCLIDES. Greg Quinting, Gary E. Maciel, Stephen Dec, Bruce L. Hawkins and Robert Wind, Colorado State University.

4:30 262. SOLID STATE NMR IN A CONTROLLED ATMOSPHERE. R. R. Eckman.

Tuesday Morning, August 5

Century Room

MAS HARDWARE, TECHNIQUES, AND SIDEBAND SUPPRESSION
R. A. Wind and B. L. Hawkins, Presiding

8:30 263. CONTROL AND MANIPULATION OF SIDEBANDS IN MASS NMR SPECTRA. D. P. Raleigh, E. T. Olejniczak, S. Vega and R. G. Griffin, Massachusetts Institute of Technology.

9:00 264. HIGH SPEED MAGIC ANGLE SPINNING. S. F. Dec, R. A. Wind and G. E. Maciel, Colorado State University.

9:30 265. MAGIC-ANGLE SAMPLE SPINNING - PRACTICAL CONSIDERATIONS. E. O. Stejskal, Monsanto Company.

10:00 **BREAK**

10:30 266. DESIGN CONSIDERATIONS FOR VERY HIGH TEMPERATURE MAS. D. Doty.

11:00 267. LOW TEMPERATURE CPMAS-NMR OF METASTABLE MOLECULES. C. S. Yannoni. IBM Almaden Research Center.

11:30 268. CHEMAGNETICS MAGIC ANGLE SPINNING: DESIGN CRITERIA. V. J. Bartuska. D. H. Lewis. and A. R. Palmer. Chemagnetics. Inc.

Tuesday Afternoon. August 5

Century Room

EXPERIMENTAL TECHNIQUES
F. Miknis. Presiding

1:30 269. EFFECTS OF SAMPLE SPINNING ON CROSS POLARIZATION. Maziar Sardashti and Gary E. Maciel. Colorado State University.

2:00 270. EXPERIMENTAL CONSIDERATIONS IN VARIABLE TEMPERATURE CP/MAS NMR. Richard C. Crosby. Gordon C. Campbell. and James F. Haw. Texas A&M University.

2:30 271. MULTIPLE QUANTUM NMR OF LIQUID CRYSTALS. K. Schenker. N. Gochen. D. Hugi-Cleary and A. Pines. Univ. of Calif.

3:00 **BREAK**

3:30 272. SOLID STATE DEUTERIUM NMR SPECTROSCOPY. A POWERFUL TECHNIQUE FOR ASSESSING MOLECULAR MOTION IN SOLIDS. Lynn W. Jelinski and Joseph J. Dumais. AT&T Bell Laboratories.

4:00 273. A COMPARISON OF THE RESOLUTION OF THE CRAMPS (COMBINED ROTATION AND MULTIPLE-PULSE SPECTROSCOPY) EXPERIMENT AT TWO FIELDS. Charles E. Bronnimann. Bruce L. Hawkins. and Gary E. Maciel. Colorado State University.

4:30 274. ALTERNATIVE WAYS OF POLARIZATION TRANSFER FOR SOLIDS. R. A. Wind. S. F. Dec. S. E. Emery. G. E. Maciel. and C. S. Yannoni. Colorado State University.

Wednesday Morning. August 6

Century Room

NON-MEDICAL NMR IMAGING
A. R. Palmer. Presiding

8:15 275. LINE-NARROWING FOR MAGNETIC RESONANCE IMAGING IN SOLIDS. J. B. Miller. G. C. Chingas and A. N. Garroway. Naval Research Laboratory.

8:45 276. NMR IMAGING OF DILUTE NUCLEI IN THE SOLID STATE. Mark Davis, Robert Wind, Steve Dec, Steve Emery, Maziar Sardashti, and Gary E. Maciel, Colorado State University.

9:15 277. MULTIPLE QUANTUM AND POLARIZATION TRANSFER TECHNIQUES IN NMR IMAGING AND SPECTROSCOPY. C. L. Dumoulin, General Electric Corporate Research and Development Center.

9:45 278. NMR IMAGING USING LOOP-GAP RESONATORS. J. P. Hornak, J. Szumowski and R. G. Bryant, Rochester Institute of Technology.

10:15 **BREAK**

10:30 279. MAGNETIC RESONANCE IMAGING OF POLYMER RHEOLOGY. J. Crowley.

11:00 280. NMR IMAGING AND RELAXATION STUDY OF POLYMER SWELLING AND CHAIN DYNAMICS. T. H. Mareci, S. Donstrup and A. Rigamonti, University of Florida.

11:30 281. NMR IMAGING OF SOLID INTERFACES. D. L. Foxall, Varian.

Wednesday Afternoon, August 6

Century Room

SPIN DIFFUSION AND CHEMICAL EXCHANGE

1:00 282. NATURAL ABUNDANCE C-13 SPIN EXCHANGE AS A PROBE OF MORPHOLOGY AND MOLECULAR TRANSPORT IN POLYMERS. D. L. VanderHart, National Bureau of Standards.

1:40 283. ORTHOGONAL INDIRECT DETECTION OF NMR SPINOR TRANSITIONS. Dieter Suter, Alex Pines and Michael Mehring, University of Stuttgart.

2:10 284. CHEMICAL SHIFT PERTURBATIONS IN ION-CONTAINING COPOLYMERS, LIQUID CRYSTALS, AND POLYMER BLENDS - MISCIBILITY DETECTION VIA HYDROGEN BONDING. Laurence A. Belfiore, Colorado State University.

2:40 285. CHEMICAL EXCHANGE IN ZERO-FIELD NMR. P. Jonsen, M. Luzar, A. Pines, M. Mehring, P. Meier and G. Kothe, University of Stuttgart.

1 RECENT ADVANCES IN THE USE OF ARRAY DETECTOR TECHNOLOGY FOR ATOMIC SPECTROSCOPY
M. Bonner Denton and Robert B. Bilhorn, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Rapid quantitative elemental analysis of complex mixtures by optical emission spectrometry requires sensitive simultaneous multiwavelength detection. The need for such a multichannel detector which is also compact, rugged and easily operated has long been recognized. In an attempt to satisfy these needs a charge injection device (CID) array camera system along with a reduced image size echelle spectrometer have been designed and evaluated for atomic emission spectrometry. Critical operational parameters of the camera system such as noise, quantum efficiency and detector to detector cross talk have been evaluated, and the results will be presented. Methods to reduce the system noise will be discussed, along with characteristics of the camera system to spectrometer interface such as spectral coverage and resolution. Detection limits for a number of elements will be reported. These detection limits have been found to be at least comparable to, and in many cases, to exceed photomultiplier tube detection limits. The system's unique ability to perform line and readout mode selection, background correction and system diagnostics optimized for the current sample during the actual analysis of the sample will be described.

2 MERCURY DETERMINATION IN MULTI-ELEMENT ICP-AES, ROUTES TO INCREASED SENSITIVITY IN GEOLOGICAL ANALYSIS. T. L. Fries, P. J. Lamothe, U.S. Geological Survey, Menlo Park, CA, 94025 and K. D. Summerhays, A. Tewari, University of San Francisco, San Francisco, CA, 94117.

The determination of mercury in geological samples can be important in studies of the environment, minerals exploration and transport processes connected with hydrothermal solutions. Mercury concentrations in such studies are in the low μg/g or ng/g range requiring separation and preconcentration procedures which do not allow the use of the multi-element capability of ICP-AES. The techniques outlined here provide a 50 to 60 fold increase in sensitivity for mercury when compared to reported detection limits and background equivalent concentrations (BEC) for aqueous mercury solutions. This is achieved by generating volatile mercury species either during sample introduction or as part of a split stream introduction system with two different sample preparations. Both approaches maintain multi-element capability with increased sensitivity for mercury. Optimization of the systems for either mercury or other elements is possible, and compromise conditions are not different than those used normally. Wavelength selection for mercury determination is dependent on the volatile species production method and on expected inter-element interferences. Detection limits for mercury range from 0.24 μg/L, using the 253.7 nm wavelength with the system optimized for mercury, to 1.0 μg/L at the same wavelength using compromise conditions. BEC and detection limits for Al, B, Ca, Cu, Li, Mg, Mn, Na, Pb and Zn are unchanged from those we normally obtain using compromise conditions but are degraded by a factor of 2-5 using conditions optimized for mercury.

3 ANALYTICAL STATUS OF A PRACTICAL INDUCTIVELY COUPLED PLASMA-FOURIER TRANSFORM SPECTROMETER (ICP-FTS). M. W. Tikkanen and M. W. Routh, Applied Research Laboratories, Sunland, CA 91040.

Inductively Coupled Plasma Atomic Emission Spectrometry has been routinely used for elemental analysis for the past decade. An ICP-AES system that utilizes a Fourier Transform interferometer offers unique analytical capabilities as compared to the conventional optically dispersive ICP-AES. Because of its unique data acquisition characteristics, the ICP-FTS allows the freedom of element and wavelength choice afforded by a sequential ICP, as well as the simultaneity of a "direct-reading" ICP system. With the ICP-FTS, several modes of analysis are available. Quantitative analysis with precision on the order of 1% RSD, and linear dynamic range of 3-4 orders of magnitude is possible. Additionally, because of the same unique data gathering capabilities, the ICP-FTS is well suited to such analytical possibilities as qualitative analysis ("finger printing"), pattern recognition and correlation techiques, multiple line confirmation, and data archiving (for post-run data evaluation). Several of these data evaluation techniques will be discussed and applications to a number of standard reference materials will be presented.

4

ANALYSIS OF ORGANIC SOLVENTS BY ICP EMISSION SPECTROMETRY

Danton D. Nygaard, Jack Roberts, and David A. Leighty. Allied Analytical Systems, 590 Lincoln Street, Waltham, MA 02254

This paper examines the potential for direct analysis of the solvents of interest to the electronics industry (acetone, methanol, 2-propanol, xylene, toluene, halocarbons, etc.) by nebulization into an inductively coupled plasma emission spectrometer. Among the topics discussed will be: (1) the compatibility of various solvents with materials used in the ICP sample introduction system, especially with peristaltic pump winding materials such as silicone rubber, Viton rubber, and other polymer materials; (2) the ability of the plasma discharge to consume various solvents without being extinguished, especially with regard to the effect of a newly designed autotuning power supply on plasma performance with organic solvents; (3) preparation and stability of standard solutions in various organic solvents; and (4) the detection limits obtainable in various organic solvents for analyte elements of interest to the electronics industry, as compared to the standards established by the Semiconductor Equipment and Materials Institute.

5

DETERMINATION OF TRACE METALS IN SEMICONDUCTOR PROCESSING CHEMICALS.

K. Fredeen, G. Carnrick, E. Pruszkowski, and D. Yates
Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0906

Advances in semiconductor technology have made it increasingly important to know the concentrations of metallic contaminants in the chemicals used in semiconductor manufacturing processes. Atomic emission and atomic absorption techniques are typically the methods of choice for determination of trace levels of metallic species in a wide variety of materials. However, the nature of several semiconductor processing chemicals precludes the use of the sample preparation and sample introduction techniques normally used in AES and AAS methods. Problems such as reactivity with air, water, and laboratory equipment, along with the thermal instability, volatility, and toxicity of some of these chemicals, require special sample preparation and introduction techniques.

This paper discusses techniques used for determination of trace metals in some semiconductor processing chemicals via ICP-AES and GFAAS. The inherent advantages and disadvantages of these two methods for such determinations are compared and contrasted. While the advantages of rapid, multielement determinations for ICP-AES, and small sample size and low detection limits for GFAAS are important considerations, there are other unique requirements for these determinations which merit attention.

6

THE SIMULTANEOUS DETERMINATION OF 19 MAJOR AND TRACE ELEMENTS IN GEOCHEMICAL SAMPLES BY ICP-AES.

Liu Zen, Zhu Yong Ping, Ni Tong Wen, Testing Center of Gansu, 77 S. Ding Xi Road, Lanzhou, Gansu, Peoples Republic of China.

A method for using ICP-AES for the determination of 19 major and trace elements in geochemical samples will be described. A sample preparation procedure involving full dissolution of the samples is suggested. The method is ideal for geochemical samples. In addition, interelement effects resulting from spectral overlap and stray light are quantified for the instrument used, a Shimadzu ICPQ-100. Performance in terms of long term precision and accuracy is assessed. Examples will be presented of general geochemical investigations undertaken at the Testing Center of Ganzu where this method has produced good results.

7 AN EVALUATION OF THE INTERFERENCE EFFECTS FOR SLURRY INJECTION OF GEOLOGICAL MATERIALS INTO AN ICP. I. B. Brenner and L. Halicz, Geological Survey of Israel, 30 Malkhe Israel Street, Jerusalem, 95501, Israel.

ICP-AES analysis using slurries offers numerous potential advantages in sample output and preparation. In this presentation we will describe the role of complex interference effects related to transport and volatization effects in the plasma column for diverse silicate rocks and clay minerals. Atomization efficiency and thermal decomposition are critically dependent on the partical size of the sample and the mode of occurrence of the analyte. Many of the particles that reach the excitation cell may be too large or even refractory to be decomposed and atomized. Scandium as an internal reference appears to compensate for some of the transport effects only, failing to compensate for chemical and mineralogic interference effects. It will be shown that the slurry technique will be an attractive possibility when textural, mineralogical and chemical compositions are restricted and known. Forethought should be applied to the selection of the calibration standards. These will have to be carefully matrix matched.

8 SELENIUM IN BIOLOGICAL MATERIALS BY GFAAS AFTER CLOSED CELL MICROWAVE DIGESTION.
Claude Veillon, K.Y. Patterson and H.M. Kingston. Human Nutrition Research Center, USDA, ARS, Beltsville, Maryland 20705 and Inorganic Analytical Research Division, NBS, Gaithersburg, Maryland 20899.

Selenium can be determined in some sample types by GFAAS with Zeeman background correction employing nickel as a matrix modifier. For many biological materials, except homogeneous liquids like plasma and serum, this procedure requires that the organic matrix be first destroyed. Acid digestions can be used, provided oxidizing conditions are maintained, but these are slow, especially when the samples contain any fat. A novel closed system employing microwave heating and high temperature and pressures is investigated for the rapid acid digestion of a variety of biological samples, with subsequent selenium determination by GFAAS. The procedure is applicable to other elemental determinations and analytical methods as well.

9 DETERMINATION OF MERCURY IN GEOLOGICAL MATERIALS BY CONTINUOUS-FLOW, COLD-VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY, J.G. Crock and K.R. Kennedy, U.S. Geological Survey, Box 25046, MS 928, Denver Federal Center, Denver, CO 80225.

To determine mercury in geological materials, the samples are first digested and oxidized using nitric acid and a 25% (w/v) sodium dichromate solution in a closed teflon vessel at 110°C for 3 hours. After bringing to a constant weight, the digest is mixed with air, a sodium chloride-hydroxylamine hydrochloride-sulfuric acid solution, and finally the Hg(II) is reduced to Hg^0 with a stannous chloride solution in a continuous-flow manifold. The mercury vapor is then separated and measured using cold-vapor atomic absorption spectrophotometry. This method proves to be sensitive, precise, accurate, and relatively free from interferences. For a 100-mg sample, the limit of detection is 0.02 ppm Hg. The limit of detection is usually blank-limited at this level. To obtain a 1% absorption signal, the described method requires 0.21 ppb Hg solution. Precision is acceptable at less than 1.2% RSD for a 10 ppb Hg aqueous standard. Accuracy is demonstrated by the results of the analysis of standard reference materials. Several elements do interfere--producing low results--but either the digestion procedure does not dissolve them (such as Au or Pt) or they are normally of low abundance in geological materials (such as Se or Te).

10 REAL-LIFE ACCURACY OF BACKGROUND CORRECTION IN GRAPHITE FURNACE AAS.

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Nonspecific background absorption can be a significant source of error in atomic absorption analyses. The occurrence of this problem is particularly apparent in applications of the graphite furnace AAS technique. There are four methods currently used for background correction: a) the two-source method (i.e. HCL and a continuum source), b) the Zeeman-effect method, c) the wavelength-modulation continuum source method, and d) the pulsed hollow cathode lamp method. The following requirements can be specified for each of these methods: accuracy of correction must be very good, there should be no analytical sensitivity loss connected with the correction, and it should be possible to correct for fast background signals as well as for structured background and for high nonspecific absorbance. In the asymmetric method for the calculation of corrected signal a single pair of measurements "AA + BG" and "BG only" are used. As the two measurements are made at different times (Δt = 5-10 ms), compensation errors will occur if the background changes rapidly. Three measurements, BG_1, AA + BG, and BG_2 are used in the bracketing method for calculation of the corrected signal. The two background measurements before and after the AA + BG measurement are averaged. The averaged BG value corresponds more closely to the true background at the time when the AA + BG measurement was made. Through application of this method the quality and accuracy of background correction can be improved always when peak height is measured and under certain conditions when integrated absorbance, i.e., peak area is used.

11 GRAPHITE FURNACE AA: NEW APPROACHES TO MATRIX MODIFICATION.

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Matrix modification techniques have been widely used in GFAAS to minimize interferences. For example, nickel is typically used to stabilize arsenic and selenium to higher temperatures.

Palladium can be used to stabilize elements to temperatures several hundred degrees higher than those attained with nickel. However, it was found that the performance of palladium was strongly effected by the sample matrix. The interaction of palladium with various sample matrices was investigated.

A new matrix modification method will be presented. With the proper use of a mixed modifier, ash temperatures for many elements can be raised an average of 400°C. Preliminary interference performance for 15 elements in sea water and sodium sulfate matrices was excellent.

12 FURNACE ATOMIC ABSORPTION SPECTROMETRY WITH DISPOSABLE CHARRING/ATOMIZATION SURFACE.

Thomas W. Brueggemeyer, Fred L. Fricke, and Carlos A. Bonnin. Elemental Analysis Research Center, U.S. Food and Drug Administration, 1141 Central Parkway, Cincinnati OH 45202.

A problem frequently encountered in the direct analysis of foods and biological substances by graphite furnace atomic absorption spectrometry is the buildup of carbonaceous residue in the tube or platform. Such a difficulty could be eliminated if the charring/atomization surface were disposable and used only for the analysis of a single sample. Furthermore, if such a surface were introduced on a probe into a pre-heated graphite furnace, the interference reduction experienced in constant-temperature furnaces would be obtained. Because the probe is not heated resistively, atomizer surface materials need not be limited to electrical conductors such as graphite. Among the charring/atomization surfaces which have proven useful are zirconia (ZrO_2) cloth and felt. Zirconia is oxidation-inert and can withstand furnace temperatures greater than 2000 °C. Atomization behavior of Pb, Cd, and Cu from zirconia is similar to that from a graphite surface in terms of sensitivity, reproducibility and linearity. The work to be described utilizes a batch charring of samples in a muffle furnace (each sample deposited on a separate zirconia cloth) followed by sequential probe atomization. Charring and atomization parameters will be discussed, as well as precision and detection limits for a number of real samples.

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13 COMPUTER ENHANCED AUTOMATIC METHODS DEVELOPMENT IN ATOMIC ABSORPTION SPECTROMETRY.

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The need to select the correct temperature profile for the dry, ash and atomize steps when performing an electrothermal atomization on a sample with a complex matrix is well known. The usual method of determining the appropriate thermal program involves a labor intensive series of experiments where by a single parameter is changed and the results are noted. Central processor controlled atomic absorption instrumentation combined with a flexible extended BASIC language specifically tailored to atomic absorption applications allows software to be developed which can automate these tedious optimization procedures.

This same language can be used with the centrally controlled instrumentation to automatically optimize the stoichiometry of the flame for the maximum sensitivity of a particular element in a given matrix, or to select the stoichiometry which yeilds the minimum interference from matrix materials.

The implimentation and application of such graphite furnace and flame optimization software will be discussed.

14 OPERATION AND PERFORMANCE OF A NEW COMPUTER-CONTROLLED FURNACE AA SYSTEM

Danton D. Nygaard, Jack Roberts and David A. Leighty. Allied Analytical Systems, 590 Lincoln Street, Waltham, MA 02254

The purpose of this paper is to describe a new furnace AA system with respect to operator interfacing and its performance for both simple and complex sample types. The new system consists of the actual cell head, a "black-box" control module, and an AA spectrophotometer which is programmed to control the furnace. The system combines the delayed atomization cuvette and infrared temperature sensor with the FASTAC aerosol deposition technique and Smith-Hieftje background correction. The analytical performance of this overall furnace AA system was evaluated using NBS SRM 1643b and results will be presented.

15 EVALUATION OF A HIGH RESOLUTION SPECTROMETER AND INTERNAL REFERENCES FOR DIRECT TRACE ELEMENT ANALYSIS OF TUNGSTEN POWDERS.

S. Erlich and I. B. Brenner, Geological Survey of Israel, 30 Malkhe Israel Street, Jerusalem, 95501, Israel.

The emission spectrum of tungsten is particularly complex in the ICP. Trace element analysis of such materials requires the time-consuming separation of the matrix element or the analyte elements to avoid spectral interferences. In this presentation we will present data on line selection and the use of the matrix element as an internal reference for the compensation of spectral interferences and physical effects in the introduction system for solutions containing high concentration of hydrofluoric acid. A method will be described for the direct trace element determination in pure tungsten powders.

16 MODERNIZATION OF A SPECTROGRAPHIC DARKROOM.

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In order to improve the utility of a 30-year old spectrographic darkroom several changes were made. The manual film and plate processor was replaced with an automated processor and a large capacity dryer was intalled. Conversion was made from a single use to a multiple use darkroom through the addition of a revolving door and an electrical warning system. All changes were made with commercially available components. Problems encountered with the modernization and their solutions will be discussed.

17 SEGREGATED DISCHARGES: A NEW LOOK AT SOME OLD SPECTROSCOPIC TOOLS.

David M. Coleman. Department of Chemistry, Wayne State University, Detroit, MI 48202.

Numerous investigators over the past several years have discovered the value in segregating the "sampling" from the "excitation" step in various forms of atomic emission spectroscopy. In general one 1.) uses a first discharge to create an atomic reservoir from a sample of interest then 2.) uses a second discharge to controllably and selectively re-excite that material for purposes of analytical observation. A brief historical review of segregated experiments will be included. Specific examples developed in the WSU Emission Spectroscopic Laboratories including 1.) high voltage spark sampling followed by 200 Mhz. high frequency re-excitation and 2.) a new tandem (dual) ICP discharge will be discussed. In general one observes significant reduction in background levels; enhanced signal-to-noise, detection limits, and intensity linearity; and relative freedom from interferences.

18 CHARACTERIZATION OF BOUNCE AND EFFICIENCY IN A SINGLE-STAGE INERTIAL IMPACTOR UTILIZING A GRAPHITE FURNACE AS THE COLLECTION SUBSTRATE.

K. H. Dewhurst, D. R. Parker, Sandia National Laboratories, Org. 3311, Albuquerque, New Mexico 87185; Y. S. Cheng, ITRI, Loveland Biomedical and Environmental Research Institute, P.O. Box 5890, Albuquerque, New Mexico 87115 and T. M. Niemczyk, Department of Chemistry, University of New Mexico 87131.

Open-faced filter samples are used routinely to collect aerosol samples in the work place for industrial hygiene purposes. However, sample losses during the transfer and dilution of the collected material from the filter substrate reduce the accuracy of this method. In the work to be discussed here the collection efficiency of a single-staged impactor which utilizes a graphite furnace as the impaction substrate is determined. The collected sample is analyzed directly by electrothermal atomization atomic absorption spectroscopy. Losses of collected sample are minimized because no sample transfer is made. The aerosol materials include di-octyl phthalate (liquid form) and ammonium fluorescein (solid form). A vibrating orifice aerosol generator was used to produce monodisperse aerosols ranging in size from 1 to 10 microns. Particle bounce and internal losses have been characterized.

19 TWO GEOLOGICAL SAMPLE PREPARATION TECHNIQUES USING LABORATORY ROBOTICS

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Increased sample workloads in our laboratory have stimulated interest in laboratory robotics as a means of increasing sample preparation capacities. Because automated sample introduction and dedicated computers are the norm with most modern analytical instruments, the major bottleneck is no longer the analysis but sample preparation. Sample preparation is time-consuming, tedious and exposes laboratory personnel to potentially dangerous reagents. Five major advantages in sample preparation by laboratory robotics are (1) uniform sample handling; (2) large number of samples prepared; (3) decreased personnel exposure to dangerous reagents; (4) faster sample preparation; and (5) results comparable with traditional sample preparation. Two robotic systems have been set up in the U.S. Geological Survey, analytical chemistry laboratory. One system is a multiple-acid digestion of rocks for inductively coupled argon plasma analysis. The other system is a hydrobromic acid, methyl isobutyl ketone extraction of rocks for the determination of gold by atomic absorption. We have characterized each of the five advantages for each robotic system.

20 AUTOMATED DETERMINATION OF TRANSITION METALS IN BRINES AND OTHER IONIC MATRICES

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Sunnyvale, CA 94088-3603

The determination of transition metals in sea water and other highly ionic solutions has historically been a troublesome analysis. While modern atomic spectroscopy techniques are beginning to address this type of analysis, "direct" methods are still a rarity. In most cases, some form of selective preconcentration is necessary to increase the transition metal-to-brine ratio in order to avoid interferences and instrument mechanical problems with the high amounts of dissolved solids. The preconcentration step usually involves separation on an ion exchange or chelating resin and is therefore amenable to Ion Chromatography (IC) instrumentation. Since IC has also proven capable of stand-alone transition metals determination, it is possible to devise an automated IC instrument capable of performing the entire metals in brine analysis procedure. This paper will describe an automated IC which may be used either by itself or as a sample preparation device for atomic spectroscopy. Applications will include sea water, industrial brines, and soils.

21 CHEMICAL AND EXCITATIONAL CHARACTERIZATION OF NITROGEN SOURCES FOR METASTABLE TRANSFER EMISSION SPECTROSCOPY. Hwei-Chen Yang and T. M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131.

The chemical properties of an active nitrogen source used for Metastable Transfer Emission Spectroscopy (MTES) are generally attributed to the nitrogen atom concentration. We will present a method for the absolute determination of nitrogen atom concentrations in gaseous systems. The results of the application of this method to three different active nitrogen sources used in MTES will be presented. These results will be correlated with the metastable N_2 concentrations in the different sources.

22 INTERFEROMETRIC/SCHLIEREN OBSERVATION OF MAGNETICALLY-INFLUENCED SPARK DISCHARGES. David M. Coleman, Wu-hwa Hsu, and Vahid Majidi. Department of Chemistry, Wayne State University, Detroit, MI 48202.

A new instrument has been developed for refracted light observation of luminous electrical discharges. This instrument can function to provide 1.) schlieren, 2.) interferometric, and 3.) combined schlieren/interferometric views of continuous and transient discharges. Application of this technology to investigate new approaches to magnetically-influence a high voltage spark's post discharge torus will be presented. Discovery of a new ionic filamental structure, formed under magnetic control, will be discussed.

23 THE CHARACTERISTICS OF A LOW-POWER N_2-Ar ICP FOR MULTIELEMENT ANALYTICAL EMISSION SPECTROMETRY. S. Erlich and I. B. Brenner, Geological Survey of Israel, 30 Malkhe Israel Street, Jerusalem, 95501, Israel.

The analytical application of the high and medium power (>2-3 KW) Ar-nitrogen plasma is well documented. Owing to the improved thermal conductivity of mixed Ar-nitrogen plasmas and the reported enhancement in intensity of low power Ar-nitrogen plasmas, we decided to make a detailed analytical evaluation of a low-power Ar-nitrogen plasma operating in the power range of 1-1.75 KW. Our preliminary data for argon plasmas containing 1-2% nitrogen in a Trassy-Mermet demountable torch and in a low consumption MAKtorch clearly show that although the background continuum is higher, the signal-to-background ratio is also significantly higher than for a low power argon plasma. This presentation will include spatial behavior of line intensities in the plasma column as a function of ICP operating conditions and the effect of easily ionized elements.

24 PHOTOCHEMICAL AMPLIFIER FOR DETECTION IN HPLC. Curtis Shellum and John W. Birks, Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309.

A detection scheme for HPLC has been developed that makes use of a post-column photochemical reaction sequence to enhance the sensitivity of u.v. and fluorescence detectors. Any organic molecule which absorbs light in the photochemical reactor and undergoes intersystem crossing to an excited triplet state will produce a response in this system. The excited triplet state of the eluite is quenched by oxygen to form electronically excited singlet oxygen, $^1O_2^*$. The $^1O_2^*$ reacts with either 2,5-dimethyl- or 2,5-diphenylfuran to form oxidized products. A change in absorbance or fluorescence of either the reactant or product is monitored by the detector. The reaction sequence is catalytic in that an analyte molecule can repeatedly trigger the reaction sequence during its residence time (~2 min) in the photoreactor. The result is a large absorbance or fluorescence change and a large enhancement in detection sensitivity. Lower limits of detection in the range 1-50 pg of compound are obtained for both fluorescent and non-fluorescent analytes.

25 PHOTOCHEMICAL REACTION-DETECTION OF ANTHRAQUINONES AND NAPHTHOQUINONES IN HPLC. James R. Poulsen and John W. Birks. Department of Chemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder CO 80309.

The unique photochemistry of quinone compounds can be used to improve their detection properties in HPLC. Two reaction-detection methods which are selective and sensitive will be introduced. In the first, a photooxygenation of the mobile phase by the quinone analyte catalytically produces hydrogen peroxide which is subsequently detected by peroxyoxalate chemiluminescence. Typically, the detection limits for these analytes are in the low to mid picogram range. A second approach to quinone detection utilizes their anaerobic photoreduction to fluorescent hydroquinones. Selectivity is lower in this mode since compounds which are natively fluorescent interfere. Performance of these detection schemes in their application to quinone detection in extracts of paper products will be compared to more conventional HPLC detectors.

26 THE USE OF TERBIUM(III) and EUROPIUM(III) AS LUMINESCENT CHROMOPHORES FOR LIQUID CHROMATOGRAPHIC DETECTION, Thomas J. Wenzel and Elsie E. DiBella, Bates College, Department of Chemistry, Lewiston, ME 04240

Tb(III) and Eu(III) have been employed as luminescent chromophores for liquid chromatographic detection. The detection is based on the principal of sensitized luminescence. Certain organic compounds, particularly aromatic ketones and aldehydes, have the ability to transfer energy to terbium and europium ions. Dissolved oxygen quenches the lanthanide luminescence and must be removed from all mobile phases. The method is suitable in mobile phases containing methanol, acetonitrile, and water. Higher temperatures increase the frequency of collisions resulting in an increase in sensitivity. Using broadband excitation, the lanthanide ions have a sizeable background luminescence. Some organic compounds will quench the background luminescence, rather than transfer energy, and will appear as a negative peak in the chromatogram. The positive or negative nature of a peak provides useful information for compound identification. Potential applications of this method for the detection of biologically important compounds will be presented.

27 A RATIONAL APPROACH TO THE DESIGN OF CHIRAL STATIONARY PHASES FOR ENTANTIOMER SEPARATION. W. H. Pirkle, T. C. Pochapsky and D. S. Reno, Department of Chemistry, University of Illinois, Urbana, IL 61801.

Beyond its ability for separation and analysis, HPLC can be used to study subtle details of intermolecular interactions. A systematic study of the relationship between structure of N-aryl amino acid derivatives and the enantioselectivity noted on a chiral HPLC column led to a chromatographically-derived chiral recognition model. Support for the model is provided by NMR and ultraviolet-visable absorption spectroscopy. The basic concepts of the model have been incorporated into a transition state model for enantioselective reaction. These results will be presented.

28 LIQUID CHROMATOGRAPHIC SEPARATION OF CR-BETA-DIKETONATES WITH SYSTEMATICALLY MODIFIED LIGANDS. Peter Schultze and Bernd W. Wenclawiak, Dept. of Chemistry, University of Toledo, 2801 W. Bancroft Street, Toledo, OH, 43606.

In reverse phase (C18) liquid chromatography the retention of Cr-beta-diketonates depends not only on the mobile phase composition but also on the ligands bonded to the chromium(III).
We have sytematically investigated the influence of the residual groups (R1, R2) of the ligand on the retention time of the Cr-complex. For symmetric ligands (R1 = R2) an equation $\ln t_R = X + YL + ZB$ can be derived, which includes the length (L) of the side chain and the number of branchings (B). It can be used to calculate the retention times of Cr-beta-diketonates with different beta-diketone ligands. For Cr-beta-diketonates with unsymmetrical or mixed ligands minor deviations from the equation are noted. The degree of deviation indicates the symmetry of the complex.

29 REVERSED PHASE POLYMERS FOR HPLC

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Conventional macroporous polymers for reversed phase chromatography utilize highly cross-linked poly(styrene-divinylbenzene) without further derivatization. We report on two new polymeric packing materials that have been structurally modified to reduce the shortcomings of these underivatized polymers, while maintaining their advantages of high chemical stability. Underivatized polymers are characterized by a high density of pi electrons that interfere with polar and aromatic analytes. Tailing, asymmetry and long retention times result. The ACT-1 column contains a macroporous polymer to which C18 groups have been covalently bonded. The ACT-2 column contains a similar macroporous polymer, but covalently bound nitrogen has been inserted into the matrix in place of the C18. Both polymers are stable from pH 0 to 14, so reversed phase chromatography can be accomplished at very low or very high values of pH. These new polymers should be particularly useful in analysis of mixtures of drugs and their metabolites, since at elevated pH values, nitrogens are deprontonated and, unlike silica columns, the separation can occur via a pure reversed phase mechanism. No associated tailing or inappropriate retention times are observed.

30 CHROMATOGRAPHIC DETERMINATION OF TOTAL NITROGEN FOLLOWING KJELDAHL OXIDATION. S. Moldoveanu, Dowell Schlumberger, Post Office Box 2710, Tulsa, Oklahoma 74101.

Total nitrogen determination in organic and some inorganic materials can be done by means of a new gas chromatographic method following Kjeldahl oxidation. A significant increase in sensitivity, in comparison with the classical Kjeldahl method, can be obtained using a thermal detector on the gas chromatograph. Even higher sensitivity would be expected using a nitrogen-phosphorus flame ionization detector. The method is based on the fact that at a temperature of 130° to 140°C, a solution of ammonium acetate behaves in the chromatographic column like a mixture of ammonia and acetic acid. The nitrogen determination is done by collecting in acetic acid the ammonia resulting from the addition of a strong base solution to the sample, after the application of the Kjeldahl oxidation. The concentration of the resulting ammonium acetate solution is then chromatographically determined. To allow a more rapid release of ammonia, the solution of the strong base has been made in 2-propanol instead of water. Known samples containing nitrogen in the range of 0.001 meq to 0.05 meq have been analyzed; this compares to the minimum 1 meq nitrogen detectable by the classical Kjeldahl method.

31 SUPERCRITICAL FLUID JET EXPANSIONS USING A SHEATH FLOW NOZZLE. Bruce D. Anderson and Murray V. Johnston, Department of Chemistry and Biochemistry, and CIRES (Cooperative Institute for Research in Environmental Sciences), Campus Box 215, University of Colorado, Boulder, CO 80309.

A sheath flow nozzle is used to obtain fluorescence excitation spectra of compounds cooled in supersonic jet expansions of supercritical fluids. Preliminary work was done on naphthalene in supercritical carbon dioxide at 2000 psi and 40°C. Under these conditions, the full width at half maximum for the 8^1_0 transition of naphthalene is 5 cm^{-1}. The method is compatible with capillary supercritical fluid chromatographic flow rates, and contributes little or no bandbroadening. The properties and applications of jet cooled spectra of non-volatile compounds dissolved in various supercritical fluids will be discussed.

32 DIFFERERENT MODES OF DENSITY CHANGES IN CAPILLARY SUPERCRITICAL FLUID CHROMATOGRAPHY OF OIL AND GAS SAMPLES. Bernd W. Wenclawiak, Dept. of Chemistry, University of Toledo, 2801 W. Bancroft Street, Toledo, OH, 43606.

Standards and samples of gasoline and oils have been separated with capillary column supercritical fluid chromatography (SFC) and detected with a flame ionization detector (FID).

Density changes of the fluid CO$_2$ were obtained by three different modes: 1) pressure increase of the CO$_2$ cylinder; 2) negative temperature gradient of the column oven; 3) a combination of 1 and 2.

All modes will be dicussed in detail and the effects on the separation will be shown.

33 SUPERSONIC JET SPECTROSCOPY WITH A CAPILLARY GAS CHROMATOGRAPHIC INLET. Steven W. Stiller and Murray V. Johnston, Department of Chemistry and Biochemistry/CIRES, University of Colorado, Boulder, CO 80309-0449.

Supersonic jet spectroscopy is a highly selective molecular detection method that has suffered from relatively poor sensitivity. Sensitivity problems arise in part from the sample dilution effect of a free jet expansion. We will discuss a new type of jet nozzle based upon sheath flow gas dynamic focusing that enriches the central core of the jet with analyte to provide better sample overlap with the incident laser beam. This method allows subnanogram detection limits to be achieved, can allow molecular selective detection, and provides a simple way to couple a capillary gas chromatograph to a supersonic jet expansion. The focusing and cooling properties of analyte enriched jets will be presented and spectral selectivity will be illustrated for the detection of naphthalene in unleaded gasoline.

34 THE REDOX CHEMILUMINESCENCE DETECTOR: HOW DOES IT WORK? S. A. Montzka, R. M. Barkley, and R. E. Sievers, Dept. of Chemistry and Biochemistry and the Cooperative Institute for Research in Environmental Sciences, Campus Box 449, Univ. of Colorado, Boulder, CO 80309.

The Redox Chemiluminescence Detector (RCD) involves the detection of analytes that can be oxidized by nitrogen dioxide over a heated gold or palladium catalyst. Downstream detection of nitric oxide produced in the redox reaction provides for a sensitive and selective chromatography detector. The mechanism by which these redox reactions occur, however, is poorly understood. Temperature Programmed Desorption and other surface techniques have been employed at catalyst operating pressures to observe the behavior of nitrogen oxides on a catalyst surface. Different support materials and catalyst metals have also been investigated to observe their effect on the redox reaction. The mechanistic implications of these and other results for RCD catalysis will be discussed.

35 DEVELOPMENTS IN REDOX CHEMILUMINESCENCE DETECTION. R. L. Shearer and R. E. Sievers, Cooperative Institute for Research in Environmental Sciences and Dept. of Chemistry and Biochemistry, Campus Box 215, Univ. of Colorado, Boulder, CO 80309.

The redox chemiluminescence chromatography detector (RCD) was invented by Nyarady and Sievers in our laboratory. (Nyarady, S. A. and Sievers, R. E., JACS, 1985, 107, 3726) Since that time, much effort has been directed toward a more comprehensive understanding of chemistry integral to the redox reaction. The principal factors controlling selectivity and sensitivity of the RCD are reagent gas, catalyst bed material, and catalyst bed temperature. Through judicious choice of reaction conditions, the selectivity of this detector can be tailored to a particular analysis. A great deal of effort is also being made to further develop the RCD for new applications. One such application is to use the RCD in a cylinder-less GC configuration. In this configuration, the ozone reaction chamber vacuum is used to draw air through the column, thus eliminating the need for a compressed carrier gas. The RCD in this configuration has been successfully used to analyze H_2 and CO in automobile exhaust and alcohol in breath samples. Further developments will yield a portable detector useful for these and other applications.

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The Analysis of Oxygenates by the Redox Chemiluminescence Detector for GC

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The redox chemiluminescence detector (RCD^{TM}) can selectively detect oxygen-containing compounds in the presence of much higher levels of other compounds such as water and saturated hydrocarbons. The detector is based on gold-catalyzed oxidation/reduction reactions of various reducing agents with nitrogen dioxide to form nitric oxide, which is subsequently detected by the ozone chemiluminescence technique. By judicious selection of the catalyst temperature, the RCD can be operated as a highly selective detector, or as a more general detector. At relatively low catalyst temperatures, only compounds that are easy to oxidize (e.g., alcohols, phenols and aldehydes) will produce a response, while at higher catalyst temperature, the RCD becomes sensitive to a wide array of compounds, including olefins and aromatic hydrocarbons.

37

DETERMINATION OF STRYCHNINE IN TISSUE SAMPLES USING REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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Strychnine (strychnidin-10-one) is a pesticide registered for use in controlling a variety of animals including porcupines, pigeons, pocket gophers, cotton rats, kangaroo rats, and ground squirrels. A convenient, reliable method for the quantitative analysis of strychnine is needed to investigate suspected poisonings in non-target species, secondary poisoning hazards, and illegal use of this chemical. A method has been developed that utilizes liquid/solid extraction followed by analysis using reversed-phase high-performance liquid chromatography. The method is applicable to a variety of sample matrices, including liver and muscle tissues, and allows for the determination of strychnine at less than 0.2 ppm in tissue samples. Ease of sample preparation and reduction in the amount of solvent used during extraction make this method attractive for routine analyses. Examples of the utility of this procedure for the determination of strychnine in a variety of matrices will be presented and discussed.

38 HYDROLYSIS OF SAMPLES FOR AMINO ACID ANALYSIS USING MICROWAVE DIGESTION,

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Amino acid analysis of proteins requires that they be hydrolyzed to free amino acids. Traditional methods of hydrolyzing proteins involve vigorous heating of samples in concentrated acids for long periods of time. Lack of reproducibility, low recoveries of specific amino acids, and the long sample preparation times required have been problematic in obtaining reliable and rapid amino acid analyses of samples with complex matrices. Use of microwave ovens for digestion and ashing of samples for metals analysis by ICP or AA has been reported. Development of procedures using microwave technology for amino acid analysis and selected results of that work will be reported in this paper. Samples worked with include grain meals, animal feed, calf collagen and insulin.

39 APPLICATION OF AQUEOUS SIZE EXCLUSION CHROMATOGRAPHY TO OIL-FIELD POLYMERS.

G. R. McGowan and G. W. Hawkins, Dowell Schlumberger, Post Office Box 2710, Tulsa, Oklahoma 74101.

The measurement of the molecular-weight distribution (MWD) of water-soluble polymers by size-exclusion chromatography is in general not straightforward due to interactions between the polymer, the eluant and the column packing. These interactions include adsorption, membrane and viscosity effects. We have assembled a system in which these interactions are minimized for a wide range of polymers used in oil-field applications. Generally, the simple analysis of the chromatogram from SEC does not provide the quantitative correlation with polymer properties needed. The system software written for our application is optimized for ease of use and flexible data treatment. It includes smoothing, baseline subtraction, data editing and storage, interactive graphics control, single injection calibration, and calculation and plotting of the MWD. We have applied the system to studying several types of polymers, including polyacrylamides, guar, hydroxypropylguar and synthetic copolymers. We have found that the MWD for a polymer fracturing fluid can be correlated with its viscosity and history, and can be used to predict its performance in specific applications.

40 ADSORPTION ON THE SURFACE OF ICE.

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The adsorption of low concentrations of substances on the surface of ice has important implications for the storage and transport of pollutants in the environment because of the large amount of ice surface in snow. The surface of ice has anamolous properties at normal temperatures which have been interpreted as a quasi-liquid layer. The use of frontal development chromatography with ice as a column allows the measurement of adsorption isotherms of substance at low concentrations and helps to elucidate important properties of the ice surface. Preliminary measurements of SO_2 adsorptions at -3°, -11°, and -30° C provide an example.

42 CONFIRMATION OF ZERANOL/ZEARALENONE RESIDUES BY GC/MS.

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Bovine tissue extracts containing residues of alpha, beta zearalenol and zearalenone were analyzed by capillary GC/MS as their corresponding TMS derivatives. Incurred sample residues ranged from 0.1 ppb to 10 ppb. The metabolic conversion of the administered alpha zearalenol to zearalenone and back to both alpha and beta zearalenol is discussed. In addition, capillary GC/MS separation and identification of all six isomers, alpha and beta (taleranol) zearalanol, alpha and beta zearalenol, zearalanone and zearalenone, is shown.

43 DETERMINATION OF DIMETRIDAZOLE/IPRONIDAZOLE METABOLITES IN ANIMAL TISSUE BY GC. M. C. Pullano and C. Andres Geisler, Food and Drug Administration, Veterinary Analytical Section, Denver, Colorado 80202.

A 2 ppb method for the extraction and quantitation of 2-hydroxy Ipronidazole and 2-hydroxy Dimetridazole in animal tissue has been developed. The method consists of an extraction of 10 g of tissue with water, cleanup using ultrafiltration membrane and acid-base extraction followed by capillary GLC. Recoveries ranged from 80-90% for both nitroimidazoles.

44 CONFIRMATION OF TETRACYCLINE RESIDUES IN ANIMAL FEEDS BY HPLC/UV AND TLC. E. E. Martinez and W. Shimoda, Food and Drug Administration, Animal Drug Researh Center, Denver, Colorado 80202.

Chlortetracycline, oxytetracycline and tetracycline are antibiotics commonly used in animal feeds. A confirmatory method is described. Procedures for their detection in animal feeds by HPLC/UV and TLC are reported. Tetracyclines are extracted in McIlvaines buffer, cleaned using Amberlite XAD-2, and separated on a reverse-phase C_{18}, 5 micron, Nova-Pak column. Parameters such as recoveries, detection limits, HPLC conditions, mobile phase and detector conditions are reported.

45 A MULTIRESIDUE METHOD FOR BETA-LACTAM ANTIBIOTICS IN MILK AND TISSUE BY HPLC. R. K. Munns and W. Shimoda, Food and Drug Administration, Animal Drug Research Center, Denver, Colorado 80202.

A method of determining total penicillins begins with an enzymatic hydrolysis of the B-lactam ring to form their respective penicilloate product. Acetonitrile precipitates much of the casein and protein, which are then separated from the liquid by centrifugation. The lipids are removed from the aqueous fraction with methylene chloride. Mercuric chloride is added, which reacts with the penicilloate to liberate the side chain that has a terminal aldehyde. These penilloaldehyde products are extracted with methylene chloride and are subsequently reacted with dansyl hydrazine. The resulting fluorolabeled side chains are separated by liquid chromatography on a C_{18} column with acetonitrile-water as mobile phase. The fluorescence is measured by the mercury line at 254 nm excitation wavelength and a 500 nm filter on the emission side. The overall average recoveries from milk spiked at 25, 50, and 100 ppb are benzyl penicillin 79.4%; phenoxymethyl penicillin 59.7%; phenethicillin 75.9%; nafcillin 87.7%; methacillin 47.5%; oxacillin 57.6%; cloxicillin 37.3%; and dicloxicillin 26.4%.

47 HIGH PRESSURE LIQUID CHROMATOGRAPHIC-ELECTROCHEMICAL DETERMINATION OF ZERANOL/ ZEARALENONE AND THEIR METABOLITES IN EDIBLE ANIMAL TISSUE. J. E. Roybal, R. K. Munns, J. A. Hurlbut, W. J. Morris and W. Shimoda, Food and Drug Administration, Animal Drug Research Center, Denver, Colorado 80202.

A sensitive method for the detection and confirmation of zeranol and zearalenone, as well as their isomers and metabolites, in edible animal tissue is described. The analytes are extracted from tissue with methanol, enzymatically hydrolyzed, cleaned up by acid-base partitioning, quantitatively detected by HPLC/EC and confirmed by GC/MS. HPLC/EC is performed by isocratic elution with buffered mobile phase via Nova-Pak reverse phase C_{18} column with amperometric electrochemical detection at +0.90V.

48 DETECTION OF SELECTED VETERINARY DRUGS BY HPLC USING ELECTROCHEMICAL DETECTION. J. A. Hurlbut, J. E. Roybal, R. K. Munns, E. E. Martinez, W. J. Morris, and W. Shimoda, Food and Drug Administration, Animal Drug Research Center, Denver, Colorado 80202.

High performance liquid chromatography with electrochemical detection has proven itself to be a very useful technique for the determination of electrochemically oxidizable or reducible compounds in complex matrices. A number of veterinary drugs such as tetracyclines, penicillins and zeranol related compounds were investigated. They were separated using a reverse phase, C_{18}, Nova Pak, 5 micron column, and they were detected using a Bioanalytical Systems amperometric controller. Parameters such as extraction conditions, recoveries, oxidation/reduction potentials, and detection limits are reported.

49 FT SPECTRAL DECONVOLUTION IN 1-DIMENSIONAL EPR IMAGING.

Martin M. Maltempo, Physics Department, University of Colorado at Denver, 1100 14th Street., Denver, CO 80202

In the most common form of the EPR imaging experiment performed with static field gradients, the spectral width of most paramagnetic species results in significant overlap of absorption peaks from spatially separated species. Consequently, there is an inherent difficulty distinguishing between the spatial information necessary for spin mapping and the spectral information that will yield the EPR spectrum specific to a particular spatial site. One response to this difficulty is to consider the restricted problem in which one assumes that the EPR signal of the paramagnetic species is spatially invariant. The task of obtaining spin mapping then becomes a problem in spectral deconvolution. The use and limitations of FT deconvolution, and associated filtering, will be discussed. This research was supported, in part, by a grant from the National Science Foundation (#CHE-8421281).

50 MICROCOMPUTERS APPLIED TO NMR DATA PROCESSING,

James W. Cooper, IBM Instruments, Inc.
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Increasingly, laboratory instruments such as NMR spectrometers are controlled by a cluster of microcomputers and microprocessors, so that each is dedicated to the task it performs most effectively. In addition, offline data handling is becoming more common with remote computers used for processing, plotting, data manipulation and report generation. A summary of recent work in this field will be presented.

51 THE COMPUTER NETWORKING AND WORKSTATION ENVIRONMENT IN NMR,

David W. Mehaffy,
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Abstract: The time required to perform an nmr experiment is generally short compared to the time required to process the acquired data. It is becoming more effective to move the data to a remote computer for data manipulation and plotting, freeing the nmr control computer for further data collection. The data can also freely move about a network that is connected to the nmr spectrometer. A summary of recent work of implementing a network of PC-ATs with nmr spectrometers will be presented.

52 PHOTOACOUSTIC SPECTROSCOPY APPLIED TO WHOLE COLUMN DETECTION CHROMATOGRAPHY.

K.L. Rowlen, J.W. Birks, J. Avery, CIRES and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0449.

A new chromatographic technique, Whole Column Detection Chromatography (WCDC), is to be developed for high performance liquid chromatography (HPLC). In this technique the eluites are detected along the entire length of the column, and thus the separation process is continuously monitored. Photoacoustic spectroscopy (PAS) is ideally suited to WCDC in that the same compounds detected in HPLC by uv absorption would be detected, and PAS would be relatively immune to scattering of light by the column and the column packing. Specifically, here we propose to implement the use of a chopped, frequency-doubled argon laser to stimulate a photoacoustic signal on a quartz, microbore HPLC column. The *photoacoustic signal will be detected by a piezoelectric crystal and demodulated via a* lock-in amplifier or boxcar integrator. The resolution element will be determined by the width of the laser beam, and the beam will be swept along the length of the column to obtain each whole column chromatogram.

53 THE ROLE OF COMPUTERS IN THE DESIGN OF ANALYTICAL INSTRUMENTATION

James P. Avery, Dept. of Electrical and Computer Engineering, University of Colorado-Boulder, Boulder, Colorado 80309-0425

The role of the computer in the analytical laboratory and particularly in analytical instrumentation has changed as the price of computers has come down, and the capabilities of the computers has risen. Tasks once too costly for computer control are now too costly to do manually; many measurements now made routinely could not be made at all without the computer systems imbedded in the instruments. I would like to present a somewhat subjective and incomplete review of the role that computers have played in the past, are playing now, and will play in the future of analytical instrumentation. In many cases, the historical precedents have colored our current perceptions of what computers can and should do for us. The current trends towards multi-instrument analysis systems and distributed computer systems in instruments deserves some comment and analysis. The future role of artificial intelligence and particularly expert systems in analytical instrumentation systems is another topic I will discuss. I am particularly interested in how these systems will be designed, who will do the design, and what training these individuals or teams will need to have. In my view, the answer is that a much more multi-disciplinary approach to the problem will be required than has traditionally been "allowed" in academic chemistry. I hope to be able to discuss the ramifications of the changes I see as necessary in the organization of chemistry departments and their curricula. Industrial and research analytical chemists will also be affected by the changes in the technology used in future instrumentation, although perhaps not so severely.

54 EXPLORATORY CHEMOMETRIC TECHNIQUES APPLIED TO ANALYTICAL DATA.

Robert J. Sistko, Center for Environmental Sciences, University of Colorado at Denver, Denver, Colorado 80202.

Over the past six years the chemical subdiscipline, chemometrics, has become an increasingly valuable tool for chemists involved in measurement interpretation. The need for chemometrics has arisen in response to several current data management problems. The advent of automated and computer assisted analyses has increased data production to an unprecedented rate. The sheer volume of samples analyzed (and variables determined on each) can adversely affect the likelihood of elucidating a useful answer for a specific chemical problem. Also, analytical chemists are realizing that data are not information; and data reduction accomplished via traditional statistics often increases the amount of data while only minimally increasing the amount of chemical information. While chemometric techniques are being used with increasing frequency, many chemists view the methodology as being too complex for routine use. This paper will present three exploratory processes which have found widespread application in the analytical laboratory. Only minimal statistical and mathematical training is necessary to apply these techniques. Examples will illustrate cluster analysis, principle component analysis and classification analysis as they relate to analytical chemistry.

55 THE APPLICATION OF PATTERN RECOGNITION IN CHARACTERIZATION OF SOLID PRODUCTS IN AUTOXIDATION OF HYDROCARBON MIXTURES.

Kaveh Zarrabi and Stephen R. Daniel, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401.

Hydrocarbon fuels in contact with air produce insoluble solids of very complex composition. Simple binary mixtures of hydrocarbons exhibit similar behavior yielding solids too complex for characterization by conventional analytical methods. The nature of such solids has been studied by HPLC, GPC and pyrolysis mass spectrometry in conjunction with pattern recognition techniques. The influence of hydrocarbon composition, temperature, and the presence of various trace compounds on the nature of solids produced is discussed using linear projection and non-linear mapping.

56 APPLICATION OF AN INTEGRATED SOFTWARE SYSTEM FOR PROCESSING OF ANALYTICAL DATA.

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The availability of integrated software systems incorporating spreadsheets, business graphics, database management and word processing provides valuable tools to the analyst to manage the reporting of information from the laboratory. This paper describes the interface of analytical data from a simultaneous inductively coupled plasma (ICAP) into an integrated environment. The trace metal analysis format generated by the ICAP can now be modified by the user without the knowledge of computer languages. Predefined reporting templates can be constructed to generate forms required by regulatory agencies. Direct insertion of these forms into the word processor provides a finished document from the laboratory. The use of the database manager and the graphics package provides the means to plot trend analysis or control plots.

57 LANGUAGE CONSIDERATIONS FOR WRITING A CUSTOM LIMS

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Writing a custom LIMS requires the software meet certain design requirements such as speed, adaptability and portability to other CPUs. Using common database management programs such as dBaseIII or Rbase 5000 leave much to be desired in terms of speed and portability onto other CPUs. The C programming language offers great speed, flexibility and portability to other CPUs. Run-time critical modules can be written in assembly and easily linked to C modules. C modules are easily ported to other CPUs as necessity dictates. By using C programming language, built-in obsolescent is minimized. These factors combined give the user maximum return on his software investment.

58 MICROCOMPUTER BASED LABORATORY INFORMATION MANAGEMENT SYSTEMS (LIMS)

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Collecting, analyzing, correlating, and managing laboratory data has historically been a costly, labor-intensive function in an analytical laboratory. Using the powerful microcomputers currently available in conjunction with carefully selected software can give laboratory personnel a powerful management tool. This paper will review several of the most popular commercial laboratory software packages and describe the planning and installation of a LIMS package.

59 DESIGNING A CUSTOM LIMS FOR A HIGH VOLUME LABORATORY ON AN IBM PC

Richard Hardenstein, General Government Computer Center, 2002 S. Colorado Blvd., Denver, CO 80222.

Designing an IBM PC based LIM system capable of managing a laboratory with a large annual sample volume requires careful design considerations. A methodical evaluation of the current flow of data (on paper) through the lab combined with feedback from the client enables us to design a custom system which eliminated the "choke-points" from the traditional flow of data. Large labor savings were made since it was estimated that over 50% of the chemists time was spent manipulating paper before the LIMS was installed. Sample tracking, accounting functions and retrieval or archived information were all improved due to the LIMS. The system was designed with portability to larger machines as one design condition.

60 BARCODE AS A KEY ELEMENT FOR LIMS EFFICENCY

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A properly designed LIM system is capable of vastly improving the flow and control of data in the laboratory. A major impediment to efficient LIMS operation is data input to the system. There are also problems associated with updating records already on the system with results from analysis. An experienced keypunch operator averages about 10k strokes per hour with about a 1% error rate. By using barcoded sample request forms, worksheets and other documents, an inexperienced operator can input in excess of 25k characters per hour with virtually no errors. This obviously is an efficient manner of data entry into the LIM system as it is fast and does not require any special skills. Many companies offer barcode add-ons; however, there are some significant pitfalls to avoid.

61 ENDOR STUDIES OF METALLOENZYME ACTIVE-SITE STRUCTURE AND FUNCTION.

Brian M. Hoffman, Department of Chemistry, Northwestern University, Evanston, Illinois 60201.

In electron-nuclear double resonance (endor) spectroscopy, a radiofrequency field induces nuclear transitions in a paramagnetic center whose epr signal is being monitored. The occurrence of a nuclear transition is detected by a change in the epr signal intensity. Thus, endor provides an nmr spectrum of those nuclei which interact with the electron spin of the center. The measurement is inherently broad-banded: In work to date we have observed resonances from ^{1}H, ^{14}N, ^{17}O, ^{33}S, ^{57}Fe, $^{95,97}Mo$, $^{63,65}Cu$. Thus endor studies of isotopically labelled metallo-protein samples offer the possibility of characterizing every atom of an enzyme active site and of bound substrate. Although most studies involve frozen solution samples, our theory of polycrystalline endor spectra provides a means of obtaining full tensor information. Among our results from this technique is a description of the properties of the molybdenum-iron cofactor of nitrogenase, as well as the discovery of key elements in the mechanism by which aconitase converts citrate to isocitrate.

62 EPR STUDIES OF THE ROLE OF NON-HEME IRON IN OXYGENASES.

Betty Jean Gaffney, D. V. Mavrophilipos, A. S. Yang and Leslie M. Bloom, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

The enzymes phenylalanine hydroxylase and lipoxygenase depend on iron for catalysis but the iron is not associated with either heme or acid-labile sulfur. Both proteins present interesting problems regarding the structure of the iron center and the way in which iron participates in catalysis. EPR studies of high-spin ferric iron in these proteins have revealed multiple geometries around the metal. Thus, EPR may be used to determine which factors give a unique iron geometry, a necessary condition for studies of the iron center by other techniques. EPR studies have also been used to determine the stoichiometry of reduction of iron in phenylalanine hydroxylase and to show that two titratable groups near iron may influence catalysis by lipoxygenase. Both of these proteins exhibit substantial rapid passage signals which may provide additional information about the iron centers.

63 EPR SATURATION STUDIES OF METAL ION CENTERS IN PROTEINS AND ENZYMES.

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Studies in our laboratory characterizing the immediate ligand coordination environment and structure of metal ion centers in enzymes and proteins will be reviewed. The parameter $P_{1/2}$, the microwave power at which the saturation factor equals 0.5, provides a direct monitor of spin lattice relaxation time T_1. Under conditions of constant T_2, the temperature dependence of the parameter $P_{1/2}$ is employed to estimate the zero-field splitting (ZFS) high-spin metal ions. For the high-spin Co^{2+} ion, the value of the ZFS is a direct signature of coordination number. Based on the ranges of values found for structurally defined small molecule complexes in crystals, the coordination number of the active site metal ion is assigned in catalytically competent enzyme reaction intermediates of Co^{2+}-reconstituted forms of carboxypeptidase A and liver alcohol dehydrogenase. In both enzymes the coordination number is increased to accommodate a water molecule as a fifth ligand in catalytically competent states although the coordination number in the free enzyme is shown to be four. We have also observed that the parameter $P_{1/2}$ is sensitive to the presence of oxygen-17 enriched into inner-sphere coordinated oxygen-donor ligands. This effect is ascribed to the influence of contact hyperfine interactions on the correlation time of the local field through spectral diffusion. This interpretation is supported through pulse saturation and recovery experiments. The observation of a change in cw power saturation properties upon introduction of ^{17}O-enriched oxygen donor ligands confirms the assessment of metal ion coordination environment made on the basis of ZFS measurements. (Supported by GM 21900 and AA 06374).

64 PULSED ELECTRON PARAMAGNETIC RESONANCE STUDIES OF COPPER BINDING SITES IN AMINE OXIDASES.

J. McCracken, D. Dooley and J. Peisach. Albert Einstein College of Medicine, Bronx, NY 10461 and Amherst College, Amherst, MA 01002.

Pulsed EPR spectroscopy utilizing the electron spin echo (ESE) envelope modulation technique has been used to study Cu(II) binding sites in both porcine kidney and bovine plasma amine oxidases. The purpose of this study was to determine what structural changes occur at the Cu when the anion inhibitors, CN^- and N_3^-, are present, and when the enzyme substrate, benzylamine, is added. For the native enzyme, ESE spectra demonstrate the presence of bound histidyl residues in two distinct magnetic environments. From an ESE comparison with enzyme exchanged against D_2O, we show that water is coordinated to Cu(II). When benzylamine is added to the enzyme, no alteration in metal-ligand structure is noted. However, the addition of the anion inhibitors produces changes in the spectrum indicating that H_2O is no longer coordinated to Cu(II). Also, there is a significant alteration in the magnetic couplings for bound histidyl residues, and magnetic coupling between the Cu(II) and the ^{14}N of CN^- is observed. These experiments provide direct evidence that the action of CN^- and N_3^- in the inhibition of porcine kidney and bovine plasma oxidases involves binding to the Cu(II) cofactor by displacing a H_2O ligand.

65 SPIN LABEL STUDIES OF THE ACTIVE SITES OF AMINE OXIDASES.

Frederick T. Greenaway, Peter Spacciapoli, Coleen M. Young, Department of Chemistry, Clark University, Worcester, MA 01610

The active site of the amine oxidases contains an aldehyde cofactor whose identity has not been established in all cases. In order to investigate the environment of the aldehyde cofactor in the amine oxidases, lysyl oxidase and bovine plasma amine oxidase, we have labeled the aldehyde with a hydrazide nitroxide and have investigated the EPR spectra under a variety of experimental conditions. Such labelling destroys all activity, consistent with reaction at the aldehyde. The results can also be used to discuss the relationship between the aldehyde site and the copper(II) which is also required for activity. The results show that the copper is not close to the aldehyde, in contrast to most mechanistic model predictions.

66 CW AND PULSED EPR STUDIES OF CYCLIC DIPEPTIDE Cu(II) COMPLEXES.

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Cu(II)-cyclo(methionine-histidine) and Cu(II)-cyclo(histidine-histidine)complexes are useful models for the copper site of several copper containing proteins. For example, the Cu(II)-cyclo(histidine-histidine)complex has been shown to have superoxide dismutase activity (S. Kubota & Yang, 1984, PNAS 81, 3283). We have used CW EPR, X-Band and S-Band, and electron spin echo envelope modulation, X-Band, to study superhyperfine interactions between Cu(II) and ligands. Echo envelope modulation and superhyperfine spectral analysis yields hyperfine and nuclear quadrupole coupling parameters for pyrimidine and pyrrole nitrogens of the ligated histidines. The magnetic coupling parameters are used to suggest possible ligand binding in these cyclic dipeptide Cu(II) complexes.

67 ELECTRON SPIN ECHO AND SATURATION TRANSFER EPR STUDIES OF POLYMER STATE SICKLE HEMOGLOBIN.

Michael E. Johnson*, Leela Kar*, P. Thiyagarajan*+ and Michael K. Bowman+, *Medicinal Chemistry Department, University of Illinois, Chicago, IL 60680; and +Chemistry Division, Argonne National Laboratory, Argonne, IL 60439.

The motional behavior of spin-labeled deoxygenated sickle hemoglobin (dHbS) has been studied using 9 and 35 GHz saturation transfer (ST) EPR, and electron spin echo (ESE) spectroscopies. We find that the ST-EPR spectra for the dHbS gel state cannot be described as a simple superposition of spectra from immobilized Hb plus solution state Hb, but instead suggest that the individual dHbS molecules exhibit limited, probably anisotropic, wobbling or rotational oscillation within the polymer fiber. Interpretation of the ST-EPR spectra is complicated in that the observed spectra are a superposition from the polymeric and monomeric dHbS components in the system. We have also used ESE techniques to obtain the first direct relaxation measurements on a spin-labeled protein at physiological temperatures, and have partially circumvented the superposition problem, in that the monomeric dHbS exhibits a very short relaxation time, and most of its signal decays within the instrumental dead time. The resultant ESE spectra thus primarily report the behavior of the polymer dHbS component. Generation of 2-D contour plots and comparison with reference ESE spectra from Hb that has been approximately immobilized either by ammonium sulfate precipitation or by siloxane entrapment also indicates that polymer dHbS exhibits a limited, complex motional behavior. Computer simulations to describe the behavior are in progress.

68 REACTION YIELD DETECTED MAGNETIC RESONANCE (RYDMR) AND MAGNETO-OPTICAL DIFFERENCE SPECTROSCOPY (MODS) OF PHOTOSYNTHETIC REACTION CENTERS

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Two new techniques for the study of radical reactions are described. Photolytic reaction yield detected magnetic resonance (RYDMR) is carried out in low magnetic fields (10 to 20 mT), using cw illumination and a cw microwave field B_1 of no more than 0.1 mT in the rotating frame. The technique is applied to reaction centers of photosynthetic bacteria in which the radical pair $^1[D^+A^-]$ is photo-induced. Through singlet-triplet mixing the $^3[D^+A^-]$ state is created. Application of microwaves resonant between the Zeeman levels of this state perturbs the spin dynamics in the pair, thereby influencing the yield of recombination products. These are measured by monitoring the optical absorption. From the B_1 dependence and line shape simulations we conclude that in the radical pair the exchange interaction is about 0.8 mT and the dipolar interaction $|D| < 2$ mT, whereas the sum of the singlet and triplet decay rate constants is $< 0.42 \pm 0.02$ ns^{-1}.
Magneto optical difference spectroscopy (MODS) of the reaction centers utilizes the dependence of the spin dynamics of the pair D^+A^- on a small laboratory field B_0 (0 - 30 mT). A modulated $B(t) = B_0 \sin \omega t$ field generates absorbance changes $A(\omega,t) = A_0(\omega) \sin 2\omega t$. By lock-in detection and scanning the wavelength of the monitoring light we have measured with sensitivity up to $\Delta A_0/A_0 = 10^{-7}$ triplet-minus-singlet absorbance difference spectra. The spectra are interpreted using exciton theory of the coupled pigment systems of the reaction center.

69 SPIN-LABELLED 8-HYDROXYQUINOLINE.

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The first spin-labelled chelate was prepared in the late 1960's. Since then, less then 100 spin-labelled chelates have been prepared and evaluated either for their analytical applications or study of metal-radical interactions. With a few exceptions, previous spin-labelled chelates were prepared by attaching a chelating functionality to a spin label molecule. The present work describes the results of the opposite approach. A spin label was attached to an established and extensively researched chelator, 8-hydroxyquinoline, and its ESR properties with various metals investigated.

70 ELECTRON SPIN RESONANCE AND ELECTRON SPIN ECHO STUDIES OF Rh(II) SPECIES IN X AND Y ZEOLITES.

Daniella Goldfarb and Larry Kevan, Department of Chemistry, University of Houston, Houston, Texas 77004.

The characterization of Rh species formed in X and Y zeolites in terms of their location and interaction with adsorbates is important due to their catalytic activity. Rh(II) species are generated in X and Y zeolites through exchange with $[Rh(NH_3)_5Cl]Cl_2$ and subsequent activation by heating in flowing oxygen. The paramagnetic Rh(II) species formed after various treatments were studied by electron spin resonance (ESR) and electron spin echo modulation (ESEM) spectroscopies. The zeolites which have been studied are NaX, NaY, CaX and CaY. Comparison of the Rh(II) species formed following similar treatments gives information about the effect of the cocation, i.e. Na^+ and Ca^{2+}, and the Si/Al ratio, $\sim$1.2 and $\sim$2.4 in X and Y respectively, on the location of Rh(II).

In NaX and NaY activation in the 350-400° C range generates species A whereas activation to 450-500° C generates species C. On the basis of the interaction distance with adsorbates obtained from ESEM data and on the effect of O_2 on the ESR linewidth these species were assigned to the β-cage and to the hexagonal prism respectively in the zeolite structure. In contrast, in CaX and CaY following activation the spin concentration is very low due to formation of Rh(II) dimers. However, adsorption of H_2O, NH_3, CO and O_2 increased the ESR signals by 1-2 orders of magnitude indicating the dissociation of the dimers. In NaY, CaX and CaY zeolites Rh cations interact with oxygen to form a paramagnetic adduct which further reacts with water and methanol, whereas adsorption of O_2 has no effect in NaX. These differences are interpreted in terms of the number and preferred location of Na^+ and Ca^{2+} in X and Y Zeolites.

71 CONDUCTING PROPERTIES AND ELECTRON SPIN RESONANCE OF POLYPHENOTHIAZINE AND POLYPHENOXAZINE,

M. D. Pace and O.-K. Kim, Naval Research Laboratory, Code 6120, Washington DC, 20375-5000

Polyphenothiazine (PTL) and Polyphenoxazine (POL) are conducting polymers which have a conjugated ladder structure. They differ by one chain linkage which is sulfur in PTL and oxygen in POL. The electrical conductivity of doped versus undoped PTL increases by ca. 10^4 (ranging from 5×10^{-6} ohm^{-1} cm^{-1} for undoped PTL to 2.1×10^{-2} ohm^{-1} cm^{-1} for PTL doped with $ClSO_3H$). For POL the conductivity increases by ca. 10^3 for doped versus undoped samples. Electron paramagnetic resonance (EPR) spectra of PTL and POL were recorded and compared with EPR spectra of PTL doped with H_2SO_4 or $CLSO_3H$ or AsF_5. In all cases the EPR signal consists of a single first-derivative lineshape. The spin concentration of undoped PTL is 2.5×10^{15} and it becomes 10 times greater when doped. A discussion of the conductivity and EPR lineshape analysis of these polymers will be presented.

72 EPR STUDY OF PHASE TRANSITIONS IN $NH_4Pr(SO_4)_2.4H_2O$ MONOCRYSTALS. V. M. Malhotra, Southern Illinois University, Carbondale; R. Chatterjee and H. A. Buckmaster, Univ. of Calgary, Calgary and W. R. M. Graham, Texas Christian Univ., Fort Worth.

The 9.4 GHz electron paramagnetic resonance (EPR) of Gd^{3+} impurity ions in $NH_4Pr(SO_4)_2.4H_2O$ monocrystals has been studied at 10-300 K. The Gd^{3+} impurity ions are found to substitute for the trivalent Pr ions in two inequivalent magnetic complexes, corresponding to the tetramolecular unit cell. The EPR spectra at 296 K have been analyzed, using an orthorhombic symmetry spin-Hamiltonian. The observed zero field splittings of Gd^{3+} impurity ions in nine coordinated double sulfates and in other hydrated host lattices indicate the inadequacy of the splittings mechanisms based only on symmetry. Using the temperature dependence of the EPR zero field splitting, linewidths and intensities, it has been shown for the first time that $NH_4Pr(SO_4)_2.4H_2O$ monocrystals have first order phase transitions at 250 and 137 K. FTIR spectrum shows that the NH_4^+ ion freely rotates in the lattice at 296 K. The temperature dependence of the linewidths suggests that water molecules show an onset of fluctuation near 250 K. Below 137 K, two unit cells collapse to form a new unit cell whose dimensions are twice that of 296 K.

73 USE AND ABUSE OF MICROWAVE EQUIPMENT IN THE NAME OF SCIENCE. Ira B. Goldberg, Rockwell International Science Center, 1049 Camino Dos Rios, Thousand Oaks, California 91360.

In all but a few electron spin resonance (ESR) experiments, a microwave resonant structure (typically a cavity or helix) is needed to maintain the sufficiently high sensitivity so that measurements can be made. Very often, the transient behavior of a sample subjected to an excitation or perturbation needs to be studied, and in this case the microwave cavity or resonant structure needs to be adapted to allow the appropriate experiment to be carried out. This typically results in degradation of microwave performance. This discussion provides a brief review of the types of cavities and helicies which have been built, and presents some of the constraints on types of cavities from the points of microwave, chemical and spectroscopic performance.

74 ELECTRON PARAMAGNETIC RESONANCE AT HIGH PRESSURE USING A DIAMOND ANVIL CELL
Nobuko Sakai and Joe H. Pifer
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We have developed an X-band electron resonance apparatus incorporating a diamond anvil cell to generate pressures up to 100 kbar. The system can operate down to 1.5 K and the pressure can be changed and calibrated via ruby fluorescence while at low temperature. The system differs from a conventional EPR cavity system in that the pressure gasket acts as the microwave resonator. For an initial application, the system is used to examine the pressure dependence of the magnetic properties of a chromium chalcogenide spinel, $CdCr_2Se_4$.

75 QUANTITATIVE STUDIES OF RADICAL DYNAMICS IN LIQUID JETS. David M. Bartels and Alexander D. Trifunac, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

Experiments at Argonne National Laboratory have demonstrated the feasibility of using free-flowing liquid jets rather than glass tubes to introduce samples into an EPR cavity. This technique has two primary advantages for pulse radiolysis/EPR studies in liquids. First, the signal (at $g \approx 2.00$) generated in quartz sample tubes by radiation damage is eliminated, which, in many cases, allows detection of weak radical lines that would otherwise be obscured. Second, the liquid jets are quite immune to damage from an electron beam, and higher beam currents and repetition rates are possible. We are presently exploring the possibility of simultaneous optical and EPR detection with this geometry. Some recent applications include the study of fast radiolysis chemistry, the study of diffusion controlled reactions of radicals, and the quantitative study of relaxation in transient radicals.

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76 APPLICATION OF A HIGH-PRESSURE-HIGH TEMPERATURE ESR CAVITY TO THE STUDY OF ENERGETIC REACTIONS,

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A microwave cavity has been constructed to permit study of systems at high pressures and temperatures. The sample heater is located within the cylindrical cavity and is shielded from the microwave field by a cylindrical metallic sheath so that the composite system behaves as a coaxial cavity operating in the cylindrical TE_{011} mode. It is possible to heat the sample from room temperature to 800° within 20 sec.

This system has been used in coal liquefaction studies to determine the variation of free radical concentration with hydrogen pressure and reaction temperature. Comparison spectra obtained when deuterium gas is substituted for hydrogen will be shown.

Free radicals are formed during the thermal decomposition of many high explosives and the high pressure cavity provides a safe environment for study of such systems. Spectra obtained during decomposition of trinitrotoluene (TNT) and nitramine explosives (HMX and RDX) will be presented.

77 A SPIN LABELLED ELECTRODE.

K. di Gleria, H.A.O. Hill, D.J. Page and D.G. Tew, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, England.

The study of electrode surfaces has attracted many chemists, with a number of spectroscopic techniques being used to study electrode interfaces *in situ*. Unfortunately they do not readily give information on the mobility of electrode bound species or the dynamics of electrode reactions.

We have prepared a spin label from the condensation of di-N,N-*tert*-butoxycarbonyl-2-cysteine with 4-amino-tetramethyl-piperidine-1-oxyl. This label can be bound to a gold electrode and its spectra may be observed in an electrochemical e.s.r. flat cell.

Two distinct spin label environments are observed. The effect of potential, electrolyte and various solution additives on the populations of the two environments will be presented. This study introduces spin labelled electrodes and shows how they may be applied to the study of the electrode interface.

78 MEASUREMENT OF ROTATIONAL MOLECULAR MOTION BY SATURATION RECOVERY EPR.

P. Fajer, J. Feix, J. Hyde and D. Thomas, Dept. of Biochem., Univ. of Minnesota, Minneapolis and National Biomedical ESR Center, Medical College of Wisconsin, Milwaukee.

We have used saturation-recovery EPR (SR-EPR), a time-resolved EPR technique, to measure directly the microsecond rotational diffusion of spin-labelled proteins. SR-EPR utilizes an intense microwave pulse to saturate a spin population having narrow distribution of orientations with respect to the magnetic field. The time evolution of the signal is then observed. The signal increases in time as saturation is relieved by spin-lattice relaxation (T_1) as well as by spectral diffusion (τ_{sd}) which is a function of rotational diffusion (τ_r) and spectral position. In the presence of both events, the recovery is biphasic, with the initial phase related to both τ_r) and T_1, and the second phase determined only by T_1. We have measured the saturation recoveries of spin-labelled haemoglobin tumbling in media of known viscosities, as a function of rotational correlation time (τ_r) and pulse duration (t_p). The τ_r values estimated from the initial phase of recovery were in good agreement with theory. Variation of the pulse time can also be used to determine τ_r. For $t_p < \tau_{sd}$ the recoveries were observed to be biphasic, for $t_p > \tau_{sd}$ a single-exponential. T_1 values were determined from the recoveries following pulses quenching spectral diffusion or from the second phase of recovery after shorter pulses. These results demonstrate that SR-EPR is applicable to the study of motion of spin-labelled proteins. Its time-resolution should provide a significant advantage over steady-state techniques, particularly in the case of motional anisotropy or system heterogeneity.

79 ESR, ENDOR AND TRIPLE RESONANCE STUDY OF RADICALS FORMED FROM 9,10-ANTHRAQUINONE-SULFONATES AND 2-METHYLANTHRAQUINONE IN SOLUTION. R. Mäkelä and M. Vuolle, Department of Chemistry, University of Jyväskylä, Finland.

ESR, ENDOR, and TRIPLE resonance spectra have been recorded for 2-methylanthraquinone, anthraquinone-1-sulfonate, anthraquinone-2-sulfonate, anthraquinone-1,5-disulfonate and anthraquinone-2,6-disulfonate anion radicals, and in strongly acidic medium for 2-methylanthraquinol, anthraquinol-1- and anthraquinol-2-sulfonate, anthraquinol-1,5- and anthraquinol-2,6-disulfonate cation radicals. The hyperfine coupling constants and g factors are given. The coupling constants were calculated by the INDO method and their assignment is discussed. The ENDOR spectra show that there are more coupling constants than were detected earlier by ESR. The dideutero radicals of the anthraquinols were studied by ESR.

80 ESR AND ENDOR STUDY OF PHOTO OXIDATION OF PORPHYRINS. S. Stepanovich and H. van Willigen. Department of Chemistry, University of Massachusetts at Boston, Boston, MA 02125.

Photo excitation of metalloporphyrins in the presence of electron acceptors in frozen matrices can give rise to electron transfer. The rate of electron transfer as function of light intensity, solvent medium, and acceptor concentration was studied using the ESR signals of the photogenerated doublet radicals and of the photoexcited porphyrin triplets. The identity of the free radicals was established with the aid of ENDOR measurements.

81 AN ELECTRON SPIN RESONANCE INVESTIGATION OF RADICAL INTERMEDIATES IN CHOLESTEROL. Cynthia L. Sevilla, David Becker, and Michael D. Sevilla, Department of Chemistry, Oakland University, Rochester, MI 48063

An ESR investigation of the free radical chemistry of cholesterol and a number of cholesterol derivatives and analogs is reported. The initial radicals formed in solid oxygen free cholesterol samples after γ-irradiation at 77K are found to be a tertiary side chain radical and an allylic radical in the cholesterol A and B rings. At 300K only the allylic radical is found. The structure of the allylic radical is confirmed by experiments on two analogs of cholesterol, 7-OH cholesterol and the selectively deuterated 7-D-7-OH cholesterol, both of which produce the allylic radical after γ-irradiation by loss of the hydroxyl group. Cholesterol samples with oxygen present provide evidence for formation of two distinct peroxy radicals originating with the two carbon radicals found in the oxygen free samples. These peroxy radicals are suggested to have different reactivities resulting from the different motional freedom each possesses. It is found for four cholesterol esters, one cholesterol derivative, and one sterol, that the only radical stable at room temperature in oxygen free samples is the allylic radical. In only one ester, cholesterol chloroacetate, is the allylic radical not the stable room temperature radical.

82 **EFFECT OF CHOLESTEROL ON THE TRANSPORT OF A COPPER SQUARE PLANAR COMPLEX IN MEMBRANES.** W. K. Subczynski,[a,b] W. E. Antholine,[a] and J. S. Hyde[a], National Biomedical ESR Center, Medical College of Wisconsin, Milwaukee, WI 53226 and [b]Department of Biophysics, Jagiellonian University, Krakow, Poland.

We have previously defined the oxygen transport parameter: $W(O_2) = T_1^{1}(AIR) - T_1^{1}(N_2)$, where the T_1's are the spin-lattice relaxation times of nitroxide radical spin labels in the presence and absence of oxygen. In this work oxygen was replaced by the copper complex 3-ethoxy-2-oxobutyraldehyde bis(N^4-dimethylthiosemicarbazanato)Cu(II), $CuKTSM_2$. The $CuKTSM_2$ transport parameter, $W(CuKTSM_2) = T_1^{1}(CuKTSM_2, N_2) - T_1^{1}(N_2)$, was measured in the membranes using the saturation recovery technique. The parameter $W(CuKTSM_2)$ is proportional to the product of the concentration of $CuKTSM_2$ and its translational diffusion constant in the local environment of the nitroxide moiety of the spin labels. $W(CuKTSM_2)$ was measured in DMPC, DSPC, and EYPC membranes containing 0 and 27.5 mole % cholesterol. Spin labels 16-SASL (the nitroxide moiety close to the center of the bilayer), 5-SASL (close to the surface) and T-PC (within the polar head groups) were employed. In the fluid phase the effect of cholesterol on $W(CuKTSM_2)$ depends on the distance from the membrane surface, phospholipid alkyl chain length, unsaturation, and temperature. At the main phase transition for DMPC, $W(CuKTSM_2)$ drops by a factor of 3-5 in the absence of cholesterol but does not change abruptly in the presence of 27.5 mole % cholesterol. Supported by NIH Grants GM35472, GM22923 and RR01008.

83 **ESR OF CUPRIC HISTIDINE COMPLEXES IN THE LIQUID PHASE.** M. Pasenkiewicz, W. Froncisz, R. Basosi, W. E. Antholine, and J. S. Hyde, National Biomedical ESR Center, Department of Radiology, Medical College of Wisconsin, Milwaukee, WI 53226

Copper histidine complexes in frozen aqueous solution in the presence of excess histidine are comprised of four nitrogen donor atoms (previous results). All the donor atoms arise from the imidazole moiety of histidine. Thus, the stoichiometry is four histidines per cupric ion. This study reaffirms a study by Goodman et al. (J. Chem. Soc. Dalton, 822, 1981) in which two histidines per cupric ion form complexes even in the presence of excess histidine under conditions where four histidines per cupric ion form a complex in the frozen state. Nitrogen superhyperfine structure is resolved for ^{63}Cu in D$_2$O in the presence of excess histidine. These spectra are computer simulated using a program for fast tumbling copper complexes in an isotropic environment. Simulations as well as Fourier analysis of the ESR spectra for ^{63}Cu in the presence of excess histidine or excess histidine, for which ^{15}N is substituted for ^{14}N in the imidazole ring, characterize two Cu(Histidine)$_2$ complexes in solution. The primary complex has a copper-histamine like structure in which an amine and an imidazole nitrogen donor atom are bound to cupric ion for each of the two histidine ligands. Supported by NIH Grants GM35472 and RR01008.

84 EPR AND SPECTROSCOPIC STUDIES OF CONFIGURATIONAL CHANGES IN COPPER(II) COMPLEXES OF 1,4-DIAZACYCLOHEPTANE. M. S. Hussain and J. S. Hwang, Department of Chemistry, University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia.

EPR and spectroscopic studies of the square-planar bis(1,4-diazacycloheptane)copper(II) perchlorate and the square pyramidal bromobis(1,4-diazacycloheptane)copper(II) were carried out in nitromethane, dimethylsulfoxide, and water solutions as well as in the polycrystalline state. The ligation of the bromide ion to bis(1,4-diazacycloheptane)copper(II) along the Z axis was investigated by quantitative titration of the latter against tetramethylammonium bromide in nitromethane solution. The EPR spectra are explained in terms of energy changes involving the electronic ground state and the lowest excited state as a function of ligation of nucleophiles to the metal atom along the Z axis. The degree of tetragonal distortion for copper(II) increases in the order: perchlorate < DMSO < water ≈ bromide, as nucleophiles. In the polycrystalline state, the weaker the apical interaction (square-planar species) the lower the g-value and the higher the copper(II) hyperfine coupling constant. In the liquid state, the g-values observed in non-coordinating solvents such as nitromethane, are similar to those for the polycrystalline material suggesting similarity of structures in the two states. The electronic absorption maxima for the three complexes in the liquid state increase with an increase in tetragonal distortion around the copper(II). In strongly coordinating solvents the EPR spectra and absorption maxima are independent of the anion present. In the solvent series studied here, the solvent basicity increases in the order nitromethane < DMSO < water. The increasing strength of solvation results in an increase in the wavelength of the optical transition and the g-values, and a decrease in the copper(II) hyperfine coupling constant. It therefore appears that increasing the basicity of the solvent has the same effect on the d-orbital energy levels and on the unpaired electron density on copper(II) as does increasing the electronegativity of the substituents on the ligand.

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85 EPR STUDIES ON THE REACTION BETWEEN NITROSYL-HEMOGLOBIN AND OXYGEN: A COMPARISON OF *IN VITRO* AND *IN VIVO* NO-EXPOSURE. K.Kon, N.Maeda and T.Shiga. Dept. Physiol., Sch. Med., Ehime Univ., Shigenobu, Onsen-gun, Ehime, 791-02 Japan.

Among the nitrogen oxides, NO_2 causes the airway-injury, while NO enters into blood to yield nitrosyl-hemoglobin (Hb-NO), which is then converted to methemoglobin (metHb), and reduces the oxygen transport function. In order to clarify the mechanism of hemoglobin (Hb)-injury by NO, both *in vitro* and *in vivo* studies were carried out. (A) The time course of the reaction between Hb-NO and O_2 in a closed chamber, monitoring dissolved O_2 (by oxygen electrode), Hb-NO and metHb (by EPR) and NO_2^- and NO_3^- (by chemical method), revealed that Hb-NO was converted to metHb by consuming O_2 and producing NO_3^-. The reaction consisted of branched, successive reactions: (i) dissociation of Hb-NO to deoxyHb and NO was rate-limiting step, then NO in solution changed to NO_2^-; (ii) at high O_2, deoxyHb was transiently formed and reacted with NO_2^-, yielding metHb and NO_3^-; (iii) at low O_2,deoxyHb reacted with NO_2^-, yielding Hb-NO, metHb and NO_3^-; (iv) NO_3^- production was accelerated by metHb; (v) as proceeding metHb formation from Hb-NO, the amount of Hbα-NO augmented over Hbβ-NO and Hbα-NO in T-state developed (especially upon dithionite reduction). (B) The time course of Hb-NO and metHb production in NO-exposed rat revealed that (i) the amount of metHb was always higher (ca. 10 times) than that of Hb-NO, (ii) metHb reductase activity seemed to decrease, as increasing NO concentration, and (iii) both Hb-NO and met Hb disappeared by inspirating fresh air. A simplified kinetic scheme of *in vivo* reaction was obtained, accordingly, as far as the reductase activity was maintained, the Hb-injury in red cells was much less than that of purified Hb in solution.

86 SUPERHYPERFINE COUPLINGS IN VANADYL COMPLEXES WITH S-ADENOSYLMETHIONINE SYNTHETASE. G.D. Markham, The Institute for Cancer Research, Philadelphia, PA 19111

EPR of VO(IV) complexes with S-adenosylmethionine (AdoMet) synthetase has been used to investigate the structure of the divalent metal ion binding site of the protein. 2 classes of spectra have been observed: the enzyme-VO(IV), enzyme-VO(IV)-methionine and enzyme-VO(IV)-AdoMet complexes have rhombic ^{51}V hyperfine coupling and g tensors; complexes with polyphosphate substrates or products (i.e. enzyme-VO(IV)-ATP-methionine and enzyme-VO(IV)-AdoMet-PPi) show axial symmetry with larger ^{51}V coupling constants and reduced g values due to coordination of 2 phosphate groups to VO(IV). In all cases linewidths in H_2O solutions have substantial contribution from unresolved superhyperfine coupling (SHFC) to exchangeable protons therefore most studies were conducted in D_2O. To investigate the feasibility of unambiguously determining the protein ligands to VO(IV) by EPR, enzyme uniformly enriched with ^{13}C (99%) was produced biosynthetically. Spectra of the [^{13}C]enzyme-VO(IV)-AdoMet complex show inhomogeneous broadening from coupling to ^{13}C, demonstrating the potential for elucidation of the ligands by selective ^{13}C enrichment. In complexes with ATP or PPi, couplings to 2 equivalent ^{31}P nuclei are resolved; solution spectra give an isotropic ^{31}P coupling constant of 23 MHz, while frozen samples display $\sim$3 MHz anisotropy in ^{31}P SHFC. Experiments with [^{17}O]PPi show that there is little unpaired spin density on the oxygen in the V-O-P bond. AdoMet synthetase also binds one monovalent cation such as Tl^+. Isotropic SHFC to Tl^+ has been observed in various complexes, with coupling constants ranging from 24 to 67 MHz, demonstrating close proximity of the two metal binding sites. Supported by USPHS grant GM31186.

87 A pH-DEPENDENT EQUILIBRIUM AROUND IRON IN LIPOXYGENASE. D. V. Mavrophilipos and B. J. Gaffney, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Soybean lipoxygenase catalyses the hydroperoxidation of unsaturated fatty acids. The role of protein-bound iron in the enzyme action is not clear. EPR spectra of the enzyme at 4 K reveal an equilibrium between three different iron geometries. Using pH variation, it is found that there are two titratable groups near iron. The pH optimum in enzyme activity occurs at a pH on the basic side of the pK's of both titratable groups. The EPR spectra are also sensitive to changes in protein concentration and other variables. While not all of these responses are well understood, they provide a phenomenological solution to the problem of variability in published EPR spectra of lipoxygenase.

88 BINDING STUDIES OF TRANSITION METALS WITH BISDIOXOPIPERAZINE ANTITUMOR AGENTS AND THEIR HYDROLYSIS PRODUCTS. George C. Yang, Eugene H. Herman and Antoine N. El-Hage, Food and Drug Administration, Washington, D. C. 20204.

The bisdioxopiperazines (ICRF compounds) may act as potent intercellular chelating agents toward transition metal ions. Some of these compounds were found to elicit antitumor activity against sarcoma 180 and leukemia L1210. Furthermore, ICRF187 [(+)-1,2-bis-(3,5-*dioxopiperzin-1-yl) propane] was shown to reduce the chronic cardiotoxic* effects of doxorubicin in animals. Since the role of chelation in the cellular environment is obscure, we have studied the binding affinity of several ICRF compounds and some of their hydrolysis products for certain transition metal ions by electron spin resonance spectroscopy. The affinity constants of Mn(II), Cu(II), Fe(III), Zn(II), Mg(II) and Ca(II) were obtained by measuring the broadening of ESR spectral lines resulting from chelation of transition metals with the compounds. For the non-paramagnetic ions, Mn(II) was used as an indirect, competitive probe for binding constant determination. Most ICRF compounds exhibited weak binding initially. Upon standing in solution over a period of time, the binding affinity improves. The hydrolysis products of ICRF 187 which were isolated by HPLC, exhibited the strongest affinity toward Cu(II) ($K \geqq 6x10^4 M^{-1}$). No binding was detected for either Ca(II) or Mg(II).

89 DETECTION OF ISOLATED AND PAIRED Cu(II) IONS IN NAFION MEMBRANES BY ESR SPECTROSCOPY, S. Schlick and M.G. Alonso-Amigo, Dept. of Chemistry, University of Detroit, Detroit, MI 48221-9987.

Acid Nafion membranes were neutralized completely by immersion in 0.1 M solutions of Cu^{2+} and Zn^{2+} ions and studied by Electron Spin Resonance (ESR) spectroscopy as a function of the Cu^{2+}/Zn^{2+} ratio and the amount of water present, in the temperature range 77 K to 300 K. At low Cu^{2+} concentrations isolated Cu^{2+} ions were detected in two sites differing in their $g_{//}$ and $A_{//}$ values. Analysis of the ESR parameters indicates that in site I Cu^{2+} is ligated to two SO_3^- groups of the polymer backbone and is in the "rigid" motional limit in the entire temperature range studied. In site II Cu^{2+} is ligated to water oxygens. The relative populations of Cu^{2+} in the two sites is very sensitive to variations in the water content of the membranes. All samples were therefore measured under conditions of controlled relative humidity. In the hydrated complexes, ligation to "mobile" and "bound" water is detected by comparing ESR spectra of fully hydrated samples with those in which part of the water was removed by heat treatment. Ligation to "mobile" water leads to averaging of the g- and hyperfine anisotropy and is evident from the appearance of an isotropic line in hydrated membranes at 298 K. For Cu^{2+}/Zn^{2+} ratios of 0.1 and larger Cu^{2+}-Cu^{2+} are detected and identified by the $\Delta m=2$ transition at a magnetic field of ~1600 Gauss. The signals from the pair suggest that the interion distance is 5.5 Å, based on the intensity ratio of the $\Delta m=2$ and $\Delta m=1$ transitions.

90 EPR OF MEDIUM MOLECULAR WEIGHT CLUSTER COMPOUNDS. G. Kokoszka, D. Palahnuk, SUNY Plattsburgh, NY 12901, A. Siedle, 3M, St. Paul, MN 55144.

EPR studies may be used to distinguish inter- and intramolecular interactions and to clarify the role played by these interactions in determining the bulk physical properties of molecules in the medium molecular weight (MMW) (10^4-10^7 g/mole) range. Several examples of cluster compounds (i.e., compounds containing two or more metal ions) will be discussed which focus on (1) electronic exchange interactions in well-defined molecular solids, (2) dynamical vibronic or pseudorotational processes, and (3) magnetostructural correlations. The degree of magnetic isolation of the paramagnetic center(s) in MMW complexes can be used to monitor dynamical or electronic effects. Such effects may not be truly representative of the host molecular species or ionic solids if the EPR probes are produced by doping paramagnetic impurities into a diagmagnetic host lattice.

91 TEMPERATURE DEPENDENCE OF THE ZERO-FIELD SPLITTING PARAMETERS OF Ni(II) AND Mn(II) IN $ZnSiF_6 \cdot 6H_2O$ and $ZnSiF_6 \cdot 6D_2O$. John E. Drumheller, Stuart L. Hutton, and R. S. Rubins*, Department of Physics, Montana State University, Bozeman, MT 59717.

EPR X-band studies of crystals of Ni(II) in $ZnSiF_6 \cdot 6H_2O$ and $ZnSiF_6 \cdot 6D_2O$ and Mn(II) in $ZnSiF_6 \cdot 6D_2O$ at temperatures from 4K to above 100K were done to test the long wavelength Debye model of the zero-field splitting parameter, D. Data below 70K for all crystals were fit to the theoretical model of Shrivastava and yielded values for the Debye temperature Θ_D of 130K for $ZnSiF_6 \cdot 6H_2O$ and 99K for $ZnSiF_6 \cdot 6D_2O$. The value of Θ_D for the hydrated salt is roughly 30% larger than the more direct estimate of Vasyukov et al. from measurements of the stress coefficients. The deviations from the theoretical curves for both crystals are appreciable above 75K. The zero-field parameters for Mn(II) in the deuterated salt showed qualitatively similar dependences with the expected isotropic g and hyperfine tensors.

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92 EPR SPECTRA OF MANGANESE IN MgO POWDERS. S. Eidels-Dubovoi* and V. Beltrán-López**, *Instituto Mexicano del Petroleo, Mexico, and **Centro de Estudios Nucleares, Universidad Nacional Autonoma de Mexico, Mexico.

EPR spectra of $MgO:Mn^{2+}$ powders previously treated in air and in vacuum at various temperatures, were analyzed assuming a tetragonal distortion of the cubic environment of the manganous ion. The same analysis was used on spectra from powders which had been compressed at high pressures (U. Kretzschmar et al., Crystal Res. and Technol. 17, 257 (1982); M. V. Vlasova et al., J. Mat. Sci. 18, 245 (1983)). The spectrum of the six central hyperfine lines was calculated to third order for the line positions and to first order for the transition probability, in a computer simulation. This shows that the variation of the asymmetry of the lines can be reproduced only if the usually neglected axial term of the fourth degree is included in the spin Hamiltonian. It is also shown that the variations of intensities and widths of the central lines are due mainly to the random orientations of the spins.

93 EPR AND RESONANT CAVITY MEASUREMENTS OF FREE ELECTRONS AND METASTABLE N ATOMS PRODUCED IN $He\text{-}N_2$ MICROWAVE DISCHARGE. E. López-Moreno and V. Beltrán-López, Facultad de Ciencias and Centro de Estudios Nucleares, Universidad Nacional Autonoma de Mexico, Mexico.

Metastable nitrogen atoms and free electrons produced by a microwave discharge in a $He\text{-}N_2$ gas stream were observed by means of EPR. Free electron densities were also determined by resonant cavity frequency measurements. Downstream decay curves of free electrons from a pure He discharge and curves of the decay of free electrons with N_2 content in the gas stream were obtained. Reactions which may be responsible for the observed drop of free electrons with N_2 are discussed. Metastable $N(^2D_{5/2})$ in the afterglow could be detected in a conventional straight discharge tube. Downstream decay curves of $N(^2D_{5/2})$ suggest that reactions leading to metastable atomic nitrogen occur in the afterglow.

94 MAGNETIC RESONANCE STUDIES OF SOLID BARIUM TITANATE. C. E. Forbes,* W. B. Hammond,** and N. Cipollini**. * Celanese Research Co., 86 Morris Ave., Summit N. J. 07901 and **Allied-Signal Inc., Box 1021R, Morristown, N. J. 07960.

EPR and NMR spectroscopies have been used to study samples of barium titanate doped with either niobium or lanthanum and trace manganese. $BaTiO_3$ belongs to a group of ferroelectric materials with crystal structures of the perovskite type. At temperatures above the Curie point (118°C), the unit cell is cubic with barium atoms on the cell corners, a titanium atom at the cell center, and oxygen atoms on the cube faces. Below the Curie point, the unit cell is distorted with tetragonal symmetry. As expected, the EPR and NMR spectroscopies are sensitive to the site environments of the host lattice and dopents. The Mn^{2+} EPR spectrum indicates a cubic site symmetry at elevated temperatures and, surprisingly, also at low temperatures (~70 to 4K). The cubic symmetry of the lattice also permits observation of several NMR resonances with conventional high resolution instrumentation. NMR resonances for ^{137}Ba, ^{93}Nb, and ^{139}La have been obtained for this material at temperatures greater than the Curie point.

95 MAGNETOHYDRODYNAMICS OF NEMATIC MESOPHASES BY ESR, Michael Eastman, Bassam Freiha, Thomas Mayhew, Miin-Liang Horng, Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968.

The transient time dependent behavior of the director of a nematic mesophase subject to spinning at frequency Ω in an applied magnetic field has been investigated by ESR. All experiments reported were conducted for $\Omega > \Omega_C$ where $\Omega_C = (\Delta\chi \, Ho/2\lambda_1)$. Here $\Delta\chi$ is the anisotropic magnetic susceptibility and λ_1 the rotational twist viscosity of the nematic. The theory of Leslie, Luckhurst and Smith (LLS) is used to analyze Fourier transformed time domain data and their result for the dependence of ω, the director rotation rate, on Ω ($\omega = \Omega - \Omega_C$) is confirmed for a range of values of Ho and Ω. Values of Ω_C for Phase IV, MBBA and the alkylcyanobiphenyls K15, K18 and K21 are reported. Linewidths in the frequency domain are shown to depend on the twist viscosity of the mesophase and possible evidence for microdomains in Phase IV is presented. The values of Ω_C reported for Phase IV and MBBA differ by a constant from the values calculated using literature values of $\lambda 1$ and ΔX.

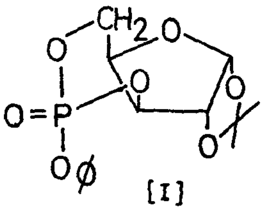
96 ESR OF DISCOTIC LIQUID CRYSTALS CONTAINING CU(II). Michael Eastman, Minn-Liang Horng and Bassam Freiha, Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968.

The discotic liquid crystals bis[1,3-di (p-n- octylphenyl) propane-1,3--dionato] copper(II)(A) and bis[1,3-di (p-n-octyloxyphenyl)propane-1,3-dionato] copper(II)(B) were prepared by methods described in the literature and were studied by ESR. In chloroform at 77 K the magnetic parameters for (B) are $g_\perp$=2.048, $g_\parallel$=2.245, $A_\perp$=29.4 G and $A_\parallel$ =184.8 G. Powder spectra of the pure compounds showed little change as a result of crystalline to discotic phase transitions. Single crystal spectra of (B) showed molecules stacked at an angle of 55° with respect to the long axis of the crystal. The crystalline to D_1 phase transition produced spectral changes which were reversible upon cooling below the phase transition temperature; the D_1 to D_2 transition produced spectral changes which were not reversible. The results are interpreted in terms of possible structures for the discotic phase.

97 EPR STUDY OF PHOSPHORUS CENTERED RADICALS TRAPPED IN AN X-IRRADIATED SINGLE CRYSTAL OF A PHENOXYPHOSPORYL XYLOFURANOSE DERIVATIVE

by Alice CELALYAN-BERTHIER, Théo BERCLAZ and Michel GEOFFROY
Department of Physical Chemistry, 30 Quai E. Ansermet, 1211 Geneva 4
(Switzerland)

Single crystals of 1,2-o-isopropylidene 3,5-o-phenoxy-phosphoryl-α-D-xylofuranose [I] were x-irradiated at low temperature (~77°K) and we followed the angular dependence of the EPR signals at low temperature. This led us to the identification of four radicals : a phosphoranyl type radical, two phosphonyl species and a radical pair whose one component is a phosphonyl type radical.
The ^{31}P-hyperfine tensor has been calculated for each species as well as the electron-electron dipolar interaction for the radical pair. The radiation damage process is shown to involve electron capture by a P=O bond and homolytic scissions of various P-O bonds.



[I]

98 EPR STUDY OF THE ORIENTED $[C_2Cl_6]^-$ RADICAL IN X-RAY IRRADIATED HEXACHLOROETHANE SINGLE CRYSTALS: AN ON-LINE ANALYSIS. Lowell D. Kispert, Kenneth G. Ezell, Joy Joseph and Eric Bradford, Dept. of Chemistry, Univ. of Alabama, Tuscaloosa, AL 35486.

Freon matrices are often used as hosts for cation radicals. If a solute is dissolved in a freon matrix with an ionization potential lower than that of the freon matrix, a cation of the solute is produced upon X-ray irradiation. During an attempt to create the carotene cation by this technique, it was found that resolved spectra from x-ray irradiated hexachloroethane crystals at 77 K could be assigned to the $[C_2Cl_6]^-$ radical. The radical is characterized by 6 equivalent chlorine nuclei at 77 K with g and chlorine hyperfine tensor components of 2.030, 2.031, 2.010 and 10.3, 5.3 and -3.6 Gauss respectively. An INDO molecular orbital calculation showed that the unpaired electron is largely located in the C-Cl antibonding orbital and that upon electron addition, the C-Cl bond length has increased approximately 0.4 Å with the CCl_3 groups undergoing rapid reorientation at 77 K. The $[C_2Cl_6]^-$ radical is very sensitive to room light, completely decaying within 1 hour. EPR data in three orthogonal planes was acquired and analyzed by an on-line IBM personal computer interfaced to a Varian E-12 spectrometer with the angular dependent spectra analyzed using computer programs written in ASYST. A complete description of this system will be given.

99 PROTON COUPLING CONSTANT EXTRACTION: A FAST METHOD FOR ANALYZING ESR SPECTRA BY COMPUTER, A.G. Motten*, D.R. Duling+, and J. Schreiber+, *Duke University, Department of Chemistry, Durham, NC, 27705 and +NIEHS, Research Triangle Park, NC, 27709.

Proton Coupling Constant Extraction (PCCE) is a novel computer method for obtaining all the proton hyperfine coupling constants in an electron spin resonance spectrum. PCCE works well on spectra which are poorly resolved, and thus appears to complement the recently developed correlation approach used for very well-resolved spectra. No prior knowledge of radical structure is needed, and proton splittings are clearly discriminated from spin one splittings. The program consists of two parts: SEARCH, to identify the proton hyperfine splittings, and SEPARATE, to simplify the ESR spectrum. PCCE is readily programmed and run on a small laboratory computer. Copies of the Basic subroutines are available on request.

100 **APPLICATION OF LOOP-GAP RESONATORS TO NUCLEAR MAGNETIC RESONANCE IMAGING AND SPECTROSCOPY** W. Froncisz,* Andrzej Jesmanowicz, Thomas M. Grist, J. Bruce Kneeland and James S. Hyde, Department of Radiology, Medical College of Wisconsin, Milwaukee, WI 53226, and *Institute of Molecular Biology, Jagiellonian University, Krakow, Poland.

Since the loop-gap resonator concept was introduced into the field of radiospectroscopy many EPR and NMR loop-gap resonators have been built in the frequency range of 10 MHz to 36 GHz. Three different types of loop-gap resonators have been designed and tested: counter rotating current coil, planar-pair coil, and butterfly coil. Each of them is intrinsically isolated from homogeneous transmission fields of arbitrary direction and can be used without active decoupling in circularly polarized rf fields. Using these three types of resonators as building blocks and adjusting their dimensions to provide suitable regions of sensitivity, numerous local probes for different anatomic regions have been constructed and evaluated. The studies of both normal anatomy and pathology have shown that local probes based on the principle of the loop-gap resonator enhance the capabilities of magnetic resonance spectrometers used for imaging and in-vivo spectroscopy.

101 FERROMAGNETIC GRADIENT PRODUCING DEVICES J. P. Hornak, Department of Chemistry, Rochester Institute of Technology, Rochester, NY 14623

ESR imaging is capable of providing useful information on the nature of paramagnetic systems. The resolution in an imaging experiment is a function of the magnetic field gradient, the line width, and the sampling interval of the CW spectrum. The relatively large field gradients required necessitate the use of large power supplies and elaborate coil cooling schemes, which complicate the imaging experiment. The appropriate geometry ferromagnetic wedge could be used in place of an electromagnetic coil for producing the field gradient. The geometries of several wedges and their corresponding gradient are presented.

102 SPECTRAL AND SPATIAL COMPONENTS IN ONE DIMENSIONAL EPR IMAGING.

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In the most common form of the EPR imaging experiment performed with static field gradients, the spectral width of most paramagnetic species results in significant overlap of absorption peaks from spatially separated species. Consequently, there is an inherent difficulty distinguishing between the spatial information necessary for spin mapping and the spectral information that will yield the EPR spectrum specific to a particular spatial site. It has been suggested that it would be possible to distinguish between spectral and spatial components by the accumulation of data obtained for different magnitudes of the static field gradient (S.S. Eaton and G.R. Eaton, Spectroscopy 1, 32, 1986). Indeed in this communication, the one-dimensional EPR imaging problem involving a static, linear gradient, in which one seeks the spectrum and spin density specific to each spatial site, is shown to involve one spatial dimension and one spectral dimension, and to be mathematically isomorphic to a class of image reconstruction problems involving two spatial dimensions for which algorithms are readily available. The extension to the general EPR imaging problem involving two spatial dimensions appears straightforward. There is the likelihood that the results noted in this communication may facilitate current work in NMR imaging, as well. This research was supported, in part, by a grant from the National Science Foundation (#CHE-8421281).

103 APPLICATION OF L-BAND ESR TECHNIQUES TO IN VIVO ANALYSIS

T. OGATA, M. ONO, E. YOSHIDA,* and H. KAMADA, Faculty of Engineering, Yamagata University, Yonezwa 992, and *JEOL Ltd., Akishima 196, Japan

Recently, we have developed an L-band ESR spectrometer equipped with a loop-gap resonator (29 mm in diameter and 28 mm in length) having an inner electric shield in order to measure wet biological systems at room temperature. At the beginning of the study, L-band ESR spectra of several kinds of paramagnetic species were measured and were compaired with their X-band spectra. L-band spectra of TEMPOL, DPPH, and Cu(II) ion solutions were similar to X-band spectra. On the other hand, six hfs signals of Mn(II) ion did not appeared at L-band region, where only one broad signal was obtained. This means that the splitting of energy levels at low magnetic field is different from the separation at high field.

As an example of in vivo analysis, the behavior of the absorption of TEMPOL radical in fresh celery was examined. The stalk of about 20 mm in diameter was inserted in the resonator and the bottom of stalk was soaked in 0.1 M radical solution. After a short time, typical hfs signals of TEMPOL molecule appeared and increased with time. The line shape indicated that the radical in the stalk has been diluted to less than 0.001 M. TEMPOL in celery disappeared finally in the leaves according to first order reaction.

L-band ESR techniques will be very useful for in vivo analysis in future. Various living things are now being measured and furthermore L-band ESR imaging is now under consideration by using three pairs of magnetic gradient coils in our laboratory.

104 A RADIO FREQUENCY ELECTRON SPIN RESONANCE SPECTROMETER FOR IN VIVO IMAGING.

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Electron Spin Resonance (ESR) spectroscopy at radio frequencies has several advantages for medical/biological applications. Dielectric losses that limit sample sizes for aqueous or tissue samples are greatly reduced. The lower frequencies allow larger samples and even whole limbs or animals to be studied rather than excised tissue samples.

We describe a 260 MHz ESR spectrometer designed for in vivo measurements and ESR imaging of small animals. The combination of low dielectric loss, high filling factor and large sample size make the minimum detectable concentration of free radicals in aqueous or tissue samples similar at 260 MHz and x-band.

The spin relaxation of nitroxides in water at room temperature is comparable at 260 MHz and at x-band. Similar results are expected for free radicals whose relaxation is dominated by rotational modulation of anisotropic hyperfine interactions.

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy under contract W-31-109-ENG-38 and the American Cancer Society Research Grant PDT-262.

DEVELOPEMENT OF A LOOP-GAP RESONATOR AND A SURFACE COIL WITH AN ELECTRIC SHIELD

105 M. ONO, T. OGATA, Kou-Chang HSIEH, M. SUZUKI, E. YOSHIDA,* and H. KAMADA, Faculty of Engineering, Yamagata University, Yonezawa 992, and *JEOL Ltd., Akishima 196, Japan

An L-band ESR system using a loop-gap resonator with an electric shield has been constructed in order to analyze the large quantities of wet samples at room temperature. The electric shield, which shuts out the electric line of force between hot ends of the loop, is composed of the multiple metal plates placed inside the loop. As the result, a residual electric field in the loop is extremely decreased. Therefore, there is no deterioration of the quality factor of the resonator with a physiological salt solution of a high filling factor.

Secondly, surface type split ring resonators with the Faraday shield between the ring and the samples have been investigated. The shield is realized by a rectilinear type screen or an electric line of force type one. The electric field was reduced in both cases. Particularly, the magnetic field was efficiently given to the sample in the latter case.

These resonators are useful for ESR measurements of biological samples at in vivo state. Furthermore, these resonators will be applied to non-destructive analysis of various materials.

106 NITROXYL RADICALS AS INTERMEDIATES IN THE ELECTRON TRANSFER BETWEEN CARBON-CENTERED RADICALS AND NITROAROMATICS.

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Reactions between heteroatom-substituted carbon-centered radicals $\bar{Y}-\dot{C}<$ and nitroaromatics $ArNO_2$ that proceed ultimately by electron transfer between $\bar{Y}-\dot{C}<$ and $ArNO_2$ have been studied by in-situ-radiolysis or photolysis ESR and pulse radiolysis techniques with optical and conductance detection. It was found that in many instances these reactions proceed in aqeuous solution via the intermediate formation of nitroxyl radicals. These radicals are able to undergo heterolysis, which may proceed by spontaneous or by catalyzed paths. The heterolysis reaction is characteristic for, and a consequence of, the acetal character of the nitroxyl radical. The products of the heterolysis of the nitroxyls are $O=C<$, the one-electron oxidized radicals, and $ArNO_2^{\cdot-}$, the one-electron-reduced nitroaromatics. The overall reaction thus consists in a one-electron transfer from the radical to the molecule.

Reactions of this type were studied in detail with substituted nitrobenzenes and α-hydroxy, alkoxy, and amido-substituted radicals (pyrimidine-6-yl radicals). From the substituent effects on the rates of spontaneous heterolysis of the nitroxyl intermediates it is concluded that the heterolysis proceeds by a push-pull mechanism. Activation parameters and solvent effects indicate that the transition state for the heterolysis is highly polar, and that solvent reorganization is very important.

STIMULATED HUMAN NEUTROPHILS LIMIT HYDROXYL RADICAL FORMATION AS DETECTED BY ESR: INVESTIGATION OF THE ROLE OF NEUTROPHIL LACTOFERRIN.

107 G.M. Rosen, B.E. Britigan, Y. Chai, B.Y. Thompson and M.S. Cohen. Duke University, Durham, NC and University of North Carolina, Chapel Hill, NC.

Superoxide ($O_2^{\cdot-}$) and hydrogen peroxide interact in an Fe^{+3}-catalyzed reaction to form hydroxyl radical ($HO\cdot$). In the presence of DMSO and the spin trap 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), $HO\cdot$ formation leads to the generation of 2,2,5-trimethyl-1-pyrrolidinoxyl ($DMPO-CH_3$). $DMPO-CH_3$ accumulated in sequential ESR scans following the interaction of xanthine oxidase (XO), hypoxanthine (HX), Fe^{+3}, DMPO, DMSO and DTPA. Stimulation of human neutrophils (PMNs) by either phorbol myristate acetate (PMA) or opsonized zymosan in the presence of DMPO, DMSO and DTPA lead to the spin trapping of only $O_2^{\cdot-}$. Inclusion of Fe^{+3} in the above reaction gave HO; as detected by the presence of $DMPO-CH_3$. In contrast to the $HX/XO/Fe^{+3}$ system, even in the presence of Fe^{+3}, PMN stimulation failed to induce sustained $DMPO-CH_3$ accumulation in spite of the fact that $O_2^{\cdot-}$ production was ongoing. This finding suggested that $HO\cdot$ formation was limited by the PMNs. PMN stimulation leads to the discharge of their cytoplasmic granule contents into the phagocytic vacuole and extracellular space. Enucleated PMNs (cytoplasts) lack cytoplasmic granules but retain capacity to form $O_2^{\cdot-}$. Stimulation of cytoplasts with PMA in the presence of Fe^{+3} resulted in sustained accumulation of $DMPO-CH_3$. Cell free supernatants obtained following PMA stimulated PMNs inhibited $DMPO-CH_3$ generation by the $HX/XO/Fe^{+3}$ system, which was inhibited by a lactoferrin antibody. These results suggest PMNs limitation of Fe^{+3}-catalyzed $HO\cdot$ formation via the release of PMN associated lactoferrin.

108 SPIN-TRAPPING METABOLICALLY FORMED FREE RADICAL PRODUCTS FROM HALOGENATED HYDROCARBONS. J. L. Poyer, Biomembrane Research Laboratory, Oklahoma Medical Research Foundation, 73104, Walter H. Massion and Paula Downs, Department of Anesthesiology, University of Oklahoma Health Sciences Center, Oklahoma City, OK 73190.

Chemical compounds termed "spin-trapping" agents have recently been used to detect and identify metabolically formed reactive free radicals. The trapped radical product, a 'spin-adduct' can be examined using EPR techniques. When rat liver microsomes were incubated (in vitro) in the presence of NADPH (reduced ß-nicotinamide adenine dinucleotide phosphate), the free radical spin-trapping agent PBN (phenyl-t-butylnitrone) and CCl_4, $CHBr_3$, 1,1,1-trichloroethane or the clinically used anesthetic halothane (1,1,1-trifluoro-2-chloro-2-bromoethane), a 6 line EPR spectrum, expected for a PBN aminoxyl adduct was observed. These same EPR signals were observed in vivo, in a liver lipid extract from a rat which was administered PBN and the appropriate halocarbon. The use of C-13 labelled CCl_4 and $CHBr_3$ confirmed both in vitro (microsomal) and in vivo that the PBN-radical adducts observed are due to the metabolism of these halocarbons to free radical products. When metyrapone (2-methyl-1,2-di-3,pyridyl-1-propanone), an inhibitor of the 52,000 MW cytochrome P-450 in the liver endoplasmic reticulum, was given prior to the PBN and halocarbon, the intensity of the EPR signals of the resulting spin-trapped adducts was greatly diminished. This free radical formation is probably the result of the direct donation of an electron from reduced cytochrome P-450 to the halogenated hydrocarbon molecule, to form a free radical product and the halide anion:

$$\text{Cyt. P-450 }(Fe^{2+}) + R\text{-}X \longrightarrow \text{Cyt. P-450 }(Fe^{3+}) + R\cdot + X^-$$

SPIN-TRAP HPLC AND RESOLUTION-ENHANCED ESR STUDIES ON ORGANIC FREE RADICALS PRODUCED 109 FROM ELECTRODE-SURFACE REACTIONS. H. Hatano, S. Okazaki, A. Naito, T. Nagaoka, and K. Nozaki, Department of Chemistry, Kyoto University, Kyoto 606, Japan.

The spin-trap HPLC (High Performance Liquid Chromatography)-ESR method was first developed by the authors (1975) and applied to the separation and detection of various kinds of short-lived radicals produced in gamma-irradiated aqueous solutions of amino acids, peptides, and nucleotides. Further applications of this technique require development of resolution-enhanced ESR techniques for obtaining further information about more complex radicals even after separation by the spin-trap HPLC method.

The resolution-enhanced ESR was carried out in two ways: one is a second harmonic +90° out-of-phase detection technique and the other involves Fourier transformation of the spectra, application of line-narrowing algorithms, and reverse Fourier transformation. In this report the latter technique was developed experimentally according to Glarum's theoretical principle. The spin-trap resolution-enhanced ESR system was employed for separation and detection of organic short-lived radicals produced from electrode-surface reactions. New spin trapping reagents for nitrogen compounds were synthesized for studying electrode-surface reactions. Spin-trapped neutral radicals such as p-nitrophenyl radicals, were separated and detected by the spin-trap HPLC resolution-enhanced ESR method. Nitrobenzene anion radicals produced from p-nitrophenyl radicals in the course of electrolysis were characterized by the ESR method.

110 A DIRECT EVIDENCE FOR THE RADICAL PAIR MODEL IN A MAGNETIC FIELD-DEPENDENT PHOTO-REACTION. M. Okazaki, S. Sakata,* R. Konaka,* and T. Shiga.
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Magnetic field dependent chemical reactions have been interpreted with the "radical pair model". However, the characteristics of the radical pair have not been clearly shown. In this study, spin trapping was applied to probe the radical pair model, and a direct evidence was obtained for the model: (1)the radical pair exists, (2)the product yield is modified by the external magnetic field due to the change in the rate of triplet-singlet mixing of the radical pair. In the photoreduction of naphthoquinones in SDS micellar solution, spin adduct of SDS radical was obtained. The spin traps used were PBN and perdeuterio-dimethylnitrosobenzenesulfonate (DMNS). Yields of the spin adducts were highly dependent on the external magnetic field. Upon irradiating the microwave at the same time during the photo-reduction of menadione (a naphthoquinone) in SDS micellar solution, the spin adduct yield decreased considerably at particular magnetic fields. The yield as a function of the static magnetic field ("porduct yield-detected ESR"; PY-ESR) showed the ESR patterns of both the SDS radical and the protonated semiquinone radical of menadione. This result is the direct evidence for the radical pair model refered above. The "PY-ESR" spectrum indicated that the exchange interaction and the electronic dipole interaction between the component radicals are smaller than the hyperfine interaction appeared in the spectrum.

111 **ESR IN MICROBIAL TECHNOLOGY** B. Kalyanaraman,[1] P. J. Kersten,[2], M. Tien,[2] K. E. Hammel,[2] and T. K. Kirk[2], [1]National Biomedical ESR Center, Medical College of Wisconsin, Milwaukee, WI 53226 and [2]Forest Products Laboratory, U.S.D.A.1, Madison, WI 53705-2398.

Lignin is a biologically recalcitrant phenylpropanoid polymer that constitutes about 20% of the terrestrial biomass. Some 90% of all photosynthetically fixed terrestrial carbon is either present as lignin or shielded from biodegradation by lignin, thus giving this material a disproportionate and central importance in the global carbon cycle. For this reason, the mechanisms of biological systems that can degrade lignin are of particular significance. Predominant among ligninolytic organisms are certain basidiomycetous fungi that cause white-rot of wood, and, of these, P-chrysosporium secretes a ferric hemoprotein ligninase which oxidatively cleaves both natural lignin and synthetic lignin model compounds and environmental compounds. In this talk we present evidence for production of radicals during ligninase-catalyzed degradation of lignin model compounds as studied by ESR and ESR-spin trapping.

112 MEDIUM EFFECTS ON HYDROGEN BONDING OF SOLVENTS WITH NITROXIDES. I. Bala'a and R.D. Bates, Jr., Department of Chemistry, Georgetown University, Washington, D.C 20057.

ESR measurements of changes in nitroxide hyperfine coupling constants can provide an effective means by which to determine formation constants of transient complexes that exist between the spin probe and hydrogen donating solvents. Interpretation of observed hyperfine coupling constants is complicated by changes in the uncomplexed radical hyperfine coupling constant with the polarity of the medium. Correlation of these shifts with $(\varepsilon-1)/(\varepsilon+1)$ for non-donor solvents provides an effective means of correcting for this shift for TMPO according to:

$$a_{obs} = 14.39 + (\varepsilon-1)/(\varepsilon+1)\cdot(0.554).$$

With this correction, improved determinations of the formation constants that correlate well with pKa of the solvent for donors such as alcohols and phenol are obtained. Larger formation constants and bigger hyperfine coupling constants are observed for fluorinated hydrogen donor solvents of special interest in NMR and double resonance (DNP) studies of the same systems.

113 SPIN LABEL EPR STUDIES OF SICKLE CELL MEMBRANES

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A fatty acid spin label, 5 doxyl stearic acid, has been used to label the erythrocytes from both normal adults and sickle cell anemia patients via a bovine serum albumin labeling procedure. The erythrocytes, with spin labeled fatty acids on the outer leaflet, were then either deoxygenated or CO-gassed at 4 ^{0}C. The concentrations of the spin labels of the normal and sickle cells were monitored by EPR at 20 ^{0}C and 37 ^{0}C, and compared with those of samples after incubation at 37 ^{0}C for one hour. The spin labels in the normal cells were reduced more than those in the sickle cells, presumably by intracellular materials. The motions of the spin labels in the membranes of normal and sickle cells were studied by saturation transfer (ST) EPR. The C'/C values were larger in sickle cells than in normal cells. Both the concentration data and the ST EPR spectral parameters suggest that the fatty acid spin labels in the sickle cell membranes are less mobile than those in normal erythrocyte membranes.

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114 ACTIVATION AND REVERSIBLE COVALENT MODIFICATION OF BOVINE LIVER FRUCTOSE 1,6 BISPHOSPHATASE BY DISULFIDE-THIOL EXCHANGE: CONFORMATIONAL CHANGES IN THE REGION OF THE ESSENTIAL CYSTEINE RESIDUE OBSERVED BY MEANS OF SPIN LABEL.

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Bovine liver fructose 1,6 bisphosphatase (E C 3.1.3.11) is markedly activated at pH 9.0 by certain disulfides, e.g., L-cystine and oxidized glutathione. However, D-cystine appeared to be ineffective. The enzyme is markedly inhibited by both L-cysteine and reduced glutathione. Pre-incubation of the enzyme with the substrate prevented the enzyme's activation by disulfide agents. Treatment of the activated enzyme with dithiotheritol, L-cysteine, or reduced glutathione reduced the extent of activation. A thiol-disulfide exchange reaction with an essential sulfhdryl group on the enzyme forming either a mixed disulfide or an intramolecular protein disulfide could account for the enzyme activation. The environment of the essential sulfhydryl group as seen by ESR-spin labelling, appears to undergo a significant conformational change following modification of the enzyme by disulfide agents. From the change of the ESR spectra, it is suggested that the local environment of the essential sulfhydryl group is in equilibrium between two conformational states. Activation of the enzyme by disulfide alters the enzyme to the most favorable conformational state. These findings suggest that modulation of bovine liver fructose 1,6 bisphosphatase by thiol-disulfide exchange may be an important physiological mechanism for regulation of the enzyme's activity.

115 EPR SPECTROSCOPIC EVIDENCE FOR SPATIALLY SEQUENTIAL AMIDE BOND FORMATION IN PLANT POLYGALACTOPYRANURONIDES.

Peter L. Irwin‡ and Michael D. Sevilla¶; ‡USDA, Eastern Regional Research Center, 600 E. Mermaid Ln., Philadelphia, PA 19118; ¶Department of Chemistry, Oakland University, Rochester, MI 48063.

To further investigate the physicochemical properties of plant polygalactopyranuronides (PGA), solutions and solid suspensions of this polymer were reacted with a carbodiimide reagent in the presence of a paramagnetic nucleophile. However, upon reaction we discovered that when as few as 2.5% of the carboxylate groups had been labeled, the nitroxide-amide EPR powder patterns were significantly broadened. This broadening effect was the same for reactions occurring in either solution or the solid state. Dimer-only interspin distances (d) were estimated to be12-14Å, which were approximately the same as intercationic distances observed previously for PGA-paramagnetic ion lattices in plant cell walls. These findings are likely due to an internitroxide spatial effect since line width-related parameters approached those of nitroxides randomly spaced in a lattice upon competitive reaction with a nonparamagnetic amine or by the partial reduction of the labeled lattice with ascorbate. These data indicate that the reaction at some initial site creates a greater potential for nucleophilic attack by the paramagnetic nucleophile with near-neighbor sites than other sites along the polyanion's main chain.

116 BINDING OF MANGANESE TO SPIN-LABELED SARCOPLASMIC RETICULUM VESICLES

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The ATPase in Sarcoplasmic Reticulum (SR) vesicles can be stoichiometrically spin labeled (1:1) with N-(1-oxy-2,2,6,6-tetramethyl-4-piperidinyl)iodoacetamide (ISL). Mn^{2+} binds to SR vesicles, and the binding can be followed due to the different EPR spectra of bound an non-bound Mn^{2+}. When Mn^{2+} is added to ISL spin-labeled SR vesicles there is a reduction in the amplitude of the ISL EPR signal which may be due to spin-spin interaction with the bound $S=5/2$ Mn^{2+}. The Mn^{2+}/ISL-SR system is being studied to ascertain if the observed changes in the nitroxyl spectra are in fact due to a manganese-nitroxyl spin-spin interaction and if so, whether information on the distance between the spins can be obtained. There are many potential binding sites for Mn^{2+}. Preliminary data indicate that the observed manganese-nitroxyl interaction follows a binding curve for Mn^{2+} to the ATPase, and studies are in progress to determine the specific Mn^{2+} binding site(s) involved.

117 EPR SPECTRA OF SPIN-LABELED PYRIDINES COORDINATED TO CHROMIUM(III) TETRAPHENYLPORPHYRIN CHLORIDE (S=3/2).

K. M. More, G. R. Eaton, and S. S. Eaton, Departments of Chemistry, University of Denver, Denver, CO 80208 and University of Colorado at Denver, Denver, CO 80202.

EPR spectra were obtained for thirteen spin-labeled pyridines coordinated to chromium(III) tetraphenylporphyrin chloride. In fluid solution weak electron-electron exchange interaction caused broadening of the nitroxyl signal and stronger interaction caused resolved splitting. Resolved spin-spin splitting was observed in frozen solution. Values of the exchange coupling constant, J, between ±0.005 and ±0.27 cm^{-1} were obtained by computer simulation of the frozen solution spectra. The stronger exchange interaction for 4-substituted pyridines than for analogous 3-substituted pyridines is consistent with π-delocalization of the unpaired spin density from the metal into the pyridine ring. π-delocalization was also dominant in the vanadyl(trifluoroacetylacetonate) complexes of these spin-labeled pyridines. The values of J for the Cr(III) ($S=3/2$) complexes will be compared with values obtained previously for these ligands coordinated to Cu(II), vanadyl, and low spin Co(II).

118 AN ENDOR STUDY OF MOLECULAR GEOMETRY OF SPIN-LABELED COMPOUNDS IN FROZEN SOLUTION.

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Using fluorine and proton electron-nuclear double resonance (ENDOR) spectroscopy, we have developed a procedure which determines the geometry of randomly oriented paramagnetic molecules. ENDOR spectra of 2-fluoro-, 3-fluoro- and 4-fluoroanilide derivatives of the spin label 2,2,5,5-tetramethyl-3-pyrroline-1-oxyl-3-carboxylic acid in frozen solutions of perdeuterated methanol exhibit resonance absorptions from the fluorine and protons of the anilide group. From analysis of the dependence of the ENDOR spectra on H_0, we have identified maximum and minimum ENDOR shifts. Because of the small **g** anisotropy in the EPR spectrum of the nitroxide group, these shifts can be identified as the principal hyperfine coupling (hfc) components. The hfc components of the fluoro-substituents exhibit axial symmetry. Under the point-dipole approximation, the anisotropic hfc components yield estimates of the nitroxide-fluorine and nitroxide-proton separations for each isomer. We have interpreted these distances with computer-based molecular graphics and derived the structures of these molecules in solution. The procedure can be extended to determine the geometry of enzyme-bound substrates in kinetically competent enzyme-substrate complexes. (Supported by GM 21900).

119 **STRUCTURE-FUNCTION RELATIONSHIPS IN F_1-ATPase AND DEHYDROGENASES AS STUDIED BY SPIN-LABELED NUCLEOTIDES.** I.G. Atchatchloui, S. Fleischer, C. Karim, J.O. McIntyre, R. Mink, J.H. Park, B. Rudy, P. Vogel, J. Wiese and W.E. Trommer.
Department of Chemistry, University of Kaiserslautern, D-6750 Kaiserslautern, F.R.G.
Spin-labeled and photoaffinity-spin-labeled derivatives of NAD, ATP, AMP-PNP, ADP and AMP were employed in studies of glyceraldehyde-3-phosphate dehydrogenase (GAPDH) from sturgeon and rabbit muscle and of mitochondrial β-hydroxybutyrate dehydrogenase and F_1-ATPase. Binding of AMP to GAPDH (8 per tetramer) is controlled by P_i, GAP and NAD^+. One equivalent of NAD^+, only, replaces four equivalents of AMP, thus, corroborating earlier findings that conformational changes in all four subunits are induced upon binding of the first cofactor molecule. NAD binding studies to the lecithin-requiring BDH by various techniques revealed two tight and two weaker sites per tetramer. Tight NAD binding is confined to the enzyme embedded in mitochondrial phospholipids, whereas various synthetic phospholipid mixtures can be employed for activation of the enzyme under saturating (NADH) conditions. BDH was covalently labeled with a NAD derivative spin-labeled at N^6 and carrying a diazirino ring in the nicotinamide moiety now allowing for investigations under conditions of weak coenzyme binding. Binding of spin-labeled nucleotides to F_1-ATPase gives rise to spin-spin interactions allowing for distance measurements between their various combining sites.

120 TIME RESOLVED IN SITU RADIOLYSIS ESR STUDIES OF SPIN TRAPPING

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Although the spin trapping technique has been widely and successfully used to detect and identify many kinds of unstable radicals, it is sometimes difficult to identify the precursor radical without kinetic information about the spin trapping reaction. To obtain some of this kinetic information, time-resolved ESR experiments have been initiated. Spin trapping reactions of $\cdot OH$, $\cdot CH_2OH$, $\cdot CH_2CO_2^-$ and $\cdot CO_2^-$ with nitromethane aci-anion (NMA) were examined as model reactions. From preliminary results, the spin adduct radical, $^-O_2C\text{-}CH_2NO_2\cdot^-$ is produced slowly, with a pseudo first order rate constant of approximately $2x10^7$, and is stable on the millisecond time scale. Acetate radical shows quite different behavior under identical radical production conditions, with fast adduct production (pseudo first order rate approximately $1.4x10^8$), and a slow decay of same, decaying to 0.77 of its original intensity in 200 microseconds. Considering the similarity in charge and carbon center configuration in these radicals, the difference in trapping kinetics is surprising. The spin adduct radicals, $HO\text{-}CH_2NO_2\cdot^-$ and $HOCH_2\text{-}CH_2NO_2\cdot^-$ are produced fast and show a fast decay on the order of 10 μs followed by a slower decay. One explanation for this fast decay involves electron transfer from the radical adduct to NMA.

121 **PHOTOLYSIS OF PHEOMELANIN PRECURSORS: AN ELECTRON SPIN RESONANCE-SPIN TRAPPING STUDY** Barbara Pilas,[2] Christopher C. Felix,[1] Tadeusz Sarna,[2] and B. Kalyanaraman[1], [1]National Biomedical ESR Center, Medical College of Wisconsin, Milwaukee, WI 53226 and [2]Department of Biophysics, Institute of Molecular Biology, Jagiellonian University, Krakow, Poland.

The photolysis of 5-S-cysteinyldopa, 2,5-S,S-dicysteinyldopa, 4-hydroxybenzothiazole and cysteinyldopa melanins has been studied by electron spin resonance - spin trapping methods using 5,5-dimethyl-1-pyrroline-1-oxide and 2-methyl-2-nitrosopropane as spin traps for hydrated electrons, hydrogen atoms, and carbon-centered alanyl radicals. *The photochemistry of these materials is shown to resemble dopa in that both* photoionization and photohomolysis occur. However, unlike dopa, the cysteinyldopa also forms the carbon-centered alanyl radicals via photodecomposition of the cysteinyl group. Action spectra and quantum yields are reported. Mechanism(s) of radical formation are discussed.

122 SPIN TRAPPING WITH *alpha*-2,4,6-TRIMETHOXYPHENYL N-*tert*-BUTYL NITRONE Coit M. DuBose, Oklahoma Medical Research Foundation, 825 NE 13th St., Oklahoma City, OK 73104 and Edward G. Janzen, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Aminoxyls derived from anion (Grignard and organolithium) and radical addition to *alpha*-2,4,6-trimethoxyphenyl N-*tert*-butyl nitrone, $(MO)_3PBN$, have been studied. Radicals studied include those generated by hydrogen atom abstraction, photolysis or thermolysis from aldehydes, ketones, ethers, halogenated methanes and ethanes, azoisobutyronitrile, phenylazotriphenylmethane, benzoyl peroxide and di-*tert*-butyl peroxalate. The effect on hfsc's of bulk, length and level of halogenation of spin adducts of $(MO)_3PBN$ nitrone will be presented. Also the effect on hfsc's of solvent polarity on the methyl and butyl adducts of (MO)3PBN will be presented. The hfsc's of carbon-centered adducts of *alpha*-2-hydroxy-4,6-dimethoxyphenyl N-*tert*-butyl nitrone, $HO(MO)_2PBN$, produced by anion addition will be given as well as hfsc's of the oxygen-centered adduct from the addition of *tert*-butoxy radical. The formation of 2H,3H-(4,6-dimethoxy)benzo[b]furan-3-yl *tert*-butyl aminoxyl, $(MO)_2BFBA$, derived from $(MO)_3PBN$ in the presence of monooxygen-centered radicals (hydroxy, alkoxy and benzophenone triplet) via intramolecular spin trapping will be presented.

123 EPR STUDY OF HYDROGEN PEROXIDE PRODUCING OXIDASES. Y. Sakagishi*, T. Hanada**, M. Sonoda*, and K. Yamanishi**, *Saitama Medical School, Moro-Yama 350-04, Japan and **Wako Laboratory, Kawagoe 350, Japan.

Many oxidases produce hydrogen peroxide upon reaction with substrates. Xanthine oxidase, cholesterol oxidase, and glucose oxidase belong in this category. These enzymes are also able to produce superoxide anion ($O_2^{\cdot-}$). This intermediate is detected by the spin trapping method employing a thiol (reduced glutathione) in heavy water - DMSO (dimethylsulfoxide). From these results we proposed a mechanism of H_2O_2 production from oxidases via superoxide anion (EPR Symposium, 1984).

Using the conditions described above, $O_2^{\cdot-}$ adducts were observed with uricase, glycerol-3-phosphate oxidase, and pyruvate oxidase. However, no detectable $O_2^{\cdot-}$ was found with galactose oxidase, pyranose oxidase or sarcosine oxidase. The tetrazorium reduction method, however, confirmed the generation of superoxide anion for all of the oxidases. Another interpretation of these phenomena based on EPR and chemical luminescence data will be presented.

124 THE CHEMISTRY OF PENTAVALENT ORGANOBISMUTH REAGENTS. PART VII. THE POSSIBLE ROLE OF RADICAL MECHANISMS IN THE PHENYLATION PROCESS FOR Bi^{V} AND RELATED Pb^{IV}, I^{III} AND Sb^{V} REAGENTS. Derek H. R. Barton, Jean-Pierre Finet, Charles Giannotti and Frank Halley. Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France.

The phenylation reactions of $bismuth^{V}$, $lead^{IV}$ and $iodine^{III}$ have been examined to test the presence or absence of phenyl radicals. In the case of several $bismuth^{V}$ reactions the presence of phenyl radicals has been detected, but it has been shown, by use of a large excess of radical trapping agent, that these radicals have nothing to do with the phenylation process. In the same way all the other phenylation reactions do not respond to a large excess of a radical trap.

125 THE SPIN TRAPPING CHEMISTRY OF CARBON TETRACHLORIDE IN RAT LIVER MICROSOMES. Rheal A. Towner and Edward G. Janzen. Department of Chemistry and Biochemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Ontario N1G 2W1, Canada.

The spin trapping chemistry of carbon tetrachloride ($^{13}CCl_4$) has been previously investigated in rat liver, both *in vitro* and *in vivo*. In addition to the trichloromethyl radical ($^{13}{\cdot}CCl_3$), both a carbon-centred and an oxygen-centred radical were detected *in vitro*. These spin adducts have been assigned to be "lipid" (L·) and "lipid oxy" (LO·) radicals, without specific structural characterization to date. The spin trapping chemistry of this system is being reinvestigated using deuterated PBN (α-phenyl N-*tert*-butyl nitrone) to obtain better spectral resolution. Results of this study will be reported.

126 THE LOCATION OF SPIN TRAPS IN MICELLAR SOLUTIONS AS DETERMINED BY HIGH FIELD NMR SPECTROSCOPY. James Hilborn, D. Larry Haire, Henry J. Stronks, Gregory A. Coulter and Edward G. Janzen. Department of Chemistry and Biochemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

The use of spin traps for the investigation of radical and radical ion diffusion has been demonstrated. A question which remains undetermined is the location of the various spin traps in these studies. By comparing the solvent effect on the proton and carbon-13 chemical shifts of the spin traps PBN (α-phenyl N-tert-butyl nitrone) and DMPO (5,5-dimethyl-1-pyrroline-N-oxide) with the chemical shift of these nuclei in a micellar solution, it is possible to make some conclusions as to the location of these spin traps. Results are most illuminating when the carbon-13 of the nitrone function is used as the probe.

127 GC/MS ANALYSIS OF TRIMETHYLSILYLATED SPIN ADDUCTS. Peter Krygsman, D. Larry Haire and Edward G. Janzen. Department of Chemistry and Biochemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

The HPLC separation of PBN (α-phenyl N-tert-butyl nitrone) spin adducts has been demonstrated. Additional structural determination involves GC/MS methods. In order to enhance parent ion intensities, the possibility of trimethylsilylation has been investigated. GC/MS results with PNB spin adducts will be presented.

128 ENDOR SPECTRA OF SPIN ADDUCTS. D. Larry Haire, Yashige Kotake, Uwe M. Oehler and Edward G. Janzen. Department of Chemistry and Biochemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

Few examples exist of aminoxyl (nitroxide) radicals with a β-hydrogen which have been investigated by ENDOR spectroscopy. The reported studies to date involve aminoxyls which are spin adducts of nitrone or C-nitroso compounds. Alkyl and aryl spin adducts of PBN (α-phenyl N-tert-butyl nitrone) can be made at concentrations suitable for ENDOR investigation. Using deuterated PBN's, the magnitude and sign of the hyperfine splittings from the hydrogens on the phenyl ring could be ascertained. From these studies, the preferred conformations of the spin adducts were deduced.

No examples of ENDOR spectra of cyclic aminoxyl radicals with a β-hydrogen are available in the literature. ENDOR results on DMPO (5,5-dimethyl-1-pyrroline-N-oxide)-type spin adducts will be presented.

129 ENDOR SPECTRA OF ACYL AMINOXYLS. Uwe M. Oehler and Edward G. Janzen. Department of Chemistry and Biochemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada.

ENDOR spectra of acyl and aryl or tert-butyl aminoxyls have been obtained for the first time. The magnitude of the hyperfine splitting constants confirms the previously recognized fact that very little spin density resides on the carbonyl carbon atom. The relative intensities of the ENDOR doublets of proton or flourine and aminoxyl nitrogen follow the Cross Relaxation Intensity Sequence Pattern (CRISP) rule. The signs of the hyperfine splitting constants of the nuclei around the N-aryl group are found to be consistent with predictions. However, the sign of the tert-butyl protons are found to be opposite (namely +ve) to the sign of the tert-butyl protons of simple dialkyl aminoxyl. This is in agreement with an NMR result previously reported.

130 SPECTRAL ROTATION IN PULSED ESR SPECTROSCOPY J.P. Hornak and J.H. Freed.
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Baker Laboratory of Chemistry, Cornell University, Ithaca, NY 14853.

The technique of pulsed Fourier transform (FT) NMR spectroscopy is well developed and understood. However, the equivalent technique for ESR has experienced slower development. Recent developments in ESR instrumentation have now made FT ESR possible. Background information and the instrumental requirements for rotating the magnetization associated with an ESR spectrum by a microwave pulse will be presented. In addition, techniques for reconstructing the frequency domain spectrum from the time domain spectrum are described. Examples of the application of these techniques will be given for obtaining a frequency domain spectrum from both a FID and an electron spin echo.

131 FOURIER TRANSFORM ESR: TWO DIMENSIONAL ESR OF NITROXIDES

Jeffrey P. Gorcester and Jack H. Freed. Department of Chemistry, Cornell University, Ithaca, New York 14853.

Microwave pulses of width on the order of 5-10 nsec. combined with low Q resonators enable irradiation of entire nitroxide spectra with spectral extent as large as 60 Gauss. A fast two-channel digitizer enables us to collect a single spectrum in less than 2 ms. An entire 2D experiment can be completed in less than 5 minutes including signal averaging and 1 ns. time resolution of the FID. A combination of selective and non-selective pulses in a given pulse sequence enables direct observation of magnetization transfer in the time-domain using the technique of Fourier Transform ELDOR. In the FTELDOR experiment we irradiate a single hyperfine line of a 3 line nitroxide spectrum with a selective (bandwidth limited) 180° pulse. Then at later time tau we rotate the entire spectrum with a non-selective 90° pulse and collect the FID. By repeating the sequence for selected values of tau and Fourier Transforming the FID's a 2D spectrum is generated which displays the ELDOR response from each resonance line. We are also exploring the applications of the full-irradiation techniques to the study of the dynamics of liquid crystals and model membranes by other 2D sequences.

132 TIME-RESOLVED FOURIER TRANSFORM EPR OF FREE RADICAL REACTIONS

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Fourier Transform EPR is a pulsed EPR technique in which the free induction decay (FID) is directly digitized and the EPR spectrum is obtained by Fourier Transformation. When combined with a pulsed excimer laser, such an FTEPR spectrometer provides greater sensitivity and spectral resolution than the usual CW and pulsed techniques employed for time-resolved photochemical studies. As we will show, time-resolved FTEPR can be readily employed to study the kinetics of biologically relevant free radical reactions in solution. The free radicals under study include some which are formed in pentoses and quinones in both aqueous and non-aqueous solution. Chemical reactions of quinones are easily observed, and followed for over four orders of magnitude in time. Also, several radicals, which are not directly detectable by CW techniques, are directly observable, and their reaction kinetics can be studied.

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy under contract W-31-109-ENG-38 and the American Cancer Society Research Grant PDT-262.

133 SENSITIVE EPR OBSERVATION BY USING A COMPUTERIZED SPECTRUM ANALYZER.

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A single-oscillation heterodyne ESR spectrometer equipped with a high-frequency spectrum analyzer has been constructed in the course of development of new systems measuring accurate spin susceptibility. Field-modulated ESR signals are detected as the amplitudes of the sidebands of intermediate frequency down-converted from the carrier frequency. By tracing the amplitudes of the sidebands as functions of magnetic field one can observe sensitively absorption signals which are different from first-derivative signals measured by conventional ESR spectrometers. This methodology is interpreted theoretically by a vector model of the signal amplitude II:

$$\frac{\partial |E|}{\partial u} = \omega_0 T_2 \chi''$$

The lineshape, the relative amplitudes of the hyperfine lines, and the modulation-amplitude dependences of the first and second sidebands observed by this method support the appropriateness of the theoretical model.

134 **STIMULATED QUANTUM BEATS IN MAGNETIC RESONANCE.** R. D. Kendrick and C. S. Yannoni, *IBM Almaden Research Center, San Jose, California.*

We have observed stimulated quantum beats (SQUABS) in a magnetic three-level system. Beats like this were first observed in optical three-level systems some time ago. Since then, a number of similar effects have been reported in the optical regime, and also for systems with mixed optical and magnetic interactions. In the mixed as well as the pure optical case, the response has been detected as an optical signal. In contrast, the beats reported here have been stimulated in a three-level system in which the energies and responses are determined solely by magnetic interactions involving nuclear spins. The possibilities for observation of SQUABS in ESR will be discussed.

135

DETERMINATION OF ENVIRONMENTAL URANIUM EMISSIONS
BY LIQUID SCINTILLATION ALPHA COUNTING

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A technique utilizing liquid scintillation alpha counting has been developed for determination of trace level airborne uranium emissions from an enrichment plant. Atmospheric discharges are continuously sampled by a caustic bubbler train. Uranium is extracted from solution into trioctylphosphine oxide (TOPO) dissolved in xylene. Uranium is quantitatively determined by direct counting of the TOPO-xylene extract in a commercial liquid scintillation system.

Alpha detection efficiency approximates 100%, thereby avoiding window absorption and geometry losses inherent in conventional proportional counting. Uranium concentrations as low as 1 x 10^{-10} molar have been determined from an air sample size of one cubic meter.

136 PRECONCENTRATION AND DETERMINATION OF AQUATIC SULFIDE, Dennis DeSalvo, Stepan Co., Northfield, IL 60093 and Kenneth W. Street, Jr., Department of Chemistry, Kent State University, Kent, OH 44242.

The level of sulfide in aqueous environmental samples was determined by first preconcentrating on a cadmium (II) exchanged zeolite sorbent then converted to methylene blue and finally quantified by visible spectrometry. The various parameters affecting the sulfide recovery of this method such as flow rate, zeolite column bed height, sample volume and aspiration time were investigated. An evaluation of this method versus the currently accepted sulfide spectrophotometric method indicates that the preconcentration technique yields a lower limit of detection, less uncertainty in results and the highest sensitivity. Application of the standard addition technique as a means to circumvent potential sample matrix problems is also discussed.

137 THE DETERMINATION OF PPB LEVELS SULFIDES IN TURBID WATERS BY GAS DIALYSIS/ION CHROMATOGRAPHY. L.R. Goodwin, D. Francom, and F.P. Dieken, Alberta Envrionmental Centre, Bag 4000, Vegreville, Alberta, Canada T0B4L0

The determination of part per billion levels of sulfide in turbid waters is difficult or impossible using the Standard Method: Methylene Blue Spectrophotometric Method, even after employing the recommended pretreatment procedures. As well, most sulfide in water samples presented to the environmental laboratory have been preserved in the field by zinc ion (or equivalent) thus complicating the direct determination of sulfide by ion chromatography. Utilizing the electrochemical detector and recommended pretreatment procedures, unstable baselines and sample matrix effects were noted in direct IC determinations on environmental water samples. A pretreatment step is presented which converts the zinc preserved sulfide to H_2S and separates the gas from the sample matrix by a gas dialysis membrane using a continuous flow procedure which traps the gas in a dilute sodium hydroxide solution for presentation to the ion chromatograph. Calibration data, parallel runs against the Standard Method for turbidity free waters, the effect of kaolin turbidity on the two test methods and recovery data on synthetic and natural waters is presented. The use of antioxidants to stablize the H_2S is supported by recovery data.

138 ABSTRACT NOT AVAILABLE

139 A QUALITY ASSURANCE PROGRAM FOR THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM AND NATIONAL TRENDS NETWORK. Myron H. Brooks, LeRoy J. Schroder, and Timothy C. Willoughby, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002

External quality-assurance monitoring of the National Atmospheric Deposition Program and National Trends Network is conducted by the U.S. Geological Survey and has been divided into three main areas. 1) The precision and accuracy of site-operator measurements of pH and specific conductance have been periodically tested since October 1981 by an intersite comparison program using solutions with known pH and specific conductance. Test results from these intersite comparisons indicate that the network goal for accuracy of pH measurements of + or - 0.1 pH unit is not being met by the majority of network site operators, whereas the network goal for accuracy of specific conductance measurements of + or - 4 microsiemens per centimeter is being attained by the majority of site operators. 2) The effects of network sample collection, handling, and shipping procedures have been examined by a blind-audit sample program since August 1980. Results from this program are summarized on an annual basis, and indicate that network sample collection, handling, and shipping procedures introduce a positive bias for many of the constituents routinely analyzed in wet-deposition samples. The magnitude of this bias is estimated for each analyte and possible contributing factors are examined. 3) Network analytical results have been monitored since November 1982 through an interlaboratory comparison program. The network's Central Analytical Laboratory, located at the Illinois State Water Survey in Champaign, Illinois, has been compared to other laboratories involved in the routine analysis of wet-deposition samples. Results of these comparisons indicate that, in general, the Central Analytical Laboratory achieves better precision and accuracy, and introduces less bias than the other laboratories involved in the comparison program.

140 AN INDIVIDUAL WATER SAMPLE QUALITY ASSURANCE PROGRAM. Richard D. Robinson, Daryl Knab, Daniel R. Perrin, Los Alamos National Laboratory, P.O. Box 1663, MS K484, Los Alamos, NM 87545

This report documents the development and implementation of a flexible Individual Water Sample Quality Assurance (IWSQA) program. The management of the data obtained from the chemical characterization of a water sample is described. These data are used to calculate the IWSQA ratios used to evaluate the data for possible errors and indications of which chemical constituents should be reanalyzed before reporting. The theory, definitions, tables for calculation, and guildlines for interpretation of the ratios are given.

141 STABILITY OF NITRATE IN PRESERVED AND UNPRESERVED NATURAL SURFACE WATERS, F. X. Suarez, D. C. Hillman, Acid Deposition Methods Group, Lockheed Engineering and Management Services Company, Inc., 1050 E. Flamingo Rd., Las Vegas, Nevada, E. M. Heithmar, U.S. Environmental Protection Agency, 944 E. Harmon, Las Vegas, Nevada

The United States Environmental Protection Agency is currently operating a program known as the National Surface Water Survey (NSWS) in which lakes and streams across the United States are characterized for a number of analytes, including nitrate. During the Eastern Lake Survey (ELS, one phase of NSWS), the holding time for nitrate analysis was seven days. However, for a number of samples the holding time was exceeded by 110 days. As a result, a project was initiated to review the literature on the stability and the preservation of nitrate and to evaluate the holding time for nitrate analysis in natural surface waters. The evaluation consisted of two experiments to study the effect of mercuric chloride ($HgCl_2$) preservation, of post sampling filtration, and of storage temperature on low level nitrate stability. The first experiment was designed to study nitrate stability in a deionized water matrix, and the second experiment was designed to study nitrate stability in low ionic strength natural surface waters. All nitrate analyses were performed using ion chromotography. In the first experiment, deionized water samples spiked at concentrations of 25 and 200 ppb NO_3-N were stored at 4°C and 30°C. In the second experiment, aliquots of three lake samples were treated in four different manners: filtered, filtered and preserved with $HgCl_2$, unfiltered and preserved with $HgCl_2$, and unfiltered. The samples were stored at 4°C and at room temperature. After determining the initial nitrate concentration, the nitrate concentration in each sample was determined periodically over 150 days.

142 DEVELOPMENT OF NATURAL MATRIX STANDARDS FOR USE IN THE ANALYSIS OF ENVIRONMENTAL MATERIALS.

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The National Bureau of Standards has developed a series of natural matrix Standard Reference Materials (SRM's). These matrices include: rocks, ores, soils, fuel oils, simulated rainwater. These SRM's are intended for use in the evaluation of methods and the calibration of equipment used for the determination of constituent elements in environmental materials. In this paper a description of the methods/techniques used in the certification of these SRM's is presented along with the data base used to certify constituent elements that are environmentally important. The methods/techniques to be discussed include: neutron activation analyses, atomic absorption-emission ion chromatography, optical emission x-ray fluorescence, mass spectrometry, gas chromatography and many others.

143

DETECTION LIMITS FOR ENVIRONMENTAL SAMPLES

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Detection limit is an important topic for trace analysis work. Although detection limit values are often found in literature, a universal definition for detection limit is lacking. This paper examines several literature definitions for detection limit, how error effects detection limit values and why no universal detection limit definition exists. Errors of the first and second kind and random and determinate errors are defined. Experimental examples are included along with illustrations.

144 THE DETERMINATION OF AVAILABLE ARSENIC (III) AND ARSENIC (V) IN STREAM SEDIMENTS.

Walter H. Ficklin, USGS, Box 25046, DFC, MS 955, Denver, CO 80225.

Inorganic arsenic occurs in environmental waters and stream sediments in two oxidation states: As (III) and As (V). An investigation of the chemistry of arsenic in the aqueous environment requires an analytical method for the determination of the concentration of arsenic in each oxidation state, especially that arsenic which is easily extracted from stream sediments. The usual metal extractants are either 1.0 N HCl or 0.2 M oxalic acid/ammonium oxalate buffer. However, recovery of added As (III) in each of these extraction media is less than 50%. An analytical method for the determination of "available" As (III) and As (V) in stream-sediment samples has been developed using 1.0 N HCl and 0.05 M oxalic acid. About 1 gm of stream sediment (wet) is added to a preweighed volume of 1.0 M hydrochloric acid and 0.05 M oxalic acid in a polyethylene bottle. After the sediment is added, the bottle is reweighed to determine the amount of wet sediment used. Following a suitable extraction period, 5 ml of the solution are passed through a column containing Dowex 1 x 8 resin in the acetate form. The As (III) and As (V) are selectively eluted with 0.12 N hydrochloric acid. Each species of arsenic is determined by graphite furnace atomic-absorption spectrophotometry. An average of 85% of the added As (III) and 92% of As (V) was recovered from stream sediments using this procedure. The lower limit of detection for either species is 0.1 μg/gm. The addition of the sample to the preweighed bottle is made at the sample site to avoid any changes in the concentration of As (III) or As (V), which may occur when samples are stored.

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145 DETERMINATION OF TRACE TRANSITION METALS AND ORGANICS IN SEAWATER AND BRACKISH ESTUARINE WATER BY MATRIX ELIMINATION -- A COMPARISON OF CLOSED AND OPEN MARINE SYSTEMS

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The determination of trace levels of transition metals in brines poses a very difficult analytical problem. The high sodium chloride concentrations create sampling problems for Atomic Absorption and the presence of calcium and magnesium, create matrix difficulties with typical Ion Chromatographic separations of metals and organic constituents. This paper will address the use of buffered samples passed through and concentrated on Iminodiacetate resins as a means of eliminating the matrix interferences. The determination of organic acids in closed and open marine systems and the effect of the matrix upon this analysis will also be addressed.

146 INVESTIGATION OF SELENIUM AND OTHER TRACE ELEMENTS IN SOILS FROM THE SAN JOAQUIN VALLEY OF CENTRAL CALIFORNIA

Stephen Wilson, Ron Tidball, D. Brooke Hatfield and Paul Briggs, U.S. Geological Survey, Box 25046, MS 928, Denver Federal Center, Denver, CO 80225

The U.S. Geological Survey is currently conducting selected geochemical studies in the San Joaquin Valley of California in an attempt to understand the processes which have resulted in the accumulation of selenium in the Kestersen National Wildlife Refuge. Initially, two soil surveys were conducted to define the natural distribution of elements in the soils, establish background values, discover areas of unusual trace element concentrations and identify potential source areas for selenium. The first study was conducted using a 10-kilometer sampling cell (10 km x 10 km) and covered the entire San Joaquin Valley. Elevated concentrations of selenium in the soil were observed in two areas on the west side of the valley: The Panoche-Cantua Creek fans in western Fresno County and the Antelope Hills area in western Kern County. The Panoche-Cantua Creek fans were further sampled (1-mile sampling cell; 1 mi x 1 mi) to verify the earlier observations and to precisely delineate the source area. Results from both soil surveys will be presented along with recent selenium mobility investigations. The discussion will focus on the mobility of selenium and the association of selenium with other trace elements.

147 ABSTRACT NOT AVAILABLE

148 CHANGES IN STRATOSPHERIC OZONE CHEMISTRY RESULTING FROM A NUCLEAR WAR,

Sherry L. Stephens, John W. Birks, Michel Rossi, and David Golden, CIRES, Campus Box 449, University of Colorado at Boulder, Boulder, CO 80309

Fires ignited by the thousands of nuclear explosions of a major nuclear war would inject huge quantieties of smoke aerosol and other noxious chemical species into the atmosphere. Nuclear explosions would also raise large quantities of dust. Recent studies have shown that light scattering and adsorption by the dust and smoke would initially block large fractions of incident solar radiation with consequent cooling of land surfaces, and effect now referred ot as "nuclear winter". Heat adsorption by the dust and smoke would drastically alter the dynamics of the atmosphere allowing for interactions between high surface area particulates and stratospheric ozone.

Damage to the ozone layer following a nuclear war is possible through heterogeneous and homogeneous reactions. Our studies have shown that ozone is decomposed on carbon surfaces in a very fast initial reaction which is slowed by surface oxide formation. Increases in temperature decrease surface oxide formation and increase the duration of fast initial ozone decomposition. Other studies have shown oxides of nitrogen produced by nuclear explosioins act as homogeneous catalysts to destroy ozone. Decreases in light levels could also slow the rate of production of ozone. The combination of these and other reactions are being investigated.

149 SOURCES, TRANSPORT, AND PHOTOCHEMICAL PRODUCTION OF ORGANIC COMPOUNDS IN ATMOSPHERIC AEROSOL PARTICLES.

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The use of a new technique for aerosol particulate sampling has enabled us to collect hourly atmospheric samples and measure their volatile constituents. The method has allowed frequent enough sampling to show rapid, synchronous changes in the concentrations of volatile organic constituents. This has provided information about aerosol particle sources, transport, and photochemical products. The data were subjected to principal component analysis to determine the inter-relationships among variables. In one study, 138 aerosol samples were collected in Boulder, Colorado, and 45 compounds were quantified. At least three important factors were extracted from the data: a group of compounds associated with photochemical activity, a set of compounds that are known to arise from biogenic sources, and a series of paraffins known to be generated by vehicular sources. A second study has involved the collection of aerosol particles along the northern East Coast of the U.S., using an aircraft sampling platform.

150 *A THEORETICAL ASSESSMENT OF POLLUTANT DEPOSITION TO INDIVIDUAL LAND TYPES DURING A REGIONAL SCALE ACID DEPOSITION EPISODE.*

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Using a mesoscale model of pollutant transport, transformation and deposition, a detailed analysis of acidic deposition to the states of New York and Ohio was performed for a three day springtime deposition episode. With this model, it is possible to assess the roles of wet and dry deposition to individual land types in the removal of pollutants from the atmosphere. Over two-thirds (67%, Ohio; 78%, New York) of the acidic deposition during this rainy period fell as wet deposition, primarily in the form of sulfuric acid. Dry deposition of SO_2 accounted for 70 - 75% of the total dry acidic deposition in both areas, and most of the remaining dry deposition occurred as HNO_3. Over both deposition areas, particulate sulfate deposition accounted for less that 1% of the total acid deposition. Due to the highly surface-specific nature of the dry deposition process, individual land types displayed unique patterns of pollutant uptake. Water surfaces absorbed primarily SO_2, while rougher forested areas absorbed a larger proportion of nitric acid vapor. Urban areas with their associated material surfaces were found to absorb significantly less acid in the dry form, and most of this deposition occurred as nitric acid vapor. These model results suggest that dry pollutant fluxes to individual surface types will show significant variability from any "averaged" flux estimates over larger areas encompassing numerous land types.

151

A COMPARISON OF TWO MODELS LINKING CHLORINE CHEMISTRY WITH ANTARCTIC OZONE DEPLETIONS

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Strong circumstantial evidence suggests that the dramatic ozone depletions recently observed in Antarctica are caused by heterogeneous interconversion of chlorine species on stratospheric ice clouds. Rapid springtime recycling of the major chlorine reservoirs through the cross reaction $HCl + ClONO2 -> Cl2 + HNO3$ has already been explored as a possible depletion mechanism. An intriguing alternative involves slow redistribution of both odd nitrogen and chlorine families through simultaneous hydrolysis of $ClONO2$ and $N2O5$ during the polar winter. The hydrolyses have the combined ozone destructive effect of sequestering nitrogen as photo-insensitive $HNO3$, and shifting chlorine to readily photolyzed $HOCl$.

152 FORMATION OF HUMIC ACID-LIKE SUBSTANCES FROM NON-TRADITIONAL PRECURSORS

Kaveh Zarrabi, Wen-Chia Chen, James A. Rice, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401

Humic acid-like substances were formed from a Tetralin-Dodecane mixture (1/10, V/V) and a petroleum-based fuel (Jet-A) during autoxidation. These humic acid-like substances are compared to humic acids produced by natural processes. The solubility, elemental analysis, infrared, 13C NMR and pyrolysis-mass spectra of these humic acid-like substances are compared and cotrasted to literature characterizations of humic acids. This comparison is discussed with reference to the processes of organic matter oxidation.

153 MULTIRESIDUE DETERMINATION OF CORN PRODUCTION PESTICIDES BY CAPILLARY GLC.

T. D. Spittler, J. B. Bourke, D. L. Snook and H. C. Leichtweis. New York State Experiment Station, Cornell University, Geneva, NY 14456.

The movement of applied pesticides through soil and into groundwater is being studied in a series of paired watersheds -- one of each set producing corn by conventional techniques, the others under conservation or "No-Till" methods. Four soil types are under investigation in NY, PA, DE and MD. Water samples are obtained via measured surface runoff through calibrated flumes, wells, suction lysimeters and pan lysimeters. Soil samples are derived from waterborne silt and horizon cores. Filtered water samples (0.45 µm) are concentrated on C-18 Sepak cartridges which have been activated with methanol and water rinses. Cartridges are eluted with benzene for glc, with 1.0 ppb chlorothalonil as internal standard. 50g subsamples of air-dried and ground (20 mesh) soils are extracted 20 min with 100 mL of 90% methanol/water. 20 mL aliquots representing 10g of soil are removed and clarified by centrifugation. The supernatants are diluted 1:10 with water, and the resulting ca 8% MeOH solutions of pesticides are concentrated on Sepaks, as above. Determination is by splitless injection on an SGE SE-54 column, 25M x 0.22 mM; He carrier at 35 cM/sec. Program: 3 min at 130°C; 7°C min to 210°C; hold 7 min; 10°C/min to 250°C; hold 5 min. Detection limits for water samples are 0.1 ppb for atrazine, simazine, propazine, cyanazine and metolachlor, and 0.01 ppb for alachlor. Soil detection is 10-fold less sensitive.

154 ACID-NEUTRAL CONTINUOUS LIQUID-LIQUID EXTRACTION OF EPA PRIORITY POLLUTANT AND HAZARDOUS SUBSTANCE LIST COMPOUNDS.

Joseph L. Slayton, E. Ramona Trovato, USEPA - Region 3, Central Regional Lab, 839 Bestgate Road, Annapolis, Md. 21401.

Continuous liquid-liquid extraction is compared to manual extractions per EPA Method 625, but employing an acid-neutral scheme. The results from EPA performance evaluation, wastewater, Superfund, and RCRA samples are compared using the two extraction techniques. Continuous liquid-liquid extractions following an acid-neutral scheme are compared to those following a base-neutral scheme. The distribution of target compounds in the acid-neutral and base fractions is detailed. All identifications and quantitations are performed using a GC/MS system with a fused silica capillary columns.

155 INFRARED DETERMINATION OF POLYMERIC SIZING AGENTS ON COTTON YARNS.[1]

Nancy M. Morris and Jerry P. Moreau, Southern Regional Research Center, New Orleans, Louisiana 70179.[2]

The quantification of warp size on textile yarns is important in assaying the ease of removability from fabrics before the fabrics are subjected to commonly used textile wet processes. Equally important is the extent of durability of permanent sizing agents throughout various stages of wet processing. This paper reports the use of computerized dispersive infrared spectroscopy to quantify acrylate and urethane polymers and mixtures of these polymers on cotton warp yarns. The method is very accurate for quantification of known polymer systems and provides useful information on the presence of carbonyl containing polymers even when the identity of the polymer is unknown. Fourier transform photoacoustic infrared spectroscopy was also used to examine these yarns and proved to be a useful tool for the study of location of polymer on the yarn.

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[1] To be presented at the 28th Rocky Mountain Conference of Society for Applied Spectroscopy, Denver, Colorado, Aug. 3-7, 1986.

[2] One of the facilities of the Mid South Area, Agricultural Research Service, U.S. Department of Agriculture.

156 EXTENDED CALIBRATION CURVES AND EXCITATION AND EMISSION SPECTRA FOR STUDYING THE LUMINESCENCE OF BENZO(f)QUINOLINE ADSORBED ON SILICA GEL

G. J. Burrell and R. J. Hurtubise, Chemistry Department, University of Wyoming, Laramie, WY 82071

Room-temperature solid-surface fluorescence (RTF) and room-temperature solid-surface phosphorescence (RTP) have been employed considerably in trace organic analysis. Although both fluorescence and phosphorescence may be exhibited by the same compound, significant differences may exist in the surface interactions and microenvironment requirements for fluorescence and phosphorescence. In this study, benzo(f)quinoline (B(f)Q) was used as a model compound to investigate some of the interactions of B(f)Q with a silica gel chromatoplate. Specifically, the work involved obtaining RTF and RTP calibration curves well beyond the linear portions of the curves to obtain insights into some of the interactions of B(f)Q for strong RTF and RTP signals with a silica gel chromatoplate containing a polyacrylate binder. In addition, several luminescence excitation and emission spectra were obtained for B(f)Q at moderate to high levels of adsorbed B(f)Q. The RTF and RTP results were quite different which showed that dissimilar interactions are needed for enhanced RTF and RTP. The overall results allowed the development of an analytical model which partly described the important conditions for strong RTF and RTP signals.

157 STABILITY OF pH AND DIC IN SEALED SYRINGE SAMPLES

E. M. Burke, D. C. Hillman, Acid Deposition Methods Group, Lockheed Engineering and Management Services Company, Inc., 1050 E. Flamingo Rd., Las Vegas, Nevada. E. M. Heithmar, United States Environmental Protection Agency, 944 E. Harmon, Las Vegas, Nevada

Logistics in future phases of the National Surface Water Survey of the Environmental Protection Agency may necessitate a holding time for pH and DIC determinations in syringe samples of up to seven days. Therefore, a series of experiments was performed which measured the pH and DIC of synthetic and natural samples over approximately a seven day time period. Synthetic samples contained dissolved CO_2 levels 0, 1, 10, and 100 times the atmospheric CO_2 level. Synthetic samples were stored in open beakers at room temperature and in sealed syringes at both 4°C and room temperature. Natural water samples that initially contained dissolved CO_2 levels 0.1, 1.6, and 2.5 times the atmospheric CO_2 were stored in sealed syringes and in aliquot bottles at both 4°C and room temperature. This study indicated that it is necessary to store samples in sealed containers. When contained in sealed syringes, the pH and DIC of synthetic and natural samples stored at 4°C did not change significantly over a seven day time period regardless of initial dissolved CO_2 concentration. The results from samples stored in aliquot bottles were not so definitive. Although the pH appeared to be stable, the DIC was only marginally stable at each storage temperature.

158 CHEMICAL AND BIOLOGICAL STUDIES OF DRINKING WATER SOURCES OF WESTERN ILLINOIS RURAL COMMUNITIES.

Robert E. Neas, Te-Hsiu Ma, Charlotte Cook and
Mary Harris. Water Laboratory - Department of Chemistry,
Environmental Mutagenisis Laboratory - Department of
Biological Sciences, and Institute for Environmental
Management, Western Illinois University, Macomb, IL 61455.

Water samples collected weekly from two groundwater sources of drinking water and one surface impoundment source of drinking water were examined by chemical analyses and biological assays. The samples obtained from rural communities in McDonough and Fulton counties in western Illinois were analyzed for fourteen chemical parameters including nitrate, nitrite, ammonia, manganese, selenium and cadmium. Both a plant bioassay (Trad-MCN) and a mammalian bioassay (Mus-MCN) were also performed to test for the mutagenicity of the samples. Several samples exhibited relatively elevated concentrations of chemical constituents (e.g. nitrate, nitrite, ammonia, selenium) and relatively elevated levels of mutagenicity by the Trad-MCN bioassay. The Mus-MCN bioassay also revealed relatively elevated mutagenicity, on a cumulative basis, in the latter stages of the six-month study. Limited correlations between chemical concentrations and bioassay results were noted. (Research supported by the Illinois Department of Energy and Natural Resources Grant No. EH-25).

ANALYSIS OF VOLATILE PRIORITY POLUTANTS BY CAPILLARY GAS CHROMATOGRAPHY

159 N.H. Mosesman, R.J. Bartram, L.M. Sidisky, J. Brown

Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048

Wide bore (0.75mm ID), thick film (1+μm), bonded phase capillary columns offer several advantages over both narrow bore capillary columns and packed columns, for analyses of volatile organics involving purge and trap techniques. Although narrow bore capillary columns offer better resolution and faster analysis time than packed columns, they must be operated at low flow rates (0.5-2ml/min.). Thus, when a narrow bore column is interfaced to a standard purge and trap system and specialized injection port, a secondary trapping system or a splitter is required. In contrast, wide bore columns accept high flow rates (5-15ml/minute). This makes them more amenable to direct coupling with a purge and trap device. In addition, wide bore columns have much higher sample capacity (∿15,000ng/component, vs. ∿500ng for 0.32mm ID columns).

A 1.0 to 1.5 μm film on a wide bore column retains volatile compounds better than a standard (0.2 to 0.3 μm) film, yet does not cause band broadening of later eluting compounds. Bonded phases provide better thermal stability and resist water vapor damage inherent with purge and trap techniques. Wide bore columns do not require specialized capillary injection systems. They can be interfaced to virtually any gas chromatograph with a 1/4" or 1/8" injection port fitting by using a simple direct injection kit.

The performance of a VOCOL wide bore column (60m x 0.75mm ID, 1.5μm film) will be compared to that of the packed column currently cited in EPA methodols for volatile organics analyses. The VOCOL column can resolve the 34 volatile pollutants and internal standards listed in EPA Method 624 in approximately 30 minutes.

NON-DESTRUCTIVE ANALYSIS OF PLUTONIUM BEARING SAMPLES BY CALORIMETRY AND GAMMA SPECTROSCOPY

Barbara M. Hardin and Noralynn J. Caduff

160 Rockwell International, P.O. Box 464 Golden, CO 80401

Non-destructive analysis (NDA) is rapidly becoming an important tool for quality control and safeguards measurements. NDA techniques currently in use in the Analytical Laboratories at Rocky Flats Plant are calorimetry and gamma-spectroscopy. The instruments are capable of measuring Plutonium in any type of Plutonium-bearing material, as well as indicating amounts of Americium, Neptunium, and Uranium and the presence of several other elements and their isotopes. The systems can handle variable sample sizes and sample throughput.

161 BEYOND THE ONE HUNDRED PERCENT LINE; A SIMPLE METHOD FOR DETECTING LOW LEVEL ARTIFACTS IN FT-IR SPECTROMETERS,

J.J. Rafalko and T. Davidson, Celanese Research Company, 86 Morris Ave., Summit, N.J. 07901.

Test data provided by instrument manufacturers for new FT-IR's are not adequate to determine their quality. A user is normally given background and polystyrene spectra and a 100% line spectrum which highlight an instrument's overall performance. However, it has been previously shown by computer methods that these tests do not detect subtle problems with individual components (1,2). We have been able to detect defects by simply ratioing an unattenuated background spectrum versus a sample spectrum that has been recorded with a beam spot size at the sample postion that has been reduced to 20 to 40% of the unattenuated beam. The results of this test and their relationship to artifacts in real sample spectra will be discussed for several instruments.

1. J. DeHaseth, Appl. Spectrosc., 36, 544(1982).
2. D. Saperstein and W. Golden, Appl. Spectrosc., 39, 1032 (1985).

162 ANALYTICAL ROOM-TEMPERATURE LUMINESCENCE FROM COMPOUNDS ADSORBED ON A α-CYCLODEXTRIN-NaCl MIXTURE.

J. M. Bello and R. J. Hurtubise, Chemistry Department, University of Wyoming, Laramie, WY 82071.

A α-cyclodextrin-NaCl mixture was investigated as a solid-surface substrate for room-temperature phosphorescence and fluorescence. The optimum conditions for inducing room-temperature luminescence were explored extensively for four model compounds. Experimental conditions such as the solvent used to adsorb the compounds, drying temperature, surface atmosphere of the sample, and mixing the cyclodextrin with salts like NaCl had substantial effects on the luminescence intensities of the compounds. Furthermore, the analytical aspects of cyclodextrin induced solid-surface room-temperature luminescence were explored. Spectral characteristics, linear dynamic range, reproducibility of luminescence signals, and limits of detection were obtained. Also, studies were undertaken to explain the α-cyclodextrin-analyte interactions responsible for the luminescence phenomenon. One spectroscopic technique employed was diffuse reflectance spectroscopy. The diffuse reflectance spectra of model compounds were obtained under several experimental conditions. In addition, the α-cyclodextrin inclusion complexes of model compounds were prepared. The luminescence properties of the inclusion compounds and the compounds adsorbed on the α-cyclodextrin-NaCl mixture were compared.

163 EFFECT OF TEMPERATURE ON THE LUMINESCENCE PROPERTIES OF p-AMINOBENZOIC ACID ADSORBED ON SODIUM ACETATE.

S. M. Ramasamy and R. J. Hurtubise, Chemistry Department, University of Wyoming, Laramie, WY 82071.

The fundamental reasons for the room-temperature phosphorescence (RTP) of organic compounds adsorbed on solid surfaces is not completely understood. In an attempt to elucidate some of the interactions responsible for RTP, a cryogenic system was designed which permitted nitrogen gas to be cooled to about -180°C. With this system and with liquid nitrogen, the luminescence properties of p-aminobenzoic acid adsorbed on sodium acetate were determined over selected temperature increments in the range of 23°C to -196°C. The luminescence properties obtained over the above temperature range included fluorescence and phosphorescence intensities, fluorescence and phosphorescence excitation and emission spectra, phosphorescence lifetimes, and fluorescence and phosphorescence quantum yields. The determination of fluorescence and phosphorescence quantum yields was based on a relative comparison method using sodium salicylate as a reference standard. With the fluorescence and phosphorescence quantum yields and the phosphorescence lifetime results, it was possible to estimate the triplet formation efficiency of p-aminobenzoic acid and various rate constants related to the luminescence processes. The results were used to explain some of the interactions needed for observing the RTP of p-aminobenzoic acid adsorbed on sodium acetate.

164 SULFUR ANALYSIS OF COMPLEX ORGANIC COMPOUNDS USING MICROWAVE OVEN DIGESTION.

C.L. Fisher, BASF Corporation Chemicals Division, Holland, Michigan 49423

The sulfur content of copper phthalocyanine blue (PCN) pigment affects the performance of the finished product. The oxygen bomb digestion of PCN is both time consuming and capable of only a single analysis per bombing. A microwave oven method has been developed that reduces the digestion time and also allows up to twelve digestions per run. The CEM Corporation MDS-81D microwave digestion system is used to digest the PCN samples. Each sample is pre-treated with 30% hydrogen peroxide, digested with concentrated nitric acid, and the resulting sulfur oxides are totally oxidized to sulfate with another 30% hydrogen peroxide treatment. The sample is brought to a suitable volume for either gravimetric or ion chromatography sulfate quantitation.

165 COMPARISON OF ION-TRAP, FLAME-IONIZATION AND NITROGEN-PHOSPHORUS DETECTORS FOR PESTICIDE RESIDUE DETERMINATIONS BY CAPILLARY GAS CHROMATOGRAPHY, Sharon M. Johnson and Thomas R. Steinheimer, U. S. Geological Survey, P.O. Box 25046, Mail Stop 407, Denver Federal Center, Denver, Colorado, 80225

Three different standard mixes containing 20 different pesticides and five degradation products were utilized to develop capillary gas chromatographic separations. Two different column polarities and three detector types were evaluated on two separate gas chromatographs. A Hewlett-Packard 5890A gas chromatograph configured with a single injector but dual (identical) DB-17 columns was connected independently to a flame-ionization detector and an ion-trap detector. The second gas chromatograph, a Hewlett-Packard 5840A, contained a single, less polar DB-5 column and used a nitrogen-phosphorus detector. All 25 standard compounds could be at least partially resolved in one chromatographic run on either system.

Extracts from environmental samples and spiked samples were analyzed to determine practical detector utility for pesticide residue determinations. The nitrogen-phosphorus detector showed a lower minimum detectability than either the flame-ionization detector or the ion-trap detector in full-scan mode, with fewer interferences. However, the multiple-ion-detection mode and/or the mass-chromatograms data-analysis programs of the ion-trap detector greatly increased its sensitivity and versatility, especially when used in conjunction with a second or third independent detector system to give additional information.

166 DEPTH AND TIME PROFILING OF TIN IN ANTIFOULING RUBBERS BY DC ARGON PLASMA ATOMIC EMISSION SPECTROMETRY. Rm. Panayappan, John C. Cooper, and Caroline C. Houston, Naval Research Laboratory, Washington, DC 20375-5000

Neoprene rubber in marine use often contains tert-butyltin oxide (TBTO) to prevent barnacle attachment. Effectiveness and expected lifetime as well as disposal considerations are dependent upon TBTO concentrations remaining in the rubber. To allow such determinations, an analytical method was developed for tin in antifouling rubbers. The method allows for depth and time profiling of tin by coring and slicing the samples. Individual samples from cored multilayer rubber were digested in acid and analyzed for tin by DC Argon Plasma Emission Spectrometry (DCP). Time profiling of the digestion process allowed determination of minimum digestion time. Results of analyses of several multi-layer rubber samples of varying age and sea-water exposure will be described. Resolution of potential interferences and application to analyses of other "composite" materials will be discussed.

168 ION CHROMATOGRAPHIC ASSAY OF COMBUSTION BOMB AND FUSION PRODUCTS. Raaidah Saari, Ewa Dabek, and James Cox, Department of Chemistry, Southern Illinois University, Carbondale, IL 62901.

Direct ion chromatographic assays of oxygen combustion bomb products where Eschka's mixture is used and carbonate fusion products are generally not possible because of the high electrolyte level that results. Dilution prior to ion determinations is an acceptable procedure unless the analytes are at trace levels. The use of dual ion-exchange permits such determinations. Here, the carbonate-containing products are passed through a cation-exchange membrane tube that is immersed in a slurry of cation-exchange resin in the hydrogen-form. Carbonic acid is metathesized in the tubing which lowers the electrolyte level. The dual ion-exchange process does not alter the analyte concentration and does not introduce interferents to the sample stream. The method is illustrated by the determinations of chloride and sulfur in coal, a study on citrus leaves, and measurements on various food products. Results with both the single column and suppressed modes of ion chromatography will be presented.

169 ABSTRACT NOT AVAILABLE

170 ANALYSIS OF ORGANIC CONTAMINANTS IN PRECISION QUARTZ RESONATOR PACKAGES BY GC-MS.

Richard M. Sheeley, Dickinson College, Carlisle PA 17013; William P. Hanson, Robert A. Beers, Charles J. Jensik, Piezo Crystal Company, Carlisle PA 17013.

Premature aging of quartz crystal resonators has been attributed to the presence of organics as impurities on the crystal surface. 10 MHz precision quartz resonators of various types which had exhibited accelerated aging were drilled open and flushed with HPLC grade dichloromethane. The extract was reduced in vacuo to approximately 20μl, and injected into the GC-MS. The resulting chromatograms and mass spectra were compared with those of fluids such as vacuum pump oils, silicones, and solvents used on the production lines. Definite identification of contaminants in individual resonator packages could be made at nanogram levels by this method.

171 ANALYSIS OF ORGANIC CONTAMINANTS IN EXTENDED WEAR CONTACT LENSES WORN BY MILITARY AIRCREW PERSONNEL.

Richard M. Sheeley, Dickinson College, Carlisle PA 17013; W. Jeffrey Hurst, Consultant, Mount Gretna PA 17064; Herbert E. Halliday,O.D., Wayne M. Yorkgitis,O.D., David D. Glick, O.D., Carlisle PA 17013.

As part of a feasibility study on the use of extended wear contact lenses by military aircrews, lenses that has been worn from 24 to 60 days by active duty Army National Guard helicopter flight and maintenance personnel were examined for toxic fume uptake. Lens extracts were compared with a series of 12 commonly used aircraft maintenance fluids using GC-MS. Although extraneous compounds were found in most of the lenses examined, only a few were shown to be directly associated with known fluids. Lenses worn by flight engineers, crew chiefs, and ground crew personnel were more severely affected than those of pilots, with hydrocarbons, particularly lubricating oils, being the major contaminants.

172 STATE OF THE ART CONTINUOUS FLOW ANALYSIS: TO BUBBLE OR NOT TO BUBBLE

Cissy Hepburn, Carl Meuser ALPKEM Corporation P.O. Box 1260 Clackamas, OR 97015

Automated continuous flow analysis has been a major tool in colorimetric ion analysis since its introduction in the late 1950's. The need of an air bubble segmenting the analytical stream went without question until the 1970's when non-segmented flow injection analysis was first introduced. Since then the controversy has developed over which is the preferred method. Clearly one method is not totally superior over the other and each technique has its advantages and disadvantages. The purpose of this poster session is to compare the two methods, segmented CFA and non-segmented FIA, in terms of various analytical and operational parameters on the same chemistries. Using ALPKEM's RFA-300 system eliminates any instrument bias since the RFA-300 system is capable of running in either mode.

173 AN APPROACH TO THE QUANTITATIVE ANALYSIS OF SOLIDS BY LA-ICP-MS,

A.L. Gray, Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 5XH, UK.

The introduction of solid samples into an ICP ion source for mass spectrometry by laser ablation offers an attractive prospect of rapid direct solids analysis with detection limits well below the 1 μg/g level. Much of the work reported to date has been of a qualitative nature and although this is of considerable value for survey analysis its use will be limited unless quantitative measurements can be made.

Recent studies of the problems involved in quantitative analysis will be described and results in different matrixes reported.

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174 ANALYSIS OF SOLID SAMPLES BY LASER ABLATION ICP-MS, R.C. Hutton, J.E. Cantle, and D. Hall, VG Isotopes, Ltd, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, England.

Both arc and laser ablation have previously been used to introduce solid samples into an ICP for emission analysis. The use of an ICP-MS system with ablation sampling improves the detection limits of solid samples by several orders of magnitude. The laser can be used directly on insulating and conducting samples alike, and the high sensitivity coupled to the rapid scanning facility of the quadrupole allows multi elements analyses to be carried out in a few minutes on the transient signal from a laser shot.

The use of both a ruby and a Nd-YAG laser for this purpose will be discussed and quantitative results obtained from a varied of samples presented.

175 ANALYSIS OF HIGH PURITY QUARTZ AND POLYCRYSTALLINE INDIUM PHOSPHIDE BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY, G.A. Laing and J.J. Larkin, Eagle Picher Industries, Inc., 200 9th Avenue NE, Miami, Oklahoma 74354.

Inductively coupled plasma mass spectrometry was studied as an analytical tool in the analysis of high purity quartz and polycrystalline indium phosphide. Effects of sample preparation are discussed with special consideration given to contamination and volatility of analytes. Instrumental parameters are presented with their interaction with the sample matrices. Factors affecting instrumental performance are presented.

176 DETERMINATION OF THE RARE EARTH ELEMENTS IN GEOLOGICAL MATERIALS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY, F.E. Lichte, A.L. Meier[1], and J.C. Crock, U.S. Geological Survey, Branch of Analytical Chemistry, Box 25046 MS 928 DFC, Denver, CO 80225, [1]Branch of Geochemical Exploration, Box 25046 MS 955 DFC, Denver, CO 80225.

A method of analysis of geological materials for the determination of the rate earth elements using the inductively coupled plasma mass spectrometric technique (ICP-MS) has been developed. Samples are analyzed directly, following an acid digestion, without the need for separation or preconcentration with limits of detection of 2 to 11 ng/g, precision of 2.5δ relative standard deviation, and accuracy comparable to other methods. A commercially available ICP-MS instrument is used with modifications to the sample introduction system, torch, and sampler orifice to reduce the affects of high salt content of samples prepared from geologic materials. Corrections for isobaric interferences from oxide ions and other diatomic and triatomic ions are made mathematically. Special internal standard procedures are used to for compensate for drift in oxides ratios and sensitivity. Reference standard values are used to verify the accuracy and utility of the method.

177 ANALYTICAL METHODS UTILIZING INDUCTIVELY-COUPLED PLASMA-MASS SPECTROMETRY SPECTROMETRY FOR HYDROLOGIC INVESTIGATIONS, John R. Garbarino and Howard E. Taylor, U.S. Geological Survey, 5293 Ward Road, Arvada, CO 80002.

Inductively-coupled plasma-mass spectrometry has been implemented for the analysis of hydrologic samples using several different instrumental methods. Each method utilizes the multielement determination capabilities of the instrument. The methods differ only in the data acquisition technique employed, the degree of accuracy desired, and the required scope of the analysis. Analytical methods routinely employed are (1) Rapid, semi-quantitative, mass spectral scan from 6 to 238 atomic mass units; (2) quantitative, multielement analysis based on calibration curves; and (3) multielement, isotope dilution analysis. A complete mass spectral scan provides an estimate of the concentration of most elements in the mass range in about 3 minutes. The estimate can be based either on multielement standards previously analysed or on adjusted intensities based on isotopic abundances. Multielement quantitative analysis requires calibration based on internal standard ratios; the required number of internal standards is dependent on the analyte mass range. Calibration curves are nearly linear throughout several orders of magnitude below 1 part per million. Multielement isotope dilution analysis provides for highly accurate determinations. Currently, copper, nickel, strontium, cadmium, barium, thallium, and and lead are determined by this technique in about 3 minutes. The relative standard deviations attainable for these analytes at part per billion levels is better than 1 percent for triplicate determinations. Each method has been evaluated in terms of its accuracy and precision based on results from analyses of several standard reference materials. The methods described above are applied to sample types ranging from meteorological precipitation to fulvic and humic acids isolated from surface water.

178 TRACE METAL ANALYSIS OF WATERS BY ICP-MS, Richard Robinson, Los Alamos National Laboratory, P.O. Box 1663 MS K484, Los Alamos, NM 87545.

The ICP-MS's analytical capabilities make it a desirable technique for the rapid multielement enviornmental surveillance of drinking waters. An ICP-MS was used to analyze drinking waters and reference materials for As, Ba, Cd, Hg, Pb, Se, Cu, Mn, Fe, and Zn. A comparison of recoveries materials obtained by several different data acquisition modes. The data acquisition modes include scans of the full atomic mass spectrum, of selective mass regions, and the use of internal standards in selective mass regions to determine the best operational parameters.

179 ANALYSIS OF RESOURCE CONSERVATION AND RECOVERY ACT SAMPLES BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY, D. Knab, M.Bell, Los Alamos National Laboratory, P.O. Box 1663 MS K484, Los Alamos, NM 87545.

The RCRA requirements call for quantitation of eight primary pollutants; Cr, As, Se, Ag, Cd, Ba, Hg, and Pb; from soil extracts and water samples. A fast, accurate, multi-element procedure is ideal for analyzing these samples. Results are usually wanted soon after sampling and the samples either pass or fail the maximum allowable concentration level (MCL) criteria. The RCRA have high dissolved solids and complex matrices which cause interferences. ICP-MS is a technique for quantitative multielemental determinations that also gives a complete mass scan of all elements. It is possible to simultaneously quantitate the eight primary metals, and obtain semiquantitative information on major and minor elements including anions. Theoretically, ICP-MS is selective, sensitive, interference free and fast, in practice it suffers from several limitations that must be accounted for. Preliminary data indicate that all of the primary pollutants have at least one mass line that is free of spectral interferences. Se is the most difficult to determine because it has a low MCL, and the mass line at 78 AMU is only 24δ abundant. Cr lies in a very matrix contaminated region of the spectrum, but its most abundant isotope at 52 AMU is almost free of interferences. At the levels of concern, each of the primary pollutant elements can be determined.

180 THE INFLUENCE OF ICP EXCITATION SYSTEMS ON ANALYTICAL PERFORMANCE IN ICP-MS, A.L. Gray, Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 5XH, UK.

A number of differences in the performance characteristics of the two commercially available ICP-MS systems have been reported. In particular these relate to the production of doubly charged ion and oxide species and to the manner in which these change with aerosol flow rate and plasma power.

The differences appear to be related to load coil geometry and the effect this has on plasma potential and consequently on the energy of ions extracted from the plasma.

The effect of a number of alternative load coil geometries on performance will be described and the choice of an optimum system discussed.

181 ICP MASS SPECTROMETRY: A DISCUSSION OF THE IMPORTANT SPECTROMETER PARAMETERS, R.C. Hutton, J.E. Cantle, and T.O. Merren, VG Isotopes, Ltd., Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, England.

The use of the ICP as an ion source for mass spectrometry is a recent revolutionary development in elemental and isotopic analysis. To date, however, the focus of attention has been directed towards characterization of the ICP and little attention has been directed towards the spectrometer.

In the spectrometer, both the vacuum interface and the quadrupole have not previously been used in such an application. In this paper, several important features of each will be shown. The effect of sampler geometry on observed molecular ions will be shown. Also, the influence of abundance sensitivity and resolution will be discussed with particular reference to the demands of heavy matrix analysis.

182 CURRENT STATUS AND RECENT DEVELOPMENTS IN ICP-MS, G. Gillson, J. Fulford, D. Douglas, SCIEX, 55 Glen Cameron Road, Thornhill, Ontario, L3T 1P2, Canada.

Inductively coupled plasma-mass spectrometers have been commercially available since 1983. Over the past 3 years ICP mass spectrometry has matured noticeably as evidenced by increased understanding of the fundamentals of the technique, and improvements in its analytical capabilities.

This point will be illustrated by discussion of ion energies, ion signal response to changes in experimental parameters, matrix effects and the ability to handle refractory oxide matrices.

Innovations such as miniature and low flow torches are gaining commercial acceptance in ICP emission spectrometry. Generators of various frequencies are available, as are a wide range of nebulisers and spray chambers. Undoubtedly some of this hardware will find application in ICP-Mass Spectrometry.

Improvements to the sampling interface will also occur as critical factors in the design of samplers and skimmers are elucidated and new high temperature materials become available.

The latter part of the talk then, will include a discussion of the progress that has been made at SCIEX in exploring some of these avenues.

183 RECENT DEVELOPMENTS IN ELECTROTHERMAL VAPORIZATION FOR ICP/MS, Peter B. Stockwell, PS Analytical Ltd, U.K. and Angelo C. Grillo, Questron Corporation, Box 2386, Princeton, NJ, 08540.

Electrothermal Vaporization apparatus has been described as a highly efficient sample introduction system for optical emission spectroscopy with an inductively coupled argon plasma source. Kirkbright et al have reported good detection levels and have explored the interfacing requirements between ICP and the graphite filament.

This paper describes the criteria for a commercial electrothermal vaporizer, the flexibility of its control cycles, the most recent applications to ICP/MS, the physcial characteristics of the ETV cell and the operation of a newly developed transport mechanism.

184 HOW TRANSIENT NEED THE SIGNAL BE FOR MULTI-ELEMENT ICP-MS, R.C. Hutton, J.S. Gordon and P.D. Blair, VG Isotopes, Ltd., Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, England.

Current analytical technology by ICP-MS has been based around nebulization systems where the analytical signal is, to all intents and purposes, continuous, lasting from several seconds to several minutes. However, there are many extremely powerful sampling systems which generate liquid or vapor over a discrete time window. Examples of these include HPLC, laser ablation, electrothermal sampling, flow injection etc. With these applications it is necessary to acquire as much data as possible over the short duration of the signal.

There are three modes of data acquisition in ICP-MS which can be successfully utilized for this purpose. These are:

1. rapid scanning
2. peak jumping
3. scanning and jumping in one cycle

Each of these techniques has been used successfully in ICP-MS and in this paper the applicability of all three techniques will be demonstrated and the limitations in sampling will be discussed.

185 DETERMINATION OF ULTRA-TRACE PLATINUM IN BIOLOGICAL SAMPLES USING AN ELECTROTHERMAL VAPORIZATION DEVICE FOR SAMPLE INTRODUCTION INTO AN INDUCTIVELY COUPLED ARGON PLASMA SPECTROMETER, Lynn Charney, Analytical Consulting Services, 6251 Corporate Drive, Houston, Texas 77036 and Alan Forster, Shell Development Company, P.O. Box 1380, Houston, Texas 77251-1380.

An application of electrothermal vaporization-inductively coupled argon plasma-mass spectrometry (ETC/ICP-MS) capable of determining picogram amounts of platinum in micro amounts of biological samples has been developed. Inductively coupled plasma mass spectrometry provides a very effective means for the determination of ultra trace levels with most elements being detected well below one part per billion. In addition, due to the simplicity of the mass spectra, ICP-MS is often the method of choice for samples having complex matrices.

In order to perform the analysis of micro-amounts of biological samples, the sample introduction system on a Sciex "Elan" ICP-MS has been replaced with a HGA 500 graphite furnace atomizer. The introduction of the dry aerosol from the furnace tube into the ICP, was accomplished by connecting "Tygon" tubing directly to the torch injector. Ten microliters sample aliquots are injected into the ETV device and subsequently heated to 2400 degrees C. The dry solvent aerosol is transported with flowing argon directly into the ICP injector tube.

Analytical capabilities of the graphite furnace ETC/ICP-MS technique for the analysis of real biological samples were investigated by the analysis of several samples. Detection limits for platinum were calculated to be in the 0.05 picogram range. Since spectral interferences are absent with the ICP/MS analytical system, the ETC/MS sample introduction offers unlimited possibilities for ultra-trace work in complex matrices.

186 EQUIVALENCY TESTING OF A COMMERCIAL INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER AND GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETER IN ENVIRONMENTAL SAMPLES, G.A. Laing, G.K. Ward, and R.E. Perrin, Eagle Picher Industries, Inc., 200 9th Avenue NE, Miami, Oklahoma 74354.

Analysis of Sb, As, Cd, Cr, Pb, Se, Ag, and Tl by inductively coupled plasma mass spectrometry (ICP/MS) are compared to graphite furnace atomic absorption spectrophotometry (GFAA) in the analysis of environmental samples. Comparison of ICP/MS is also made with cold vapor hydride generation in the analysis of mercury. Methods for the analysis of these metals in water, wastewater, and soil samples will be presented.

187 THE REDUCTION OF POLYATOMIC ION INTERFERENCES IN ICP-MS ANALYSIS IN THE PRESENCE OF MINERAL ACIDS, A.L. Gray, Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 5XH, UK.

First reports of analytical studies using ICP-MS instruments have drawn attention to the interferences which arise from polyatomic ions thought to be formed by ion molecule reactions between the more abundant species in the plasma. Well known examples are the $^{56}ArO^{+}$ interference on $^{56}Fe^{+}$ and the $^{51}ClO^{=}$ interference on $^{51}V^{+}$. In many cases these have been found to occur at levels which completely obscure the ion peaks of interest from the analyte and are difficult or near impossible to correct for.

Attention to the detail of interface design shows promise of reducing these interferences to levels where correction is more practicable. Quantitative values of interfering species are reported for nitric, hydrochloric and sulphuric acids and comparative spectra shown for typical interference examples obtained on the research instrument at Surrey.

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188 LOW FREQUENCY INFRARED AND RAMAN ASSIGNMENTS OF CAMPHOR AND CAMPHOR DERIVATIVES BY DEUTERIUM LABELING; R. D. Freeman, S. B. Kim*, W. G. Fateley, R. M. Hammaker, C. E. Meloan; Kansas State University, Department of Chemistry, Manhattan KS 66506; *University of Oklahoma, Department of Chemistry, 620 Parrington Oval, Room 208, Norman OK 73109

This work focuses on the low frequency vibrational spectroscopy of camphor and some camphor derivatives, particularly bornyl acetate and isobornyl acetate. Deuterium labeling and model compounds have been used to assign observed vibrational bands below 850 cm^{-1}. Kim et al. (Spectrochim. Acta, Vol. 40B, Nos. 10-12, pp. 1295-1330, 1985) have labeled the C-2 and C-3 ring positions and the C-10 methyl position of the camphor skeleton. This deuterium labeling is continued with the preparation of d-1, d-2, and d-3 analogs for the C-8 methyl group only and for the C-9 methyl group only for the following compounds: camphor, borneol, isoborneol, bornyl acetate, isobornyl acetate, bornyl acetate-d-3, and isobornyl acetate-d-3. All of these compounds are naturally occuring, dissymetric, in some cases biologically active, and have interesting vibrational spectra. The insertion of deuterium also produces some interesting spectral phenomenon. This talk will describe some of the vibrational modes of these compounds and some of the effects of deuterium labeling on these modes.

189

FTIR ANALYSIS OF METAL ACETATES IN AQUEOUS SOLUTION.
J. E. Tackett and B. D. McCarty. Marathon Oil Company, Exploration and Production Technology, P.O. Box 269, Littleton, Colorado 80160.

In the solid state, X-ray crystallography and infrared spectra have been used to characterize acetate groups in a variety of metal acetates into several types: ionic, unidentate, chelating, and bridging.(1) We have run selected metal acetates in aqueous solution by FTIR to determine if the types of acetate groups found in the solid state persist in aqueous solution. We will discuss two techniques for obtaining aqueous solution spectra: thin film between silver chloride disks, and a cylindrical internal reflection cell.

We have found that for many metal acetates only ionic acetate groups appear to exist in solution, however, in some cases the other types of acetate groups may be present.

(1) G. B. Deacon and R. J. Phillips, Coord. Chem. Rev. 33 (1980) 227-250.

190 ABSTRACT NOT AVAILABLE

191 FTIR SPECTROSCOPY OF PH_3 AND HCN. J.-I. Choe$^{(a)}$, T. Tipton$^{(b)}$, and S.G. Kukolich. Department of Chemistry, University of Arizona, Tucson, AZ 85721.

High-resolution vibration-rotation spectra of PH_3 and HCN were measured using the Fourier Transform Spectrometer developed by Jim Brault at the National Solar Observatory at Kitt Peak, Arizona. This system has a large dynamic range and resolution of 0.01 cm^{-1} and produces very high quality spectra. A six-meter, multipass White cell was used to provide long absorption path lengths. The $2\nu_2$ and $\nu_2 + \nu_4$ bands of phosphine were measured and analyzed. The 1900 - 2100 cm^{-1} region of the PH_3 spectrum is of interest due to recent astronomical observations. Spectroscopic constants obtained from the data analysis will be reported. Results on combination and hot bands in HCN will also be discussed.

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a) Department of Chemistry, Chung-Ang University, Seoul, Korea 151.
b) Department of Chemistry, University of Florida, Gainesville, FL 32603.

192 Title: Quantitative Determination of Dopant Levels in Phosphosilicate and Borophosphosilicate Thin Films by IR Techniques

Authors: Ronald Carpio and Charla Bertrand, Inmos Corp.
1110 Bayfield Dr., Colorado Springs, CO 80906

The properties of PSG and BPSG thin films which have widespread use in the semiconductor industry are chiefly controlled by their phosphorus or boron and phosphorus content, respectively. In this paper, a low cost, dispersive infrared spectroscopic approach will be outlined for rapidly measuring the dopant levels in these silicate glasses. This procedure overcomes the problem in BPSG films associated with the overlapping P=O and B-O bands whose maximia are 1316 cm-1 and 1370 cm-1, respectively. The accuracy and detection limit for the phosphorus analysis in the case of PSG films are improved. This approach will be compared with other analytical techniques which are currently being utilized for this analysis.

193 PHOTOSTABILISATION AND ATMOSPHERIC SOILING RESISTANCE STUDIES OF SILVER-BACKED POLYMER FILMS FOR SOLAR THERMAL SYSTEMS. C.A. Sergides, A.R. Chughtai and D.M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208; P. Schissel, Solar Energy Research Institute, 1617 Cole Boulevard, Golden, CO 80401.

Fourier transform infrared reflection absorbance (FTIR/RA) spectroscopy has been used to study the photodegradation and photostabilisation of silver-backed polyacrylonitrile (PAN) films for the last several years. In addition to the photodegradation, atmospheric soiling of these films over a period of time has a damaging contribution to the decrease in the specularity of the reflector systems. The specularity of these films was determined using the new Specular Reflectometer NSR-SERI. A combination of Irganox 1010 (antioxidant) and Irgastab 2002 (quencher) in PAN films was found to significantly retard the photodegradation of the polymer without affecting specularity of the PAN/Ag surface. Durability tests show that the Irgastab 2002 was partially depleted in aqueous media, while no corresponding depletion products were detected from PAN. The presence of about a 100 Å SiO surface layer on PAN/Ag film was found to increase its specularity, retard to some extent its photodegradation, and increase its atmospheric soiling resistance and cleaning ease.

194 EFFECTS OF PHASE TRANSFORMATIONS ON THE WATER WETTING PROPERTIES OF MONTMORILLONITE.* A. A. Ogloza and V. M. Malhotra, Physics Department, Southern Illinois University, Carbondale, Illinois 62901.

A thorough understanding of the structure and behavior of smectite clays under conditions typical of enhanced oil recovery processes is important in developing and maintaining the productivity of oil fields. These clays swell, migrate, and disperse when contacted with fresh water. The Ca-montmorillonite clay was subjected to thermal ($293\ K \leqslant T \leqslant 1180\ K$) and/or KOH/crude treatment to modify its water wetting properties. The effects of treatment parameters on the structure and water wetting properties of clay were monitored by recording their FTIR spectra. The clay samples were fired at 60 K intervals in the temperature range of $293\ K \leqslant T \leqslant 1180\ K$ for both 1 and 24 hours. The systematic FTIR study of the lattice hydroxyl and internal water absorption bands showed that: 1) one hour heating is a statistically unreliable parameter for studying the thermal behavior of this clay, 2) there are four phase transformations in this condensed system, and 3) the dehydration and rehydration of this clay show thermal hystersis in its water wetting properties. The clay samples were also treated with KOH and crude and KOH/crude. All these treatments modified the water wetting properties of montmorillonite clay, but the crude treatment showed the most promise in stabilizing these clays under water flooding.

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195 QUANTITATIVE ANALYSIS OF CEMENT, CLAYS, AND FLY ASH BY INFRARED SPECTROSCOPY
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The current waste management strategy for ultimate disposal of low-level radioactive liquid wastes at Hanford is immobilization of the wastes in the form of cementitious grouts. For fixing the waste, grout formulations consisting of cement, attapulgite clay, indian red pottery clay, and fly ash are tailored for the type of Hanford waste of interest. To ensure that the grout mix meets acceptable emplacement requirements and the finished grout possesses thermal and chemical stability for long-term public safety, an accurate characterization of the dry cement, clays, and fly ash, as well as monitoring of the mixing proportion during grouting operations is important. A Fourier Transform Infrared Spectroscopic (FTIR) method was developed to support process control and conformance to materials specifications. The procedure involved the sequential analysis of each of the components of a blend with minimum sample preparation. Using potassium bromide (KBr) pellets prepared from the blend or reference materials, the absorption spectra in the region (4600 to 400 cm^{-1}) are scanned and analyzed. By nulling unique low-absorbing bands of a component of the blend/material of interest by computer subtraction, the proportion of this component/material in the blend or its equavalency to a reference material can be determined. Details of the procedure and the results obtained are discussed.

196 TROPOSPHERIC SO_2 MEASUREMENTS BY TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY *Elizabeth A. Mishalanie, Michael T. Coffey, and William G. Mankin, National Center for* Atmospheric Research, P.O. Box 3000, Boulder, Colorado 80307

Infrared spectroscopy has proven to be a useful technique for monitoring major and minor constituents in the atmosphere. The development of tunable diode lasers has made possible the in-situ, real-time monitoring of many atmospheric constituents at the ppbv level. A tunable diode laser absorption spectrometer (TDLAS) is a highly selective and sensitive instrument for performing trace gas analyses. The laser line width is sufficiently narrow to scan a single rotational line in the vibrational absorption spectrum of molecules with resolved fine structure. The infrared absorption intensity is detected while a gas sample flows through a multiple-reflection White cell. The gas is maintained at low pressure to avoid the collisional broadening of absorption lines. High sensitivity is achieved through signal modulation techniques that enable the measurement of small absorbances (10^{-3}-10^{-5}). A TDLAS has been constructed in our laboratory for use on a jet aircraft to measure tropospheric SO_2. The design and operational principles of the TDLAS will be presented in addition to the calibration procedure for small quantities of SO_2 in air.

197 APPLICATIONS OF THE INFRARED MICROSCOPE
W.D. Perkins, The Perkin-Elmer Corporation, 411 Clyde Avenue, Mountain View, CA 94043

The ability to work with minute samples has long been an advantage of infrared spectroscopy. With the high energy throughput of Fourier Transform Infrared (FT-IR) Spectrometers, it is now possible to use infrared microscope accessories to further enhance this capability. The microscope can be used in both transmission and reflection modes, and good spectra can be obtained from samples as small as 10-20 micrometers across. Typical examples include small imperfections or inclusions in polymers, coatings, and paper samples, corroded areas on opaque substrates, and minute single crystals, paint chips, or fiber fragments. Among the advantages of the microscope over the traditional beam condenser are the ability to view the sample under magnification through an ocular, to position it in the field of view on the adjustable mechanical stage, and to precisely limit the area to be examined through the use of an independently adjustable four-bladed aperture. This paper will describe a variety of examples in which the infrared microscope has been applied to difficult microsamples.

198 AUTOMATED QUANTITATIVE INFRARED ANALYSIS USING MODERATE-COST FT-IR SPECTROMETERS

Robert C. Williams, B. F. Goodrich Chemical Group, Avon Lake Technical Center, POB 122, Avon Lake OH 44012.

It is only within the last fifteen years that infrared spectroscopy has been widely used as a quantitative analytical tool. Prior to this period, infrared spectrometers were considered excellent qualitative tools, but inherent variations in their (vacuum-tube) electronics rendered any quantitative results suspect. The advances in detector electronics in conventional instruments, and the advent of Fourier Transform (FT) systems which are mechanically simpler and optically more reliable, have given credibility to quantitative infrared analyses.

The major remaining stumbling block to the use of quantitative infrared analysis has been the complex algebra necessary to solve in order to analyze multi-component systems containing overlapping peaks. The advent of minicomputer-based data systems and appropriate software which automatically set up and solve the simultaneous calibration equations of the multi-component system have now removed this last obstacle. Moreover, infrared analysis now offers several advantages over many other techniques; among these are the speed and ease of analysis (typically less than ten minutes, once a method has been established), high reliability and accuracy, and the minimal technician training necessary (many analyses can be run by pushing one of two buttons).

Several moderate-cost FT-IR's and the associated quantitative analysis software have been purchased at Avon Lake and other BFG plants. These systems are intended for primary use in quantitative analyses necessary to assure product quality conformance. The procedures necessary to do this are described, using as an example, the recently developed method which analyzes for percent chlorine in a chlorinated polyvinyl chloride (CPVC) resin.

199 ABSTRACT NOT AVAILABLE

200 SOLUBILITY AND DIMERIZATION IN XANTHINES.

Douglas M. Sheeley, Richard Gilkey, Richard M. Sheeley, Gerald C. Roper, Dickinson College, Carlisle PA 17013, and W. Jeffrey Hurst, Robert A. Martin, Jr., Hershey Foods Corporation, Hershey PA 17033.

Previously reported thermodynamic data have suggested that the extreme solubility differences within the xanthines may be attributed to dimerization. Application of group theory to their FTIR spectra supports this explanation, and indicates that dimerization occurs mutually across either the 1- and 6- or the 1- and 2-positions of the pyrimidine ring. Through use of a temperature-controlled CIRcle cell it has been shown that the xanthines which are dimerized in the solid state are monomeric in D_2O solution at 85°C. It can be inferred from these data that the greater water solubility of some xanthines, such as caffeine and theophylline, is due to the preclusion of dimerization, which in the less soluble xanthines, such as theobromine, doubles their size and eliminates the more hydrophilic groups from interaction with the solvent.

201 ION EXCHANGE CHROMATOGRAPHY - CAPABILITIES, APPLICATIONS, FUTURE NEEDS.
V. T. Turkelson, Michigan Applied Science & Technology Laboratories, The Dow Chemical Company, 1602 Bldg., Midland, Michigan 48674.

Ion chromatography (IC) has been extensively employed in this laboratory over the past ten years for the separation and determination of anions and cations in numerous inorganic and organic sample matrices. In addition, the IC technology has been successfully transferred to on-site usage for process control, product development, quality control, and environmental and industrial hygiene monitoring. Automated analyzers have also been utilized in on-line applications. This diverse usage of IC has been achieved by "re-shaping" the technology as originally developed in the early 1970's in order to maximize overall system flexibility. Additional detection schemes including direct UV, indirect UV, electrochemical and visible have been introduced into routine use resulting in (1) enhanced specificity and sensitivity for the analysis of complex sample matrices and (2) greater eluent selection for expanded separation capabilities. This paper will focus on multiple developments which have made IC more versatile, and consequently more effective, in day-to-day analytical problem-solving. The impact of these developments on the current capabilities of IC will be demonstrated in selected applications of the technology.

202 MICROLITER SAMPLE INJECTIONS AND EFFECTS OF ELUENT MODIFICATIONS IN ION CHROMATOGRAPHY. Dutt V. Vinjamoori, Corporate Research Labs., Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, MO 63167.

The capability of direct injection of microliter samples into the ion chromatographic column will be valuable for the analysis of expensive biotechnology products. Since the normal fixed sample loop used in the instrument is 0.1 ml, at least 0.5 ml of sample is needed to flush and fill the sample loop from the injection port. We have devised a simple two segmented injection loop for the Dionex injection valve routed through a four port Hamilton valve which offers great flexibility and eliminates sample waste. Simple 90° rotation of the valve gives direct access to the injection port cavity. The eluent in the cavity is partially or completely emptied with a microsyringe and any sample size from nanoliters up to five microliters could then be injected into the cavity. The valve is then rotated 90° to restore the original flow path. This arrangement also permits loop loading from the injection port and complete or half loop loading directly at the injection valve. Illustrations of the modified injection valve and some interesting observations on the effects of halate-laced standard eluent on the anion signals will be presented.

203 ANALYSIS OF SUGARS USING PULSED AMPEROMETRIC DETECTION COMBINED WITH ISOCRATIC AND GRADIENT ANION EXCHANGE SEPARATIONS
W.T. Edwards and C.A. Pohl, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94088

The analysis of sugars using Liquid Chromatography is often hampered by the detection methods available. Pulsed amperometric detection (PAD) is both sensitive and specific and combines well with the eluants used in anion exchange separations. Unlike Refractive Index detection, the PAD does not respond to many classes of compounds found in typical samples and eluants. This offers two major advantages: Firstly it minimizes the amount of sample preparation needed, and secondly it allows the use of gradient elution. The versatility of anion exchange also allows the separation of different classes of carbohydrates on the same column. Various examples of the separation of monosaccharides and oligosaccharides using both isocratic and gradient elution will be discussed.

204 ELUANT OPTIMIZATION IN ION EXCLUSION CHROMATOGRAPHY.

D. T. Gjerde, D.W. Togami, J. H. Nguyen; Wescan Instruments, Inc., 3018 Scott Blvd., Santa Clara, Calif. 95054

Ion Exclusion Chromatography as developed by Harlow and Morman (Anal. Chem., 36, 2438, (1964)) and further refined by Turkelson and Richards (Anal. Chem., 50, 1420, (1978)) has proven to be an extremely useful technique. Organic acid and other weak acid separations are typically carried out on high capacity polystyrene-based cation exchange resins using dilute mineral acid eluants. The combination of mineral acid and organic modifiers such as acetonitrile was used by Jupille, et. al. (Amer. Lab, 1981) to elute organic species such as phenols. Deionized water eluant has been found to be effective for bicarbonate analysis. More recently, a new class of eluants for ion exclusion chromatography have been found by Tanaka and Fritz of Ames Laboratory (In Publication). These eluants offer increased sensitivity over the traditional eluants. Examples of each type of eluant and the types of compounds separated by it will be discussed.

205 RECENT ADVANCES IN THE ANALYSIS OF ORGANIC ACIDS BY ION CHROMATOGRAPHY

Joseph D. Olechno, D. G. Gillen, R. W. Slingsby,
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Many common carboxylic acids including those of the Krebs cycle can be separated by either anion exchange or ion exclusion chromatography and detected by chemically suppressed conductivity. Mono-, di-, and triprotic acids can be separated by anion exchange using gradient elution. Isocratic ion exclusion chromatography allows most important organic acids to be separated in a single run. Both anion exchange and ion exclusion chromatography use cation based membrane suppressors to reduce the conductivity of the eluant while enhancing the conductivity of the organic acid analytes. The ability to choose between ion exclusion and anion exchange increases the analysts range of capabilities to fit the particular analytical problem.

206 TRANSITION METAL CONTAMINATION FROM STAINLESS STEEL AND ITS EFFECTS ON ION CHROMATOGRAPHIC AND HPLC SEPARATIONS

L. Henry, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3603

Stainless steel, although frequently touted as inert, is known to leach metal ions and is sensitive to corrosion even with organic solvents. Trace contamination can cause peak tailing in traditional HPLC separations where the analyte forms complexes with the metal. Metal ions can contaminate ion exchange resins, causing a loss of column performance. Most important, contamination from stainless steel is particularly deleterious to trace determinations of transition metals. This paper will discuss the problems associated with stainless steel especially where they adversely affect trace transition metal analyses and suggest solutions using non-metallic systems.

207 NEW POLYMER-BASED ION-EXCHANGE COLUMNS

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Several columns for single column anion-exchange separations have been developed for use on an HPLC equipped with a conductivity detector, or using direct or vacancy UV detection. These low capacity columns offer advantages in reduced instrument complexity and cost over "suppressed" ion chromatography. Silica columns have been employed for non-suppressed ion chromatography, but these are of limited utility due to their instability at extremes of pH. Some commercial polymeric columns exhibit improved chemical stability, but column efficiencies are low and analysis times relatively long. However, the chemical composition of the polymer backbone supporting the ion-exchange sites on these columns leaves them subject to decomposition at even moderate pH values. We report our ongoing work to develop improved resin-based ion-exchange packings. Columns packed with these materials exhibit excellent chemical and physical stability. They show improved resolution and decreased retention times, indicating the good mass transport effects of these columns. Column selectivity is readily influenced by changing eluents, a feat not possible with "suppressed" methods.

208 SEPARATION MODES AVAILABLE FOR ION CHROMATOGRAPHY.

Petr Jandik, W.R. Jones, D. Cox, J. Oberholtzer, Waters Chromatography Division of Millipore Corporation, 34 Maple Street, Milford, Ma. 01757

Ion Exchange, even though it is very important, is only one of the many available separation modes for ion chromatography. At present, successful separations of ions are performed using ion exclusion; reverse phase; ion pairing, reverse phase; ion suppression, reverse phase. Separations of ions have also been reported on normal phase stationary phases. For each known mode set of rules governing the retention behaviour will be presented. Applicability of various detection techniques will be discussed. Usage of optimization software for separations will be illustrated on several selected applications.

209 THE CARE AND FEEDING OF YOUR COLUMN

Joe Machamer, Ken Rice, Denise R. Eubanks, Dionex Corporation,
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The lifetime of Ion Chromatography columns can be dramatically extended through the use of sound column care techniques. Proper column care begins with the use of correct initial start-up procedures and continues with the application of proper sample pretreatments such as sample filtering and the removal of hydrophobic organic compounds. When a loss of column capacity is observed due to poisoning, proper column clean-up procedures may rectify the problem. In addition to column problems caused by particulate plugging and chemical poisoning, macroscopic column deterioration such as headspace, column voids, column leaks, and bed support compression will manifest themselves as a loss in column performance. This paper describes the proper care and treatment of Dionex columns as well as the effects of macroscopic column problems on chromatography.

210 GRADIENT ELUTION IN ION CHROMATOGRAPHY: PREDICTION OF GRADIENT PARAMETERS FROM ISOCRATIC DATA

R. D. Rocklin, J. A. Schibler, C. A. Pohl, Dionex Corporation,
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Gradient elution has recently been introduced as a new technique in Ion Chromatography. By varying the concentration of the eluant it is possible in one run to separate weakly retained ions such as fluoride and acetate, as well as elute strongly retained ions such as citrate. As a new technique, the theoretical basis for gradient elution in IC has not been readily available. In this presentation, it will be shown that retention in gradient elution can be predicted from parameters derived from isocratic separations. Results from several different Dionex separator columns and eluants will be compared.

211 DETERMINATION OF CATIONS AND AMINES BY INDIRECT PHOTOMETRIC CHROMATOGRAPHY

D.L. McAleese, BASF Corporation, Analytical Research Laboratories, Wyandotte, Michigan 48192

An indirect photometric chromatography (IPC) technique, coupling cation exchange chromatography with indirect photometric detection, was developed for the determination of selected cations and alkylamines. The method employs a surface sulfonated polystyrene/divinylbenzene copolymer cation exchange column, an aqueous benzyltrimethylammonium chloride solution as the mobile phase, and indirect absorbance detection at 275 nm. Inverted absorbance peaks are observed as the UV-transparent analyte ions are selectively displaced from the column by the UV-absorbing benzyltrimethylammonium eluent ions. The order of elution, peak resolution, and detection limits of the analytes by IPC are compared to ion chromatographic (IC) determinations on the same column. The IC method utilizes an aqueous hydrochloric acid solution as the mobile phase, a cation hollow fiber suppressor column, and conductivity detection. Although the IC detection limits are superior, the IPC technique is favored for certain separations. IPC is, thus, a useful alternative for the determination of "transparent" ionic species that are normally not thought to be amenable to photometric type detection.

212 NEW HIGH PERFORMANCE FIVE MICRON PACKING MATERIALS FOR ION CHROMATOGRAPHY

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Common column packing materials for Ion Chromatography are currently mostly 10 or 15 micron in size. While such packing materials are adequate for simple separations of inorganic ions, these column materials lack the resolving power for use in the analysis of complex mixtures of inorganic and organic ions. A new class of 5 micron packing materials has been developed which utilizes micropellicular resin design. The columns exhibit high efficiency and good permiability. They are suitable for both complex samples as well as rapid analysis of inorganic ions.

213 ION CHROMATOGRAPHY OF ORGANICS.

Robert E. Smith, Allied Corporation Bendix Kansas City Division, Kansas City, Missouri 64141

Although ion chromatography was originally developed for determining inorganic ions, it also has recently been demonstrated to be a powerful technique used for organic compounds. The first technique used for the analysis of organics was ion chromatography exclusion (ICE) which is specially suited for aliphatic carboxylic acids. The acids are detected by chemically suppressed conductivity. Another method that has been developed is mobile phase ion chromatography (MPIC). This technique is similar to reverse phase liquid chromatography, except that the MPIC column is packed with a microporous polystryrene/divinyl benzene (S/DVB) resin that is stable from pH 0-14. In addition, MPIC usually implies the use of chemically suppressed conductivity detection. Applications of MPIC to the determination of benzoic acids, aliphatic and aromatic amines, nonionic detergents, and plating bath additives will be discussed. More recently, a gradient elution system has become available, enabling a wider range of separation and detection modes. The use of this gradient system for separation by both ion exchange and ion pair chromatography will be illustrated.

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214 SEPARATION OF ETHANOLAMINES BY SINGLE COLUMN ION CHROMATOGRAPHY.

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Ethanolamines are often found in industrial effluent streams. The monitoring of these ethanolamines by ion chromatography has been simplified by the use of cation exchange chromatography. Previous methods have used ion pair chromatography to accomplish this analysis. The use of a fixed site exchange column allows the use of dilute nitric acid as the only eluant needed, thus eliminating the need for ion pairing agents in the mobile phase. Monoethanolamine, diethanolamine, and triethanolamine are separated on the Wescan Silica Cation column with nitric acid eluant and conductivity detection.

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SELECTIVE AND SENSITIVE DETERMINATION OF TRIVALENT, HEXAVALENT AND TOTAL CHROMIUM IN AIR, WATER AND HAZARDOUS WASTE SAMPLES

S. S. Heberling, M. J. Doyle, and R. J. Joyce, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3603

The toxic nature of chromium, especially hexavalent chromium, is well documented. Accordingly, analytical methods to measure trivalent, hexavalent and total chromium have been refined over the years. However, despite this refinement period, the elimination of interferences such as iron, vanadium, mercury, and chloride has been cumbersome in some cases and impossible in others. This report will highlight the ability of Ion Chromatography (IC) to eliminate such interferences while providing ppb level detection limits for the three environmentally important chromium parameters, trivalent, hexavalent and total. The advantages and limitations of determining chromium by IC using conductimetric, photometric and post-column reaction/photometric detectors will be presented.

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EVERYTHING YOU EVER WANTED TO KNOW ABOUT BORIC ACID ANALYSIS BY ION CHROMATOGRAPHY- PART 2

Denise R. Eubanks, Robert J. Joyce, and Gary F. Lee, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3603

Boric acid analysis is of interest in several industrial areas. For example, in the nuclear power industry boron as borate, is monitored from the ppb to ppm levels, where it is used as a neutron absorber. Furthermore, this same industry must monitor their boric acid solutions for trace contaminants such as fluoride, chloride and sulfate. Manufacturers of boric acid are interested in assaying the purity of their product as well as trace contaminants which might be present. Boric acid can be determined as borate by Ion Chromatography (IC) using either anion exchange or ion exclusion, depending on matrix and concentration levels of interest. Anionic impurities in boric acid can also be determined using IC. This report will discuss the Ion Chromatographic separations used to evaluate trace contaminants in boric acid. It will also deal with current IC methods for measuring both high and low levels of borate in aqueous matrices.

217 TRACE METAL ANALYSIS VIA CONDUCTIVITY DETECTION. Donald Cox, Waters Chromatography Division of Millipore Corporation, 34 Maple St., Milford, MA 01757

A method for quantitative analysis of pg/ml levels of metal ions using conductivity detection is presented. Single Column Ion Chromatography using a resin based trace enrichment cartridge and a silica based cation exchange column is employed to separate metal ions. The results show that with low sample volume (30ml) the detection limits are in the pg/ml range. Example applications are illustrated.

218 ION CHROMATOGRAPHY OF ALKALINE SULFITE SCRUBBING SOLUTIONS, E.L. Grove, IIT Research Institute, 10 West 35th Street, Chicago, IL 60616

Strongly alkaline sulfite solutions were used to scrub nitrogen oxides. Ion chromotography with AS3 type columns were used to monitor the concentration changes of nitrite, nitrate, sulfite and sulfate. A weakly basic eluent provided the resolution between the nitrate-sulfite peaks. Standards were prepared with and samples were diluted to 0.05N NaOH; 0.1% formaldehyde solutions. The influence of base and formaldehyde on the formate ion formation and sulfite peak response were briefly studied. Species with a strong affinity for the column resin are formed in the scrubbing reactions so columns must be periodically cleaned.

219 DETERMINATION OF ORGANICS IN COMPLEX MATRICES: ADDITIVES & BRIGHTENERS IN PLATING BATHS, Mike Doyle, Shawn Heberling, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3603

Standard Reverse Phase HPLC methods suffer from limitations when applied to the determination of carboxylic acids and sulfonates. The lack of chromaphore functional groups and the polar nature of the molecules result in conditions not ideal for separation by conventional R.P. HPLC. Ion Chromatography has been applied to determination of these species in complex matricies of metal plating solutions. Monovalent and divalent carboxylic acids are separated and detected in Ni and Cu baths as well as sulfonates in Ni and Sn baths. The Ion Chromatographic methods are superior for determination of these compounds in high salt content plating baths.

220 ANALYSIS OF NICOTINE BY CATION MPIC, by John D. Lamb, Delbert J. Eatough, Brenda Sedar, Department of Chemistry, Brigham Young University, Provo, UT, 84602 and Norman L. Eatough, Department of Chemistry, California Polytechnic State University, San Luis Obispo, CA, 93401

Nicotine is an important potential tracer of ambient tobacco smoke. Sampling for nicotine by acidic denuder and subsequent extraction into water solution prohibits analysis by gas chromatography. Mobile phase ion chromatography (MPIC) offers an attractive alternative. Nicotine was successfully determined in such water extracts with a Dionex Ion Chromatograph using cation MPIC with 25% acetontrile/ 5.0 mM octanesulfonic acid in water. Conductivity detection was facilitated by a fiber suppressor using barium hydroxide suppressant. It was found that the retention time (10-12 min.) was affected little by the concentration of octanesulfonic acid, whereas acetonitrile concentration had a strong effect. Experiments detected no interference from ammonia even at high ammonia concentrations. Using benzenesulfonic acid denuders followed by MPIC analysis, it was shown that approximately 90% of the nicotine in environmental tobacco smoke exists in the gas phase, with 10% in the suspended particle phase.

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QUANTITATIVE ANALYSIS FROM SUB-PPB TO PERCENT LEVELS BY ION CHROMATOGRAPHY

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Two factors limit the working range of all Ion Chromatography (IC). At the low end, the background noise determines the minimum analyte signal that can be measured. At the high end, column capacity limits the amount of analyte that can be chromatographed without loss of resolution and/or deterioration of peak shape. The total analytical range can be extended by sample preconcentration or dilution. Such pretreatments have been successfully used in a variety of applications in which direct injection could not be used. However, these techniques have distinct disadvantages, such as increased sample handling, poorer reproducibility, and more potential for contamination. Therefore, it is desirable to use direct-injection methods whenever possible. In this paper, several common methods for determining anions and cations using chemically suppressed Ion Chromatography will be discussed. Data that show the linear working range and the total analytical range will be presented.

222 INTEGRATED SEPARATION SCHEMES IN ION CHROMATOGRAPHY. W.R. Jones, P. Jandik, A.L. Heckenberg, D. Wong, Waters Chromatography Division of Millipore Corporation, 34 Maple Street, Milford, Ma. 01757

Instrumental configuration consisting of two columns, one switching valve and two detectors helps to solve numerous separation and sample pretreatment problems. For example, boron and chloride analysis, as required in the nuclear power industry, can be carried out at widely varying concentrations of both analytes. Another application is a simultaneous determination of anions and cations in drinking water. On-line sample pretreatment will be shown on the example of determination of the traces of common inorganic anions in concentrated caustic solutions.

223 ION CHROMATOGRAPHIC DETERMINATION OF ALKALINE EARTH METALS WITH POST-COLUMN REACTION AND SPECTROPHOTOMETRIC DETECTION. V. T. Turkelson, S. W. Barr, Analytical Laboratories, Michigan Applied Science & Technology Laboratory, Midland, MI 48674.

The capabilities of ion chromatography (IC) for the determination of the alkaline earth metals (i.e., Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}) can be notably enhanced with the use of spectrophotometric rather than conductimetric (COND) detection. This is accomplished by coupling cation exchange separation and spectrophotometric detection via post-column reaction (PCR) of the separated species with an appropriate colorimetric complexing reagent. As compared to the determination of these cations via IC/COND, the IC/PCR technology provides marked improvements in both specificity and sensitivity. Parts per billion (ppb) concentrations can be routinely monitored and a common conductimetric interference, encountered in many inorganic materials and process streams (e.g. high sodium concentrations), can be effectively eliminated. In addition, IC/PCR yields faster analyses, improved system stability, expanded linear dynamic range and greater flexibility in eluent selection. This paper considers the ion exchange column technology, eluents, complexing reagents and system designs available for the most effective IC/PCR determination of the alkaline earths. The colorimetric reagents most commonly cited for these metals are compared with a series of "neglected" pH indicator-based reagents. In addition, applications of this IC/PCR technology are presented as an indication of the scope and impact of its usage to date.

224 **ENHANCEMENT OF SENSITIVITY AND SELECTIVITY OF CLASSICAL COLORIMETRIC METHODS BY ION CHROMATOGRAPHY**

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The colorimetric determination of analytes is one of the oldest and most widely used of the analytical chemist's techniques. In its simplest form colorimetry may be only a qualitative or semiquantitative test tube reaction. In its more sophisticated forms colorimetry may be employed on a routine industrial scale for on-line monitoring of process streams. Ion Chromatography significantly enhances the colorimetric method since it not only separates the analyte of interest from potential interferences but also concentrates the analyte into a chromatographic band, substantially enhancing the signal. Chromatography may take advantage of the lack of specificity to provide a broad spectrum approach to the determination of many elements, or a highly specific colorimetric method may be used with matrix elimination and preconcentration to provide trace determinations in complex sample matrices. This paper will address a variety of classical colorimetric techniques and demonstrate their use as highly efficient detection schemes in conjunction with Ion Chromatography.

225 SELECTIVE DETERMINATION OF CR(III) IN PLATING SOLUTIONS, Daniel N. Rubel, The Armoloy Corporation, 1325 Sycamore Road, Dekalb IL 60115.

A method has been developed for the separation of determination of trivalent chromium in concentrated chromium bath solutions. Common metallic impurities may include iron, copper, zinc, nickel, aluminum, and trivalent chromium. Of these, trivalent chromium is the most difficult to quantify due to relatively low concentrations and matrix interferences. Cr (III) can be separated by dilution (1:50) and selective precipitation with 50% NH_4OH and followed by recovery under vacuum and acid digestion with hot 12 mM 2,6-pyridinecarboxylic acid. The determination of Cr (III) (Dionex procedure) is then made by using an eluent of 6mM of 2,6-pyridinecarboxylic acid, adjusted with LiOH, and post column reaction with 4-(2-pyridylazo) resorcinol and UV-Vis detector. The reproducibility of precipitated and acid digested samples is approximately ±2%.

226 THE ION CHROMATOGRAPHIC ANALYSIS OF BORON AND PHOSPHORUS IN CHEMICAL VAPOR DEPOSITED GLASS FILMS. Raymond M. Merrill and Mary T. Kay, Sandia National Laboratories, Albuquerque, NM 87185

Ion chromatography has been used to simultaneously determine the boron and phosphorus content of vapor deposited borophosphosilicate glass (BPSG), and the phosphorus content in phosphosilicate glass (PSG). The glasses were deposited by various chemical vapor deposition techniques on silicon substrates, and ranged in thickness from 5000 to 8000 angstroms. The boron content of the glasses ranged from 0.5 to 5 weight percent, while phosphorus content ranged from 2 to 8 weight percent. The samples were prepared for analysis by etching the glasses from the substrates with hydrofluoric acid. Boron was then determined as the tetrafluoroborate ion and phosphorus determined as the orthophosphate and ortho-phosphite ions. The results of the analyes were used to optimize instrument parameters for the vapor deposition, to calibrate a non-destructive FTIR analysis technique, and to speciate phosphorus compounds within the glass films. This work performed at Sandia National Laboratories supported by the U. S. Department of Energy under Contract Number DE-AC04-76-DP00789.

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ION CHROMATOGRAPHY SEPARATION OF INORGANIC SULFONIC ACIDS. Richard J. Williams, Allied-Signal Corporation, P. O. Box 1021R, Morristown, N. J. 07960

A large number of inorganic sulfonic acids are produced from the reaction of nitrite and bisulfite ions. A number of ion chromatographic methods have been developed to separate many of these inorganic sulfonic acids, including: hydroxylaminedisulfonate, hydroxylaminemonosulfonate, aminetrisulfonate, aminedisulfonate, sulfamate, etc. The discussion will address column, eluent and detector selection. A single column cationic separation of hydroxylamine will also be presented.

228 DETERMINATION OF ARSENITE AND ARSENATE USING INDIRECT PHOTOMETRIC DETECTION

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A single injection, simple method has been developed to determine arsenite and arsenate using indirect photometric detection at 280 nm. The eluent, boric acid-potassium acid phthalate adjusted to pH 9.0 with potassium hydroxide, separates the anions in conjunction with various HPIC columns in under 10 minutes. Resolution is adequate to detect arsenite in the presence of high levels of chloride, phosphate, arsenate and sulfate. Sensitivity for arsenate and phosphate is increased 5-10 fold over conductimetric detection.

229 ANALYSIS OF SOME ELECTROACTIVE ANIONS BY ELECTROCHEMICAL DETECTION IN A FOOD MATRIX. Don Cox, Petr Jandik, Waters Chromatography Division of Millipore Corporation, 34 Maple St., Milford, MA 01757

Analysis of electroactive anions, sulfite, iodide, nitrite, sulfide in food, beverage, and process waters is discussed. The sample preparation necessary when preparing a food sample for analysis is a critical factor. This parameter is discussed in relation to labor intensive sample preparation schemes i.e., The Monier-Williams Analysis for Sulfite in Dried Foods. The chromatographic alternative to classical wet chemical techniques is presented. These alternatives will deal with electroactive species detected by an amperometric detector.

230 CONFIRMATION OF THE CHROMOTROPIC ACID DETERMINATION OF FORMALDEHYDE USING ION CHROMATOGRAPHY, J.T. Pierce and R.G. Howard, Occupational and Environmental Health Laboratory, University of North Alabama, Florence, AL 35632-0001.

Formaldehyde analysis has been devised using spectroscopic, electroanalytical, chromatographic, and other means. Ion chromatographic (IC) means of formaldehyde analysis have appeared particularly attractive on account of sample preparation considerations and the inherent resolving power of a chromatographic system. Due to the widespread use of the chromotropic acid procedure, the present study focuses upon its verification. Early attempts at formaldehyde analysis using IC focused upon the oxidation of formaldehyde to formate ion, which could then be detected using anion techniques. More recently DuVal, Rogers and Fritz (Anal. Chem. 57: 1583-1586 (1985)) have proposed the IC determination of aldehydes and acetone as alpha-hydroxyalkane sulfonate derivatives. Using a single-column system based upon a citric acid eluent they were able to detect low-ppm (solution measurements) levels of formaldehyde and related compounds. The present work provides an adaptation of this study to a two column (separator/suppressor) system.

231 COMBINING ION CHROMATOGRAPHY AND FLOW INJECTION ANALYSIS FOR ONLINE MONITORING Gary F. Lee and Michael E. Potts, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94088

Online monitoring of water contaminants and additives is becoming increasingly more important. Chemically suppressed ion chromatography has become the method of choice for the determination of inorganic anions and cations. Ion chromatography allows the simultaneous determination of several anions and cations in a single injection. Flow injection analysis offers important features such as high sample throughput, versatility and high precision. By integrating conventional flow injection techniques with ion chromatography, a variety of chemical compounds can be analyzed with interference-free results. Combining ion chromatography with flow injection analysis offers several distinct advantages for online monitoring of contaminants and additives in process streams. Ion chromatography is a sensitive and specific analytical procedure, but has the disadvantage of low sample turnaround while flow injection analysis is more prone to the interferences and is less sensitive than ion chromatography. Benefits of combining ion chromatography with flow injection analysis includes matrix interference elimination by separating the compounds prior to analysis and preconcentration techniques increases sensitivity.

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APPLICATIONS OF ION CHROMATOGRAPHY TO THE ANALYSIS OF NON-CHROMOPHORIC PHARMACEUTICALS AND THEIR METABOLITES

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Many drugs and their metabolites are difficult to separate by GC or RP-HPLC due to their extremely polar, hydrophilic natures. Likewise, many of the new pharmaceuticals are not easily detected by UV absorbance due to the lack of chromophores. Ion Chromatography coupled with amperometric or suppressed conductivity detection allows for the selective and sensitive determination of a variety of compounds including aminoglycosides and penicillin-related antibiotics as well as some of the metabolites of these various physiologically active substances. Various applications will be shown using the suppressed conductivity and Pulsed Amperometric Detector (PAD).

233 PYROLYTIC GAS CHROMATOGRAPHY MASS SPECTROMETRY OF MOLDING COMPOUND FOR THE PLASTIC ENCAPSULATION OF SEMICONDUCTOR DEVICES

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Molding compound for the plastic encapsulation of semiconductor devices is the most important assembly material in the back end of the semiconductor manufacturing process. Epoxy molding compound is a complex blend of phenolic, epoxy resins, flame retardants, release agents, catalyst and fillers. Defective molding compound has been implicated in several process problems and reliability failures. Hydrolyzable or extractable anions, especially chloride, have contributed to corrosion failures. Molecular weight differences have been shown to produce flash and bleed problem resulting in solderability failures. Release systems are responsible for mold scumming problems resulting in the need for additional mold cleaning cycles resulting in decreased productivity. Molecular weight differences are also responsible for flow problems resulting in non-fill of large molds resulting in production losses. Molecular weight differences are also suspected of being the cause of the void problems as well. Compositional differences may result in curing mechanism variations which affect cycle time and add to process control problems. This paper reports on studies using PGCMS designed to characterize molding compound formulations so that good and bad molding compounds can be differentiated. The data gathered was treated in a statistical fashion in such a way as to allow statistical determination of differences between samples. Correlation between PGCMS measurements and molding compound failures will be discussed.

234 APPLICATIONS OF DIRECT MOLECULAR BEAM MASS SPECTROMETRY TO PYROLYSIS AND CATALYSIS

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A technique will be described which combines the features of analytical pyrolysis-mass spectrometry with the ability to sample directly from realistic, high-temperature, ambiant pressure, reactive environments. This is accomplished with free-jet sampling followed by molecular-beam introduction of stable, reactive and condensible species directly into the ion source of a quadrupole mass spectrometer. Primary and secondary molecular processes in wood pyrolysis will be illustrated as well the use of zeolites to catalytically upgrade primary oil vapors to a highly aromatic product slate. A distinction between wood oils and wood tars, of interest to woodstove emissions, will be made.

236 DEVELOPMENTS IN GLOW DISCHARGE MASS SPECTROMETRY.

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The combination of a glow discharge source with a high resolution mass spectrometer has resulted in a powerful analytical technique forinorganic elemental analysis. Since its inception the VG 9000 G.D.M.S. has undergone constant development in both hardware improvements and analytical applications. The current performance of the VG 9000 will be discussed in terms of its application to:-

1. The determination of major components in high temperature alloys.
2. The determination of minor/trace elements in a wide range of materials.
3. The determination of non metallic consitutents.
4. The analysis of non conducting powders.

Data will be presented to illustrate the limits of detection and levels of precision that are attainable.

237 MASS DISCRIMINATION PHENOMENA IN FAST ATOM BOMBARDMENT MASS SPECTROMETRY OF METAL STABLE ISOTOPES:

L.V. Miller, P. Peirce, C. Goss, K.M. Hambidge, and P.V. Fennessey; University of Colorado Health Sciences Center, Denver, CO 80262

Fast atom bombardment (FAB) mass spectrometry, without a liquid matrix, has found application as a simple, sensitive, and widely available technique for measurement of stable isotope ratios of metals in such fields of study as nutrition and archaeological sample analysis. Our experience with FAB mass spectrometry in isotope dilution studies of zinc nutrition has uniformly demonstrated an isotope discrimination effect. Data in the published reports of other investigators performing FAB or secondary ion mass spectrometry of metals often show similar effects as well, though little discussion of the phenomena has been forthcoming. Prompted by our experience with zinc, measurements of the natural isotope ratios of Ca, Ti, Ni, Mo, and Sn revealed that isotope ion currents decreased from their expected levels as isotope masses increased and that the magnitude of this mass discrimination effect on isotope ratios was roughly proportional to the mass difference between the isotopes. Furthermore, the magnitude of the mass discrimination varied from metal to metal, exhibiting a range from 1.5% per a.m.u. mass difference for Mo to 2.4% per a.m.u. for Sn. Further efforts have been directed towards 1) determining whether this mass discrimination is attributable to mass fractionation, other instrument-related mass discrimination phenomena, or a combination thereof; and 2) developing a detailed characterization for purposes of explanation and prediction. We report here on the findings of our investigation of these mass discrimination phenomena.

238 MEASUREMENT OF PLATELET ACTIVATING FACTOR BY GC/MS.

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The recent elucidation of the structure of platelet activating factor (PAF) as 1-O-hexadecyl, 2-O-acetyl, sn-glycero-3-phosphocholine has enabled the development of assays for this specific chemical entity to replace the assays based on biological activity. The GC/MS procedure described in this report is faster, more sensitive and more accurate than the bioassays it supplants.

Stable isotopic variants of PAF molecular species have been synthesized and are added at the beginning of the assay procedure to act as internal standards in an isotope dilution assay. PAF is extracted from the experimental matrix with chloroform/methanol and then further purified by silica acid chromatography, either through a column, or on thin layer plates. The PAF-containing fraction is then subjected to phosphate ester hydrolysis with 50% hydrofluoric acid. The diglyceride thus produced is extracted, derivatized and subjected to GC/MS selected ion monitoring analysis.

Depending on the amount of PAF extracted, various derivatives can be formed to exploit the characteristics of different ionization and fragmentation moles. For routine assay of PAF in amounts greater than one nanogram, the trimethylsilyl derivative and electron impact ionization is preferred. For amounts less than one nanogram, very good results can be obtained with the pentafluorobenzoyl derivative measured under negative ion chemical ionization conditions.

This assay has been used to quantitate PAF in various tissues and fluids, including isolated neutrophils, macrophages and lung tissue. It has also been used to demonstrate the presence of PAF in mouse brain tissue and in human urine.

239 STRUCTURE ELUCIDATION OF THE ANTIGENTIC OLIGOSACCHARIDE ISOLATED FROM CELL WALL OF STREPTOCOCCUS SANGUIS (MITIS) Ss34: A. Bush, P. Fennessey, F. McIntire and S. Tjoa; University of Colorado Health Sciences Center, Denver, CO 80262.

Gel chromatograph of the crude mixture formed from lysozyme treatment of Streptococcus sanguis Ss 34 cells yielded a fraction which showed antigenic activity. The crude fraction which inhibited aggregation and coaggregation contained much less cell wall constituents and more polysaccharide. This fraction was further purified using HPLC into 3 peaks (1 major and 2 minor) which were collected and analyzed as follows. A portion of the sample was completely hydrolized and treated with $NaBH_4$ followed by acetic anhydride. GC/MS of the derivatized sample gave 4 major components. Using the mass spectra and the capillary gc retention indices the components were identified as Rhamnose, Glucose, Galactose, and N-Acetylgalactosamine. Fast Atom Bombardment was used to determine the molecular weight of each of the HPLC peaks. This data also gave sequence information on the major component (a hexasaccharide). Further analysis of the original fraction using permethylation followed by reduction and acetylation gave a gas chromatogram with six components. Mass spectra of these compounds revealed the linkage points of 5 of the six sugars including the non-reducing terminal. Further work with $NaBD_4$ was needed to separate isomeric possibilities in the final sugar linkage. NMR data was used to identify the stereochemistry of the sugar linkages. Finally, GC/MS of derivatives made using optically active butanol (R and S) were used to reveal the configuration (D or L) of each sugars.

240 NIRA: A WELL-KEPT SECRET IN SPECTROSCOPY
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Analytical chemists working in the so-called classical (mid) infrared region of the spectrum think it's bad enough that some of us are content to examine only the overtones and combination bands which fall in the near infrared (NIR) region. Worse than that, information is often gathered by reflectance methods, thus giving rise to the phrase Near Infrared Reflectance Analysis (NIRA). Even though absorption peaks are broad and their intensities may be 2-3 orders of magnitude lower in the 1100-2500 nm region, the combination of low-noise instruments and sophisticated computer algorithms may be a route to rapid (would you believe 30 seconds?) and non-destructive analyses, quite often without sample preparation. Over 6000 instruments are currently in use (some with filters, others with scanning monochromators), but most of the users are quietly solving their analytical problems without broadcasting the virtues of the technique. Nevertheless, NIRA is doing both quantitative and qualitative analyses in such diverse fields as foods, beverages, agriculture, textiles, tobacco, petrochemicals, pharmaceuticals, and polymers. Samples may be liquids (aqueous or organic media) or solids, including powders, granules, films, pastes, slurries, etc. This presentation will serve as a background for the others in the NIRA symposium.

241 CHEMICAL SENSING WITH NEAR-INFRARED REFLECTANCE ANALYSIS. David L Wetzel, Kansas State University, Dept of Grain Science and Industry, Manhattan KS 66506

Near-infrared reflectance analysis is particularly well suited to chemical sensing because it operates on "as is" samples and yet has chemical specificity. The adsorptions observed originate from vibrations of a relatively few chemical groups whose overtones and combination bands appear in the near infrared region. These groups are commonly found in natural and synthetic materials and their quantitation is possible at major component levels. Chemical sensing by near-infrared techniques does not usually require complete scanning since information for quantitation is found in select wavelength responses incorporated into a mathematical analytical expression. Correlation transformation between laboratory pre-analyzed samples (training set) and the optical data collected allows statistical wavelength selection and assignment of regression coefficients. The result is a select calibration for an analyte in a particular matrix or commodity. Quantitative chemical sensing occurs when the built-in computer of the near-infrared analyzer simultaneously calculates multiple component concentrations by solving prediction equations which use multiple wavelength intensity ratioed data for individual samples. Similarly, qualitative sensing information by discriminant analysis is obtained by use of a discrete wavelength multiterm function. Preselected wavelengths and dedicated preprogrammed microcomputers are ideal for numerous sensing and ultimately control functions.

242 UNDERSTANDING A SAMPLE PROPERTY-TO-NIRA RELATIONSHIP. Joseph G. Montalvo, Steven M. Buco*, Devron P. Thibodeaux and Sherman E. Faught, Southern Regional Research Center, P.O. Box 19687, New Orleans, LA 70179; *Louisiana State University, Baton Rouge, LA 70803.

A systematic procedure is presented to identify what physical or chemical changes in a sample are being detected by NIRA in the correlation with a property of that sample. The property of interest may be physical, chemical or biological. The approach is to destroy the physical structure of the sample (e.g., milling or melting) and to fractionate the original and physically modified specimens into simpler subsamples by solvent extraction. Derived samples are tested for a correlation between the property under investigation and NIRA. If a correlation is observed, these materials are subjected to qualitative and quantitative analyses, physical and chemical. For specific physical structures, correlation between results of the analyses and the property of interest is an indicator of cause of the property-to-NIRA relationship in the original samples. Small sample sizes are recommended, < 10 samples, due to the resources needed to complete the work. Two problems with NIRA analysis of a small number of samples are instrument noise and chance correlations. Instrument noise was overcome by developing an appropriate test statistic to test for a relationship between the variables. This test statistic is a function of successive values of the correlation coefficient r at adjacent wavelengths. Chance correlations were assessed by means of a randomization test to determine significance of the test statistic. The procedure is demonstrated on artificial and real-world samples.

243 SPECTRAL MATCHING IN THE NEAR INFRARED (NIR)
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Spectral matching algorithms for the identification of unknown mid-infrared spectra have been the topic of considerable interest, as well as debate. However, significant research in this area for NIR spectra has been lacking. The emergence of NIR spectroscopy, with its inherent advantages over its mid-infrared counterpart for certain applications, now requires that this situation be rectified. The algorithm used here involves treating each NIR spectrum or some mathematical transformation of the spectrum (e.g., log 1/R, log 1/T, or first, second or higher order derivatives of log 1/R or log 1/T, or Fourier transforms of log 1/R or log 1/T), as an N-dimensional vector, where N is the number of wavelengths, i.e., data points, in each spectrum. Comparison of an unknown spectrum to that of a known spectrum is accomplished by calculating the cosine of the angle between the two vectors which represent the known and unknown spectra. The value of that cosine can be considered as a "match index" which describes the similarity, or lack of similarity, between the spectra. It is possible to search data bases consisting of hundreds of NIR spectra within minutes using this algorithm. The effectiveness of the different mathematical transformations of the spectral data and the use of limited spectral windows for sample identification will be discussed. Several applications involving NIR spectral matching will be presented.

244 QUALITATIVE NIR ANALYSIS USING MULTIDIMENSIONAL DISTANCE MEASURES, Howard Mark, Technicon Instrument Corp., Industrial Systems Division, 511 Benedict Ave., Tarrytown NY 10591.

Many methods of matching spectra of unknown samples to spectra in a library have been devised. Use of many of the standard methods is complicated by the effects of particle size and repack that are inherent to reflectance measurements, leaving only a small subset of methods suitable for qualitative analysis via NIR reflectance.

Use of Mahalanobis and normalized Mahalanobis distances is one technique that overcomes the difficulties encountered when reflectance measurements are made. In addition, it allows matching to be performed both when full NIR spectra are available, or when only a small subset of wavelengths, such as are obtained from instruments based on interference-filter technology, are available.

Theoretical descriptions will supplement examples from agricultural and pharmaceutical applications.

245 QUANTILE BEAST ATTACKS THE FALSE-SAMPLE PROBLEM IN NIRA

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The multiple linear regressions typically used during the calibration procedure in NIRA yield equations in which any amount of reflectance at the analytical wavelengths leads to a corresponding composition value. When a sample contains a component not present in the training set, erroneous composition values can result without any indication of this situation. The Quantile BEAST (Bootstrapped Error-Adjusted Single-sample Technique) provides a method of detecting any number of false samples, and can be used for qualitative analyses. The BEAST constructs a multi-dimensional form in space using the reflectances of each training-set sample at each wavelength. New samples are then projected into this space, and an asymmetric, nonparametric confidence test is executed to determine whether the new sample is part of the training set form. This method is more tractable in its theory than conventional discriminant analysis and yet is potentially capable of producing more accurate results.

246 MONITORING HYDROCARBONS BY NEAR-INFRARED SPECTROSCOPY

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The near-infrared has characteristics that make it useful for process measurements. The transitions in this region are classically forbidden. but occur because of the deviation of real vibrations from the harmonic oscillator model. The forbidden nature of the transitions causes the absorptivities to be weak. typically 0.1-10 percent of the absorptivities of the fundamental bands. Because of the weak signals of the near-infrared. compared to the mid-infrared. Beer's law remains linear over a wider concentration range and longer pathlengths. Regression techniques allow the extraction of information from complex spectra. The large number of calculations that are needed to find the best correlations can now be done on microcomputers available in most laboratories. We have applied these methods in a fiber optic system to remotely measure hydrocarbons. The investigation of both a simple mixture of hydrocarbons and a more complex petroleum blend has been done.

247 NEAR INFRARED REFLECTANCE METHOD FOR WHEAT-FLOUR GLYCOLIPIDS.

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The near infrared (NIR) reflectance method cannot accurately determine flour glycolipid because its concentration is too low (approximately 0.2%). For this reason a new method for presentation of the glycolipid in the instrument cell was developed and tested. For laboratory analysis, glycolipid was hydrolyzed with methanolic HCl (Kates 1964) followed by analyzing for sugar by the phenol sulfuric acid method (Dubois et al 1956). For NIR measurements Whatman GF/A glass fiber disks, powdered silica, and crystalline sodium chloride and potassium bromide were coated with lipid by wetting these materials with extracted lipid solution followed by evaporation of the petroleum ether solvent. The lipid coated materials were used in the instrument cell for developing and testing of glycolipid calibrations. In comparisons to the best calibration obtained on flour, the glycolipid calibrations on coated materials had much higher correlation coefficients and lower coefficients of variation. Calibrations on glass fiber disks are statistically the best ones for determining glycolipid content of wheat flour. This new method of coating an extracted material on fiber disks or small particle materials for NIR measurements might also be used in analyzing for minor constituents in other types of samples.

248 A STRATEGY FOR THE USE OF NIRA IN LIQUID FORMULA QUALITY CONTROL APPLICATIONS, Tom M. Jones and Lana R. Rademacher, Nutritional Quality Control, Mead Johnson and Company, 2404 Pennsylvania Avenue, Evansville, IN 47721

Mead Johnson has successfully utilized NIRA for protein, fat, and total solids determinations in liquid formula products for several years (1980). Its use was initially limited to finished product quality control applications. Recently, a new strategy was developed to more effectively employ NIRA technology in our quality control operations by introducing its use for testing of in-process formula samples. In order to develop an effective NIRA program with application to both finished products and in-process goods, recalibration was necessary. The results of calibration efforts on two infant formulas, Enfamil (a milk-based formula) and ProSobee (a soy-based formula), are presented. These new calibrations included formula samples from all stages of processing, as well as sterilized product. The various caloric levels (dilutions) into which each product line is formulated were incorporated into a single product calibration. Relative accuracy is within 3% for each constituent (protein, fat, and total solids) for both product types when compared with reference methods. A system developed for monitoring the performance of NIRA calibrations in an in-process laboratory environment is also discussed.

249 COMPARISON OF THE PERFORMANCE OF INTERFEROMETERS AND DISPERSIVE SPECTROPHOTOMETERS IN THE NEAR INFRARED (NIR)

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NIR spectroscopy offers distinct advantages over mid-infrared spectroscopy for applications involving the quantitative analysis of complex mixtures, especially when diffuse reflectance measurements are required. Interferometers, as compared to dispersive spectrophotometers, have been shown to provide significant improvements in signal/noise ration (S/N) and wavelength repeatability when operated in the mid-infrared. As the use of NIR spectroscopy for quantitative analysis expands, questions concerning the relative merits of interferometers and dispersive instruments arise. This paper will attempt to address the performance requirements for successful quantitative analysis in the near infrared and the suitability of current instrumentation for meeting those requirements.

250 FOURIER ANALYSIS OF NIR SPECTRA: DERIVATIVE ENHANCEMENTS IN FOURIER SPACE

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Analysis of NIR spectra in wavelength space has several problems. Wavelength spectra occupys an excessive amount of space in the computer and on magnetic media. The data points in the spectra are highly correlated which makes wavelength domain calibrations unstable. Fourier analysis is suggested as a means of overcoming the above problems while at the same time accruing several other advantages. Fourier Domain analysis: (a) cuts storage requirements by 98%, (b) slashes calibration times by 98%, (c) enhances estimates of composition by using Fourier coefficients, (d) reduces the multicollinearity problem, (e) makes it easy to correct for particle size, (f) makes it easy to do spectral matching and product identification, (g) makes calibration maintenance much easier, and permits derivative enhancements in Fourier space. Emphasis will be placed on theory and techniques for achieving enhancements.

251 LAPLACE TRANSFORM SPECTROSCOPY

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Laplace Transform Spectroscopy (LTS) is a novel technique that uses a translucent material, known as the filter, to effect a transformation of the sample spectrum. In LTS the sample spectrum is convolved with the transmittance spectrum of the filter. The filter transmittance spectrum is modulated in the exponential manner by changing the optical pathlength of the filter material. As the pathlength of the filter increases the transmitted power decreases exponentially. The observed decay depends on the sample spectrum. In LTS, this exponential decay is the analog to the Fourier Transform interferogram. The sample spectrum can be extracted from the decay by an inverse Laplace transform and a mapping operation. This mapping operation is defined by the filter absorbance spectrum. As a result of this mapping operation, resolution in LTS is not constant but is defined by the first derivative of the filter absorbance spectrum. LTS, unfortunately, creates degeneracies in the sample spectra. These degeneracies result from points in the filter spectrum that have the same transmittance values. A full development of the theory of LTS will be presented, with several simulated examples to clarify the aspects of LTS. The design of a prototype Laplace Transform spectrometer and initial results will be shown.

252 DNP-NMR AS A PROBE OF INTERNAL SURFACES.

H. Seidel, R. D. Kendrick and C. S. Yannoni, IBM Almaden Research Center, San Jose, California, M. E. Galvin, AT&T Bell Laboratories, Murray Hill, New Jersey.

We have used dynamic nuclear polarization (DNP) to study a composite of polyacetylene in low density polyethylene in order to probe the intimacy of mixing in this material. Our results confirm that the DNP spectra are sensitive to both the degree and nature of the contact between components as well as the details of local electronic structure in such composites.

253 SMALL-MOLECULE ^{31}P NMR PROBES OF SURFACES.

Laima Baltusis, James Frye and Gary E. Maciel, Department of Chemistry, Colorado State University, Ft. Collins, Colorado 80523.

Previous NMR studies of Bronsted and Lewis acid sites on amorphous catalysts with trialkylphosphine probes reveal the importance of pulse mode (FT vs. CP) and substituent bulk in assaying quantitatively the number of active sites on the surface. Current work with trialkylphosphine oxide probes reveals the importance of carefully examining spin lattice relaxation times for correct quantitative analysis of surface sites. The ^{31}P resonances of trialkylphosphine oxides bound to different types of surface sites are better separated in terms of chemical shift than are the corresponding trialkylphosphines. Model compound studies confirm ^{31}P chemical shift assignments of surface species. Provided attention is paid to relaxation parameters, single-pulse Bloch-decay experiments better represent the true stoichiometric amounts of phosphine oxide molecules bound to various surface sites than do cross-polarization (CP) experiments, which discriminate against more mobile physisorbed species. Plots will be presented that show novel results of the variation of ^{31}P spin-lattice relaxation time as a function of fractional surface area coverage by phosphine oxide probe molecules. The role of variable temperature MAS NMR techniques for characterizing chemical exchange among the various phosphine oxide surface species will also be discussed.

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254 NMR STUDIES OF SUPPORTED BIMETALLIC CATALYSTS

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NMR of ^{1}H, and of ^{63}Cu has been used to characterize the state of adsorbed hydrogen on, and of copper in supported bimetallic catalysts $M-Ru/SiO_2$, with M = nothing, Cu, Ag, and Au. At least three states of hydrogen are observed from these studies; 0-H, Cu...H...Ru, and localized dipolar pairs or triplets of hydrogen on supported Ru. Hydrogen spillover from Ru to Cu allows the calculation of surface composition from NMR. The dispersion of copper in Cu/SiO_2 may be inferred from the NMR of ^{63}Cu. The lack of a signal from Cu in $Cu-Ru/SiO_2$, together with the NMR of hydrogen on $Cu-Ru/SiO_2$ indicates that Cu forms a surface layer on Ru in this system. This information, coupled with kinetic studies of the methanation reaction over $Cu-Ru/SiO_2$ indicate that neither electronic, nor geometric effects are important on this catalyst. Variations of product distributions in the Fischer-Tropsch reaction will be discussed.

255 A STUDY OF CO ADSORBED ON SUPPORTED GROUP 8-10 METALS BY 13-C MAGIC ANGLE SPINNING NMR

R. Shoemaker and T. Apple
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13-C magic- angle spinning NMR in controlled environments allows the observation of the surface-adsorbed state of carbon momoxide on supported metal catalysts. Based upon isotropic chemical shifts, differentiation of bridged, linear and dicarbonyl species is possible.

The relative proportions of surface-bound carbonyls is found to be strongly dependent upon the adsorption temperature and the make-up of the catalysts.

Reactions of surface carbonyls with water (the water-gas shift) and hydrogen (Fischer-Tropsch) can be monitored. NMR analysis can be combined with Temperature Programmed Desorption (TPD) to determine the energetics of the adsorbed species.

256 MULTINUCLEAR NMR STUDY OF THE VACUUM-CALCINATION AND REHYDRATION OF ZEOLITE NH_4-RHO.

Alexander J. Vega and Zeev Luz†, Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898.
(†Permanent address: The Weizmann Institute of Science, Rehovot 76100, Israel).

Calcination of the ammonium form of a zeolite usually results in a product with a combination of Bronsted and Lewis acid sites. The pure H-form which has only Bronsted sites is often difficult to make. In this study NMR has been used to characterize the results of various calcination procedures applied to zeolite rho which has a highly symmetric cubic crystal structure lending itself to a fairly straightforward interpretation of the NMR spectra. Its unit cell can exist in two cubic space groups with quite different geometries. Using a variety of NMR characterization methods we have determined that a two-step vacuum-calcination procedure yields a nearly perfect Bronsted-acid form of rho with essentially all the hydrogens in bridging hydroxyl positions and with a minimum degree of framework dealumination. Structural properties of the zeolite were investigated at various stages of the sample treatment, i.e., hydrated NH_4-rho, partially and fully dehydrated NH_4-rho, anhydrous H-rho, and partially and fully rehydrated H-rho. Because of the inhomogeneous nature of most zeolite structures, we have chosen to simultaneously apply a wide range of NMR methods. These include nonspinning and MAS proton NMR, proton multiple-pulse relaxation and lineshapes, Si-29 MAS with and without cross polarization, Al-27 MAS, and deuterium solid echoes. Many of the conclusions are based on the quantitative results obtained by proton Al-27, and Si-29 spectroscopy.

257 DEUTERIUM RELAXATION AND LINESHAPES IN CLATHRATES.

Alan D. Ronemus, Michael S. Greenfield, Robert L. Vold and Regitze R. Vold. Department of Chemistry B-014, University of California - San Diego, La Jolla, California 92093

Small hydrocarbons included in channel clathrates are often free to undergo a variety of restricted internal rotations and librations. When such motions occur at rates on the order of 10^3 s^{-1} to 10^7 s^{-1} it is possible to distinguish among different motional models on the basis of deuterium quadrupolar echo lineshapes. Information regarding faster processes can be obtained from spin lattice relaxation measurements, and single crystal samples allow the determination of individual spectral densities of motion; when used in conjunction with sample rotation experiments, details of the motion may be obtained. Data will be presented and discussed for powder and single crystal samples of perdeuterated and 4,4'-d2-labeled biphenyl in beta-cyclodextrin and perdeuterated nonadecane in urea. Procedures to deal with several pernicious artifacts such as the virtual FID and sampling at an arbitrary time with respect to the echo maximum will also be discussed.

258 CROSS POLARIZATION DYNAMICS IN AMORPHOUS HYDROGENATED SILICON

Nicholas Zumbulyadis, Corporate Research Laboratories, Eastman Kodak Co., Rochester, NY 14650

The incorporation of hydrogen into amorphous silicon is essential for obtaining device quality materials. Infrared electron photoemission, and theoretical studies indicate the presence of a variety of Si-H bonding environments. Nonetheless, the Si-29 CP/MAS spectrum of these materials consist of a broad and featureless line with no indication of any fine structure due to the various SiH_x moieties. We present here the application of a variant of the cross-polarization method that allows the resolution of three overlapping components within the broad Si-29 resonance. Taken together with electron photoemission studies and theoretical calculations, our results lead to a model for the structure of shallow traps at the bottom of the conduction band of a-Si:H.

259 NMR OF INORGANIC SOLIDS.

Eric Oldfield, School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, Illinois 61801.

I will discuss recent progress in obtaining and interpreting NMR spectra of inorganic solids, such as oxides and zeolites, using nonintegral-spin nuclei. Some emphasis will be given to O-17 studies, including cross polarization effects. I will discuss the uses of spin-echo methods for quadrupolar nuclei, including de-Pakeing effects. Some results of grafting of metal carbonyls onto oxide surfaces will also be given.

260 VARIABLE TEMPERATURE CP/MAS NMR STUDIES OF PARAMAGNETIC AND ANTIFERROMAGNETIC SOLIDS

Gordon C. Campbell and James F. Haw, Department of Chemistry, Texas A&M University, College Station, Texas 77843

The extent to which CP/MAS NMR techniques become applicable in inorganic and organometallic chemistry will depend, in part, on strategies for dealing with, and possibly exploiting, unpaired electrons. Many paramagnetic complexes of lanthanide and actinide metals yield informative CP/MAS spectra, and paramagnetic shift and relaxation effects are observed which can often be interpreted in a meaningful fashion. The NMR properties of these materials are also temperature dependent, reflecting the temperature dependence of the magnetic properties, dynamics, and relaxation rates. Shift and relaxation effects in paramagnetic solids can, in principle, be analyzed in terms of structural parameters.

Antiferromagnetic molecular solids approach diamagnetic behavior as the temperature is reduced and often yield useful CP/MAS spectra at low temperature, even if the signals are broad or absent at room temperature. Complicated chemical shift and relaxation effects are often observed for these solids.

Preliminary results for various classes of magnetic solids will be presented and the prospects for further work in this area will be assessed.

261 SOLID-STATE NMR SPECTRA OF METAL NUCLIDES. Greg Quinting, Gary E. Maciel, Stephen Dec, Bruce L. Hawkins and Robert Wind. Department of Chemistry and Regional NMR Center, Colorado State University, Fort Collins, CO 80523.

Solid-state NMR studies with heavy-metal nuclides in diamagnetic materials present a set of technical and phenomenological difficulties in the issues of generating spin polarization, excitation of the magnetization and detection. Reliance on spin lattice relaxation or cross polarization (CP) can often be undermined by the remoteness of the nuclei of interest from other magnetic nuclei that can serve as sources of relaxation or CP transfer, and small magnetogyric ratios can strain the applicability of CP approaches. Large ranges of chemical shift and large chemical shift anisotropy (CSA) that are typical of heavy-metal nuclides can present difficulties in the manipulation of nuclear spin magnetization, and the large CSA's exacerbate spinning sideband problems. Manifestation, of nuclear electric quadrupolar interactions for nuclei with $I > 1/2$ add additional complications. This talk will describe progress in our laboratory on strategies designed to overcome and/or circumvent these difficulties.

262 SOLID STATE NMR IN A CONTROLLED ATMOSPHERE. R. R. Eckman, Exxon Chemical Company, 5200 Bayway Dr., Baytown, TX 77520.

A cylindrical rotor system has been developed having an hermetic seal which is useful for solid state NMR in a controlled atmosphere. It can also be used for rotating heterogeneous, liquid, or liquid crystal solution samples and should be useful in a number of different areas of chemistry. The cylindrical rotor has a significant advantage in stability. The endplug provides an impermeable seal by the use of o-rings for air-sensitive, pyroforic, or hygroscopic compounds. The major advantages of this technique are that the rotor and endplug are reusable many times, sample preparation is simplified which allows efficient use of spectrometer time, and variable temperature application is routine. Applications to determine the structure of air-sensitive compounds are demonstrated.

263 CONTROL AND MANIPULATION OF SIDEBANDS IN MASS NMR SPECTRA. D.P. Raleigh, E.T. Olejniczak, S. Vega, and R.G. Griffin, Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139.

In high magnetic fields magic angle sample spinning (MASS) breaks up chemical shift powder patterns into sharp centerbands flanked by sets of rotational sidebands. Although the presence of sidebands is often regarded as an unnecessary complication, their intensities yield the principal values of the shift tensor. It will be demonstrated that these data can be important in determining the origin of isotropic chemical shift differences between samples. In recent years, several experimental methods have been developed for controlling and manipulating sidebands and thus aiding in assignments. We give a simple theoretical description of these experiments based on an analysis of the magnetization vectors of individual crystallites. This analysis leads to a simple explanation of the two π-pulse and four π-pulse experiments for eliminating sidebands, as well as the chemical shift scaling experiment for reducing sidebands. Finally, we present several interesting variations on the basic TOSS experiment.

264 HIGH SPEED MAGIC ANGLE SPINNING. S.F. Dec, R.A. Wind and G.E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

The performance of a modified version of the spinning system described in ref. 1 is presented. Rotational frequencies exceeding 20 KHz can be realized. Results obtained under high speed MAS conditions for various nuclei, such as ^1H, quadrupolar nuclei, and dilute spin systems, are discussed.

1. R.A. Wind, F.E. Anthonio, M.J. Duijvestijn, J. Smidt, J. Trommel and G.M.C. deVette, J. Magn. Reson., 52, (1983) 424.

265 MAGIC-ANGLE SAMPLE SPINNING - PRACTICAL CONSIDERATIONS.

E. O. Stejskal, Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, MO 63167.

The optimum magnetic field for routine ^{13}C-CP/MAS in non-crystalline solids is not necessarily the highest possible field. As magnetic field is increased, higher spinning speeds are required to prevent unmanageable spinning side bands. Sample payloads are necessarily smaller and sensitivity does not increase. Since chemical-shift dispersion dominates line width, resolution does not increase as magnetic field increases. Larger resonant frequencies may require larger radiofrequency field amplitudes, certainly not smaller. Such fields are harder and more expensive to produce as the frequency increases. Furthermore, just as it is desirable to spin at a speed greater than the chemical shift anisotropy width, it is also desirable to spin slowly compared to important dipolar interactions in the sample. As the magnetic field increases, the window for acceptable spinning speeds narrows. Indeed, for some less than routine experiments, such as dipolar rotational spin-echo spectroscopy, this window may be even narrower. Similar, related considerations affect the choice of field for routine ^{15}N-CP/MAS experiments as well. A short exposition of various successful magic-angle sample spinners will also be presented, along with their behavioral characteristics.

266 ABSTRACT NOT AVAILABLE

267 LOW TEMPERATURE CPMAS-NMR OF METASTABLE MOLECULES.

C. S. Yannoni, IBM Almaden Research Center, San Jose, California.

Over the last few years, we have specialized in using variable temperature CPMAS techniques to obtain well-resolved carbon-13 NMR spectra of molecules which are stable only at low temperatures. To this end, we have developed methods for preparing and transferring these species at low temperature, and have been able to obtain CPMAS spectra at temperatures as low as 6K. I will outline the considerations that led to our approach and will describe the apparatus in detail.

268 CHEMAGNETICS MAGIC ANGLE SPINNING: DESIGN CRITERIA

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The development and maturing of magic angle spinning designs as developed at Chemagnetics will be discussed. From these experiences, a set of quide lines and design criteria have developed and these will be discussed in terms of an "ideal probe" yet to be built.

269 EFFECTS OF SAMPLE SPINNING ON CROSS POLARIZATION.

Maziar Sardashti and Gary E. Maciel Department of Chemistry, Colorado State University, Ft. Collins, Colorado 80523.

Sample spinning can modulate the rate of polarization transfer from abundant to rare spins in cross-polarization experiments on solids, if the spinning speed is the order of magnitude of the dipolar couplings among the abundant spins (1). The intensity of this modulation depends on the angle of the spinning axis relative to H_0 and the size of the dipolar coupling of the abundant spins, and the frequency of this modulation depends on both this angle and the spinning speed. For example, at the magic angle (54.7°) modulation has a frequency equal to the spinning frequency, whereas at 90° it occurs at twice the spinning frequency. Examples of the above phenomena are given for both a ^{13}C-^{1}H system (adamantane) and also a ^{113}Cd-^{1}H system (cadmium formate). It is shown that advantage can be taken of the behavior for a 90° (or even better, 0°) spinning angle to broaden the CP match condition and make it less sensitive to amplifier instabilities.

1. E.O. Stejskal, J. Schaefer and J.S. Waugh, J. Magn. Res., 28, 105 (1977).

270 EXPERIMENTAL CONSIDERATIONS IN VARIABLE TEMPERATURE CP/MAS NMR

Richard C. Crosby, Gordon C. Campbell, and James F. Haw Department of Chemistry, Texas A&M University, College Station, Texas 77843

Variable temperature CP/MAS NMR is increasingly important for study of the structure, dynamics, reactivity, and magnetic properties of solids. One would like to perform such studies with a high degree of temperature accuracy and control, but various reports in the literature suggest that the uncertainties in temperature measurement can be as high +/- 20 K. The sources of these uncertainties include: temperature measurement and control when two independent gas streams are used, the necessity of having the temperature sensor(s) remote from the sample, Joule-Thompson cooling or heating, rf heating, temperature equilibration times, and possibly other factors. Some of these difficulties can be minimized or eliminated through a careful redesign of the variable temperature accessories, but a solution to many of the experimental problems in VT CP/MAS NMR requires that the sample temperature be measured directly.

We have developed ^{13}C CP/MAS chemical shift thermometry based on samarium actetate tetrahydrate, which has chemical shifts in the solid state that obey the Curie law. This thermometer allows the measurement of rf heating effects, temperature gradients, and thermal equilibration times; its use permits refinements in VT design and experimental protocol.

271 MULTIPLE QUANTUM NMR OF ISOTOPIC MIXTURES IN LIQUID CRYSTAL MATRIX.

K.V. Schenker, M. Gochin, D. Hugi-Cleary and A. Pines. Department of Chemistry, University of California, Berkeley, California 94720

NMR spectra of molecules dissolved in liquid crystals contain information about the intramolecular anisotropic dipole-dipole interaction of the spins. It is of interest to recover the dipolar coupling constants D_{ij} between each pair of spins since D_{ij} is proportional to $<(r_{ij})^{-3}>$. However the number of allowed transitions in the conventional NMR spectrum increases very rapidly with the number of active spins and the individual lines may no longer be resolvable. In case of ^{1}H-NMR, a solution of the problem is to use randomly deuterated samples which contain a mixture of all possible isotopomers of the molecule of interest. A highly deuterated sample will contain mostly isotopomers with just a few protons. Thus the task of interpreting one complex spectrum is reduced to one of analyzing a large number of simple but overlapping spectra. The crucial point is the ability to recognize the individual signals which derive from the same spin system (isotopomer). This can be achieved by the combined application of multiple quantum and two dimensional NMR techniques.

272 SOLID STATE DEUTERIUM NMR SPECTROSCOPY. A POWERFUL TECHNIQUE FOR ASSESSING MOLECULAR MOTION IN SOLIDS.

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Recent solid state deuterium NMR experiments have demonstrated that this technique is very powerful for uncovering the details of molecular motion in both biopolymers and in synthetic polymers. The deuterium NMR lineshape is sensitive to motions with correlation times in the 10^{-3} to 10^{-7} s regime, and deuterium T_1 experiments can be used to extend this range to much shorter correlation times. We illustrate the application of this technique with three examples. In the first example, solid state deuterium NMR spectroscopy is used to assess the degree of crystallinity in the conducting polymers poly-*p*-phenylene and polyacetylene. We find that the characteristic motions associated with the amorphous region in poly-*p*-phenylene are 180° flips of the aromatic rings. In the second example, deuterium NMR spectroscopy is used to associate phenyl ring flip with the β transition in polyarylene ether sulfones. Finally, deuterium NMR is used to investigate peptide-peptide aggregation that occurs during Merrifield solid phase peptide synthesis. This polymer-peptide system is a model for tethered biological systems, and shows that this technique holds much promise for the study of similarly immobilized systems in vivo.

273 A COMPARISON OF THE RESOLUTION OF THE CRAMPS (COMBINED ROTATION AND MULTIPLE-PULSE SPECTROSCOPY) EXPERIMENT AT TWO FIELDS.

Charles E. Bronnimann, Bruce L. Hawkins, and Gary E. Maciel, CSU Regional NMR Center, Dept. of Chemistry, Colorado State University Fort Collins, Colorado 80523.

The CSU Regional NMR Center is currently performing ^1H CRAMPS (Combined Rotation and Multiple-Pulse Spectroscopy) experiments on solid samples at proton frequencies of 187 and 360 MHz. In this paper we will present and discuss our approach to meeting the experimental requirements of proton multiple-pulse spectroscopy. Included will be brief discussions of the designs of the phase shifter, amplifier, probe and receiver. Experimental results at 187 and 360 MHz on a variety of compounds will be presented and compared, with the goal of determining the optimal (if any) field(s) for ^1H multiple-pulse experiments for different types of samples. Limits to resolution will be discussed.

274 ALTERNATIVE WAYS OF POLARIZATION TRANSFER FOR SOLIDS.

R.A. Wind, S.F. Dec, S.E. Emery and G.E. Maciel, Department of Chemistry, Colorado State University, Ft. Collins, CO 80523 and C.S. Yannoni, IBM Almaden Res. Center, 650 Harry Rd., San Jose, CA 95120.

Two alternative ways of polarization transfer between abundant and rare spins will be considered: (i) polarization transfer via the Nuclear Solid State Effect (1), in which polarization transfer is obtained by means of irradiation at a frequency $\omega = \omega_I + \omega_S$ or $\omega = \omega_I - \omega_S$ (ω_I and ω_S are the Larmor frequencies of the abundant and rare spins, respectively); (ii) polarization transfer via the Nuclear Solid State Effect in the rotating frame (2), which occurs when simultaneous irradiations are applied at the frequency ω_S with an amplitude ω_{1S}, and at the frequency $\omega = \omega_I + \omega_{1S}$ or $\omega = \omega_I - \omega_{1S}$. It will be shown that compared with the conventional way of polarization transfer (Hartmann-Hahn cross polarization) especially the first method has many advantages, like larger signals of the rare spins, quantitatively better results, excellent long term stability and applicability for rare spins with small γ values. The main disadvantage is the long polarization transfer time, and experiments will be described to improve this situation.

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2. N. Bloembergen and P.P. Sorokin, Phys. Rev. 110 (1958), 865.

275 LINE-NARROWING FOR MAGNETIC RESONANCE IMAGING IN SOLIDS

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NMR imaging is now recognized as an important technique in medical studies, however progress in applying this technique to materials science has been slow. The major problem has been the inherently broad resonance associated with the solid state. In this paper we will discuss methods for overcoming this problem. In particular, the use of multiple-pulse line-narrowing techniques are used to remove homonuclear dipolar broadening and/or chemical shift broadening. We will present examples of the application of these techniques to high natural abundance spin systems such as 1-H or 19-F, and to dilute systems such as 13-C, 29-Si, or 31-P.

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276 NMR IMAGING OF DILUTE NUCLEI IN THE SOLID STATE; M.F. Davis, M. Sardashti, S. Dec, S. Emery, R.A. Wind, G.E. Maciel, Department of Chemistry, Colorado State University, Ft. Collins, Colorado 80523.

In order to overcome the problems associated with the large homonuclear dipolar interactions that are associated with solid-sample NMR imaging via abundant nuclei, e.g., protons, our laboratory is generating NMR images using dilute nuclei, e.g., ^{13}C and ^{113}Cd.[1] In order to overcome the effects that rise and fall times of gradients can have on transverse magnetization in solids, $\pi/2$ "storage" pulses are used to store the nuclear magnetization along the B_0 axis during periods of gradient switching. The use of dynamic nuclear polarization (DNP) has allowed regions of a sample containing paramagnetic centers to be selectively imaged, while increasing the sensitivity of the imaging experiment.[2] In this talk we will review some of our past efforts and report on more recent results obtained in our laboratory in generating NMR images of solids using dilute nuclei.

1. N.M. Szeverenyi and G.E. Maciel, J. Mag. Res., **60**, 460 (1984).
2. M.F. Davis and G.E. Maciel, J. Mag. Res., **64**, 356 (1985).

277 MULTIPLE QUANTUM AND POLARIZATION TRANSFER TECHNIQUES IN NMR IMAGING AND SPECTROSCOPY, C. L. Dumoulin, General Electric Corporate Research and Development Center, PO Box 8, Schenectady, NY 12301

Many of the advanced experimental techniques developed for high resolution spectroscopy of chemical systems have applications to in-vivo systems as well. For example, multiple quantum filters can be used with imaging experiments to obtain images of only spin-spin coupled nuclei. Multiple quantum filters can also be used to selectively detect certain spin systems in a complicated set of spin systems. This capability is particularly important in light of the complexity of in-vivo ^1H spectra and the dominance of the water resonance. Another application of a high resolution spectroscopy technique to in-vivo spectroscopy is the use of polarization transfer between spin-spin coupled nuclei. In high resolution experiments heteronuclear polarization transfer has been typically used to increase the sensitivity of low gamma nuclei coupled to ^1H. Homonuclear polarization transfer experiments cannot be used to increase sensitivity but, can be used to selectively detect coupled spins. Information from specific spin systems can also be obtained by combining polarization transfer techniques with selective excitation methods.

278 NMR IMAGING USING LOOP-GAP RESONATORS J.P. Hornak, J. Szumowski, and R.G. Bryant. Department of Chemistry, Rochester Institute of Technology, Rochester, NY 14623. Departments of Radiology, Biophysics, and Chemistry, University of Rochester Medical Center, Rochester, NY 14642

Large volume loop-gap resonators (LGR) have been designed for use as both the transmitter and receiver probe in magnetic resonance imaging (MRI). A variety of possible designs makes the resonator suitable for imaging several anatomical parts of the body. The LGR is easily constructed and has a wide tuning range, making it useful for several nuclei. These resonators efficiently produce a uniform radio frequency magnetic field within their volume, resulting in equal rotation of all the spins within the resonator volume. This aspect makes the resonator particularly well suited for in vivo spectroscopy using MRI. Specific resonators have been constructed for imaging the head, arms, breasts, legs, and feet. A higher transmitter efficiency permits faster repetition rates in some imaging pulse sequences while adhering to the FDA specific absorption rate (SAR) limitations. Fewer averages, thinner image slices, and exceptional image clarity are possible due to an improved signal to noise ratio on the receiver side.

279 ABSTRACT NOT AVAILABLE

280 NMR IMAGING AND RELAXATION STUDY OF POLYMER SWELLING AND CHAIN DYNAMICS. T.H. MARECI, S. Dønstrup, Departments of Radiology and Physics, University of Florida, Gainesville, Florida and A. Rigamonti, Department of Physics "A. Volta", University of Pavia, Pavia, Italy

Nuclear magnetic resonance imaging has matured to the point where it has become a routine diagnostic procedure in medicine. We have been exploring the application of NMR imaging to problems in chemistry and physics. This talk will present our NMR study of the process of polymer swelling and dynamics of polymer chains in solution in real-time. In particular, a Fourier imaging sequence with T_1 and T_2 contrast was used to provide information on the phenomenology of the swelling process in the metastable states. At the same time, T_1 was measured in the high-resolution spectra of the region of the polymer being swollen to investigate local polymer chain dynamics while the concentration was changing by progressive swelling. These techniques will be illustrated with our study of the swelling of polymethylmethacrylate in normal and deuterated chloroform as solvents.

281 NMR IMAGING OF SOLID INTERFACES, D. L. Foxall, Varian-Fremont Operations, 1120 Auburn Street, Fremont, CA 94538

At the present time very few results have been published for applications of NMR imaging to non biological systems. This is unfortunate as the technique is potentially applicable to a wide variety of problems with scientific and commercial importance.

The aim of the presentation will be to explore through a series of examples the potential for NMR imaging to study the interaction between solid and liquid phases. The examples will include such diverse objects as plastics, glues, paints, rocks and wood. It is hoped that such a wide survey of materials will promote discussion on the applicability of NMR imaging to solve significant problems in materials science.

282 NATURAL ABUNDANCE C-13 SPIN EXCHANGE AS A PROBE OF MORPHOLOGY AND MOLECULAR TRANSPORT IN POLYMERS. D. L. VanderHart, Polymers Division, National Bureau of Standards, Gaithersburg, MD. 20899

This presentation will give some general perspectives on the use of C-13 spin exchange as a probe of local structure. The important topic of the relationship between exchange time and magnetization propagation distance will be addressed. We are particularly interested in exchange times in the range of a few seconds to several tens of seconds. It will be seen that even after a few tens of seconds, magnetization propagation distances are expected to be in the range of 0.6-1.0nm. This distance range is not easily probed by other NMR techniques. Based on these perspectives, an interpretation of some spin exchange data in native cellulose will be given to support the theory that certain celluloses contain two different crystalline forms. In another example, linear polyethylene, it will be shown that slow chain transport can be sensed because the transport makes the C-13 pair distribution time dependent. Up to a point, as chain transport becomes faster, the spin exchange times approach the ensemble-average spin exchange time rather than reflect the statistical distribution of pair separations. A rough modelling of these effects not only gives an estimate of the average lifetime of a chain on a lattice site, but also yields information on whether the diffusion of chains is a bounded or unbounded process. Finally, differences in C-13 spin exchange behavior with or without magic-angle spinning will be considered.

283 ORTHOGONAL INDIRECT DETECTION OF NMR SPINOR TRANSITIONS. Dieter Suter and Alex Pines, Department of Chemistry, University of California, Berkeley, California 94720 and Michael Mehring, Physikalisches Institut 2, Universität Stuttgart, D-7000 Stuttgart, West Germany.

The well-known property of a spin-1/2 particle to change sign under 2π - rotation has been exploited recently (M. Mehring, P. Hofer, A. Grupp and H. Seidel, Physics Letters, 106, 146 (1984)) in a pulsed ENDOR experiment. In this spinor-ENDOR experiment a 2π - pulse is applied to the NMR transition during an ESE sequence, thereby inverting the sign of the quantum mechanical state function and the connected ESR transition. This 200% ENDOR effect is not always realised in practice since the inverted resonance coincides with resonances which are not coupled to NMR transitions and accordingly do not change sign. This can be avoided in a modified version of the experiment where the nuclear spin is not rotated around an axis in the x,y - plane, but around the z axis. If the nuclear spin is rotated by ψ, the connected ESR transition is phase shifted by $\pm\frac{\psi}{2}$. A π_z - pulse therefore shifts the ESR echo signal into the orthogonal, otherwise empty detection channel. The rotation around the z-axis can be achieved e.g. by a composite z - pulse, phase shifted π - pulses or differential precession. The experimental scheme may be extended to spins (or pseudospins) $S > \frac{1}{2}$.

284 CHEMICAL SHIFT PERTURBATIONS IN ION-CONTAINING COPOLYMERS, LIQUID CRYSTALS AND POLYMER BLENDS--MISCIBILITY DETECTION VIA HYDROGEN BONDING. Laurence A. Belfiore, Department of Agricultural and Chemical Engineering, Colorado State University, Fort Collins, Colorado 80523

Various examples illustrate the use of high-resolution carbon-13 NMR (CP/MAS) to detect partial or complete miscibility in polymer-polymer and polymer-liquid crystal solid state blends. Intermolecular effects on the isotropic chemical shift interaction provide evidence that segments of dissimilar chains are well-mixed. Differential thermal analysis supports the NMR results and allows one to distinguish between partial and complete miscibility, particularly when one of the components exhibits solid-solid, solid-liquid, or liquid-liquid first-order thermodynamic transitions. Neutralization of ethylene/methacrylic acid random copolymers with either sodium, zinc, or thallium counterions produces a distribution of carboxyl-carbon chemical shifts, most of which are more deshielded than that in the unneutralized copolymer. This suggests that hydrogen bonding might be responsible for the chemical shift perturbations since the neutralized methacrylic acid segments of the ionomer are limited with respect to their hydrogen-bonding potential. Support for this claim is derived from the chemical shift perturbations observed in model polymer-polymer blends of poly(ethylene oxide) and poly(acrylic acid). In this system, both the carboxyl carbon of the acid and the methylene carbon of the oxide reveal chemical shifts that are more shielded in the blends relative to those in the undiluted homopolymers. The composition-dependent miscibility of this model blend is governed by the propensity for intermolecular hydrogen bonding versus the driving force for poly(ethylene oxide) crystallization.

285 CHEMICAL EXCHANGE IN ZERO-FIELD NMR. P. Jonsen, M. Luzar, and A. Pines, Department of Chemistry, University of California, Berkeley, California 94720 and M Mehring, P. Meier and G. Kothe, University of Stuttgart, West Germany.

The quadrupolar and dipolar Hamiltonians are sensitive to molecular motion. In zero-field NMR, the spectra are characterized purely by these local interactions. Theories are presented which describe the effect of molecular motion on zero-field NMR spectra and demonstrate the potential of this novel technique in the investigation of molecular dynamics.

AUTHOR INDEX

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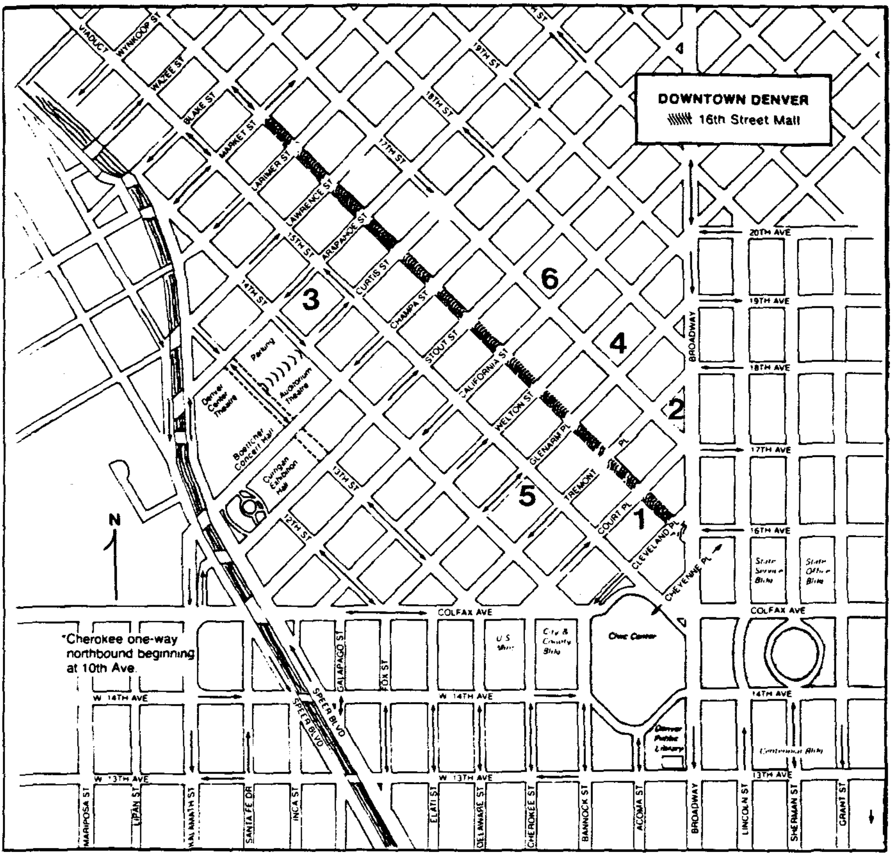


Map Legend

1 Radisson Hotel Denver

2 Brown Palace Hotel

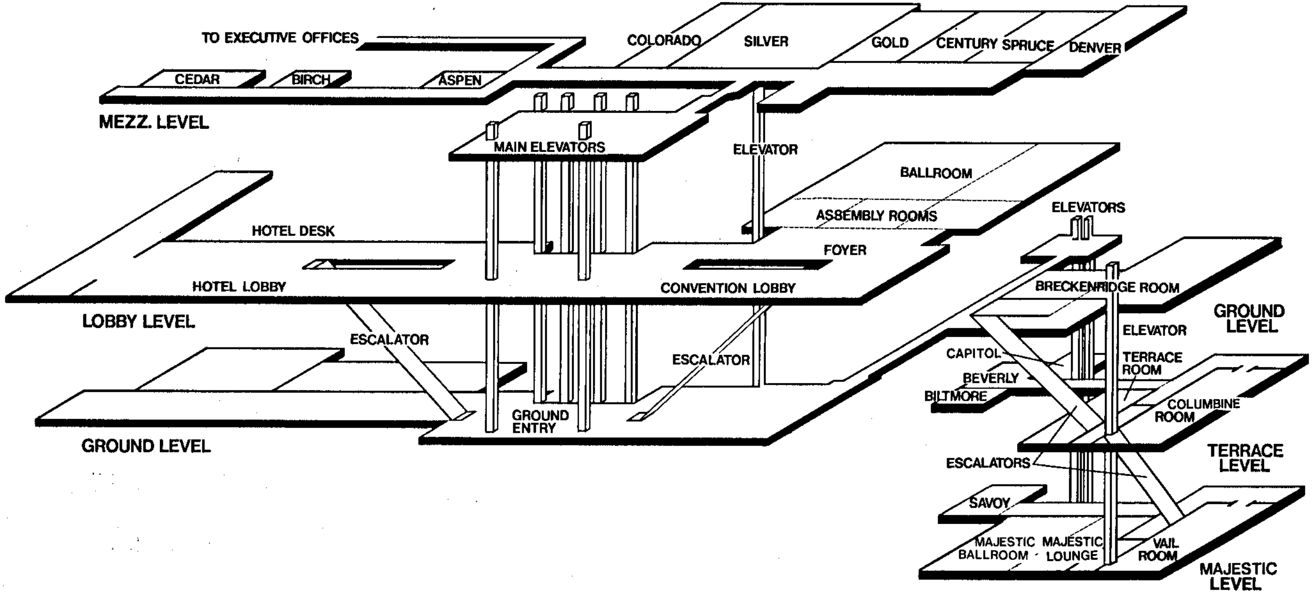
3 Executive Tower Inn

4 Fairmont Hotel

5 Holiday Inn-Downtown

6 Marriott City Center

CONVENTION CENTER COMPLEX



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