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27th Rocky Mountain Conference

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27th Rocky Mountain Conference

Abstract

Program and abstracts from the 27th 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, July 14-18, 1985.

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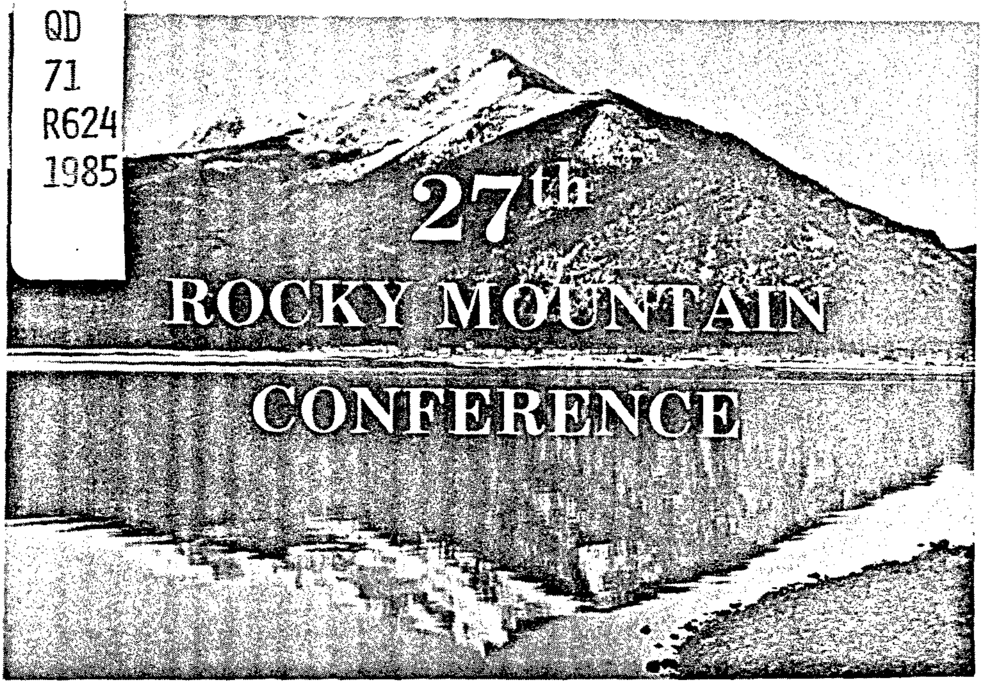
Publication Statement



27th
ROCKY MOUNTAIN CONFERENCE

Program
&
Abstracts

JULY 14-18, 1985

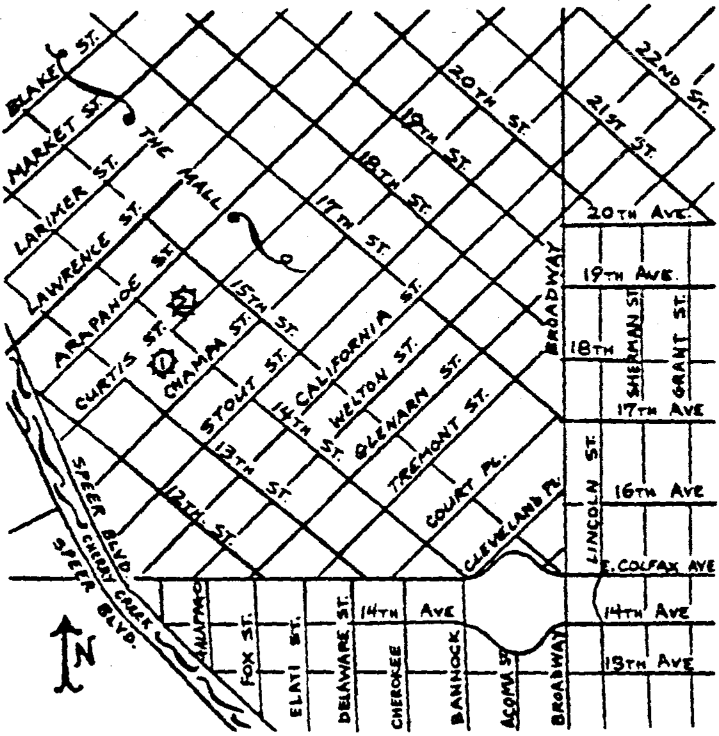
1323 Champa St.
Denver Convention Complex
Denver, Colorado

Sponsored Jointly By:

Rocky Mountain Section
Society for
Applied Spectroscopy

Rocky Mountain
Chromatography
Discussion Group

DOWNTOWN DENVER



1. CONVENTION COMPLEX
2. EXECUTIVE TOWER INN

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WELCOME

This is our 27th annual conference in Denver. The conference goal is to promote the exchange of ideas and work efforts in the sciences involving spectroscopy, chromatography and analytical chemistry.

The formal aspects of the conference appear to offer an outstanding program. There will be 357 oral and poster presentations in 12 symposia. The 72 exhibits offer a unique opportunity for you to meet with the representatives of manufacturers and service groups and discuss their latest offerings. Several social events are planned which will offer opportunities to mix and mingle. Finally, because Denver and Colorado offer great vacation opportunities, we have offered a spouses and family program to show off some of Colorado during the week.

We hope this year you will be stimulated by the people you meet and will return home excited to try out a new idea or to finish off that project that will answer the questions raised during the meeting.

We are proud to offer this conference. We thank you for participating and sharing your ideas and experiences.

Sincerely,
F E Lichte
F. E. Lichte
Conference Chairman

FUTURE ROCKY MOUNTAIN CONFERENCE DATES

August 3 - 8, 1986

July 26 - 31, 1987

July 30 - August 5, 1988

July 29 - August 4, 1989

REGISTRATION INFORMATION

Admission to all technical sessions requires a 27th Rocky Mountain Conference name badge (Vendors and conferees will have different color badges to allow vendors the opportunity to set up their booth before the area is open to the general public.).

REGISTRATION FEES

Registration at Conference	$45.00
Registration one day only	$25.00
Students	$10.00
Unemployed or retired	No charge
Vendors	Look at your packet from exhibits chairman, Vanessa Bush.

Admission to the Exhibit Area and Film Festival by conferee family members is free, but a ticket must be obtained at the registration desk. If family members of conferees want to attend technical sessions, then the appropriate fee must be paid.

REGISTRATION HOURS AND LOCATION

Sunday	July 14	Denver Convention Complex	4:00 p.m.- 8:00 p.m.
Monday	July 15	Denver Convention Complex	7:30 a.m.- 3:30 p.m.
Tuesday	July 16	Denver Convention Complex	7:30 a.m.- 3:30 p.m.
Wednesday	July 17	Denver Convention Complex	7:30 a.m.- 3:30 p.m.
Thursday	July 18	Denver Convention Complex	7:30 a.m.- 11:30 a.m.

The address for the Denver Convention Complex is 1323 Champa St., Denver, Colorado.

VISITOR INFORMATION

Information on the Denver area may be obtained from the Denver Convention and Visitors Bureau, 225 West Colfax Avenue, Denver, Colorado 80202 Phone: (303) 892-1112

27th ROCKY MOUNTAIN CONFERENCE SOCIAL FUNCTIONS

REGISTRATION NIGHT MIXER - A cash bar mixer will be held in the Beethoven Room of the Executive Tower Inn from 7:00-9:00 p.m. July 14th. Plan to meet your early arriving friends there.

CONFERENCE MIXER - All conference attendees and spouses are cordially invited to attend a mixer on Monday, July 15, 1985 from 5:00 p.m. to 7:30 p.m. at the Executive Tower Inn.

BANQUET - A Conference Banquet will be held on Tuesday, July 16th, 1985 at 7:00 p.m. in the Ballroom of the Executive Tower Inn. Tickets are $16.00 per person. There will be a cash bar in the banquet area beginning at 6:00 p.m.

Our after dinner speaker this year will be Dr. John B. Newkirk. Dr. Newkirk's title will be "Applications of Modern Materials for Repairs of the Human Machine". Dr. Newkirk is Prof. Emeritus of Metallurgical Engineering at Denver University and President of Denver Biomaterials. Following the cash bar and banquet, this speaker should have a very attentive audience.

RECEPTION AND PARTY AT COORS - On Wednesday evening July 17th, 1985 Coors Brewery will host a reception. The evening will consist of a plant tour, late evening snacks and dancing. Beer, (Coors brand only), soft drinks, cheese, and crackers etc. will be furnished by Coors. Coors hosts these parties to promote good will and provides an entire evening of entertainment free of charge. However, the conference will provide transportation from the Executive Tower Inn and return plus a continuation bus to the dormatories at Denver University. Therefore, a charge will be made of $5.00 per person attending this function. We will leave from the Executive Tower Inn at 7:00 p.m. and return around midnight. Registration is limited to 150 people, register early.

FAMILY PROGRAM

A special effort is being made this year to ensure that accompanying spouses and children have a good time while the technical sessions are being held. Hannah Goldberg will be the hostess for a variety of events Monday, Tuesday and Wednesday.

Monday July 15th There will be a guided walking tour of historic downtown Denver. This tour will begin at 2:00 p.m. and last for 2 hours. There will be a $4.00 per person charge and is well worth the cost. Meet at the Executive Tower Inn at 1:30 p.m.

Tuesday July 16th A Gray Line tour is planned that will travel into the mountains passing through Bergen Park, Idaho Springs, Echo Lake, and finally stopping in Georgetown for souvenir shopping and lunch. The tour begins at 9:00 a.m. and lasts for 6 hours. There will be a stop for lunch which is not provided in the $13.00 per person charge. Children 12 and under will be $6.50.

Wednesday July 17th Today, Hannah has planned a bus tour through and around Denver. Starting time will be 12:30 p.m from the Executive Tower Inn. Special tours will include the historic Molly Brown house and the State Capitol. The tour will end about 5:00 p.m. at the Exceutive Tower Inn. The cost will be $10.00 per person. Children 12 and under will be $5.00.

Other: Downtown Denver is alive and well. There are plenty of shops and restaurants within easy walking distance from the hotels and convention complex. The newly opened Tabor Center just adds to the life of Larimer Square and the 16th St. Mall. Your families may even have a better time than you.

FILM FESTIVAL

A series of films will be shown during the conference. The titles and schedule will be displayed on the bulletin board by the registration desk. This will be free of charge for conference attendees and families.

MESSAGE CENTER

A Message Center will be set up for conference attendees in the registration area. The telephone number is (303) 623-3838. The message center will be open from 8:00 a.m. to 4:30 p.m. (MDT) Monday through Thursday. This service is for incoming calls only.

There are numerous pay telephones in the Convention Complex for outgoing calls.

EMPLOYMENT CLEARING HOUSE

An Employment Clearing House Area will be provided in the Poster Display area during the Conference.

Bulletin board space will be provided for employers to post job announcements. There also will be a notebook provided for conferees to post resumes.

The Conference (Employment Clearing House) assumes no obligation for the qualification of job candidates, confidentiality of information exchanged, or the responsibility of employers.

EXHIBITS INFORMATION

An important facet of the Rocky Mountain Conference is the contribution made by the manufacturers and service organizations who buy space on our convention floor to specifically meet you. In the Rocky Mountain area this exhibit offers a unique opportunity to discuss with the representatives the latest innovations in instrumentation or the latest services offered by these organizations.

The exhibit area will be open to the conferees on:

Monday, July 14, 1985	10:00 a.m. to 6:00 p.m.
Tuesday, July 15, 1985	9:30 a.m. to 6:00 p.m.
Wednesday, July 16, 1985	9:30 a.m. to 3:00 p.m.

Families of conferees may visit the exhibit area free of charge, but they will need to pick up a ticket a the Registration Desk before they will be allowed entrance.

CONFERENCE EXHIBITORS

	Booth No.
Air-Row Enterprises	48
R.H. Allen Co.	44
Allied Analytical Systems	72
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Bioanalytical Systems	47
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General Electric	9
Gow-Mac Instruments Co.	17
Hach Co.	7
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Lachat	53
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Oxford Instruments North America, Inc.	68
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ORGANIZERS OF THE 27TH ROCKY MOUNTAIN CONFERENCE

Conference Chairperson - F. E. Lichte, USGS, Box 25046, MS 928, DFC, Denver, CO 80225 (303) 236-1941

Conference Chairperson (28th RMC) - R. M. Barkley, CIRES, Campus Box 449, University of Colorado, Boulder, CO (303) 492-1158

Treasurer - Glenda Brown, Rockwell International, P. O. Box 464, Golden, CO 80401 (303) 497-7817

Registration - Carol Gies, Rockwell International, P.O. Box 464, Golden, CO 80401 (303) 497-7380

Exhibits/Facility - Vanessa Bush, Adolph Coors, Golden, CO 80401 (303) 277-6078 and Jeff Otto, Cord Labs, 2555 W. Midway Blvd., Broomfield, CO 80020 (303) 469-2131 X214

Printing - Kim Zilas, Rocky Mountain Analytical, 5530 Marshall, Arvada, CO 80002 (303) 421-6611

Publicity - Mike Brooks, Rocky Mountain Analytical, 5530 Marshall, Arvada, CO 80002 (303) 421-6611

Social Functions - Greg Johnson, Molycorp, Inc., P. O. Box 37, Louviers, CO 80131 (303) 798-8355 and Larry Lockrem, Reservoirs Inc., 1827 Grant St., Denver, CO 80203 (303) 830-1986

Poster Session/Seminar - 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

Atmospheric Chemistry, D. H. Stedman, Dept. of Chemistry, University of Denver, Denver, CO 80208. (303) 871-3530

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

Chromatography, Kenneth C. Brooks, Dept. of Chemistry, University of Colorado at Denver, 1100 14th St., Denver, CO 80202. (303) 556-3202

Electrochemistry, Carl Koval, Dept. of Chemistry, Box 215, University of Colorado, Boulder, CO 80309. (303) 492-5564 and Mike Elliott, Dept. of Chemistry, Colorado State University, Fort Collins, CO 80523 (303) 491-5391

Environmental, Michael Reddy, USGS, 5293 Ward Rd., Arvada, CO 80002. (303) 236-3617

EPR, G. Eaton and S. Eaton, Dept. of Chemistry, University of Denver, Denver, CO 80208. (303) 871-2980

Flow Injection, C. B. Ranger, Lachat Chemicals, Inc., 10500 N. Port Washington Rd., Mequon, WI 53092-5593 (414) 241-3872

ICP/Mass Spec., H. E. Taylor, USGS, 5293 Ward Rd., Arvada, CO 80002. (303) 236-1928

IR/Luminescence, Marvin Goldberg, USGS, P. O. Box 25046, MS 424, Denver Federal Center, Denver, CO 80225. (303) 236-4728

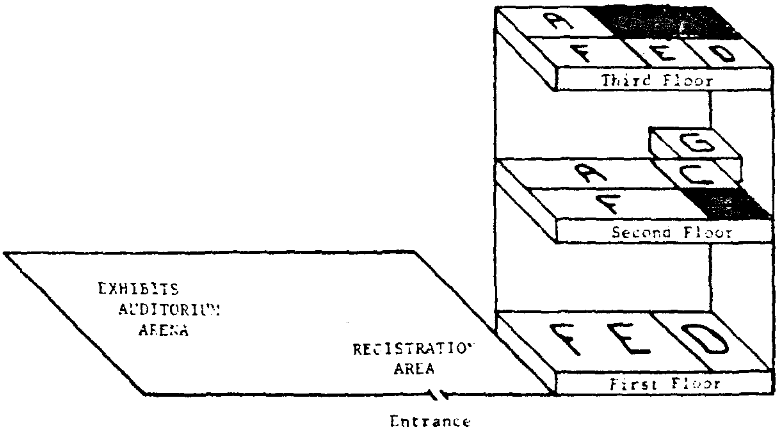
Ion Chromatography, Art Hedley, USGS, 5293 Ward Rd., Arvada, CO 80002. (303) 236-3614

Mass Spectroscopy, Mike Bergeron, Rockwell International, P. O. Box 464, Golden, CO 80401 (303) 497-4793 and Paul Fennessey, CU Medical School, 4200 East 9th Ave., Denver, CO 80220 (303) 394-7286

NMR, Fran Miknis, University of Wyoming Res. Corp., Box 3395, Laramie, WY 82071. (307) 721-2307 FTS 328-4307

TECHNICAL PROGRAM

	Floor/Room	Morning	Floor/Room	Afternoon
Monday July 15	2F	Atomic Spectroscopy	2F	Atomic Spectroscopy
	3F	Chromatography	3D	Electrochemistry
	3D	Electrochemistry	2A	Environmental
	2A	Environmental	2G/1F	EPR, Session II & III
	2G	EPR, Session I	3E	Flow Injection
	3A	Ion Chromatography	3A	Ion Chromatography
	3E	Mass Spectroscopy	3F	Mass Spectroscopy; Biomedical
Tuesday July 16	3E	Atmospheric Chemistry	3E	Atmospheric Chemistry
	2F	Atomic Spectroscopy	3F	Chromatography/Mass Spectroscopy
	3F	Chromatography		
	2A	Environmental	2A	Environmental
	2G	EPR Session IV	2G	EPR, Session V
	3A	Ion Chromatography	2F	ICP-MS
	3D	Luminescence Spectroscopy	3A	Ion Chromatography
			3D	Luminescence Spectroscopy
			2C	NMR
Wednesday July 17	3E	Atmospheric Chemistry	3E	Atmospheric Chemistry
	2F	Atomic Spectroscopy	3F	Biological Applications of Chromatography
	2A	Environmental/Mass Spectroscopy	2A	Environmental/Mass Spectroscopy
	2G	EPR, Session VI	1F	EPR, Session VII
	1F	General Session - Posters	3D	Infrared Spectroscopy
	3D	Infrared Spectroscopy	2F	ICP-MS
	3A	Ion Chromatography	3A	Ion Chromatography
	2C	NMR	2C	NMR
Thursday July 18	3A	Atmospheric Chemistry	2F	EPR, Session IX
	2G	EPR, Session VIII	2A	Infrared Spectroscopy
	2F	ICP-MS		
	2A	Infrared Spectroscopy		
	2C	NMR		



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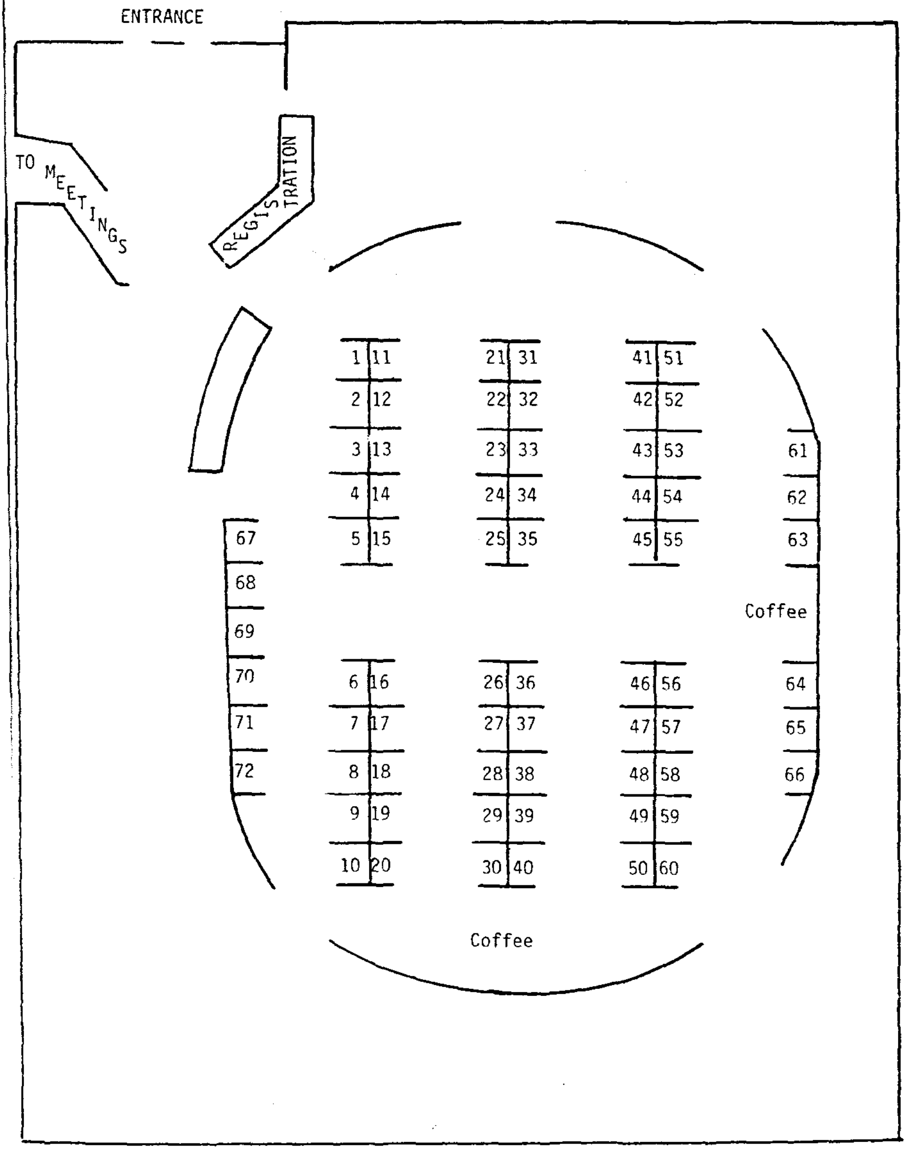
VG Instruments	26,27,36,37
Varian	57
Waters Assoc.	20
Wescan Instruments Inc.	6
Wilmad Glass Co, Inc.	42
Zymark Corp	50



4:40 25. MEASUREMENTS OF FORMATE AND ACETATE IN PRECIPITATION AND AEROSOLS. R.B. Norton, National Oceanic and Atmospheric Administration, Boulder.

THURSDAY MORNING, July 18, 1985 - Third Floor, Room A
Dr. H. Niki, Presiding

9:30 26. STUDIES AIMED AT UNDERSTANDING PHOTOCHEMICAL PRODUCTION OF OZONE IN THE NON-URBAN TROPOSPHERE. F.C. Fehsenfeld, National Oceanic and Atmospheric Administration, Boulder.

10:30 COFFEE BREAK

11:00 27. MEASUREMENTS OF NO_y IN THE RURAL TROPOSPHERE. D.W. Fahey, National Oceanic and Atmospheric Administration, Boulder.

11:30 28. MEASUREMENT OF NO AND NO_2 AT NIWOT RIDGE COLORADO. P.C. Murphy, Cooperative Institute for Research in Environmental Sciences, Boulder.

SANDWICH LUNCH BUS TO NIWOT RIDGE LEAVES AT 12:10
FROM THE FRONT DOOR OF THE CONFERENCE CENTER

SYMPOSIUM ON ATOMIC SPECTROSCOPY SYMPOSIUM

Chairman: T. M. Niemczyk

MONDAY MORNING, July 15, 1985 - Second Floor, Room F
James A. Holcombe, Presiding

8:30 29. THE ANALYSIS OF SOLID SAMPLES BY GRAPHITE FURNACE ATOMIC ABSORPTION USING ZEEMAN BACKGROUND CORRECTION. G. R. Carnrick and B. K. Lumas, Perkin-Elmer Corporation, 4036 Youngfield, Wheat Ridge, CO 80033; W. B. Barnett and R. H. Hergenreder, Perkin-Elmer Corporation, MS 906, 901 Ethan Allen Highway, Ridgefield, CT 06877

8:50 30. AQUEOUS TOTAL CHROMIUM: PROBLEMS WITH PERMANGANATE OXIDATION; A POTENTIAL SOLUTION WITH CERIUM (IV). Edward W. Matthews and Ronald C. Hooper, U.S. Geological Survey National Water Quality Laboratory-Atlanta, 6481-H Peachtree Industrial Boulevard, Doraville, GA 30340.

9:10 31. SECOND SURFACE ATOMIZATION; ANALYTICAL FLEXIBILITY AND INTERFERENCE REDUCTION FOR GRAPHITE FURNACE AA. T. M. Rettberg and J. A. Holcombe. Department of Chemistry, University of Texas, Austin, TX 78712.

9:30 32. REDUCTION OF FURNACE INTERFERENCES BY DELAYED ATOMIZATION TECHNIQUES. J. J. Roberts, G. R. Dulude, M. C. Almeida, and J. J. Sotera. Allied Analytical Systems, 590 Lincoln Street, Waltham, MA 02254.

9:50 BREAK

10:20 33. UTILIZATION OF HYDRIDE GENERATION FOR THE DETERMINATION OF AS AND SE IN COMPLEX MATRICES. L. M. Voth, K. G. Brodie, B. Frary, Varian Instrument Group, 205 W. Touhy Avenue, Park Ridge, IL 60068.

10:00 62. THE APPLICATION OF HEADSPACE, DIRECT INJECTION, AND SNIFF PORT GAS CHROMATOGRAPHY IN THE ANALYSIS OF FLAVOR COMPONENTS IN FOOD PRODUCTS. Margaret K. Conditt, The Proctor & Gample Company Food Products Division, Cincinnati, OH.

10:20 63. REDOX CHEMILUMINESCENCE DETECTION OF LIGHT GASES. R. Shearer and R. E. Sievers, University of Colorado, Boulder, CO.

10:40 64. REDOX CHEMILUMINESCENCE DETECTOR: A NEW DETECTOR FOR GAS CHROMATOGRAPHY. R. S. Hutte, Sievers Research Inc., Boulder, CO and R. E. Sievers, University of Colorado, Boulder, CO.

11:20 65. INJECTION TECHNIQUES USED IN CAPILLARY GAS CHROMATOGRAPHY. A. D. Bashall, Erba Instrument, Peabody, MT.

11:40 66. THE ANALYTICAL CHEMISTS: HOW THEY CONTRIBUTE TO THE DEVELOPMENT OF AN EFFECTIVE DRUG SUBSTANCE. Orville N. Hinsvark, Penwalt Corp., Pharmaceutical Division, Rochester, NY.

TUESDAY MORNING, July 16, 1985 - Third Floor, Room F
Session II - HIGH PERFORMANCE LIQUID CHROMATOGRAPHY
J. N. Gillis, Presiding

8:15 67. POLAR ORGANIC COMPOUND ANALYSIS--HPLC OR IC? Jack Korpi, Claudra Lincoln, Leonard Henry, Rosanne Slingsby, William Edwards, Dionex Corp., Sunnyvale, CA.

8:35 68. THE CLASS SEPARATION OF POLYCYCLIC AROMATIC HYDROCARBONS, NITROGEN HETEROCYCLES AND HYDROXYL AROMATRICS BY LIQUID CHROMATOGRAPHY. S. C. Ruckmick and R. J. Hurtubise, University of Wyoming, Laramie, WY.

8:55 69. SOLVENT SELECTION FOR METAL CHELATE SEPARATION BY LIQUID AND THIN LAYER CHROMATOGRAPHY. B. Wenclawiak, University of Munster, Munster, West Germany and R. E. Sievers, University of Colorado, Boulder, CO.

9:15 70. QUANTITATIVE DETERMINATION OF COMPOUND CLASSES IN JET TURBINE FUELS BY HPLC/DIFFERENTIAL REFRACTIVE INDEX DETECTION. C. W. Sink, Edinboro University of Pennsylvania, Edinboro, PA.

9:35 BREAK

10:10 71. **PLENARY LECTURE**
CHROMATOGRAPHIC SEPARATIONS UTILIZING COLVALENT INTERACTIONS. M. F. Burke, University of Arizona, Tuscon, AZ.

11:10 72. POLYMER SEPARATIONS USING CHEMICALLY BONDED LIQUID CHROMATOGRAPHY. Shi-Tse Lai and Michael Locke, Rockwell International, Newport Beach, CA.

11:30 73. PACKED COLUMN SUPERCRITICAL FLUID CHROMATOGRAPHY FOR THE SEPARATION OF METAL CHELATES. B. Wenclawiak, University of Munster, Munster, West Germany.

TUESDAY AFTERNOON, JULY 16, 1985 - Third Floor, Room F
Session III: Detection in HPLC
Jointly Sponsored by Symposia on Chromatography and Mass Spectrometry
B. Wenclawiak, Presiding

1:20 74. **PLENARY LECTURE** - NEW DEVELOPMENTS & RECENT APPLICATIONS OF THERMOSPRAY LC-MS. M. Vestal, University of Houston, Houston, TX

2:20 75. MASS SPECTRAL CHARACTERIZATION OF PAF AND OTHER PHOSPHOLIPIDS. K. L. Clay and R. C. Murphy, University of Colorado Health Sciences Center, Denver, CO.

2:40 76. SELECTIVE DETECTION OF ORGANOSULFUR COMPOUNDS ON HPLC VIA FLUORINE-INDUCED CHEMILUMINESCENCE. E. A. Mishalanie and J. W. Birks, University of Colorado, Boulder, CO.

3:00 BREAK

3:40 77. HPLC DETECTION OF SINGLET OXYGEN SENSITIZERS. Curtis Shellum and John W. Birks, University of Colorado, Boulder, CO.

4:00 78. WHOLE COLUMN DETECTION: A MULTIDIMENSIONAL SEPARATION TECHNIQUE. PART I. David G. Gelderloos, Kathy L. Rowlen, John W. Birks, James P. Avery, and Christie G. Enke. University of Colorado, Boulder, CO.

4:20 79. WHOLE COLUMN DETECTION: A MULTIDIMENSIONAL SEPARATION TECHNIQUE. PART II. David Gelderloos, Kathy L. Rowlen, John W. Birks, James P. Avery, and Christie G. Enke, University of Colorado, Boulder, CO.

4:40 80. ION CHROMATOGRAPHIC DETERMINATION OF OXALATE IN URANIUM RECOVERY SOLUTIONS. S. J. Van Hook, III, R. W. Smithwick, III, and N. J. Williams, Martin Marietta at Oak Ridge, Oak Ridge Y-12 Plant, Martin Marietta Energy Systems, Inc., P. O. Box Y, Building 9995, Oak Ridge, TN.

WEDNESDAY AFTERNOON, July 17, 1985 - Third Floor, Room F
Session IV: Biomedical Applications of Chromatography
K. C. Brooks, Presiding

1:10 81. HPLC AS A TOOL FOR THE STUDY OF BACTERIA. Robert W. Looyenga and Jane Roseland, South Dakota School of Mines and Technology, Rapid City, SD.

1:30 82. AN IMMUNOAFFINITY CHROMATOGRAPHIC ASSAY WITH AMPEROMETRIC DETECTION. U. de Alwis and G. S. Wilson, University of Arizona, Tuscon, AZ.

1:50 83. APPLICATION OF MONOCLONAL ANTIBODIES TO ANALYTICAL DETERMINATION. R. G. Nielsen and G. S. Wilson, University of Arizona, Tucson, AZ.

2:10 84. DETERMINATION OF AVERMECTIN IN CITRUS BY REVERSED PHASE LIQUID CHROMATOGRAPHY WITH FLUORESCENCE DETECTION. Jeffrey J. Jenkins and Janice Cobin, Merck Sharp and Dohme, Research Laboratories, Three Bridges, NJ.

10:40 34. DETERMINATION OF METALS AND CATIONS IN THE CLINICAL LABORATORY BY ATOMIC EMISSION AND ATOMIC ABSORPTION SPECTROMETRY. Joseph Sneedon, Janet Munro, Timothy A. Tapia, Andriana Uranga, Mark Rodriquez, and Cathy A. Hernandez, New Mexico State University, Las Crusas, NM 58003.

11:00 35. COMPARISON OF AA, ICP AND ION CHROMATOGRAPHY FOR MEASUREMENT OF METALS. Richard Rubin, Denise Eubanks, Shawn Heberling, John Riviello, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088.

MONDAY AFTERNOON, JULY 15, 1985 - Second Floor, Room F
Thomas M. Niemczyk, Presiding

1:30 36. **KEYNOTE SPEAKER**

INTERFACING LIQUIDS TO PLASMAS AND FLAMES: NEW ANSWERS TO OLD PROBLEMS. Richard F. Browner, School of Chemistry, Georgia Institute of Technology, Atlanta, GA 30332.

2:20 37. FACTORS LIMITING AEROSOL TRANSPORT IN NEBULIZATION CHAMBERS, R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, CO 80523; Kurt Kronholm, 1583 Oakwood Avenue, Des Plaines, IL 60016.

2:40 38. LATERAL DIFFUSION INTERFERENCES IN FLAMES AND PLASMAS. R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, CO 80523; S. J. Freeland, Chemagnetics, Inc., 208 N. Commerce Drive, Fort Collins, CO 80524; Kurt Kronholm, 1583 Oakwood Avenue, Des Plaines, IL 60016.

3:00 BREAK

3:30 39. SLURRY ANALYSIS BY INDUCTIVELY COUPLED PLASMA USING CONVENTIONAL NEBULIZATION. Susan E. Knauf, J. D. Nohe, Instruments SA, Inc., 173 Essex Avenue, Metuchen, NJ 08840.

3:50 40. USE OF SIGNAL VS. TIME PROFILES TO OPTIMIZE ELECTROTHERMAL VAPORIZATION-INDUCTIVELY COUPLED PLASMA SPECTROSCOPY. M. W. Tikkanen, Scientific Laboratory Division, State of New Mexico, 700 Camino de Salud, NE, Albuquerque, NM, 87106; T. M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131.

4:10 41. SENSITIVITY ENHANCEMENT OF TRACE ELEMENT DETERMINATIONS BY ELECTROTHERMAL ATOMIZATION INTO AN ICP EMISSION SPECTROMETER. R. M. Manabe, D. D. Nygaard, and D. A. Leighty, Allied Analytical Systems, 590 Lincoln Street, Waltham, MA 02254.

4:30 42. TRACE ELEMENT ANALYSIS OF SILICATE ROCKS BY DIRECT INSERTION OF A GRAPHITE CUP INTO AN ICP. I. B. Brenner, Geological Survey of Israel, and A. Lorber and Z. Goldbart, Negev Center for Nuclear Research, Beersheva, Israel.

TUESDAY MORNING, July 16, 1985 - Second Floor, Room F
Joseph A. Caruso, Presiding

8:10 43. LABORATORY INFORMATION MANAGEMENT. Art Ambrose, Perkin-Elmer Corporation, 4036 Youngfield St., Wheat Ridge, CO 80033.

2:30 BREAK

3:00 85. HPLC/EC DETERMINATION OF SELECTED VETERINARY DRUGS IN TISSUES. Jeffrey A. Hurlbut, Jose E. Roybal, Robert K. Munns, and Wilbert Shimoda, Food and Drug Administration, Denver, CO.

3:20 86. REVERSED-PHASE HPLC OF NUCLEOSIDES, NUCLEOTIDES, DI-AND TRINUCLEOTIDES. Allen M. Schoffstall, Elizabeth Miller, Eaton M. Laing and Nancy J. Getzinger, University of Colorado at Colorado Springs, Colorado Springs, CO.

3:40 87. HPLC STUDY NADH DEGRADATION PRODUCTS WITH ELECTROCHEMICAL DETECTION. Mumtaz H. Shah, Elan Pharmaceutical Research Corp., Gainsville, GA.

4:00 88. PEPTIDE SEPARATIONS USING POLYMERIC ION-EXCHANGE COLUMNS. Paula Mychak and James R. Benson, Interaction Chemicals, Inc., Mountain View, CA.

4:20 89. BEVERAGE ANALYSIS USING POLYMERIC COLUMNS. Dexter J. Woo, Bart Paulsen, and James R. Benson, Interaction Chemicals, Inc., Mountain View, CA.

SYMPOSIUM ON ELECTROCHEMISTRY

Co-Chairmen: C. A. Koval and C. M. Elliott

MONDAY MORNING, July 15, 1985 - Third Floor, Room D
C. A. Koval, Presiding

8:30 90. ELECTROCHEMISTRY, SPECTROSCHEMISTRY AND PHOTOREDOX CHEMISTRY OF MIXED PHOTOCENTER/DONOR/ACCEPTOR COMPLEXES. C. M. Elliott, R. A. Freitag and Jon Merkert, Colorado State University, Fort Collins, Colorado

9:10 91. KINETICS AND THERMODYNAMICS OF ELECTRON TRANSFER REACTIONS INVESTIGATED BY SQUARE WAVE VOLTAMMETRY. Cindy M. Reidsema and Carl A. Koval, University of Colorado, Boulder, Colorado

9:45 BREAK

10:15 92. ELECTROCHEMICAL STUDIES OF IRON PORPHYRINS AND HYDROPORPHYRINS. Steve H. Strauss and Ronald G. Thompson, Colorado State University, Fort Collins, Colorado

10:50 93. ELECTROCHEMISTRY IN TOLUENE. L. Geng, J. Jernigan and Royce W. Murray, University of North Carolina, Chapel Hill, North Carolina

11:35 94. ELECTROCHEMICAL STUDIES OF TWO-ELECTRON REDOX PROCESSES OF Ni and Pd COMPLEXES. Daniel Dubois, and Alex Miedaner, Solar Energy Research Institute, Golden, Colorado

MONDAY AFTERNOON, July 15, 1985 - Third Floor, Room D
C.M. Elliott, Presiding

1:30 95. WEIGHING AN ELECTRODE SURFACE - QUARTZ MICROBALANCE. J.G. Gordon II, K.K. Kanayawa, Owen Melroy, D. Buttry, T. Li and R. Schumacher, IBM Research Laboratory, San Jose, California

2:15 96. ION TRANSPORT IN ELECTROACTIVE POLYMER FILMS. C.M. Elliott and J.G. Redepenning, Colorado State University, Fort Collins, Colorado

2:50 BREAK

3:20 97. TRANSPORT NUMBERS IN 1-METHYL-3-ETHYLIMIDAZOLIUM CHLOROALUMINATE MOLTEN SALTS. C.J. Dymek, Jr. and L.A. King, The Frank J. Seiler Research Laboratory, USAF Academy, Colorado Springs, Colorado

3:45 98. KINETIC ASPECTS OF FACILITATED TRANSPORT THROUGH LIQUID MEMBRANES. Zelibeth E. Reyes and C.A. Koval, University of Colorado, Boulder, Colorado

4:20 99. COMBINED ELLIPSOMETRIC AND ELECTROCHEMICAL MEASUREMENTS OF Pt/Cr ALLOYS IN ACIDIC SOLUTION. Mark T. Paffett and Shimson Gottesfeld, Los Alamos National Laboratory, Los Alamos, New Mexico

4:45 100. A MODULAR MEMORY SYSTEM FOR RAPID ACQUISITION IN MULTIWAVELENGTH SPECTROELECTROCHEMISTRY. David T. Rossi, Monsanto Industrial Chemicals, St. Louis, MO; and Harry L. Pardue, Department of Chemistry, Purdue University, W. Lafayette, IN 47906.

Environmental Chemistry

Chairman: Michael M. Reddy

MONDAY MORNING, July 15, 1985 - Second Floor, Room A
Michael Reddy, Moderator

8:15 Introduction

8:20 101. CHEMICAL SEPARATION AND ANALYSIS OF OXYGENATED POLYNUCLEAR AROMATIC HYDROCARBONS FROM THE PHOTOCHEMICAL DEGRADATION OF WEATHERED CRUDE PETROLEUM. Jordan, R. E. and Chatfield, D. A., Department of Chemistry, San Diego State University, San Diego, CA 92182

8:50 102. CADMIUM SPECIATION IN NATURAL WATERS AND THEIR EFFECT ON RAINBOW TROUT. Gorman, W. C., Jr., and Skogerboe, R. K., Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Davies, P. W., Colorado Division of Wildlife, 317 West Prospect, Fort Collins, Colorado 80522.

9:10 103. NEW NBS STANDARD REFERENCE MATERIALS FOR QUALITY ASSURANCE IN ENVIRONMENTAL ANALYSIS. Gills, T. E., and Rasberry, S. D., National Bureau of Standards, Bldg. 222, Rm. B311, Gaithersburg, Maryland 20899.

9:30 104. ASBESTOS IN THE BUILDING ENVIRONMENT--THE ANALYTICAL ALTERNATIVE. Stewart, Ian M., VP McCrone Environment Services, 5500 Oakbrook Parkway, 200 Oakbrook Business Center, Norcross, Georgia 30093.

9:50 105. A CONTINUOUS FLOW ANALYZER FOR AMMONIA, NITRATE, AND TOTAL INORGANIC NITROGEN. Barthel, P. J., Jupille, T. H., and Togami, D. W., Wescan Instruments, Inc., 3018 Scott Blvd., Santa Clara, California 95054.

10:10 BREAK

10:40 106. MOLECULAR WEIGHTS OF AQUATIC FULVIC ACIDS BY VAPOR PRESSURE OSMOMETRY. Aiken, George R., U.S. Geological Survey, Water Resources Division, Denver Federal Center, MS 407, Denver, Colorado 80225.

11:00 107. MAJOR AND TRACE ELEMENT DETERMINATIONS IN ACID MINE WATERS. Ball, J. W., and Nordstrom, D. K., U.S. Geological Survey, 345 Middlefield Road, MS 421, Menlo Park, California 94025.

11:20 108. SOIL SORPTION OF ORGANIC CONTAMINANTS IN RELATION TO SOIL COMPOSITION AND MOISTURE CONTENT. Chiou, Cary T., U.S. Geological Survey, Denver Federal Center, P.O. Box 25046, MS 407, Denver, Colorado 80225.

11:40 109. DIEL CHANGES IN IRON CONCENTRATION IN AN ACIDIC ROCKY MOUNTAIN STREAM. Bencala, Ken, U.S. Geological Survey, Water Resources Division, MS 496, 3475 Deer Creek Rd., Palo Alto, California 94304. McKnight, Diane, U.S. Geological Survey, Water Resources Division, Box 25046, MS 407, Denver Federal Center, Denver, Colorado 80225.

MONDAY AFTERNOON, July 15, 1985 - Second Floor, Room A
John Garbarino, Moderator

1:30 110. MASKING, CHELATION, AND SOLVENT EXTRACTION TO IMPROVE THE DETERMINATION OF SUB-PPM LEVELS OF TRACE ELEMENTS IN HIGH IRON AND SALT MATRICES. Williams, Mary Carol, Los Alamos National Laboratory, P.O. Box 1663, MS E518, Los Alamos, New Mexico 87544.

1:50 111. ION CHROMATOGRAPHY AND EPA EQUIVALENCY. Joyce, Robert J., Eubanks, Denise, and Henry, Leonard, Dionex Corporation, 1228 Titan Way, Sunnyvale, California 94088-3 03.

2:10 112. A RAPID, FIELD PRECONCENTRATION/PRESERVATION SYSTEM FOR ROUTINE MONITORING OF TRACE METALS IN NATURAL WATERS. Heimbecker, Dana, Skogerboe, R. K., Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Kunkle, Sam H., Water Resources Field Support Lab, National Park Service, 107C Natural Resources, Colorado State University, Fort Collins, Colorado 80523.

2:30 113. PPB DETECTION OF CHROME (VI) IN DRINKING WATER AND GROUND WATER. Henry, Leonard, Dionex Corporation, 1228 Titan Way, Sunnyvale, California 94088-3 03.

2:50 114. CHARACTERIZATION OF HUMIN ISOLATED FROM DIFFERENT SOURCES. Rice, James A., and MacCarthy, Patrick, Colorado School of Mines, Chemistry and Geochemistry Department, Golden, Colorado 80401.

3:10 BREAK

3:40 115. CORROSION TESTING BY THE POLARIZATION RESISTANCE METHOD. Umana, M., Whitaker, D., Pellizzari, E. D., Analytical and Chemical Sciences, Research Triangle Institute, P.O. Box 12194, Research Triangle Park, North Carolina 27709. Fedkiw, P., and Chapman, R., Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

4:00 116. A DISCUSSION OF THE X-RAY FLUORESCENCE DATA FROM PM-10 MONITORING. Zimmerman, Margaret J., Jenks, J. Maxine, Anselmo, Vincent C., Vallarino, Hazel C., Denniston, Virginia J., Texas Air Control Board, Sampling and Analysis, 6330 Highway 290 East, Austin, Texas 78723.

4:20 117. MIGRATION OF FONOFOS FROM MUCK SOIL INTO SURFACE AND GROUNDWATER. Spittler, T. D., and Straub, R. W., New York State Experiment Station, Cornell University, Geneva, New York 14456.

4:40 118. QUANTITATIVE ANALYSIS OF PPB CONCENTRATIONS OF HYDROGEN SULFIDE IN AIR USING A GOLD FILM SENSOR. McNerney, Richard T., and McNerney, John J., Jerome Instrument Corp., P.O. Box 336, Jerome, Arizona 86331.

TUESDAY MORNING, July 16, 1985 - Second Floor, Room A
Michael Reddy, Moderator

8:30 Introduction

KEYNOTE SPEAKER

8:40 119. CHEMISTRY AND MICROPHYSICS OF FOGS AND CLOUDS IN CALIFORNIA. Hoffman, Michael R., 137-78 Caltech, Pasadena, California 91125.

9:30 120. AN AUTOMATIC-MULTICYLINDER SPLITTER FOR THE COLLECTION OF WET-ATMOSPHERIC DEPOSITION. Schroder, LeRoy J., U.S. Geological Survey, Lakewood, Colorado. Malo, Bernard A., U.S. Geological Survey, Reston, Virginia. Scott, Carl T., U.S. Geological Survey, Bay St. Louis, Mississippi.

9:50 121. ACID RAIN EFFECTS ON LIMESTONE AND MARBLE. Reddy, Michael M., and Werner, Marilyn, U.S. Geological Survey, Water Resources Division, Denver Federal Center, MS 407, Denver, Colorado 80225.

10:10 BREAK

10:40 122. A COMPARISON OF ION CHROMATOGRAPHY AND AUTOMATED COLORIMETRY FOR THE DETERMINATION OF MAJOR ANIONS IN PRECIPITATION SAMPLES. Bachman, Susan R., Illinois State Water Survey, Box 5050, Station A, Champaign, Illinois 61820.

11:00 123. CONTROLS ON SULFATE RETENTION AND MOBILIZATION IN FORESTED WATERSHED SOILS - SURFACE CHEMISTRY APPROACH. Afifi, Afifa A., U.S. Geological Survey, 432 National Center, Reston, Virginia 22092.

11:20 124. THEORY VERSUS PRACTICE IN THE DETERMINATION OF pH IN PRECIPITATION. Brennan, Carla Jo, and Peden, Mark E., Illinois State Water Survey, Box 5050, Station A, Champaign, Illinois 61820.

TUESDAY AFTERNOON, July 16, 1985 - Second Floor, Room A
LeRoy Schroder, Moderator

2:00 125. A HOMOGENEOUS GAS PHASE MECHANISM FOR USE IN A REGIONAL ACID DEPOSITION MODEL. Stockwell, William R., NCAR, P.O. Box 3000, Boulder, Colorado 80307.

2:20 126. A THEORETICAL METHOD FOR COMPUTING VERTICAL DISTRIBUTIONS OF ACIDITY AND SULFATE PRODUCTION WITHIN GROWING CUMULUS CLOUDS. Walcek, Chris J., NCAR, P.O. Box 3000, Boulder, Colorado 80307.

2:40 127. EFFECT OF STORAGE TIME AND COMPARISON OF ANALYTICAL METHODS FOR THE DETERMINATION OF ALKALINITY IN STREAM WATERS OF VARYING IONIC STRENGTHS. Kennedy, Margaret M., and Bricker, Owen P., U.S. Geological Survey, 432 National Center, Reston, Virginia 22092.

3:00 128. RAINFALL pH MEASUREMENT VARIATIONS FOR VARIOUS PROTOCOLS AT RESEARCH TRIANGLE PARK, NORTH CAROLINA. Reddy, Michael M., and See, Randolph B., U.S. Geological Survey, WRD, MS-407, Denver Federal Center, Denver, Colorado 80225. Eaton, Cary, Research Triangle Institute, P.O. Box 12194, Research Triangle Park, North Carolina 27709.

3:20 BREAK

3:50 129. QUALITY ASSURANCE OF PRECIPITATION CHEMISTRY ANALYSES USING ION BALANCE CALCULATIONS. Lockard, Jacqueline M., Illinois State Water Survey, Box 5050, Station A, Champaign, Illinois 61820.

4:10 130. SOIL CHEMISTRY IN AN ALPINE WATERSHED, COLORADO FRONT RANGE. Litaor, Michael Z., Geological Sciences Department, Campus Box 250, University of Colorado, Boulder, Colorado 80309. Thurman, E. Michael, National Water Quality Laboratory, U.S. Geological Survey, 5293 Ward Road, MS 407, Arvada, Colorado 80002.

4:30 131. ACID DEPOSITION STUDIES IN THE SAN JUAN NATIONAL FOREST. Mehs, D. M., Fort Lewis College, Durango, Colorado 81303. Story, M., San Juan National Forest, Durango, Colorado 81301. Japhet, M., Colorado Division of Wildlife, Durango, Colorado 81301.

4:50 132. THE APPLICATION OF A CONCEPTUAL LANDSCAPE ACID PRECIPITATION ENVIRONMENTAL MODEL TO ASSESSING THE IMPACT OF ACID RAIN ON DRINKING WATER QUALITY. Meranger, J. C., National Health and Welfare, Environmental Health Directorate, Ottawa, Ontario, Canada K1A 0L2. Gladwell, D. R., Barringer Research Ltd., Toronto, Ontario, Canada M9W 5G2.

Joint Session

Environmental Symposium/Symposium on Mass Spectroscopy

Wednesday Morning, July 17, 1985 - Second Floor, Room A

George Aiken, Moderator

8:30 Introduction

8:50 133. MANAGEMENT OF ENVIRONMENTAL DATA ON A PERSONAL COMPUTER. Johnson, R. Roger, Solutech Corporation, 11011 W. 6th Avenue, Suite 307, Lakewood, Colorado 80215.

9:10 134. APPLICATION OF RAPID SAMPLING AND ANALYSIS OF THE VOLATILE CONSTITUENTS OF AIRBORNE PARTICULATE MATTER. Greaves, R. C., Barkley, R. M., and Sievers, R. E., Department of Chemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), Campus Box 449, University of Colorado, Boulder, Colorado 80309.

3:50 145. EVOLUTION OF GC/MS ANALYTICAL METHODS FOR ANALYSIS OF POLLUTANTS IN WATER. Rushneck, D., Interface, Inc., Fort Collins, Colorado. Telliard, W. A., U.S. Environmental Protection Agency

4:10 146. RECOVERY AND DETECTION LIMITS OF ORGANIC COMPOUNDS IN PETROLEUM REFINERY WASTES. Phillips, M. P., Logsdon, O. J., and Lowry, J., Rocky Mountain Analytical Laboratory, 5530 Marshall Street, Arvada, Colorado 80002.

4:30 147. THE GENERATION OF CHROMATOGRAPHIC PROFILES OF WATER AND WASTEWATER SAMPLES USING A COMMERCIALLY AVAILABLE, MICROCOMPUTER-BASED, DBMS/GRAPHIC SOFTWARE PACKAGE. Peterson, Deanna, Denver Water Department, 1600 West 12th Avenue, Denver, Colorado 80254.

4:50 148. SEASONAL VARIATIONS IN THE CHEMICAL AND MUTAGENIC ACTIVITY OF A DRINKING WATER SOURCE. Neas, R. E., Ma, Te-Hsiu, Cook, C., and Harris, M., Water Laboratory-Department of Chemistry, Environmental Mutagenisis Laboratory-Department of Biological Sciences, and Institute for Environmental Management, Western Illinois University, Macomb, Illinois 61455.

8th INTERNATIONAL ELECTRON PARAMAGNETIC RESONANCE SYMPOSIUM

Chaired by G. R. Eaton and S. S. Eaton

MONDAY MORNING, July 15, 1985 - Second Floor, Room G
Session I - MULTI-FREQUENCY EPR
Robert Clarkson, Presiding

8:30 Introductory Remarks - G. R. Eaton

8:35 149. **Plenary Lecture** - THE FREQUENCY OPTION IN EPR. R. L. Belford, University of Illinois.

9:30 150. **Plenary Lecture** - MULTIFREQUENCY ESR SPECTROSCOPY. J. S. Hyde, Medical College of Wisconsin.

10:30 Coffee Break

11:00 151. **Plenary Lecture** - ESR-ENDOR SPECTROSCOPY AT V BAND. H. C. Box and H. G. Freund, Roswell Park Memorial Institute.

MONDAY AFTERNOON, July 15, 1985 - Second Floor, Room G
Session II - MULTI-FREQUENCY EPR
Robert Clarkson, Presiding

1:30 152. DETERMINATION OF STRUCTURES OF POLYCRYSTALLINE TRANSITION METAL COMPLEXES BY ENDOR. R. Kreilick, T. Henderson, S. Greiner, and D. Rowlands, University of Rochester.

2:15 153. **Plenary Lecture** - HIGH FREQUENCY EPR IN STUDIES OF FREE RADICALS AND SPIN LABELS. Ya. S. Lebedev, Institute of Chemical Physics, USSR.

Session III - POSTERS - First Floor, Room F
Sandra Eaton, Presiding
Authors present 3:00 to 4:00 for papers labeled A
Authors present 4:00 to 5:00 for papers labeled B

A 154. MULTIFREQUENCY ESR OF CU(II)-(HISTIDINE)n. R. Basosi, W. Froncisz, W. E. Antholine, and J. S. Hyde, Medical College of Wisconsin.

B 155. STUDIES OF THE INTERACTION OF Pd^{3+} AND Pd^{+} WITH ORGANIC ADSORBATES, WATER AND MOLECULAR OXYGEN IN Pd-CaX ZEOLITE BY ELECTRON SPIN RESONANCE AND ELECTRON SPIN ECHO MODULATION SPECTROSCOPY. J. Michalik, M. Narayana, and L. Kevan, University of Houston.

A 156. ESR-STUDY OF COMPLEX FORMATION OF THE ASCORBATE RADICAL WITH METAL IONS. J. N. Gex and A. V. Zelewsky, University of Fribourg, Switzerland.

B 157. MAGNETIC RESONANCE IN THE ORDERED STATES OF $(NH_3(CH_2)_nNH_3)CuBr_4$ FOR HIGH n. S. L. Hutton, G. V. Rubenacker, and J. E. Drumheller, Montana State University.

A 158. ESR STUDY OF Mn(II) IN SPIN-CROSSOVER Fe(II) COMPLEXES. P. E. Doan and B. R. McGarvey, University of Windsor, Ontario.

B 159. NATURAL ABUNDANCE ^{13}C AND ^{29}SI ENDOR STUDIES OF CYCLOPOLYSILANE RADICAL ANIONS. B. Kirste, R. West, and H. Kurreck, Free University of Berlin and University of Wisconsin.

A 160. AN ESR STUDY OF X-IRRADIATED SINGLE CRYSTALS OF 1,2-PHENYLENE PHOSPHOCHLORIDITE. M. Geoffroy and M. A. Lorente, University of Geneva, Switzerland.

B 161. THE SIMULATION OF ELECTRON PARAMAGNETIC RESONANCE SPECTRA USING RATIONAL FUNCTION APPROXIMATIONS FOR SPECTROSCOPIC LINE SHAPES. M. M. Maltempo, University of Colorado at Denver.

A 162. ENDOR STUDY OF VO(II) AND CU(II) PORPHYRIN DIMERS WITH TRIPLET GROUND STATES. H. van Willigen and T. K. Chandrashekar, University of Massachusetts at Boston.

B 163. EPR OF PARTIALLY ORDER COPPER PHTHALOCYANINE MONOLAYERS. M. D. Pace, A. W. Snow, and W. R. Barger, Naval Research Laboratory, Washington, D. C.

A 164. AN EPR STUDY OF NITROXIDE SPIN LABEL DOPED HIGH VOLATILE BITUMINOUS COAL: EXAMINATION OF PORE DISTRIBUTION. S.-K. Wuu and L. D. Kispert, University of Alabama.

B 165. ESR STUDY OF BONDING AND DYNAMICS OF PARAMAGNETIC CATIONS IN CROSSLINKED POLYACRYLAMIDE GELS. G. C. Rex and S. Schlick, University of Detroit.

A 166. FIELDS AND GRADIENTS FOR E.S.R. IMAGING. A. Sotgiu and J. S. Hyde, Medical College of Wisconsin and University of L'Aquila, Italy.

B 167. NOVEL DETECTION AND EXCITATION TECHNIQUES IN PULSED EPR. A. Schweiger, J. M. Fauth, J. Forrer, L. Braunschweiler, and R. R. Ernst, ETH-Zentrum, Switzerland.

A 168. ANALYSIS OF NUCLEAR QUADRUPOLE INTERACTION EFFECTS IN ELECTRON SPIN ECHO MODULATION SPECTRA BY SECOND ORDER PERTURBATION METHODS. M. Heming, M. Narayana, and L. Kevan, University of Houston.

9:30 135. TRACE ORGANIC COMPOUNDS IN A SEWAGE CONTAMINATED GROUND WATER. Barber, Larry B., II, National Water Quality Laboratory, U.S. Geological Survey, 5293 Ward Road, MS 407, Arvada, Colorado 80002.

9:50 BREAK

10:20 136. COMPOSITION AND ENVIRONMENTAL FATE OF HAZARDOUS ORGANIC COMPOUNDS IN WASTES GENERATED THROUGH PRODUCTION, PROCESSING AND DISTRIBUTION OF NATURAL GAS. Davini, B., and Eiceman, G. A., Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003.

10:40 137. STATISTICAL STUDIES ON THE ELEMENTAL COMPOSITION OF HUMIC SUBSTANCES. Rice, James A., and MacCarthy, Patrick, Colorado School of Mines, Chemistry and Geochemistry Department, Golden, Colorado 80401.

11:00 138. SELECTIVE DETECTION OF ORGANOSULFUR COMPOUNDS IN CAPILLARY GC VIA FLOURINE-INDUCED CHEMILUMINESCENCE REACTIONS. Tavernier,J. E., and Birks, J. W., Department of Chemistry - SCIRES, University of Colorado, Boulder, Colorado 80309.

11:20 139. AN EFFECTIVE QUALITY ASSURANCE PROGRAM FOR NPDES DATA. Nelson, James A., The Standard Oil Company (Ohio), Research Center, Cleveland, Ohio 44128.

KEYNOTE SPEAKER

11:40 140. GC-NCI MASS SPECTRAL STUDIES OF THERMAL CONVERSION OF NONCOMBUSTIBLE POLYMERS, Collazo, H., de Kanel, J., and Dougherty, R. C., Department of Chemistry, Florida State University, Tallahassee, Florida 32306, and Rappe, C., Department of Organic Chemistry, University of Umea, S-901 87, Umea, Sweden.

WEDNESDAY AFTERNOON, July 17, 1985 - Second Floor, Room A

George Aiken, Moderator

2:00 141. QUANTITATIVE ANALYTICAL SCREEN FOR THE DETERMINATION OF THE APPENDIX VIII HAZARDOUS CONSTITUENTS. Parr, J. L., and Carter, Dr. M. J., Rocky Mountain Analytical Laboratory, 5530 Marshall Street, Arvada, Colorado 80002.

2:20 142. APPLICATION OF N-OCTANOL/WATER PARTITION COEFFICIENTS IN THE EVALUATION OF A COAL-TAR CONTAMINATED, TWO-PHASE GROUND-WATER SYSTEM. Rostad, Colleen E., and Pereira, Wilfred E., U.S. Geological Survey, Box 25046, MS 407, Federal Center, Denver, Colorado 80225.

2:40 143. A MUMPS (DMS-11) DATA BASE FOR POLYCYCLIC AROMATIC HYDROCARBON MIXTURE DETERMINATION. Schwartz, T. R., and Yeager, C. J., and Petty, J. D., Columbia National Fisheries Research Laboratory, U.S. Fish and Wildlife Service, Rt. 1, Columbia, Missouri 65201.

3:00 144. APPLICATION OF THE EP OILY WASTE TOXICITY PROCEDURE TO PETROLEUM REFINERY WASTES. Wibby, C., and Bollinger, M. J., Rocky Mountain Analytical Laboratory, 5530 Marshall Street, Arvada, Colorado 80002.

3:20 BREAK

B 169. ELECTRON SPIN RESONANCE AND ELECTRON SPIN ECHO MODULATION STUDIES OF N,N,N',N'-TETRAMETHYLBENZIDINE PHOTOIONIZATION IN FROZEN MICELLAR SOLUTIONS: STRUCTURAL EFFECT OF N-BUTANOL ADDITION TO SODIUM- AND TETRAMETHYLAMMONIUM DODECYLSULFATE AND DODECYLTRIMETHYLAMMONIUM CHLORIDE MICELLES. E. Pietek, R. Maldonado, L. Kevan, and R. M. Jones, University of Houston.

A 170. ENDOR AND ESE OF DISORDERED SOLIDS. R. L. Belford, R. B. Clarkson, J. B. Cornelius, and P. A. Snetsinger, University of Illinois.

B 171. DEPENDENCE OF THE IRON(III) - NITROXYL SPIN-SPIN INTERACTION ON THE LINKAGE BETWEEN THE TWO CENTERS. K. M. More, L. Fielding, G. R. Eaton, and S. S. Eaton, University of Denver and University of Colorado at Denver.

A 172. ELECTRON SPIN ECHOES WITH A LOOP-GAP RESONATOR. J. P. Hornak and J. H. Freed, Rochester Institute of Technology and Cornell University.

B 173. STRUCTURAL AND MAGNETIC PROPERTIES OF NOVEL ONE DIMENSIONAL COPPER OXALATES - PYRIDINIUM BIS(OXALATO) CUPRATE (II) OXALIC ACID and BIS(2-METHYL IMIDAZOLE) COPPER(II) OXALATE. B. L. Ramakrishna, U. Geiser, and R. D. Willett, Washington State University.

A 174. SPIN-LATTICE RELAXATION RATES OF TRANS-POLYACETYLENE, DETERMINED BY SATURATION RECOVERY EPR. R. St. Denis, and B. H. Robinson, University of Washington; C. Mailer, University of New Brunswick.

B 175. PHASE MEMORY TIME OF TRANS-POLYACETYLENE; EVIDENCE FOR SOLITON DIFFISION. E. J. Hustedt and B. H. Robinson, University of Washington; H. Thomann, Exxon Research and Engineering, Annandale, NJ.

TUESDAY MORNING, July 16, 1985 - Second Floor, Room G
Session IV - ISOTOPICALLY SUBSTITUTED SPIN LABELS IN BIOLOGICAL INVESTIGATIONS
Jane Park, Presiding

8:30 176. DESIGN AND SYNTHESIS OF ISOTOPIC SPIN LABELS. S. D. Venkataramu and D. E. Pearson, Vanderbilt University.

9:00 177. **Plenary Lecture** - SYNTHESIS AND APPLICATION OF SPIN-LABELED AND PHOTOAFFINITY SPIN-LABELED NUCLEOTIDES: THE ADVANTAGE OF ISOTOPIC SUBSTITUTION. W. E. Trommer, Kaiserlautern University, West Germany.

10:00 Coffee Break

10:30 178. THE USE OF MOLECULAR GRAPHICS AND X-RAY CRYSTALLOGRAPHIC STRUCTURAL DATA IN THE INTERPRETATION OF EPR DATA OBTAINED FROM BIOLOGICAL MOLECULES. J. J. Birktoft and J. H. Park, Washington University and Vanderbilt Medical School.

11:00 179. EPR AND ST-EPR STUDIES OF MEMBRANE BOUND PROTEINS. A. H. Beth, Vanderbilt Medical School.

11:30 180. THE DYNAMICS OF THE MEMBRANE BOUND PROTEIN, D-β-HYDROXYBUTYRATE (DBH) AS STUDIED BY EPR AND ST-EPR. B. Robinson, O. J. McIntyre, and S. Fleischer, University of Washington and Vanderbilt University.

TUESDAY AFTEROON, July 16, 1985 - Second Floor, Room G
Session V - ISOTOPICALLY SUBSTITUTED SPIN LABELS IN BIOLOGICAL INVESTIGATIONS
Larry Dalton, Presiding

1:30 181. ELDOR STUDIES OF INTERACTIONS BETWEEN ^{14}N:^{15}N SPIN LABEL PAIRS. J. B. Feix, J. J. Yin, S. D. Venkataramu, A. H. Beth, J. H. Park, and J. S. Hyde, Medical College of Wisconsin and Vanderbilt Medical School.

2:00 182. **Plenary Lecture** -NUCLEAR MAGNETIC RESONANCE OF A MONOCLONAL ANTI SPIN LABEL ANTIBODY. J. Anglister, T. Frey, M. Whittacker, and H. M. McConnell, Stanford University.

3:00 Coffee Break

3:30 183. SPIN LABELING OF PLASMA MEMBRANES IN DISEASES. A. D. Butterfield, University of Kentucky.

4:10 184. DISORDERS IN LEUKOCYTE FUNCTION AS DETERMINED BY EPR AND SPIN TRAPPING. R. A. Haak, S. T. Barefoot, and F. W. Kleinhans, Indiana School of Medicine.

WEDNESDAY MORNING, July 17, 1985 - Second Floor, Room G
Session VI - BIOLOGICAL APPLICATIONS
Jane Park, Presiding

8:30 185. EPR SPECTROSCOPIC STUDIES OF A HIGHER PLANT CELL WALL PARAMAGNETIC ION LATTICE. P. L. Irwin, M. D. Sevilla and C. L. Stoudt, U. S. Department of Agriculture, Philadelphia.

8:50 186. SPIN-LABEL STUDIES OF THE CUTICLE OF THE SCORPION CENTRURIODES SCULPTURATUS. T. R. White and W. S. Glaunsinger, Arizona State University.

9:10 187. INVESTIGATION OF THE MOLECULAR MECHANISM OF MUSCLE CONTRACTION BY EPR SPECTROSCOPY. M. Crowder, D. Thomas, and R. Cooke, IBM Instruments, University of Minnesota, and University of California San Francisco.

9:30 188. BIS-HISTIDINE COMPLEXES IN HEMOGLOBIN: A PROBE OF THE PROTEIN CONFIGURATION IN THE HEME POCKET. J. M. Rifkind, A. Levy, P. Chuknyiski, and P. T. Manoharan, Gerontology Research Center, Baltimore.

9:50 COFFEE BREAK

10:40 189. ELECTRON SPIN ECHO STUDIES OF PHOTOSYNTHETIC OXYGEN EVOLUTION. R. D. Britt, K. Sauer, and M. P. Klein, University of California, Berkeley.

11:00 190. CA^{2+} ACTIVATION OF SPIN-LABELED SARCOPLASMIC RETICULUM ATPASE: EFFECT OF HISTIDINE MODIFICATION. C. Coan, University of the Pacific.

11:20 191. IRON AND OXYGEN FREE RADICAL INVOLVEMENT IN OXIDATIVE DAMAGE IN BRAIN. R. A. Floyd, M. M. Zaleska, and K. Nagy, Oklahoma Medical Research Foundation.

11:40 192. REDUCTION OF THE METALLOCHROMIC INDICATORS MUREXIDE AND TETRAMETHYLMUREXIDE TO THEIR FREE RADICAL METABOLITES BY CYTOPLASMIC ENZYMES AND REDUCING AGENTS. S. N. J. Moreno and R. Docampo, National Institute of Environmental Health Sciences.

WEDNESDAY AFTERNOON, July 17, 1985 - First Floor, Room F
Session VII - POSTERS AND DISCUSSIONS

1:30 INFORMAL DISCUSSION OF PROBLEMS AND EXPERIENCES WITH PULSED EPR (FOR EXAMPLE, TWT'S, LIMITERS...), John McCracken, Presiding.

Poster Session, Sandra Eaton, Presiding
Authors present 2:00 - 2:45 for papers labeled C
Authors present 2:45 - 3:30 for papers labeled D

C 193. ENDOR OF SEMIQUINONES IN VITRO AND IN BACTERIAL REACTION CENTERS. W. Lubitz, E. C. Abresch, R. J. Debus, R. A. Isaacson, M. Y. Okamura, and G. Feher, Free University of Berlin and University of California, San Diego.

D 194. ESR, ENDOR, AND TRIPLE RESONANCE OF IMIDAZOLE, 1-VINYLIMIDAZOLE, AND 2-METHYL-1-VINYLIMIDAZOLE RADICALS IN SOLUTION. M. Vuolle and R. Makela, University of Jyvaskyla.

C 195. ELECTRON SPIN RESONANCE AND ELECTRON SPIN ECHO STUDIES OF CHLOROPHYLL-A CATION RADICAL IN FROZEN VESICLE SOLUTIONS. L. Kevan and N. Ohta, University of Houston.

D 196. MICROENVIRONMENT AROUND THE ESSENTIAL CYSTEINE RESIDUES IN CHICKEN LIVER FRUCTOSE 1,6-BISPHOSPHATASE AS ANALYZED BY ESR. H. M. K. Zeidan, P. F. Han, and J. Johnson, Atlanta University.

C 197. MULTIPLE, OVERLAPPING SPECTRA FOR NON-HEME IRON OXYGENASES: BIOCHEMICAL BASIS. B. J. Gaffney, L. M. Bloom, D. V. Mavrophilipos, and S. J. Benkovic, Johns Hopkins University and Pennsylvania State University.

D 198. RELAXATION MEASUREMENTS OF LIPOXYGENASE FERRIC ESR SIGNALS. D. V. Mavrophilipos and B. J. Gaffney, Johns Hopkins University.

C 199. COMPUTER SIMULATION OF HIGH SPIN Fe(III) ESR SPECTRA OF NON-HEME IRON PROTEINS. A. Yang and B. J. Gaffney, Johns Hopkins University.

D 200. ESR STUDIES OF FREE RADICAL METABOLITES IN PERFUSED LIVERS. H. D. Connor, M. D. Galizi, R. G. Thurman, and R. P. Mason, Kentucky Wesleyan College, University of North Carolina, and National Institute of Environmental Health Science.

C 201. HYDRALAZINE FREE RADICALS PRODUCED IN RAT LIVER MITOCHONDRAL. P. K. Wong, and R. A. Floyd, Oklahoma Medical Research Foundation.

D 202. MOLECULAR DYNAMICS IN PROTEIN - SINGLE STRANDED DNA COMPLEXES. A. M. Bobst and S.-C. Kao, University of Cinncinnati.

C 203. INTERACTION BETWEEN CUPRIC ION AND SPIN-LABELED CYSTEINE 93β IN FETAL HEMOGLOBIN. W. E. Antholine and F. Taketa, Medical College of Wisconsin.

D 204. SPIN-MEMBRANE IMMUNOASSAY STUDIES OF ANTI-GANGLIOSIDE IMMUNITY IN MULTIPLE SCLEROSIS. J. B. Feix, B. Khatri, M. P. McQuillen, and S. M. Koethe, Medical College of Wisconsin.

C 205. NEUTROPHIL METABOLIC BURST PROFILE VIA ESR. F. W. Kleinhans, S. T. Barefoot, and R. A. Haak, Indiana University and Indiana University School of Medicine.

D 206. PULSED EPR STUDIES ON AXIAL LIGATION TO IRON IN HEME COMPLEXES. J. McCracken, R. S. Magliozzo, and J. Peisach, Albert Einstein College of Medicine.

C 207. SPIN-LABEL OF MEMBRANE-SKELETAL PROTEIN INTERACTIONS IN HUMAN ERYTHROCYTES. D. Allan Butterfield, T. M. Harmon, and B. T. Farmer, II, University of Kentucky.

D 208. ESR STUDIES OF THE EFFECTS OF Al^{+3}, Cd^{+2}, and H_2^{+2} ON HUMAN ERYTHROCYTE MEMBRANES. J. W. Wyse, and D. A. Butterfield, University of Kentucky.

3:30 Discussion of posters presented in Session VII, Larry Dalton - Presiding

THURSDAY MORNING, July 18, 1985 - Second Floor, Room G
Session VIII
Gareth Eaton, Presiding

8:30 209. **Plenary Lecture** - THE MECHANISM OF RADIOLYSIS PROBED BY ESR. M. C. R. Symons, University of Leicester.

9:30 210. EPR OF CYCLOSILANE ANION-RADICALS. R. West and C. L. Wadsworth, University of Wisconsin-Madison.

10:00 COFFEE BREAK

10:20 211. EPR INVESTIGATIONS OF THE EARLY STAGES OF TNT DECOMPOSITION. J. T. Swanson, R. W. Carper, and J. A. Zirrolli, USAF Academy.

10:40 212. A STUDY OF THE BOND HOMOLYSIS OF BI(3,5,5-TRIMETHYL-2-OXOMORPHOLIN-3-YL). T. H. Koch and J. B. Olson, University of Colorado.

11:00 213. EXTENDED-TIME EXCITATION ELECTRON SPIN ECHO SPECTROSCOPY. A. Schweiger, L. Braunschweiler, J. M. Fauth, and R. R. Ernst, ETH-Zentrum, Switzerland.

11:20 214. EPR STUDY OF PHASE TRANSITIONS IN Cu-DOPED $CaCd(CH_3COO)_4 \cdot 6H_2O$.
S. K. Misra and K. Kumar, Concordia University.

11:40 215. EFFECTS OF COMBUSTION ON 9 AND 34 GHz EPR OF COLD LAKE OIL SANDS. V. M. Malhotra and H. A. Buckmaster, Southern Illinois University and University of Calgary.

THURSDAY AFTERNOON, July 18, 1985 - Second Floor, Room F
Session XI - RESONATORS
Russell Lobrutto, Presiding

1:30 216. TOPOLOGIES OF THE LOOP-GAP RESONATOR. W. Froncisz and J. S. Hyde, Medical College of Wisconsin.

2:05 217. APPLICATION OF HELICAL RESONATORS TO ENERGETIC MATERIALS RESEARCH. M. D. Pace, Naval Research Laboratory.

2:25 218. RE-ENTRANT CAVITIES FOR E. S. R. SPECTROSCOPY. A. Sotgiu and F. Momo, Medical College of Wisconsin and University of L'Aquila, Italy.

2:45 COFFEE BREAK

3:05 219. CONSTRUCTION OF A COMPACT X-BAND EPR MICROWAVE RESONATOR FOR USE WITH LIQUID HELIUM FLOW SYSTEMS. R. LoBrutto and J. S. Leigh, University of Pennsylvania.

3:30 220. MICROWAVE RESONATOR PERFORMANCE IN PHOTOSYNTHETIC PULSED EPR EXPERIMENTS. C. T. Lin, R. J. Massoth, J. R. Norris, and M. K. Bowman, Argonne National Laboratory.

4:00 221. **Presentation by** - A. Grupp and M. Mehring

SYMPOSIUM ON FLOW INJECTION ANALYSIS

Chairman: C. B. Ranger

MONDAY AFTERNOON, JULY 15, 1985 - Third Floor, Room E
L. C. LeGros, Presiding

1:00 INTRODUCTORY REMARKS - L. C. LeGros

1:05 222. FLOW INJECTION ANALYSIS: AN OVERVIEW. L. C. LeGros, Lachat Instruments

1:35 223. AUTOMATIC FLOW INJECTION DETERMINATION OF AMMONIA AND NITRATE IN SOIL EXTRACTS. S. Workman, E. Brennan, and D. Shimmel, Colorado State University

2:05 224. AUTOMATIC STANDARD ADDITIONS TECHNIQUE IN ATOMIC SPECTROSCOPY USING FLOW INJECTION ANALYSIS. K. Schick, Fiatron Systems

2:35 225. AUTOMATED DETERMINATION OF NITROGEN AND PHOSPHORUS SPECIES IN WATER USING FLOW INJECTION ANALYSIS. K. Kringlie, North Dakota Public Health Laboratory

3:05 Break

3:20 226. DETERMINATION OF PHOSPHATE IN SODIUM BICARBONATE SOIL EXTRACTS USING AUTOMATED FLOW INJECTION ANALYSIS. J. Havlin, University of Nebraska

3:50 227. SIMULTANEOUS DETERMINATION OF NITROGEN AND PHOSPHORUS IN ANIMAL FEEDS AND FERTILIZERS USING A DUAL CHANNEL FLOW INJECTION SYSTEM. D. Diamond, Lachat Instruments

4:20 228. MULTI-CHANNEL ANALYSIS: EXPECTATIONS VERSUS REALITY AND INTERFACING A FLOW INJECTION ANALYZER WITH A LIMS. Mary Lou Daniels, South Florida Water Management District

4:50 229. AUTOMATED LOW LEVEL DETERMINATIONS OF NITROGEN AND PHOSPHORUS IN ACID DIGESTS OF WATER USING FLOW INJECTION ANALYSIS WITH IN-LINE NEUTRALIZATION. R. Gill, California Water Quality Control Board

10:30 240. THE EFFECT OF PLASMA OPERATING PARAMETERS ON ANALYTE SIGNALS IN INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY. G. Horlick, University of Albertal, Edmonton, Alberta, Canada

11:00 Round Table Panel Discussion

Luminescence Spectroscopy

Chairman: Dr. Marvin C. Goldberg

TUESDAY MORNING, July 16, 1985 - Third Floor, Room D

8:55 INTRODUCTION Dr. Marvin C. Goldberg

9:00 241. LUMINESCENCE SPECTROSCOPY USING A PERSONAL COMPUTER. Arnold F. Theisen, U.S. Geological Survey, Flagstaff, AZ

9:25 242. TOTAL NITROGEN DETERMINATION IN PETROLEUM USING A CHEMILUMINESCENT METHOD. J. Y. Shay, P. W. Woodward and M. L. Whisman, National Institute for Petroleum and Energy Research, Bartlesville, OK

9:50 BREAK

10:20 243. FLOW INJECTION ANALYSIS WITH CHEMILUMINESCENCE DETECTION USING THE RUTHENIUM TRIS-BIPYRIDINE COMPLEX. James B. Noffsinger and Neil D. Danielson, Miami University, Oxford, OH

10:45 244. FLUOROMETRIC DETERMINATION OF DANTHRON BY REDUCTION IN A FLOW INJECTION ANALYSIS SYSTEM. Blair E. Miller and Neil D. Danielson, Miami University, Oxford, OH

11:10 245. TEMPERATURE DEPENDENCE OF THE LUMINESCENCE OF BIACETYL VAPOR. Calvin Weiser, Grumman Aerospace Corporation, Bethpage, NY

11:35 246. THE ROOM TEMPERATURE PHOSPHORESCENCE BEHAVIOR OF SELECTED PESTICIDES AND PRIORITY POLLUTANTS. Nelson R. Herron, M. J. Zabik, and S. R. Crouch, Pesticide Research Center, Michigan State University, East Lansing, MI

TUESDAY AFTERNOON, July 16, 1985 - Third Floor, Room D
Symposium Chairperson Dr. David L. Bolton

1:25 INTRODUCTION - Dr. David L. Bolton

1:30 247. INFLUENCE OF FORSTER ENERGY TRANSFER ON FLUORESCENT LIFETIMES. Eugene R. Weiner and Marvin C. Goldberg - U.S. Geological Survey, Denver, CO

1:55 248. OXYGEN QUENCHING OF HUMIC SUBSTANCES AND ITS CONSEQUENCES FOR TERPENES IN AQUATIC ENVIRONMENTS. Kirkwood M. Cunningham and Marvin C. Goldberg, U.S. Geological Survey, Denver, CO

2:20 249. FLUORESCENCE PROPERTIES OF SYNTHETIC MELANIN. David L. Bolton, University of Denver, Denver, CO

2:45 Break

3:15 250. LASER INDUCED FLUORESCENCE OF LIGNINS FROM WOOD DIGESTION. D. J. Cietek, D. M. Hanson and W. Fookes, International Paper Company, Tuxedo Park, NY

3:40 251. DEPOLARIZATION MEASUREMENTS AS A MEANS OF DETERMINING THE MOLECULAR PROPERTIES OF FULVIC ACID. Marvin C. Goldberg, U.S. Geological Survey, Denver, CO

4:05 252. THE USE OF AN INTENSIFIED DIODE ARRAY TO DETERMINE ROOM TEMPERATURE PHOSPHORESCENCE. Nelson R. Herron, M. J. Zabik, and S. R. Crouch, Pesticide Research Center, Michigan State University, East Lansing, MI

INFRARED SPECTROSCOPY

Chairman: Dr. Marvin C. Goldberg

WEDNESDAY MORNING, July 17, 1985 - Third Floor, Room D
Symposium Chairperson Dr. A. R. Chughtai

8:55 INTRODUCTION Dr. A. R. Chughtai

9:00 253. INFRARED MONITORING OF CONDENSED PHASE PYROLIZATES PRODUCED BY CO_2 LASER PROCESSING OF PLASTICS. John M. Kokosa and Daryl J. Doyle, GMI Engineering and Management Institute, Flint, MI

9:30 254. THERMAL SHOCK OF HEAVY OIL FORMATIONS: FTIR STUDY. V. M. Malhotra and R. D. Moore, Southern Illinois University, Carbondale, IL

10:00 255. FTIR ANALYSIS OF ROSIN FLUX - METAL OXIDE INTERACTIONS. Randy W Snyder, IBM Corporation, Endicott, NY

10:30 BREAK

11:00 256. QUANTIFICATION OF BENZOYL PEROXIDE IN SILICONE ADHESIVES. Susan E. Stemporzewski, Kendall Company, Lexington, MA

11:30 257. QUALITY AND THICKNESS ANALYSIS OF THERMOPLASTIC COATING BY DIFFUSE REFLECTANCE IR SPECTROMETRY. Michael Hawkins and Howard Price, Zimmer, Inc., Warsaw, IN

WEDNESDAY AFTERNOON, July 17, 1985 - Third Floor, Room D
Symposium Chairperson Dr. W. G. Fateley

1:25 Introduction Dr. W. G. Fateley

1:30 258. THE APPLICATION OF FTIR PHOTOACOUSTIC SPECTROSCOPY AS A SURFACE ANALYSIS TECHNIQUE. C. Q. Yang and W. G. Fateley, Kansas State University, Manhattan, KS

2:00 259. IN VIVO FTIR STUDIES ON SKIN SURFACES. John Strassburger and Veronica Kreici, Gillette Research Institute, Rockville, MD

2:30 BREAK

3:00 260. THE 1600 cm^{-1} AND 700 - 800 cm^{-1} BANDS OF SOOT AS A FUNCTION OF SOURCE. J. A. Jassim, Hsay-Ping Lu, A. R. Chugtai and D. M. Smith, University of Denver, Denver, CO

3:30 261. PHOTODEGRADATION PATHWAYS OF SILVER BASED POLYACRYLONOTRILE (PAN) FILMS AS DETERMINED BY FOURIER TRANSFORM INFRARED REFLECTION SPECTROSCOPY, C. A. Sergides, A. R. Chughtai and D. M. Smith, University of Denver, Denver, CO

4:00 262. PHOTODEGRADATION INHIBITORS OF POLYACRYLONITRILE/AG (PAN/AG) FILMS, C. A. Sergides, A. R. Chughtai and D. M. Smith, Univeristy of Denver, Denver, CO

THURSDAY MORNING, July 18, 1985 - Second Floor, Room A

8:55 *Introduction* by Dr. E. R. Weiner

9:00 263. USING IR ABSORPTION SPECTROSCOPY TO HELP DETERMINE MARTIAN MINERALOGY: THE ROLE OS SUBSTRATE IN IRON OXIDE AND HYDROXIDE PRECIPITATION, J. Posey-Dowty, L. Tannenbaum, B. M. Moskowitz, D. A. Crerar AND R. B. Hargraves, Princeton University, Princeton, NJ

9:30 264. SIMULTANEOUS MULTICOMPONENT DETERMINATIONS BY VIBRATIONAL SPECTROSCOPY, Thomas J. Vickers and Charles K. Mann, Florida University, Tallahassee, FL

10:00 265. CALCULATED INFRARED TRANSITIONS FOR SOLUTION MACROMOLECULES MODELED AS ASYMMETRIC ROTO ELLIPSOIDS, John R. Riter, Jr. and Marvin C. Goldberg, U.S. Geological Survey, Denver, CO

10:30 Break

11:00 266. CHARACTERIZATION OF IMPACT MODIFIERS BY FTIR, Lee McPeters, Rohm & Haas, Bristol, PA

11:30 267. PRESENCE OF THE ACID SALT OF CALCIUM BILIRUBINATE IN CHOLESTEROL GALLSTONES SUGGESTS THAT AN ACID MICROENVIRONMENT OCCURS DURING STONE NIDATION AND GROWTH, J. M. Berman, M. A. Dabezies, P. F. Malet and R. D. Soloway, University of Pennsylvania School of Medicine, Philadelphia, PA

THURSDAY AFTERNOON, July 18, 1985 - Second Floor, Room A

1:25 INTRODUCTION: Dr. Marvin C. Goldberg

1:30 268. RECENT STUDIES ON MITOMYCIN C, Gregory L. Verdine and Koju Nakanishi, Columbia University, New York, NY

2:00 269. PROTEIN STRUCTURE BY DECONVOLVED FTIR SPECTROSCOPY, Heino Susi and D. Michael Byler, U.S. Department of Agriculture, Philadelphia, PA

2:30 BREAK

3:00 270. A MODIFIED 'QUICK' MULL TECHNIQUE, AN INNOVATION IN IR SPECTROSCOPY, Donald O. Woolf, Jr., Innovative Spectroscopy, Indianapolis, IN

3:30 271. ERROR PROPAGATION AS A CRITERION FOR OPTIMAL SPECTROPHOTOMETRIC MULTI COMPONENT ANALYSIS. John H. Kalivas

SYMPOSIUM ON ION CHROMATOGRAPHY

Chairman: by A. G. Hedley

MONDAY MORNING, JULY 15 - Third Floor, Room A
A. G. Hedley, Presiding

8:10 INTRODUCTORY REMARKS - A. G. Hedley

8:15 272. MODERN ION CHROMATOGRAPHY. J. R. Benson, D. J. Woo, D. MacBlane, and N. Kitagawa, Interaction Chemicals Inc.

8:40 273. ADVANCES IN HIGH PERFORMANCE IC OF TRANSITION AND POST-TRANSITION METALS. S. Heberling and J. Riviello, Dionex Corp.

9:05 274. DETECTOR OPTIMIZATION FOR TRANSITION METAL ANALYSIS IN ION CHROMATOGRAPHY. P. J. Barthel, T. H. Jupille, and D. W. Togami, Wescan Instruments Inc.

9:30 275. THE DETERMINATION OF TELLURIUM IN GEOLOGIC SAMPLES USING ION CHROMATOGRAPHY AND HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROPHOTOMETRY. D. B. Hatfield and S. A. Wilson, U.S. Geological Survey

9:55 BREAK

10:35 276. EXAMPLES OF TRACE ANALYSIS IN COMPLEX MATRICES. S. Stone, M. McKay, and S. Heberling, Dionex Corp.

11:00 277. RECENT DEVELOPMENTS USING IC FOR PETROCHEMICAL PROCESS AND WASTEWATER ANALYSIS. R. Rubin, P. Lanier, and D. Eubanks, Dionex Corp.

MONDAY AFTERNOON, JULY 15 - Third Floor, Room A
A. G. Hedley, Presiding

1:00 278. DYNAMIC ION EXCHANGE CHROMATOGRAPHIC SEPARATION OF LANTHANIDES AND THORIUM IN SAMPLES FROM PROCESSING OF URANIUM ORES. D. J. Barkley, Canada Centre for Mineral and Energy Technology

1:25 279. IMPROVEMENTS IN THE ANALYSIS OF CHROME PLATING BATHS. S. Stone, M. McKay, and L. Angers, Dionex Corp.

1:50 280. DETERMINATION OF ARSENIC (III) AND ARSENIC (V) IN ACIDIC FERRIC CHLORIDE OR FERRIC SULFATE LEACHING MEDIA BY ION CHROMATOGRAPHY. L. K. Tan and J. E. Dutrizac, Canada Centre for Mineral and Energy Technology

2:15 BREAK

2:55 281. ION CHROMATOGRAPHIC DETERMINATION OF BROMIDE IN GROUNDWATER AND SEAWATER. G. Schmukler, Israel Institute of Technology, M. Magaritz and A. Nadler, The Weizmann Institute of Science - Israel

3:20 282. DETERMINATION OF METAL CYANIDE COMPLEX BY ION CHROMATOGRAPHY. J. Salois and J. Gannotti, Dionex Corp.

3:45 283. ALBUQUERQUE EXPERIENCES IN USING ION CHROMATOGRAPHY FOR ANIONS AND CATIONS. E. Moore and D. Kersey, Albuquerque Water Laboratory

4:10 284. ION CHROMATOGRAPHIC ANALYSIS OF GAS SAMPLES FROM VOLCANOES AND FLUMAROLES. R. M. Merrill, Sandia National Laboratories

TUESDAY MORNING, JULY 16 - Third Floor, Room A
A. G. Hedley, Presiding

8:00 INTRODUCTORY REMARKS
A. G. Hedley

8:05 285. FACTORS AFFECTING THE PERFORMANCE OF SAMPLE PRECONCENTRATION FOR HIGH SENSITIVITY ANALYSIS. T. H. Jupille, P. J. Barthel, and D. W. Togami, Wescan Instruments Inc.

8:30 286. AUTOMATIC TRACE ENRICHMENT METHOD UTILIZING SINGLE COLUMN ION CHROMATOGRAPHY. W. R. Jones, G. Harrison, and W. T. Robinson, Waters Chromatography Division

8:55 287. PRE-COLUMN CONCENTRATION OF IONS. T. Schlabach and R. Majors, Varian Instrument Group

9:20 BREAK

10:00 288. ADVANCES IN AUTOMATION: SAMPLE PRETREATMENT AND DELIVERY. D. Gillen, S. Heberling, and D. Eubanks, Dionex Corp.

10:25 289. A GENERAL ANALYTICAL PROCEDURE FOR THE DETERMINATION OF COMMON INORGANIC ANIONS BY SINGLE COLUMN ION CHROMATOGRAPHY. T. H. Jupille, P. J. Barthel, and D. W. Togami, Wescan Instruments Inc.

10:50 290. ON-LINE ANALYSIS, A PROGRESS REPORT. L. Angers, E. Johnson, E. Gavin, K. Haak, and G. Lee, Dionex Corp.

TUESDAY AFTERNOON, JULY 16 - Third Floor, Room A
R. M. Merrill, Presiding

1:00 291. ELIMINATION OF MATRIX INTERFERENCES IN INDIRECT PHOTOMETRIC CHROMATOGRAPHY. D. Jenke, D. Brown, and R. Payton, Travenol Laboratories

1:20 292. SIMULTANEOUS DETERMINATION OF ANIONS AND CATIONS VIA INDIRECT ION CHROMATOGRAPHY. J. M. Riviello, C. A. Pohl, and M. S. Taylor, Dionex Corp.

1:45 293. ION CHROMATOGRAPHY OF SOME PHOSPHONIC AND PHOSPHINIC ACIDS. E. L. Grove, IIT Research Institute.

2:10 BREAK

2:50 294. INDIRECT DETERMINATION OF HYDROGEN PEROXIDE BY ION CHROMATOGRAPHY. D. Jenke, Travenol Laboratories

3:05 295. FLUORESCENCE DETECTION WITH FLUOROGENIC ION INTERACTION REAGENTS IN TRANSITION METAL IC. T. K. Dasgupta and K. Saroka, Texas Tech University.

3:30 296. ION EXCHANGE RESIN PACED ANNUAL DUAL MEMBRANE SUPPRESSORS IN IC. T. K. Dasgupta and M. A. Cason, Texas Tech University

3:55 297. ION CHROMATOGRAPHIC DATA REDUCTION USING A MINC-11 COMPUTER. A. G. Hedley and H. E. Taylor, U.S. Geological Survey.

WEDNESDAY MORNING, JULY 17 - Third Floor, Room A
A. G. Hedley, Presiding

8:20 INTRODUCTORY REMARKS - A. G. Hedley

8:25 298. EVOLVING APPLICATIONS OF ION CHROMATOGRAPHY: ORGANICS, METALS, AND INORGANIC ANIONS. J. Korpi and G. Franklin, Dionex Corp.

8:50 299. IMPROVEMENTS IN SELECTIVITY AND SENSITIVITY VIA CHEMICAL SUPPRESSION. R. Rocklin, C. Pohl, and E. Johnson, Dionex Corp.

9:20 BREAK

10:00 300. NEW AMPEROMETRIC DETECTOR FOR SINGLE COLUMN ION CHROMATOGRAPHY. P. Jandik, D. Cox, and W. T. Robinson, Waters Chromatography Division

10:25 301. ANALYSIS OF SOIL AND PLANT EXTRACTS. D. Eubanks and R. J. Joyce, Dionex Corp.

10:50 302. HETERO-ATOM MICROANALYSIS USING ION CHROMATOGRAPHY. G. T. Louthan, F. Block, and J. DeZwaan, The Upjohn Company

WEDNESDAY AFTERNOON, JULY 17 - Third Floor, Room A
A. G. Hedley, Presiding

1:00 303. NEW DEVELOPMENTS IN ORGANIC ANALYSIS. J. Korpi, C. Lincoln, W. Edwards, and L. Henry, Dionex Corp.

1:25 304. DETERMINATION OF ALCOHOL-AMINES AND SUBSTITUTED SACCHARIDES USING IC/EC. J. M. Frye and J. L. Buteyn, The Standard Oil Company, Cleveland, Ohio

1:50 305. PERCENT LEVEL ANALYSIS OF COMPONENTS IN INDUSTRIAL LIQUORS. R. Rocklin, Dionex Corp.

2:15 BREAK

2:55 306. APPLICATION OF ION CHROMATOGRAPHY IN THE BEVERAGE INDUSTRY. K. J. Giryluk, Pepsico

3:20 307. ANALYSIS OF FERMENTATION BROTHS. C. R. Lincoln, J. Korpi, and C. Pohl, Dionex Corp.

3:45 308. THE ANALYSIS OF FREE ORGANIC ACID AS THE DEGRADATION PRODUCT OF ITS SALT IN SUPPORT OF STABILITY STUDIES. T. Catalano, S. Dugar, and R. Faulstich, G. D. Searle

4:10 309. SAMPLE PREPARATION TECHNIQUES IN ION CHROMATOGRAPHY. R. M. Merrill, Sandia National Laboratories.

4:30 359. ION CHROMATOGRAPHY WITH POTENTIOMETRIC DETECTION USING A METALLIC COPPER ELECTRODE. P. R. Haddad, and P. W. Alexander, University of N.S.W., Kensington, Australia, and M. Trojanswicz, University of Warsaw, Poland.

SYMPOSIUM ON INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY

Chairman: Howard E. Taylor

TUESDAY AFTERNOON, July 16, 1985 - Second Floor, Room F
A. L. Gray, Presiding

1:25 Introduction and Opening Remarks

1:30 230. THE EFFECT OF EASILY IONIZED ELEMENTS ON ANALYTE SIGNALS IN INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY. G. Horlick, University of Alberta, Edmonton, Alberta, Canada

2:00 231. ICP-MS: HIGH SPEED ISOTOPE GEOCHEMISTRY. A. R. Date and Y. Y. Cheung, British Geological Survey, London, England

2:30 BREAK

3:00 232. ISOTOPIC RATIO MEASUREMENTS ON NANOGRAM SIZED OSMIUM SAMPLES BY ICP-MS. G. P. Russ, J. M. Bazan, D. A. Leich, Lawrence Livermore Laboratories, Livermore, California, and A. R. Date, British Geological Survey, London, England

3:30 233. AN IMPROVED INTERFACE FOR INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY. D. J. Douglas, Sciex, Ontario, Canada

WEDNESDAY AFTERNOON, July 17, 1985 - Second Floor, Room F
A. R. Date, Presiding

1:30 234. INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY FOR THE QUANTITATIVE ANALYSIS OF NATURAL WATERS. H. E. Taylor and J. R. Garbarino, U. S. Geological Survey, Denver, Colorado

2:00 235. SOLIDS MASS SPECTROMETRY USING SAMPLE INTRODUCTION BY LASER ABLATION INTO THE ICP ION SOURCE. A. L. Gray, University of Surrey, Guildford Surrey, England

2:30 BREAK

3:00 236. OPTIMIZATION OF ICP-MS FOR THE ANALYSIS OF SILICATE MATERIALS. F. E. Lichte and A. L. Meier, U.S. Geological Survey, Denver, CO

3:30 237. SOME OBSERVATIONS OF PERFORMANCE CRITERIA IN ICP-MS. P. J. Goddard, R. C. Hutton, C. J. Shaw and J. E. Cantle, VG Instruments, Winsford, Cheshire, United Kingdom

Thursday, July 18, 1985 - Second Floor, Room F
J. R. Garbarino, Presiding

8:55 Announcements

9:00 238. MEASUREMENT OF TRACE ELEMENT CONCENTRATION AND ISOTOPE RATIO'S IN PETROGEOLOGICAL SAMPLES BY ICP-MS. D. M. Hausler, Phillips Petroleum Co., Bartlesville, OK

9:30 239. ANALYSIS OF TRANSITION ELEMENTS IN USGS REFERENCE MATERIALS BY ICP-MS. A. L. Meier and F. E. Lichte, U.S. Geological Survey, Denver, CO

10:00 BREAK

SYMPOSIUM ON MASS SPECTROSCOPY

Co-Chairmen: P. V. Fennessey and M. Bergeron

MONDAY MORNING, July 15, 1985 - Third Floor, Room E
M. Bergeron, Presiding
Session I - General Mass Spectrometry

8:15 *Introduction*

8:30 310. THE ANALYSIS OF TRACE ELEMENTS IN METALS AND SEMI-CONDUCTORS BY GLOW DISCHARGE MASS SPECTROMETRY. P. J. Goddard, P. J. Turner and J. E. Cantle, V.G. Instruments

9:10 311. THERMAL DECOMPOSITION OF TRINITROTOLUENE: A COMBINED EPR AND MASS SPECTROSCOPIC APPROACH. J. T. Swanson, J. L. Pflug, J. A. Zirrolli, U.S. Air Force Academy, Colorado Springs, CO 80840

9:30 312. RECENT FLOWING AFTERGLOW STUDIES OF ORGANOSILICON COMPOUNDS. R. Damrauer, C. H. DePuy, and V. M. Bierbaum, Chemistry Departments, University of Colorado at Denver and Boulder, 1100 14th Street, Denver, CO 80202

9:50 313. STRUCTURAL DETERMINATION OF CARBOHYDRATES BY MASS SPECTROMETRY. M. McNeil, P. Albersheim, A. Darvill, J. Lau, L. Melton, P. Aman, L. E. Franzein, W. Dudman, W. York and A. Dell, Department of Chemistry, University of Colorado, Boulder, CO 80309

10:10 BREAK

10:30 314. THE ION TRAP DETECTOR (ITD): A NEW APPROACH TO ENVIRONMENTAL SCREENING. F. LeMunyon, Finnigan MAT, 4414 N.W. 79th Terrace, Kansas City, MO 64151

10:50 315. RESIDUAL GAS ANALYSES OF TO5 RELAYS. J. Davis Hewlett Packard, Colorado Springs, CO

11:10 316. **Plenary Lecture:** PROSPECTIVES OF MASS SPECTROMETRY IN CANCER RESEARCH AND THERAPY. Dr. John Roboz, Mt. Sinai Hospital, New York, NY

MONDAY AFTERNOON, July 15, 1985. - Third Floor, Room F
J. A. Zirrolli, Presiding
Session II - Biomedical Application of Mass Spectrometry
Jointly Sponsored by Symposia on Chromatography and Mass Spectrometry

2:00 317. QUANTITATION OF METHYLAMLONIC ACID AND OTHER DICARBOXYLIC ACIDS IN NORMAL SERUM AND URINE USING CAPILLARY GAS CHROMATOGRAPHY-MASS SPECTROMETRY. P. D. Marcell, S. P. Stabler, E. R. Podell, and R. H. Allen, University of Colorado Health Sciences Center, 4200 E. 9th Avenue, Denver, CO 80262

2:20 318. COMPARISON OF SULFONAMIDE DERIVATIVES OF CAPILLARY GC/MS ANALYSES AT 0.1 PPM RESIDUE LEVELS. W. J. Morris, G. J. Nandrea, H. R. Skinner, Food and Drug Administration, 500 U.S. Customhouse, Denver, CO 80202

2:40 319. SYNTHESIS OF DEUTERIUM LABELED INTERMEDIATES OF BILE ACID METABOLISM. G. Everson, A. Nemeth, B. Miles, University of Colorado Health Sciences Center, 4200 E. 9th Avenue, Denver, CO 80262

3:00 320. THE ANALYSIS OF STABLE ISOTOPE ENRICHMENT OF TRACE METALS USING FAST ATOM BOMBARDMENT MASS SPECTROMETRY. P. Pierce, M. Hambidge, L. Miller, and P. V. Fennessey, Department of Pedriatrics and Pharmacology, School of Medicine, University of Colorado Health Sciences Center, 4200 E. 9th Avenue, Denver, CO 80262

3:20 321. MULTIPHOTON IONIZATION MASS SPECTROMETRY OF METAL CHELATES: APPLICATION TO TRACE METAL DETERMINATIONS. Jeffrey B. Morris, and Murray V. Johnston

3:40 BREAK

4:10 322. QUANTITATION OF LYSO-PAF BY GC/S AND FAB/MS. P. E. Haroldsen, K. L. Clay, R. C. Murphy, Department of Pharmacology, University of Colorado Health Sciences Center, 4200 E. 9th Avenue, Denver, CO 80262

4:30 323. FRAGMENTATION MECHANISMS OF ORGANIC MOLECULES BY RESIDENCE ENHANCED MULTIPHOTON IONIZATION: Steven W. Stiller, Murray V. Johnston

Symposium on Nuclear Magnetic Resonance

Chaired by F.P. Miknis

TUESDAY AFTERNOON, July 16, 1985 - Second Floor, Room C

1:25 Introductory Remarks - F.P. Miknis

1:30 324. MULTIPLE-QUANTUM NMR IN DIPOLAR SOLIDS. J. Baum, M. G. Munowitz, A.N. Garroway and A. Pines, Univ. of California, Berkeley, and Naval Research Laboratories.

2:00 325. TIME DOMAIN ZERO FIELD NMR AND NQR. A. Bielecki, J.M. Millar, A.M. Thayer, D.B. Zax and A. Pines, Univ. of California, Berkeley.

2:30 BREAK

3:00 326. ECHOS OF THE PAST, AND AN ECHO OF THE FUTURE. B.C. Gerstein, Iowa State Univ., Ames, Iowa.

3:30 327. SECOND GENERATION CP/MAS TECHNIQUES: APPLICATION AND EXPERIMENTAL ASPECTS. K. W. Zilm, and G.G. Webb, Yale Univ., New Haven, CT.

4:00 328. MULTIPLE PULSE LINE NARROWING EXPERIMENTS WITH MAS. B. Hawkins, C. Bronnimann and G.E. Maciel, NSF Regional NMR Center, Fort Collins, CO.

WEDNESDAY MORNING, July 17, 1985 - Second Floor, Room C

8:25 Introductory Remarks - D.A. Netzel

8:30 329. ^{13}C CHEMICAL SHIFT ANISOTROPIES BY 2-D FT METHODS. M. Sardashti, and G.E. Maciel, Colorado State Univ., Fort Collins, CO.

9:00 330. VARIABLE TEMPERATURE C-13 CP/MAS STUDIES. J.F. Haw, R.A. Crook, S.W. Hanna, R.A. Crosby and G.C. Campbell, Texas A & M Univ., College Station, TX.

9:30 331. TRITIUM NMR-NEW PROSPECTS, PROBLEMS, AND SOME RESULTS. S. Un, G.S. Karczmar, F. Tang, H. Morimoto and M.P. Klein, Lawrence Berkeley Laboratory, Berkeley, CA.

10:00 BREAK

10:30 332. DEUTERIUM RELAXATION AND LINESHAPES IN CLATHARATES. R.R. Vold, R.L. Vold, M.S. Greenfield and A.D. Ronemus, Univ. of California, San Diego.

11:00 333. DNP-HRNMR INSTRUMENTATION: A QUASI-OPTICAL APPROACH. C.S. Yannoni, D. Singel, and R.D. Kendrick, IBM Research Laboratory, San Jose, CA.

11:30 334. NMR IMAGING OF SOLIDS VIA DNP. M. Davis, and G.E. Maciel, Colorado State Univ., Fort Collins, CO.

WEDNESDAY AFTERNOON, July 17, 1985 - Second Floor, Room C

1:25 Introductory Remarks - D.A. Netzel

1:30 335. VARIABLE TEMPERATURE MAS STUDIES OF SURFACE ADSORBED SPECIES. L. Balthusis, J. Frye and G.E. Maciel, Colorado State Univ., Fort Collins, CO.

2:00 336. SOLID STATE NMR OF SURFACE ADSORBED SPECIES: RESULTS FROM SOME MODEL SYSTEMS. L. Bonneviot, K.W. Zilm, G.G. Webb and G.L. Haller, Yale Univ., New Haven, CT.

2:30 337. STUDY OF DYNAMICS OF SMALL MOLECULES SORBED BY ZEOLITES. R.R. Eckmann, and A.J. Vega, Exxon Chemical Co, Baytown, TX and DuPont, Co., Wilmington, D.E.

3:00 BREAK

3:30 338. SOLID STATE OXYGEN-17 NMR STUDIES OF ZEOLITES. K. Kyung, C. Timken, G.L. Turner, E. Oldfield, L.B. Welsh and J.P. Gilson, Univ. of Illinois, Urbana, IL and Signal, UOP, Des Plaines, IL.

4:00 339. SOLIDS MAS NMR SPECTROSCOPY AS A PROBE OF DIAGNETIC PROCESSES. D.E. Woessner and S.E. Sommer, Mobil R & D Corp., Dallas, TX.

4:30 340. STRUCTURAL CHARACTERIZATION OF 3-AMINOPROPYLTRIETHOXYSILANE - BONDED TO SILICON WITH SOLID STATE CP/MAS NMR. G.S. Caravajal, D.E. Leyden and G.E. Maciel, Colorado State Univ., Fort Collins, CO.

THURSDAY MORNING, July 18, 1985 - Second Floor, Room C

8:25 Introductory Remarks - F. P. Miknis

8:30 341. THE TWO-DIMENSIONAL J-CORRELATED AND NOE-CORRELATED PROTON NMR SPECTROSCOPY OF POLY (METHYL METHACRYLATE). F.C. Schilling, F.A. Bovey, M.D. Bruch and S.A. Kozlowski, AT&T Bell Labs, Murray Hill, NJ.

9:00 342. CORRELATION OF NMR MEASURED STRUCTURAL PARAMETERS WITH PHYSICAL AND ELECTRONIC PROPERTIES OF AMORPHOUS CARBON FILMS. S. Kaplan, F. Jansen, and M. Machonkin, Xerox Research Center, Webster, NY.

9:30 343. SOLID STATE NMR STUDIES OF ^{13}C - ^{15}N CROSSLINKS. J.R. Garbow, J. Schaefer, E.O. Stejska., G.S. Jacob, and K.L. Kramer, Monsanto Co., St. Louis, MO and USDA, Manhattan, KS.

10:00 BREAK

10:30 344. APPLICATIONS OF DYNAMIC NUCLEAR POLARIZATION IN COAL RESEARCH. R.A. Wind, Delft Univ. of Technology, Delft, Netherlands.

11:00 345. FRACTIONATION AND MAGNETIC RESONANCE CHARACTERIZATION OF COAL-*LIQUIFACTION RESIDUUM. H.L. Retcofsky, R.F. Sprecher, M.B.* Perry, R.P. Warzinski and R.G. Lett, Pittsburgh Energy Technology Center, Pittsburgh, PA.

11:30 346. INVESTIGATION OF THE FREE SWELLING BEHAVIOR OF COAL BY IR AND NMR. T.E. Hammond and W.E. Ritchey, Standard Oil Co., Cleveland, OH, and Case Western Reserve Univ. Cleveland, OH.

GENERAL SESSION - POSTERS

WEDNESDAY MORNING, July 17, 1985 - First Floor, Room F
9:30 - 11:30

347. SPARK TESTING STEELS. F. Xavier Spiegel, Loyola College, Baltimore, MD 21210

348. AN EVALUATION OF HAMMETT RELATIONSHIPS DERIVED FROM INFRARED C=N STRETCHING DATA FOR AROMATIC SCHIFF BASES. J. J. Rafalko and E. W. Choe, Celanesa Research Co., 86 Morris Ave., Summit, N.J. 07901

349. NATURAL GOLD SOLUBILITY AND THE FORMATION OF CRYSTALLINE GOLD IN PLACERS. J. G. Crock, R. C. Severson, and B. M. McConnell, U.S. Geological Survey, Box 25046, MS 928, DFC, Denver, CO 80225

350. AN ANALYTICAL CHEMICAL APPROACH TO PROBLEMS IN ANASAZI ARCHEOLOGY. M. Schwindt, D. M. Mehs, Ft. Lewis College, Durango, CO 81301 and S.E.E. Schwindt, Edge of the Cedars Museum, Blanding, Utah 84511

351. A STREAM SURVEY IN WESTERN COLORADO. S. Krening and D. Mehs, Ft. Lewis College, Durango, CO 81301

352. A POWERFUL KJELDAHL NITROGEN METHOD USING PEROXMONOSULFURIC ACID. Clifforn C. Hach, Scott V. Brayton, and Allen B. Kopelove, Hach Technical Center, Hach Company, Loveland, CO 80539.

353. CONTAMINATION OF A SURFICIAL AQUIFER BY POLYCHLORINATED DIBENZO-P- DIOXINS. W. E. Pereira and C. E. Rostad. U.S. Geological Survey, Box 25046, Mail Stop 407, Federal Center, Denver, CO 80225

354. USE OF WIDE BORE CAPILLARY IN GAS CHROMATOGRAPH DESIGNED FOR PACKED COLUMN. James Brown and Paul Silvis, Supelco, Inc.

356. THE ANALYSIS OF GEOLOGICAL MATERIALS FOR SELECTED VOLATILE TRACE ELEMENTS BY SOLID SAMPLE ICP-OPTICAL EMISSION SPECTROGRAPHY. D. E. Detra and J. A. Dominico, U.S. Geological Survey.

357. ^{15}N-NMR INVESTIGATION OF HYDROXYLAMINE DERIVATIZED HUMIC SUBSTANCES. K. A. Thorn, U.S. Geological Survey, WRD., and J. B. Arterburn, and M. A. Mikita, Department of Chemistry, University of Colorado at Denver.

358. EXPERIENCES WITH MS/MS AT THE TEXAS AIR CONTROL BOARD, James L. Lindgren, J. Maxine Jenks, Ph.D., Texas Air Control Board, 6330 Highway 290 East, Austin, TX 78723.

1 NO ABSTRACT

2 MEASUREMENTS OF THE DRY DEPOSITION OF NITRIC ACID TO A DEVELOPING WINTER WHEAT CROP.

B. J. Huebert and James F. Galasyn, Department of Chemistry, Colorado College, Colorado Springs, CO 80903.

As one part of a cooperative experiment to study the nitrogen budget of wheat, we are using a Modified Bowen-Ratio method to measure the dry deposition of nitric acid to an Eastern-Colorado winter-wheat field. Our immediate goal is to estimate the significance of atmospheric nitrate as a nitrogen source for the crop. We will discuss the change in deposition velocities, fluxes, and surface resistances as the field changes from virtually bare soil to a mature crop, and compare our flux estimates to other sources of fixed nitrogen.

3 A NEW NITRIC ACID CALIBRATION SYSTEM

L.J. Nunnermacker, R.R. Dickerson, A. Fried, Department of Meteorology, University of Maryland, College Park, Maryland 20742.

Acid deposition is one of the most important environmental issues facing scientists today. Nitric acid comprises approximately one-third of all acid deposition and it is the primary sink for NO_x in the atmosphere. Chemiluminescence is one of the most sensitive techniques used in atmospheric chemistry. Nitric oxide, NO, reacts with ozone, O_3, to produce nitrogen dioxide which emits light measured by a photomultiplier tube. In order to use this or any other technique effectively for the measurement of nitric acid, a reliable calibration source is needed. Existing methods of calibration are difficult to use or are unreliable. We have developed a new method of calibration involving the following reaction:

$$HCl(g) + AgNO_{3(s)} \rightarrow HNO_{3(g)} + AgCl_{(s)} \quad \Delta G \approx -13.63\ \text{kcal}$$

Gaseous hydrochloric acid, HCl, is passed through solid silver nitrate contained in a teflon column. The gas stream was analyzed for HNO_3 and HCl using ion chromatography, after bubbling into deionized water. Chemiluminescence is used to measure nitric acid in the gas stream with a difference measurement obtained by alternately passing the sample directly through hot molybdenum, where it is quantitatively converted to NO, and then through a nylon filter where it is preferentially removed. The system is zeroed using ultra high purity N_2 or air. Gaseous HCl is converted to gaseous HNO_3 with an efficiency in excess of 95%.

4 MEASUREMENTS OF THE SEASONAL AND DIURNAL VARIATIONS OF NITRIC ACID VAPOR AT THE MAUNA LOA OBSERVATORY.

B. J. Huebert, James F. Galasyn, and K. L. Tschudy, Department of Chemistry, Colorado College, Colorado Springs, CO 80903.

We have made measurements of nitric acid vapor at Mauna Loa Observatory every other month since October of 1984. In each sampling period we have noted a dramatic difference between day and night average concentrations, with the higher values being in the daytime. Typical day/night averages are 54/27 pptv (Oct.'84), 23/9 pptv (Dec. 84), and 18/9 pptv (Feb. 85). We will discuss the role which meteorological factors play in causing the observed variations, with the aim of identifying the diurnal and seasonal variations in the chemistry of the remote free troposphere. We will also report measured concentrations of HCl and several inorganic aerosol species.

5 OBSERVATIONS OF NO AND OTHER ODD-NITROGEN SPECIES DURING THE STRATOZ III MISSION

A. Volz and John W. Drummond, Institut für Chemie, Kernforschungsanlage Jülich GmbH, Postfach 1913, D-5170 Jülich, FRG
M. Malejczyk, Institut für Analytische Chemie, Universität Dortmund, Postfach 500500, D-4600 Dortmund, FRG

Chemiluminescence detectors were flown aboard a Caravelle aircraft during the STRATO III campaign in June, 1984. The instrument consisted of four individual NO detectors for the simultaneous measurement of NO, NO_2 and NO_y (NO_y = NO + NO_2 + NO_3 + 2 x N_2O_5 HNO_3 + HNO_4 + PAN + aerosol nitrate). NO_2 was measured by photolysis to NO, and NO_y was measured by means of a denuder/catalytic converter system, which in principle allows the discrimination between gaseous acids and particulate nitrate. The vertica and latitudinal distribution of NO between 67° N and 60° S and preliminary data for NO_2 and NO_y will be presented. In addition, some problems associated with the measurement of NO_2 and NO_y in background air will be discussed.

6 LONG-TERM MEASUREMENTS OF ATMOSPHERIC PEROXYACETYL NITRATE (PAN) AT RURAL SITES IN SOUTHERN ONTAIRO AND NOVAL SCOTIA.

K.A. Brice, Concord Scientific Corporation, 2 Tippett Road, Toronto, Ontario M3H 2V2, Canada; and J.W. Bottenheim, K.G. Anlauf, and H.A. Wiebe, Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ontario, M3H, 5T4, Canada.

Peroxyacetylnitrate (PAN) is an important secondary pollutant formed in the ambient atmosphere during photochemical episodes. It consitutes a significant component of the atmospheric NO_x cycle, and can undergo long-range transport to remote receptor sites. The behavior of PAN has been studied using automated gas chromatographic techniques over extended periods at two sites in Eastern Canada: Longwoods in Southern Ontario (Feb. - Oct. 1983), and Kejimkujik in Nova Scotia (May 1984 - May 1985). The episodes of elevated PAN concentratiopns at these sites are examined with reference to back-trajectory analyses and, Lagrangian modelling and the apparent seasonal variations and diurnal fluctuations described and compared. Available data for other atmospheric components, such as O_3, HNO_3 and particulate nitrate are used to examine the role of PAN in the long-range transport of nitrogen species.

7 Total atmospheric sulfur gas mixing ratios can be measured by metal foil collection/flash vaporization/flame photometric detection. Sample air is passed over a palladium foil which adsorbs the sulfur gases. The loaded foil is flash heated by an electric current, and the desorbed gases are carried to a flame photometric detector. This method gives total sulfur concentrations without speciation. Ground level measurements were made at various locations in the Antarctic. A number of whole air samples were also taken in stainless steel canisters for gas chromatographic analysis. Concentrations measured were in the parts per trillion range. This data has applications to better understanding the global sulfur cycle, the contributions of natural sulfur emissions and long range transport. An assessment of the applicability of the method for atmospheric measurements will be given.

8 THE OZONE PHOTOOXIDATION OF POLYCYCLIC AROMATIC HYDROCARBONS AND OF PYRENE QUINONES. V. W. Cope, Department of Chemistry, The University of Michigan-Flint, Flint, MI 48503 Donald R. Kalkwarf, Battelle P.N.L., Richland, Washington 99352

The effect of solar-simulated radiation on the reaction of ozone with PAHs coated on glass was studied. The PAHs examined were pyrene, perylene and benzo(a) pyrene. The rates of reaction of ozone with these PAHs were not affected by radiation intensities up to 1.3 kW/m^2. However, the reaction rate of ozone with pyrene quinones was dramatically increased by exposure to solar simulated radiation. The rate of reaction is proportional to the ozone concentration and to the amount of pyrene quinone on the glass surface. The ozonation rate constant in the presence of simulated sunlight was 8.2×10^{-4} s^{-1} at 24°C and $[O_3] = 6.25 \times 10^{-6}$ mol/m^3. This is about 15 times the rate of the dark reaction. The same product results from the reaction of ozone with pyrene-1,6-quinone as with pyrene-1,8-quinone. A reaction scheme is proposed to account for the observed results.

Supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

9 ACTINIC FLUX AND PHOTODISSOCIATION RATES IN THE HIGH ALTITUDE WEST, Gerald E. Streit Los Alamos National Laboratory, Los Alamos, NM 87545

The non-urban high altitude West is widely known as a region of clean air and plentiful sunshine. To understand the potential for atmospheric photochemistry in what is now a precursor limited environment, the plentiful sunshine must be quantitatively characterized. Actinic flux (spherically integrated photochemical irradiance) calculations have been made with model atmospheres specific to the high altitude West. The parameters which are specific to the West include surface elevation, surface albedo, aerosol loading, and ozone climatology. Results of actinic flux and selected photodissociation rate calculations will be presented and compared to sea level calculations and to the available high altitude experimental j_{NO_2} determinations.

10 FORMALDEHYDE MEASUREMENTS IN NATURAL WATER SYSTEMS. Scott Elliott, Department of Chemistry, University of California, Irvine, California 92717. David C. Lowe, Department of Scientific and Industrial Research, Institute for Nuclear Sciences, Lower Hutt, New Zealand.

Atmospheric exchange dominates the formaldehyde chemistry of surface fresh waters and accounts for all observed formaldehyde concentrations and trends. With increasing depth, chemical loss processes compete with back exchange to the atmosphere. Hydroxyl attack may be the major loss pathway in surface seawater, and formaldehyde may serve as an indicator of mixed layer of hydroxyl concentrations. Coastal enrichment suggests that biological activity is a local source to seawater.

11 FLUXES OF DMS AND COS FROM THE OCEANS TO THE ATMOSPHERE.

R.J. Ferek, SRI International, 33 Ravenswood, Menlo Park, CA 94025 and M.O. Andrea, Department of Oceanography, Florida State University, Tallahassee, FL 32306.

We have extended our program of measurements of the oceanic fluxes of dimethyl-sulfide (DMS) and carbonyl sulfide (COS) into two new areas. Previously, we had found that DMS has fairly uniform concentrations over open ocean areas, and it varies diurnally with an afternoon minimum due to oxidation by photochemically produced OH. We have now measured vertical concentration profiles from an aircraft over the tropical Atlantic and found that DMS decreases with altitude at a rate consistent with expected rates of vertical transport from the sea surface and destruction by oxidation by OH.

Past measurements of COS in coastal waters of high organic content had shown that COS is produced photochemically in the uppermost layer of the ocean, and that it varies diurnally with sunlight intensity. We have recently measured dissolved COS in open ocean aeas and continue to find a diurnal cycle which has a smaller amplitude and lower concentrations than were measured in coastal waters.

12 Mechanism of the Gas Phase Oxidation of Sulfur Dioxide in the Atmosphere.

L.G.Anderson and P.M.Gates, Department of Chemistry, University of Colorado at Denver, Denver, CO 80202.

The major homogeneous gas phase oxidation process for SO_2 in the atmosphere is initiated by the attack of hydroxyl radicals upon SO_2. This process is of major importanc in the formation of acid precipitation. In many atmospheric models of acid formation, thi process is treated as

$$HO + SO_2 \longrightarrow H_2SO_4$$

Thus for each SO_2 oxidized, one H_2SO_4 is produced and one HO radical is consumed. Calvert and Stockwell have presented experimental evidence suggesting that this may not be the case. Their data suggests that under atmospheric conditions this reaction may not act as a HO radical chain termination process. They proposed the following mechanism for the reactions subsequent to the $HOSO_2$ radical formation by the addition of HO to SO_2.

$$HOSO_2 + O_2 \longrightarrow HO_2 + SO_3$$
$$HO_2 + NO \longrightarrow NO_2 + HO$$

The SO_3 produced by this mechanism would be rapidly converted to H_2SO_4 in the presence of water. This mechanism suggests that HO radical, the limiting reagent in the oxidation of SO_2 to H_2SO_4, could be regenerated in the presence of both O_2 and NO.

In this work, we are interested in testing the mechanism outlined above for the HO-SO_2 reaction under conditions appropriate for the atmosphere. Discharge flow-resonance fluorescence techniques have been used in this study. The concentration of HO radicals was monitored in the presence of SO_2, with and without added atmospheric constituents. Th effects of the added O_2, NO and O_2 + NO on the observed HO concentrations will be discuss

13 A SIMPLE MODEL OF CONVECTIVE TRACE GAS TRANSPORT

B.S. Gockel, R.R. Dickerson, G.J. Huffman, Department of Meteorology, University of Maryland, College PaRK, MD 20742.

We have studied cumulus clouds' microphysical-dynamical interaction, and the resulting trace gas transport. A time dependent, two cylinder (Asai-Kasahara) cumulus cloud model simulates the important microphysical processes and vertical transport of water vapor, carbon monoxide and ozone in the cloud-environment system. Thermodynamic and chemical input from in-situ measurements are used for comparison between the model's simulation and the observed atmosphere; we attempt to explain the observed chemical and thermodynamic profiles in terms of the cloud scale processes. In doing so, we investigate the importance of convective vertical transport to the maintenance of tropospheric trace gas profiles.

14

A NUMERICAL SIMULATION OF THE FORMATION AND TRANSPORT OF SULFATE IN CLOUDS

- R. A. Sarma, Institute of Atmospheric Sciences, South Dakota School of Mines and Technology, Rapid City, SD 57701-3995.

A two-dimensional, time dependent cloud model is used to study the interactions between cloud scale motions and some significant chemical reactions which help form sulfates and acidity in clouds. Aqueous phase oxidation of SO_2 by ozone, scavenging of sulfate aerosol through Brownian motion, inertial impaction and nucleation processes are modeled. The reaction rates are made temperature dependent. Typical values are used for initial background aerosol field. Gas-to-particle conversion rates of ~1% h^{-1} and evaporation of cloud water and rainwater are modeled as sources of ambient aerosol. Simulations are made of convective clouds and stratiform clouds. The relative significances of the various scavenging mechanisms modeled are investigated for either type of clouds. The effects of including a source at low levels such as a coal-fired power plant are studied. Current results indicate that nucleation scavenging and production of aerosol through evaporation of cloud droplets are dominant mechanisms. The simulations also show the ability of convective clouds to transport pollutants from the boundary layer to upper levels. The time evolution of the vertical fluxes of SO_2, H^+ and aerosol are also examined.

15

A FAST CHEMILUMINESCENT METHOD FOR DETECTION OF ATMOSPHERIC OZONE

John D. Ray and D. H. Stedman, Chemistry Dept., University of Denver, Denver, CO 80208

An instrument for measuring atmospheric ozone has been developed that uses chemiluminescent dyes in solution. The detection cell is designed so that a thin layer of dye solution flows over an absorbant target material which is exposed to sample air. Light produced by the reaction with ozone is measured with a photomultipier tube. The dyes rhodamine-B, safranine-O, eosin-Y, and fluorescein have been found to be effective for ozone detection. Other atmospheric compounds, such as NO, NO_2, or PAN, gave no response. The detector was calibrated with known concentrations of ozone and had linear response over the range of 0.1 to 500 ppb ozone. Several solvents have been examined to determine both the effect on sensitivity and the stability of the solutions. Measurements of ambient air in Denver have been compared to a commerical detection instrument. The chemiluminescence detector is more sensitive and has a faster response.

16

OZONE CONSERVATION IN CUMULUS CLOUDS

C. WEAVER and R. PEARSON, JR., Department of Atmospheric Science, Colorado State University, Ft. Collins, CO 80523

The role of cloud processes in tropospheric chemistry is receiving increasing attention because clouds can sometimes provide a mechanism for mixing boundary layer air with the free atmosphere above. Ozone has many desirable characteristics as a tracer which are used to study cloud processes. It is sparingly soluble and relatively unreactive to water; in many environments the ozone mixing ratio does not change rapidly on the time scale characteristic of many cloud processes (15 to 30 min); and it can be measured from an aircraft with high spatial (ca. 10 m) and temporal resolution. To establish whether ozone is conserved during moist convection, an aircraft equipped with turbulent rate (10 Hz) meteorological and ozone sensors made multiple penetrations of an actively growing, nonprecipitating cumulus congestus turrets over SE Montana during June 1981. Measurements of ozone will be compared to properties generally accepted as approximately conserved in nonprecipitating clouds, such as a thermodynamic temperature and total water substance. Results from this analysis suggest that ozone is conserved during moist convection, and that estimates of entrainment from this chemical scalar are in general agreement with those obtained from thermodynamic quantities.

17 "MEASUREMENT OF TOTAL PEROXY FREE RADICALS BY PERCA IN BENNETT, CO"

Total atmospheric peroxy free radicals were measured at a site near Bennett, CO during the month of May 1985. The site, also used by NCAR, NASA, and Colorado College for monitoring a wide variety of parameters, proved ideal for clean air measurements. This period represents the first extended field measurement trial of PERCA (PEroxy Radical detection by Cemical Amplification) in conjunction with so many other parameters essential to model considerations. Free radical data will be presented along with instrumental considerations.

18

LATITUDINAL GRADIENTS IN TROPOSPHERIC CONCENTRATIONS OF METHANE AND C_2-C_3 HYDROCARBONS. Donald R. Blake and F.S. Rowland, Department of Chemistry, University of California, Irvine, California 92717

The latitudinal distribution (71°N - 53°S) of tropospheric methane has been measured in various seasons over the time period since 1978. Integration of these observations indicates a steady increase in CH_4 concentration by about 17 parts per billion by volume per year. The observed concentrations in the southern hemisphere are often nearly constant at latitudes below about 10°S or 20°S, but this "southern hemisphere" concentration can increase or decrease by as much as 30 ppbv in a period as short as 3 months. The latitudinal gradient for CH_4 can be fitted with transport parameters derived from the latitudinal gradients found for chlorofluorocarbons and an atmospheric lifetime of about 9 or 10 years. The tropospheric concentrations of C_2 and C_3 hydrocarbons have been measured over the same latitudinal range in 1984-85.

19 **ATMOSPHERIC PHOTOOXIDATION OF HYDROCARBONS: POTENTIAL PATHWAYS AND INTERMEDIATES.** H. Niki, Research Staff, Ford Motor Company, Dearborn, Michigan 48121.

Numerous gaseous alkane, alkene, and aromatic hydrocarbons are introduced into the troposphere from various natural and man-made sources, and undergo photochemical oxidation reactions there to yield products which are eventually removed from the gas phase by heterogeneous processes. The oxidative degradation of hydrocarbons leads to the formation of a large variety of free radicals, e.g. RO_2 and RO (R = organic group), and intermediate molecular products, e.g. aldehydes, ketones, alcohols, acids, peracids, alkyl nitrates, and peroxyacyl nitrates (PANs). The overall photooxidation of hydrocabons is extremely complex. The exact nature of the reaction pathways and intermediate species involved is highly dependent on the atmospheric conditions, i.e. solar intensity, temperature, pressure, humidity, etc. More importantly, NO_x ($NO + NO_2$) plays a crucial role in controlling the formation of these organic oxidants as well as ozone. Thus far, field studies to test these photochemical processes have been severely hampered by the lack of adequate methodologies to measure the concentrations of the key radical and molecular products. During the past several years, concerted efforts are being made in a handful of laboratories including ours to characterize the atmospheric chemistry and spectroscopy of the relevant molecular organic intermediates. Recent results from these studies will be highlighted in this talk.

20 CHARACTERIZATION OF PERFORMANCE AND APPLICATION OF A CLOSED-TUBE ION MOBILITY SPECTROMETER TO DETECTION OF SELECTED ATMOSPHERIC POLLUTANTS. G. A. Eiceman, C. S. Leasure, V. J. Vandiver and G. Rico, Department of Chemistry, New Mexico State University, Box 3C, Las Cruces, New Mexico, 88003

A closed-tube ion mobility spectrometer (IMS) with unidirectional flow of drift gas was constructed for assessment as a continuous atmospheric monitor for gaseous organic and inorganic pollutants in hostile environments. Advantages of the closed-tube IMS include, low sample clearance times and simplicity of design. Additionally, sensitivity of 1 ppb limit of detection and speed of analysis (10s for complete analysis) makes IMS potentially useful as a point source atmospheric monitor. IMS was also used in studies for determination of ion equilibria processes of selected binary and ternary mixtures of polycyclic aromatic hydrocarbon (PAH) and relative proton affinities of these PAH were measured. Relative proton affinities in air at atmospheric pressure were found to decrease in order, anthracene>phenanthrene>naphthalene>benzene as consistent with basicity values measured using high vacuum techniques. In addition, detection limits, response curves for detection of some pollutant gases, SO2, NO2, Co, Hcl, H2S, N2H4 and CH3N2H3 and limits of detection were in general from 0.01 to 10 ppb without sample pretreatment. Finally, implications from these studies to application of IMS as an atmospheric monitor of toxic pollutants will be addressed.

[illegible] LIMITATIONS ON THE GRADIENT METHOD FOR MEASURING SURFACE LAYER DEPOSITION FLUX, B. L. WOODRUFF AND R. PEARSON, JR., Department of Atmospheric Science, Colorado State University, Ft. Collins, CO 80523

With the growing interest in characterizing the dry deposition of trace gases has come the desire to find alternatives to the eddy correlation technique which is effective, but requires fast response sensors. Gradient techniques have been used although they require measuring small differences in concentration and few analytical techniques are known which are intrinsically differential. Two independent instruments can be used which is expensive and can create problems of intercalibration in differencing 2 measurements. Alternatively, a single analyzer can be used to sample alternately at 2 levels, eliminating certain calibration problems, but introducing sampling errors which are difficult to quantify and are often neglected. This paper analyzes the errors in measuring vertical flux by a gradient technique incorporating the 'down and up' sampling scheme. The errors are shown to be very sensitive to the ratios among certain time scales: the averaging time, the period of the down and up cycle, the time wasted during up/down transitions (including probe travel, plumbing lag, and instrument response) and the integral time scale of the concentration. The selection of appropriate time parameters will help to minimize errors in future flux determinations by the gradient technique.

22 NO ABSTRACT

23 ON THE ACIDITY OF DEW

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Japar, and J. M. Norbeck, Research Staff, Ford Motor Company, P.O. Box 2053,
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Nightly dew samples were collected on Allegheny Mountain in southwest Pennsylvania in August 1933. The dew was found to be acidic, with mean pH ~ 4.0. Free H^+ comprised > 8 *of the total acidity, and the composition represented essentially* a H_2SO_4/HNO_3 *combination,* with average SO_4^{2-}/NO_3^- mole ratio. ~ 1.3 (2.5 in terms of H^+ equivalents). The c mistry of the dew resembled that of rain at Allegheny, though generally more dilute.

Atmospheric species responsible for dew acidity were determined. $HNO_3(g)$, with aver deposition velocity ~ 0.24 cm/sec, was chiefly responsible for the dew NO_3^-. Both SO_2 aerosol SO_4^{2-} contributed to the dew SO_4^{2-}, with respective deposition velocities ~ 0.04 and ≤ 0.07 cm/sec. SO_2 was the source of ~ 80% of the dew SO_4^{2-}. The allocation of dew H^+ among atmospheric precursors was HNO_3 ~ 30%, SO_2 ≥ 60%, aerosol H^+ ≤ 10%.

Not all of the S(IV) in dew had been converted to SO_4^{2-} *by morning; thus, the rate* of oxidation during the night *must have been on a time scale* of hours at ambient temperatures. *We did not see* S(IV) oxidation in progress in collected rain samples.

Deposition fluxes and 21-day cumulative deposition totals involving dew, rain, and settled fogwater were compared. For all solute species, the ranking proved to be dew < settled fogwater << rain in terms of fluxes, and settled fogwater ~ dew << rain in terms of deposition totals.

24 MEASUREMENTS OF ATMOSPHERIC NITROGEN COMPOUNDS AT ALERT IN THE CANADIAN ARCTIC.

J.W. Bottenheim, A.J. Gallant, Atmospheric Environment Service, Downsview, Ontario, Canada M3H 5T4, and K.A. Brice, Concord Scientific Corporation, Toronto, Ontario, Canada.

Previous studies of Arctic air quality have shown that elevated concentrations of suspended particulate matter occur throughout the atmosphere of the northern polar region during winter. To date, more attention has focussed upon the importance of secondary sulphate formation from SO_2 oxidation in the production of this "Arctic haze". Previous efforts to examine the role of secondary nitrate production, and the speciation of atmospheric nitrogen compounds under these conditions have been largely unsuccessful because of inadequate detection limits. During March 1985, an intensive field study at Alert in the Canadian Arctic provided preliminary information on the ground-level ambient concentrations of these species. Peroxyacetylnitrate was monitored by automated gas chromatography, NO and NO_x were determined using a sensitised commercial chemiluminescent analyser, and NO_2 was measured by means of the specific chemiluminescence interaction with luminol. Supporting data for particulate nitrate, O_3 and ambient C_2-C_{10} chydrocarbons will also be presented.

25 MEASUREMENTS OF FORMATE AND ACETATE IN PRECIPITATION AND AEROSOLS

R. B. Norton (Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80303).

Formate and acetate, as well as other organic and inorganic anions, have been measured in precipitation and aerosols collected in Colorado at Niwot Ridge and Boulder, and in Hawaii on Mauna Loa. In precipitation, the organic anion concentration is usually at least 20% of the nitrate concentration and occasionally is equal to the nitrate. Formate is the dominant organic anion measured with concentrations as large as 9×10^{-5} M occurring in summer rain showers. A variety of dicarboxylic anions are observed also bu their concentration is generally much less than formate. Comparisons between these precipitation measurements and the aerosol measurements will be made. Comparisons between the sites will be made and the variability of the ions will be discussed.

This research is supported by NOAA as part of the National Acid Precipitation Assessment Program.

26 STUDIES AIMED AT UNDERSTANDING PHOTOCHEMICAL PRODUCTION OF OZONE IN THE NON-URBAN TROPOSPHERE

F. C. Fehsenfeld (Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80303).

Since the photolysis of ozone initiates most tropospheric photochemistry, the study of tropospheric photochemistry has, as a logical beginning, the investigation of the processes responsible for the production and destruction of ozone. Current understanding of tropospheric O_3 recognizes two primary sources for ozone, stratospheric injection and photochemical production in the troposphere. The photochemical production of O_3 in most of the troposphere is NO_x $(NO + NO_2)$ limited. For this reason, understanding ozone formation, as well as an assessment of the potential for alteration of the global ozone budget, depends on understanding the role played by NO_x in ozone production. The present understanding of the photochemical production of ozone will be discussed. Recent measurements of the correlation of ozone production with NO_x concentration will be presented and compared with predictions from model calculations. The use of the photochemical stationary state between NO and NO_2 as a measure of atmospheric oxidants and its implication for ozone production will be discussed, and recent measurements aimed at assessing this balance will be described.

This research is supported by NOAA as part of the National Acid Precipitation Assessment Program.

27 MEASUREMENTS OF NO_y IN THE RURAL TROPOSPHERE

D. W. Fahey (Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80303).

Laboratory and field tests have shown the suitability of a technique for measuring total gas-phase, reactive odd-nitrogen, NO_y, in the atmosphere. The technique utilizes the reduction of the higher nitrogen oxides to NO on the surface of a heated Au tube in the presence of CO and O_2. The NO produced is subsequently detected by NO/O_3 chemiluminescence. During the summer and fall of 1984, measurements of the NO_y mixing ratio were made in the rural troposphere at Niwot Ridge, Colorado. An additional Au tube was used with a Teflon filter element placed upstream to assess the contribution of particulates to the NO_y signal. Other measurements made simultaneously at the site included NO, NO_2, HNO_3, NO_3^- particulate, O_3, and peroxyacetyl nitrate (PAN). The NO_y data will be examined for the diurnal and seasonal trends with data correlations used to show the photochemical interrelationships between NO_y and the separately measured species. Finally, the data will be used to examine the mass balance between NO_y and the sum of the NO_y component species.

This research is supported by NOAA as part of the National Acid Precipitation Assessment Program.

28 MEASUREMENT OF NO AND NO_2 AT NIWOT RIDGE COLORADO

P. C. Murphy (Cooperative Institute for Research in Environmental Sciences, Boulder, CO 80309).

Niwot Ridge is located in the Colorado mountains at an elevation of 10,000 ft., approximately 50 miles west of Denver. Depending on meteorology, the air reaching this ite may be reasonably unpolluted, representative of the continental background or alrnatively, heavily polluted air that has passed over the urban area to the east. The ite and the instrumentation located at the site will be described, and the systematics and trends of the NO_x distribution at the site as a function of diurnal cycle and season will be discussed.

This research is supported by NOAA as part of the National Acid Precipitation ssment Program.

29 THE ANALYSIS OF SOLID SAMPLES BY GRAPHITE FURNACE ATOMIC ABSORPTION USING ZEEMAN BACKGROUND CORRECTON.

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Although graphite furnace atomic absorption is one of the most sensitive techiques for trace element determination, the analysis of solid materials can be challengingly difficult. For furnace analysis, solid materials are typically dry-ashed or digested with mineral acids. However, these procedures are often quite time-consuming and potentially a source of contamination and analyte loss. If the trace metal content is very low in the solid material, the dissolution procedure may dilute the analyte to concentrations near or below the detection limit. The problems of contamination, analyte loss, and dilution may be eliminated by direct atomization of solid samples. We will evaluate the usefulness for certain samples of a solid sampling device that, like platform, delays atomization relative to the tube wall. Using this device, quantitat of solid samples may often be achieved using aqueous standards. We will also characterize some alternate wavelengths which might be used with Zeeman background correction for the determination of metals in solid samples.

30 AQUEOUS TOTAL CHROMIUM: PROBLEMS WITH PERMANGANATE OXIDATION; A POTENTIAL SOLUTI WITH CERIUM(IV).

Edward W. Matthews and Ronald C. Hooper, U.S. Geological Survey National Water Quality Laboratory-Atlanta, 6481-H Peachtree Industrial Boulevard, Doraville, Georgia 30340.

The permanganate procedure used to oxidize chromium before chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone causes accuracy and reproducibility problems. The method requires excessive time and patience. The causes of the difficulties are: 1) excess permanganate chelates with APDC, and result in the precipitation of manganese oxides that clog nebulizers and may coprecipitate chromium; 2) a slight excess of azide, employed to reduce permanganate, reduces Cr^{+6} to lower valence states which are not chelated or extracted; 3) highly colored samples make it difficult to visualize when permanganate is in excess or it has been removed.

Alternatively, cerium(IV) oxidizes all lower-valenced chromium to Cr^{+6}. It can be employed with a wide variety of sample types, thus avoiding the permanganate-azide oxidation. Accuracy and reproducibility are significantly improved. The analytical range is from 1 to at least 200 ug/L. The entire procedure is easy, direct, and labor-saving.

31 SECOND SURFACE ATOMIZATION; ANALYTICAL FLEXIBILITY AND INTERFERENCE REDUCTION FOR GRAPHITE FURNACE AA.

T.M. Rettberg and J.A. Holcombe, Department of Chemistry, University of Texas, Austin, Texas 78712

A modification to a Varian GTA-95 atomizer to include a conductively cooled Ta surface permits unique analytical capabilities for graphite furnace atomic absorption. Less stringent requirements for charring temperatures, the use of char temperatures in excess of the analyte vaporization temperatures and the capability of accurately using peak height measurements with complex matrices will be demonstrated. The direct analysis of solids with calibration using aqueous standards will also be presented.

The analyte is "distilled" to the tantalum carbide-coated second surface during a high temperature char cycle and held on this surface by a flow of coolant on the backside of this surface. The furnace is raised to a high ("atomization") temperature, the coolant removed, and the rerelease of the analyte into the preheated, furnace environment occurs.

32 REDUCTION OF FURNACE INTERFERENCES BY DELAYED ATOMIZATION TECHNIQUES.
J.J. Roberts, G.R. Dulude, M.C. Almeida, and J.J. Sotera. Allied Analytical Systems, 590 Lincoln Street, Waltham, MA 02254.

In 1977 L'vov suggested that the placement of a graphite platform within a cylindrical-pulsed type furnace could reduce vapor-phase interferences by delaying atomization, which causes the atoms to be released into a hotter temperature environment. This same phenomenon of delayed atomization can be affected by a new Delayed Atomization Cuvette (DAC) design, in which the ends of the cuvette are substantially thinner than the center of the cuvette where the sample has been deposited. The result of the DAC design is that cuvette heating occurs from the ends of the cuvette inward towards the sample (as compared to the conventional design which heats the center outward), delaying atomization. This technique has the advantage that it does not require the addition of an insert, which can move and occlude the light beam during the atomization process. Furthermore, the single piece design allows more flexibility in temperature programming to accommodate elements of different volatility. Examples which demonstrate the analytical capability of the DAC design will be presented.

33 UTILIZATION OF HYDRIDE GENERATION FOR THE DETERMINATION OF AS AND SE IN COMPLEX MATRICES.
L.M. Voth, K.G. Brodie, B. Frary, Varian Instrument Group, 205 W. Touhy Ave., Park Ridge, IL 60068

Because of its extreme sensitivity for elements such as As, Sb and Hg, the vapor generation technique has been widely applied in many laboratories with atomic absorption instruments and atomic emission instruments.

The VGA-76 vapor generation accessory features a continuous flow technique in which samples and liquid reagents are pumped and allowed to mix. The gaseous reaction products are swept into an absorption cell (heated by an air/acetylene flame for hydride-forming elements) located in the optical path of the atomic absorption spectrophotometer. The accessory can be readily connected to a programmable sample changer to provide automatic presentation of up to 5 calibration standards and 67 samples.

Results from studies utilizing this accessory for the determination of As, Se, and Hg in several types of samples including waste water and geological samples will be presented. Digestion procedures utilizing nitric acid have been known to cause interferences in the determination of hydride forming elements. These interferences will be examined and the investigation of methods to control them will be discussed. Criteria for the appropriate choice of digestion procedures for the hydride analysis of real world samples will be presented.

34 DETERMINATION OF METALS AND CATIONS IN THE CLINICAL LABORATORY BY ATOMIC EMISSION AND ATOMIC ABSORPTION SPECTROMETRY.
Joseph Sneddon, Janet Munro, Timothy A. Tapia, Adriana Uranga, Mark Rodriguez, and Cathy A. Hernandez, Department of Chemistry, New Mexico State University, Las Cruces, NM 88003

The important role of a large number of metals and cations in nutritional, chemical, toxicological, and environmental health problems has long been recognized. Changes in the concentrations of essential and nonessential metals and cations in human body fluids and tissues can help in the diagnosis and treatment of diseases. This paper will describe the application of atomic absorption and atomic emission spectrometry to the determination of essential and nonessential metals in biological fluids. Included in this investigation will be the direct current plasma, electrothermal atomizer, and flame. The results of these determinations will be reported.

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35 COMPARISON OF AA, ICP AND ION CHROMATOGRAPHY FOR MEASUREMENT OF METALS.

Richard Rubin, Denise Eubanks, Shawn Heberling, John Riviello, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088.

Ion Chromatography has found practical use in alkali and alkaline earth metal analysis since about 1975. However, since the more recent advent of a sensitive automatable, post-column colorimetric detection scheme for common transition metals, Ion Chromatography can begin to be considered as a viable alternative to atomic spectroscopy. Advantages of Ion Chromatography include its capability as a multielement analyzer for a single injection, high sensitivity, minimal affectation by sample matrix, and its ability to speciate certain metal valence states. The disadvantages of Ion Chromatography are: fewer element capabilities than AA/ICP and the residence time involved in separation on-column. While this latter point means a lower specification for "elements/hour" throughput, the selectivity offered by Ion Chromatography often results in reduced time in methods developments and sample preparation. Therefore, considering total analysis time, Ion Chromatography often becomes the faster technique, especially with nonroutine workloads.

36 INTERFACING LIQUIDS TO PLASMAS AND FLAMES: NEW ANSWERS TO OLD PROBLEMS.

Richard F. Browner, School of Chemistry, Georgia Institute of Technology, Atlanta GA 30332.

This paper will describe the current state of our search for "optimum" aerosols for introduction to plasmas and flames. The criteria to be discussed will include: (1) aerosol drop size (2) analyte mass loading, and (3) solvent mass loading. The influence of aerosol drop size will be examined by showing the effect of controlled aerosol size introduction to the ICP and to an air/acetylene flame. The influence of drop size on signals, detection limits, and interferences will be described for a number of model systems. Comparison of these data with conventional pneumatic nebulization introduction will be made for a number of commonly used nebulizers (e.g. concentric, crossflow, and high-solids types). The benefits of using monodisperse aerosols, compared to conventional polydisperse aerosols, will also be described. Finally, some applications of monodisperse aerosol introduction to LC/ICP and FI/ICP interfacing will be described.

37 FACTORS LIMITING AEROSOL TRANSPORT IN NEBULIZATION CHAMBERS,

R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523; Kurt Kronholm, 1583 Oakwood Avenue, Des Plaines, Illinois 60016.

It has been previously shown that gravitational settling, inertial impaction, and turbulence phenomena may all influence the transport of analytical aerosols through nebulization chambers. However, previous publications have not quantitatively evaluated the aerosol velocity situation in such chambers and have therefore failed to offer more than qualitative judgements regarding the primary transport limitation effects. In the present discussion it will be shown that the aerosol velocity may often exceed the velocity of the transporting gas. Under these circumstances the significance of gravitational settling is diminished while the prominence of impaction and turbulence losses is enhanced. The results to be discussed consequently offer a more quantitative perspective than has been evident in the past.

38 LATERAL DIFFUSION INTERFERENCES IN FLAMES AND PLASMAS, R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523; S. J. Freeland Chemagnetics Inc., 208 N. Commerce Dr., Fort Collins, Colorado 80524; K. G. Kronholm, 1583 Oakwood Avenue, Des Plaines, Illinois 60016.

Previous publications have postulated that delays in analyte vaporization cause interferences which may be explained by consideration of lateral diffusion effects. More recent results have demonstrated, however, that the distribution of analyte aerosol in an energy medium is primarily controlled by the aerosol size distribution. Thus, the vaporization profiles observed are determined by the aerosol size distributions and the diffusion of the gaseous products is of secondary significance. The present discussion will delineate the controlling processes utilizing experimental results for verification purposes.

39 SLURRY ANALYSIS BY INDUCTIVELY COUPLED PLASMA USING CONVENTIONAL NEBULIZATION. Susan E. Knauf, J. D. Nohe, Instruments SA, Inc., 173 Essex Avenue, Metuchen, New Jersey 08840

The determination of metals in coal is difficult. Pyrolization and fusions are often used to prepare the coal for analysis of its trace constituents and the possibility of contamination is high.

The direct ICP analysis of coal using a slurry method has been successful; hence, sample preparation has been simplified to a simple grinding-screening step. 60 mesh NBS SRM 2682-5 coal standards are screened to obtain -325 mesh (44μm) powder in order to pass through ISA's conventional corrosion-resistant nebulizer. Typically 0.2 grams of this powder is added to 100 ml of de-ionized water which contains 10 μg/ml of beryllium. The beryllium will serve as an internal standard and has been found to improve reproducibility.

Data obtained for several elements, including sulfur, will be presented, as well as long term stability, accuracy, and precision.

40 USE OF SIGNAL VS. TIME PROFILES TO OPTIMIZE ELECTROTHERMAL VAPORIZATION-INDUCTIVELY COUPLED PLASMA SPECTROSCOPY. M. W. Tikkanen,† Scientific Laboratory Division, State of New Mexico, 700 Camino de Salud, NE, Albuquerque, NM, 87106. T. M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131.

Multielement determinations by electrothermal vaporization-inductively coupled plasma atomic emission spectroscopy (ETV:ICP:AES) have gained increasing attention as a useful analytical technique. Detection limits orders of magnitude improved over conventional pneumatic nebulization:ICP:AES as well as microsampling capabilities have initiated this interest. With the interface of the direct reading polychromater ICP's to the ETV, came the ability to do simultaneous multielement determinations on a single electrothermally generated signal. Using a modified Jarrell Ash 965 Atom Comp Direct Reader that has been mated to an ETV System, point-by-point millisecond-resolved signal vs. time profiles of this multielement signal have been generated. This mode of data acquisition allows the investigator the ability to monitor on a simultaneous basis, the effect of companion sample constituents on the analyte. The use of the signal vs. time profiles gives insight to the processes involved in the various matrix and/or spectral interferences observed, and allows the appropriate choice of plasma and ETV parameters to minimize these effects. Optimization of these parameters for simultaneous multielement determinations in complex and matrixed samples using ETV:ICP:AES will be detailed.

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41 SENSITIVITY ENHANCEMENT OF TRACE ELEMENT DETERMINATIONS BY ELECTROTHERMAL ATOMIZATION INTO AN ICP EMISSION SPECTROMETER. R.M. Manabe, D.D. Nygaard, and D.A. Leighty, Allied Analytical Systems, 590 Lincoln St., Waltham, MA 02254.

The analysis of the priority pollutant elements in drinking water and effuent streams is now routinely performed using ICP emission spectroscopy. Detection limits for some of the toxic heavy metals are marginal with conventional pneumatic nebulization systems in common use for the ICP. Introduction of the sample into the ICP spectrometer by electrothermal atomization improves these detection limits significantly, and permits routine analysis of these samples without preconcentration.

The process of methods development for graphite furnace electrothermal atomization into an ICP spectrometer is somewhat different than for graphite furnace atomization into an AA spectrometer. A standardized approach to methods development for the combination of a graphite furnace atomizer with a simultaneous ICP spectrometer will be discussed. Optimization of hardware subsystems including readout system design and vapor transport systems will be presented. Comparison with conventional nebulization systems for the analysis of reference materials will be made.

42 TRACE ELEMENT ANALYSIS OF SILICATE ROCKS BY DIRECT INSERTION OF A GRAPHITE CUP INTO AN ICP

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Despite the widespread use of conventional pneumatic nebulization methods of liquid sample introduction, the direct analysis of solid geological materials still poses several problems. Data will be presented on the behaviour of silicate materials in a graphite cup inserted above the top of the torch. The effects of power, observation zone and the presence of graphite on the spatial and temporal variations of the analyte lines will be described. The analytical potential of the graphite cup device for the direct multitrace element analysis of geological materials will be discussed. Although this technique is appealing due to its simplicity, our data indicate that complex mineralogical history and element volatility have adverse effect on sensitivity and accuracy. These variations can be compensated by the use of internal references.

43 LABORATORY INFORMATION MANAGEMENT, Art Ambrose, Perkin-Elmer Corporation, 4036 Youngfield St., Wheat Ridge, CO 80033

Few workplaces are as information intensive as the laboratory, and there is growing pressure to enhance chemist's productivity by effectively controlling and coordinating the voluminous amounts of laboratory data that are generated. Computers have become a very important laboratory tool and have been used for some time for data collection and reduction. Uses for laboratory computers continue to proliferate as are varieties of lab computers and application software packages. For this reason, it is important that users have a strategy for computerizing the laboratory. Failure to do so may result in a lab filled with incompatible computers and analytical equipment that cannot communicate with each other in a meaningful, efficient way. An effective strategy to lab information management combines distributed and centralized processing. In this approach dedicated benchtop microcomputers perform instrument control and real-time data collection, while a minicomputer stores all the data in a data base. Selected information can then be conveniently extracted and customized to display and report it in a meaningful manner. Thus the records for thousands of samples can be tracked and maintained with sophisticated software that also provides such benefits as audit trail capability, work list generation, results verification, label printing, backlog reports, advanced chromatography analysis, and statistical and graphical display of results.

44 APPLICATION OF A COMPUTERIZED SPREADSHEET FOR THE POST-PROCESSING OF SPECTRAL INTERFERENCE CORRECTIONS IN ICP SPECTROSCOPY. R.M.Manabe, R.L. Crawford, R.M. Brown, and D.A. Leighty, Allied Analytical Systems, 115 Constitution Drive, Menlo Park, CA 94025.

A simultaneous ICP spectrometer usually measures the analyte intensity at the peak of an emission wavelength and one or two background correction points. Another approach would be to scan a spectral region surrounding the analyte wavelength. By taking an array of information adjacent to the emission wavelength, spectral features such as interfering peaks or shifts in background can be quantified. The information gathered from this scan window permits spectral interference corrections for the major elements in the sample matrix without requiring that the interfering element be present as an analytical channel. The only hardware requirement is that the spectral scans from sample to sample exactly overlap each other in wavelength, which is readily accomplished with a simultaneous system. Multiple Linear Regression(MLR) provides an efficient method of processing the intensity arrays. A computerized spreadsheet was used for the matrix calculations. A software routine was written to directly insert the array data into the spreadsheet to eliminate manual data entry. Methods development does not require the calculation of interference correction factors since the spectral interference and background information are collected in the same spectral region as the analyte line. To correct for an interference, the MLR requires a scan surrounding the analyte wavelength of a standard containing the interferent element. Data reduction utilizing the MLR will provide the best linear combination of calibration standard scans to fit the wavelength scans of specific samples. The MLR also provides an estimate of the standard deviation of the determination with only a single scan.

45 ADVANTAGES OF USING MYERS-TRACY SIGNAL COMPENSATION TECHNIQUE FOR ICP ANALYSES. E. Pruszkowska, D. Yates, R. Ediger, and R. Hergenreder, Perkin-Elmer Corporation, MS 906, 901 Ethan Allen Highway, Ridgefield, CT 06877.

Two years ago Myers and Tracy (1) described an improved technique for internal standardization which is now incorporated in the new Perkin-Elmer Plasma II Emission Spectrometer. This technique compensates for short- and long-term analyte signal noise induced by the sampling process. The signal noise can be caused by variations in nebulizer efficiency, fluctuations in aerosol transportation, differences in sample viscosity, or the peristaltic pump. This paper describes experiments performed to determine optimum plasma parameters using the signal compensation technique for the best precision and accuracy of analytical signal. The effects of changing nebulizer flow, power, and viewing height were investigated. The technique has been applied to the determination of several elements in various matrix solutions with significant improvements in both precision and accuracy.

(1) S. A. Myers and D. H. Tracy, Spectrochim. Acta 38B, 1227 (1983).

46 LIGHT SCATTERING FROM HIGH VOLTAGE SPARKS. Alexander Scheeline, M.A. Lovik, and M.J. Zoellner, School of Chemical Sciences, University of Illinois, 1209 W. California Ave., 79 Roger Adams Lab., Urbana, IL 61801.

Particulates and free electrons are two species important to the functioning of analytical discharges which cannot be easily probed by emission or absorption measurements. Small molecules may also form in a manner not conducive to emission measurements. A thorough understanding of analytical plasmas thus is impossible without light scattering measurements on non-emitting species. Mie scattering from particulates, Thomson scattering from free electrons, and Raman scattering from molecules can all be performed using similar equipment. Preliminary data from each of these techniques applied to the high voltage spark discharge are presented. Mie scattering shows the spatial and temporal regimes in which free atoms are condensing into particulates which act as a sink for analyte vapor. Raman measurements demonstrate the substantial entrainment of atmospheric nitrogen into the argon jet used to stabilize a high voltage spark. Progress towards Thomson measurements, including stray light rejection, elimination of electromagnetic interference, and various instrument design considerations are discussed.

47 THE DETERMINATION OF NONMETALS USING METASTABLE TRANSFER EMISSION SPECTROSCOPY.

W. H. Hood and T. M. Niemczyk, Department of Chemistry, University of New Mexico,
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Metastable Transfer Emission Spectroscopy (MTES) has previously been shown to be a useful technique for the detection of several classes of analytes including metals and hydrocarbons. Nitrogen atoms present in the excitation source react with some nonmetals to form nitrides in the plasma. Other nonmetals are efficiently atomized and excited in the nitrogen plasma via pathways analogous to those previously discussed for metal atoms. We will discuss detection schemes for numerous nonmetallic species based on emission from analyte nitrides in addition to emission from nonmetal atoms. Calibration curves, details of sample introduction methods, and detection limits will be presented for representative nonmetals, including iodine, sulfur, phosphorus, carbon, arsenic, selenium, and antimony.

48 DEVELOPMENT OF AN ATMOSPHERIC-PRESSURE SURFACE-WAVE PLASMA (SURFATRON) IN HELIUM FOR ATOMIC EMISSION SPECTROMETRY.

M. Selby and G. M. Hieftje,
Department of Chemistry, Indiana University, Bloomington, Indiana 47405

In recent years surface-wave induced plasmas using a "surfatron" wave launcher at microwave frequencies (2.45 GHz) have emerged as innovative new sources for atomic emission spectrometry. In this type of source the field strength is concentrated near the discharge tube walls so that the plasma produced in He has a hollow ring appearance. The surfatron plasma promises to overcome many of the problems encountered with microwave-induced plasmas used previously. These problems have included: 1) the inability to withstand undesolvated aerosols; 2) irreproducible sample introduction into the central region of the plasma; 3) loss of sample ions by implantation in the discharge tube walls.

After a brief outline of operating principles and construction the analytical capabilities of the surfatron plasma will be compared to other types of microwave-induced plasmas such as those sustained in the TM_{010} Beenakker type cavity.

49 POLARIZATION COMPENSATION OPTICS WITH ACTIVE COMPUTER CONTROL.

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California Ave., 79 Roger Adams Lab, Urbana, IL 61801.

Control of the orientation of the major axis and ellipticity of polarized light is essential in such measurements as fluorescence depolarization, Mie scattering, and Raman depolarization. A variety of schemes have been devised over the years to guarantee that linear or circularly polarized light impinges on a sample from a known angle. We report an approach with which any general polarization state can be produced at the sample position, with complete compensation for ellipticity in reflection by mirrors and inexact phase shifting by waveplates. A pure source of polarized light (either a light source filtered through a good linear polarizer or a linearly polarized laser) is presumed. Apparatus and theory based on the Mueller calculus are described. Measurement of the agreement between calculated and observed polarization parameters for a goniometer employed for Mie scattering measurements on the high voltage spark are presented.

50 DIAGNOSTICS AND EXCITATION OF MOLECULAR VAPORS USING METASTABLE NITROGEN.

H.-C. Yang and T. M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131.

Metastable nitrogen molecules, one of the most important components of active nitrogen, have been shown to efficiently excite atomic vapors. The use of volatile metal carbonyls allows the introduction of a continuous flow of metal atoms to the flow of active nitrogen. This provides a convenient method for the measurement of excitation temperatures. Data will be presented that compares the excitation temperatures obtained under various experimental conditions as well as for the use of different sources of active nitrogen. Besides the nitrogen metastables, active nitrogen can also contain nitrogen atoms. If a molecular vapor is to be excited to produce a molecular rather than an atomic spectrum it is important that the concentration of nitrogen atoms in the active nitrogen flow be low. The excitation of molecular vapors and the effects of the nitrogen atom concentration will also be discussed.

51 A LAMINAR FLOW MICROWAVE INDUCED PLASMA TORCH FOR DETERMINATION OF HALOGENATED HYDROCARBONS BY GAS CHROMATOGRAPHY AES.

Mark L. Bruce and Joseph A. Caruso, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221.

These laboratories have been concerned with helium microwave plasma source (MIP) for exciting optical emission from organo halogens and its use for chromatographic detection of these substances. This work describes utilizing the MIP with a new low flow plasma centering torch (LFT). A background correcting computer controlled polychromator system has been used to evaluate two versions of this particular torch. Sensitivities are somewhat better than the 0.5 mm i.d. capillary quartz open tube torch and the performance is markedly improved over the tangential flow device (TFT). Detection limits fall between 8 and 60 pg/sec for several elements of importance in organic compounds. Torch lifetime and stability are comparable to or better than the TFT with RSD's as low as 2%.

The LFT has been utilized for GC detection of pyrethroids and chlorodioxin. In this investigation a careful comparison was made with the open tube torch as well as the TFT. Again the LFT showed improvements over the others investigated. Empirical formulae were readily determinable and detection levels were in the low ppb range for these compounds. These values are compared with those obtainable from the more commonly used technique —high resolution mass spectrometry.

52 **LASER EXCITED ATOMIC AND IONIC FLUORESCENCE FOR STUDIES OF ENHANCEMENT EFFECTS IN THE DIRECT CURRENT PLASMA**

R.G. Michel and Martha S. Hendrick+, Department of Chemistry, University of Connecticut, Storrs, CT 06268.

This paper reports a preliminary attempt to use Laser Excited Atomic Fluorescence Spectrometry (LEAFS) to study the analyte enhancement effect caused by Easily Ionized Elements (EIEs) in the Direct Current Plasma (DCP) . Direct line fluorescence of the barium ion, excited at 614 nm and detected at 455 nm, was used to probe the effect of an EIE on excited state populations. Enhancements of fluorescence signals at low laser powers disappeared at laser powers which were sufficient to saturate the atomic transitions. While this result does not clarify any of the mechanisms of excitation in the DCP, it does lend support to two of the fundamental postulates of a recent model of the spectrochemical excitation processes in the DCP. These are first, that the analytical region of the DCP is not in Local Thermodynamic Equilibrium (LTE) and second, that EIE enhancement proceeds by increasing the rate of collisional redistribution of energy within the analytical region of the plasma.

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53 STUDIES OF ENERGY TRANSPORT AND ANALYTE EXCITATION IN THE INDUCTIVELY COUPLED PLASMA USING A PULSED POWER WAVEFORM, Paul B. Farnsworth, Department of Chemistry, Brigham Young University, Provo, Utah 84602

The power applied to the load coil of an analytical inductively coupled plasma is being pulsed off for periods of 200 microseconds at a repetition rate of 120 Hz. The time response of emission signals from both the analyte and plasma gas species provide a means of identifying the processes that are responsible for energy transport from the load coils to the analytical zone of the plasma and the mechanisms by which the analyte is excited. Time and space resolved emission data from the pulsed plasma will be presented with a discussion of the excitation and energy transport mechanisms that are implicated by the experiments. Included in the discussion will be a comparison of data from different analyte species that, on the basis of excitation and ionization potentials, would be expected to exhibit significantly different excitation behavior.

54 GENERATION AND CHARACTERIZATION OF A HELIUM INDUCTIVELY COUPLED PLASMA OPERATED AT ATMOSPHERIC PRESSURE. Akbar Montaser and Shi-Kit Chan, Department of Chemistry, The George Washington University, Washington, D.C. 20052.

An annular helium inductively coupled plasma (He ICP) is generated at atmospheric pressure. No external cooling is used to stabilize the plasma. Preliminary results reveal that the annular He ICP is capable of exciting elements such as Cl and Br which possess high excitation energies. Atomic emission detection limits for aqueous chloride and bromide solutions are improved by factors of 65 and 33, respectively, as compared to the results obtained from the argon inductively coupled plasma.

55 DEVELOPMENT OF A THETA PINCH FOR SPECTROCHEMICAL ANALYSIS. Alexander Scheeline, G.J. Kamla, and J.S. White, School of Chemical Sciences, University of Illinois, 1209 W. California Ave., Urbana, IL 61801.

A pulsed, magnetically constricted plasma, the theta pinch discharge, has been adapted for spectrochemical analysis. The theta pinch was originally designed to simulate the conditions inside nuclear fusion weapons and reactors. We have switched from a deuterium fill gas to argon, and from megaamp to tens of kiloamp peak discharge currents These changes eliminate any possibility of neutron production. The main compression coi has been changed from a single turn sheet of copper to an 8 turn solenoid. Energy transfer is improved by this change by several orders of magnitude. Aluminum alloys have bee successfully sampled with this discharge, and other alloys are under study. Dependence of signal on such operating parameters as sample geometry, sample electrical characteristics, discharge gas pressure, and discharge timing will be discussed.

56 CHARACTERIZATION OF A LABORATORY-STANDARD ICP TORCH CONFIGURATION.

G.D. Rayson, K.A. Marshall, R. Rezaaiyaan, and G. M. Hieftje, Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Considerable effort has been made toward the elucidation of the various processes occurring within an ICP. Often these investigations have been concerned with variations in the spatial character of the ICP resulting from changes in operating conditions. Unfortunately, the elucidation of the effect of parameters has been hindered by the lack of a set of standard operating conditions. Additionally, uncontrolled inter-laboratory variation of several variables in the configuration of the ICP torch have precluded any direct comparisons of profiles obtained from various laboratories.

In an effort to minimize these variations, a standard ICP torch configuration has been designed and constructed using components of precise dimensions. Additionally, a Scott-type double-pass spray chamber is used with a Babington nebulizer.

Intra-laboratory reproducibility of measured emission profiles in addition to other operation characteristics will be discussed. A set of standard operating parameters for this torch configuration will be presented and the feasibility of their use as a reference point for future fundamental studies of the ICP will be discussed.

57 MEASUREMENT OF GROUND STATE NEUTRAL ATOM AND ION SPATIAL DISTRIBUTIONS IN THE ICP USING DYE LASER EXCITED ATOMIC FLUORESCENCE SPECTROMETRY.

George Gillson and Gary Horlick, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2.

To date, most studies of a fundamental nature with respect to the ICP have concentrated on the measurement of the spatial distribution of the emission from neutral atom and ionic species and on the spatial distribution of electron density. However, for a more complete picture the spatial distribution of ground state analyte species is also required. Atomic fluorescence and atomic absorption measurements from several laboratories are beginning to provide such information. In this presentation the results of atomic fluorescence measurements on Ca and Sr neutral atom and ion species over a wide range of measurement conditions will be reported. Complete spatial distribution maps from 9 mm to 36 mm above the load coil at powers ranging from 0.7 kW to 1.5 kW and at aerosol flow rates from 0.6 to 1.4 lpm will be presented. These spatial distribution maps provide a unique picture of the ICP and in particular illustrate the dominance of ground state ions as the main analyte species at almost all powers, heights, and aerosol flow rates. The fluorescence spatial maps will be directly compared to emission maps measured under identical conditions and results will also be correlated with ICP-MS data also measured under identical conditions.

58 THE APPLICATION OF GLOW DISCHARGE - OPTICAL EMISSION SPECTROSCOPY TO ROUTINE FOUNDRY ALLOYS

R.R. Comtois, VHG Labs, Inc., Methuen, MA
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For many years foundry spectrochemical laboratories have been equipped with arc/spark optical emission spectrometers (OES) and Xray fluorescence (XRF) spectrometers in an effort to meet their rapid throughput--high precision data requirements. The OES technique, although rapid, lacks the low coefficient of variations achievable on an XRF unit. However, the XRF cannot typically determine elements below atomic number 12 and is slower. Glow discharge optical emission spectroscopy (GD-OES) has the feature of rapid determinations plus CV's approaching those of XRF for all the elements typically determinable by OES. What's more, sensitivities for some elemental determinations in various matrices are better than either technique.

This paper will investigate the viability of replacing two spectrometer systems with one glow discharge unit for some applications. Performance data, figures of merit and limitations will be discussed on a variety of alloys using a commercially available system.

59 CHROMATOGRAPHIC AND SPECTROSCOPIC TECHNIQUES APPLIED TO THE ORGANIC ANALYSIS OF NUCLEAR WASTES.

A. P. Toste, R. B. Myers, T. R. Pahl, and R. B. Lucke, Biology and Chemistry Department, Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352

Nuclear wastes often contain organic compounds. Occasionally the organic content of such wastes can be quite high (e.g., mM) and consist of complex mixtures of organic compounds. Our laboratory is currently developing analytical procedures for the exhaustive organic characterization of nuclear wastes. Many classes of organic compounds are likely to be present in the wastes, including chelating agents and their degradation products; complexing agents such as citric and oxalic acid, low molecular weight (MW) acids like acetic and glycolic acid; polyhydroxy acids such as gluconic and tartaric acid; and extremely polar and polymeric compounds associated with nuclear operations and/or chemical/radiolytic degradation of the source-term organics originally present in the wastes. An analytical procedure is already in place for the analysis of the chelating agents; it consists of solvent extraction, organic derivatization, gas chromatography (GC), GC/mass spectrometry (MS), and GC/Fourier transform infrared spectroscopy (FTIR). Some of the chelating agents have posed analytical challenges. Functional groups have resisted derivatization or promoted intramolecular cyclization to form lactones and lactams. Analyses of nuclear wastes have already revealed the presence of several chelating and complexing agents: NTA, EDTA, HEDTA and citric acid. A variety of chelator fragments such as ED3A are also present, presumably from the chemical/radiolytic decomposition of the chelating agents. The work was supported by the U.S. Department of Energy under Contract DE-AC06-76-RLO-1830.

60 DERIVATIZATION OF INORGANIC SPECIES FOR DETERMINATION BY GAS CHROMATOGRAPHY.

K.W. Michael Siu and Shier S. Berman. Division of Chemistry, National Research Council of Canada, Montreal Road, Ottawa, Ontario, Canada K1A 0R9.

Determination of inorganic species is an underdeveloped field in gas chromatograph (GC). Unlike many organic compounds, inorganic species are often involatile, and hence incompatible with GC. To impart volatility, a derivatization step in which an organic moiety is attached to the inorganic species is necessary. Volatility aside, a desirable organometallic or metal-complex derivative should also be highly stable as well as suitable for detection with one of the more sensitive and selective GC detectors. Good examples are the piazselenol derivatives of selenium, the trifluoroacetylacetonate of chromium and the 2,3-dimercaptopropanol complex of arsenic. The derivatization of the elements is discussed, and applications to the analyses of sediments, biological materials and open ocean waters are demonstrated.

61 COMPARISON OF LOW-RANK COAL LIQUEFACTION PRODUCTS BY AUTOMATED CAPILLARY GA CHROMATOGRAPHY.

Y.R. Potts, S.A. Farnum and D.E. Raynie. UND Energy Researc Center, University Station, Box 8213, Grand Forks, North Dakota 58202.

Three bottoms recycle liquefaction runs were carried out in the continuou processing unit at UNDERC. The operating conditions were relatively constant at 440° 4000 psig (5% CO and 95% H_2 reductant), and 5 wt% H_2S catalyst based on MAF coal. Th effects of two different start-up solvents and two different low-rank coals on th products after 40-58 recycle passes were compared. Sequential samples of th distillate oil from each run were separated by column chromatography and extractions Over 100 alkanes, hydrocarbons, ethers, and phenolic compounds were quantified in fou fractions by automated capillary gas chromatography. This involved a total of 872 analyses. The dilution of solvent-related components such as phenanthrene acenaphthene, fluorene, and fluoranthene, by the products was rapid during the fir 15-18 passes, approaching equilibrium near the end of the run. Conversely, coa derived, nonsolvent components such as alkanes, and phenolic compounds gradual increased. The concentrations and distributions of these components were co specific. Large solvent effects tended to mask the coal-derived differences in produ composition until late in the run. The composition of the distillate oils from each the three runs was different at all stages of the liquefaction process.

62 THE APPLICATION OF HEADSPACE, DIRECT INJECTION AND SNIFF PORT GAS CHROMATOGRAPHY IN THE ANALYSIS OF FLAVOR COMPONENTS IN FOOD PRODUCTS

Margaret K. Conditt, The Procter & Gamble Company, Food Products Division

Two methods of sampling the olfactory (odor) and gustatory (taste) flavors in a food product are compared and contrasted. The aroma of a food product is best analyzed by purging the headspace above the sample onto an adsorbant, e.g. Tenax, and then desorbing into a fused silica gas chromatographic column. A specially designed apparatus that punctures the lid of a jar of a food product is used to obtain representative headspace samples. The less volatile flavor components, which contribute to the taste of a food product, may be extracted by simultaneous distillation/extraction (SDE) into a volatile solvent and separated using gas chromatography via direct injection of the solvent. In each separation, the gas chromatographic effluent is split between a traditional detector (FID, FPD, MS) and a sniff port at which the eluents are smelled by the human nose. Details of each analytical technique will be discussed and practical applications to food products will be demonstrated.

63 REDOX CHEMILUMINESCENCE DETECTION OF GASES FOR GAS CHROMATOGRAPHY.

R.L. Shearer and R.E. Sievers. Dept. of Chem., University of Colorado and Cooperative Institute for Research in Environmental Sciences, Campus Box 449, Boulder, CO, 80309.

The redox chemiluminescence detector (RCD) is a new selective gas chromatographic detector that was developed in our laboratory. The RCD responds to analytes which reduce nitrogen dioxide to nitric oxide by a catalyst in a post-column reactor. The nitric oxide formed in the post-column reactor is then detected by its chemiluminescent reaction with ozone.

The RCD offers some advantages over other gas chromatographic detectors for detection of gases because of its selectivity and sensitivity. The RCD responds sensitivily to hydrogen, ammonia, acetylene, ethylene, carbon monoxide, formaldehyde, hydrogen peroxide, propylene, ethylene oxide, vinyl chloride, and phosgene. It does not respond to water, carbon dioxide, helium, oxygen, nitrogen, or nitrous oxide. The RCD can be made to respond to the alkanes, or it can be made to be completely insensitive to them by modifying the catalyst in the post-column reactor.

64 THE REDOX CHEMILUMINESCENCE DETECTOR: A NEW SELECTIVE DETECTOR FOR GAS CHROMATOGRAPHY.

R.S. Hutte, Sievers Research, Inc., 2905 Center Green Court, Suite B, Boulder, Co 80301, and R.E. Sievers, Department of Chemistry and CIRES, Campus Box 449, University of Colorado, Boulder, CO 80309.

A new detector for gas chromatography has been developed and refined. The Redox Chemiluminescence Detector (RCD^{TM}) is based on catalyzed oxidation/reduction chemistry and is sensitive to species that can serve as reducing agents for No_2. The detector when used with a gold catalyst, does not respond to water, alkanes, chlorinated hydrocarbons and other frequently used extracting solvents. The RCD can also detect many inorganic species which cannot be measured by conventional GC detectors.

In the RCD, the column effluent is mix with NO_2 or HNO_3 and enters a reaction chamber where reducing agents react at a catalyst surface to form NO and an oxidized product. The NO is then detected by the chemiluminescence technique, when it is oxidized with ozone.

The principles of operation of the RCD and applications in the analysis of complex samples such as lemon oil, gasoine, wastewater extracts, and biological fluid extracts will be presented.

65 NO ABSTRACT

66 THE ANALYTICAL CHEMISTS: HOW THEY CONTRIBUTE TO THE DEVELOPMENT OF AN EFFECTIVE DRUG SUBSTANCE.

O. N. Hinsvark, W. Zazulak, J. E. O'Brien, and L. P. Amsel.
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The Pennwalt® Corporation has developed a controlled release drug delivery system which lends itself well to a wide variety of pharmacologically active substances. Included among the basic drugs which can be incorporated into the Pennkinetic™ system is the non-narcotic antitussive, dextromethorphan (DM). It is only one of many, but it is among the most interesting to study. It challenges the analyst with stability measurements, with formulation potency assays, with rate of dissolution measurements, but, most of all, with bioequivalency evaluations. The biological transformation varies widely within a "users" population from extremely rapid metabolizers to those who convert the drug very slowly. This report is intended to describe the analytical techniques employed which illustrate the role played by the Analytical Chemist in (1) the development of potency/stability assays, (2) the measurement of in vitro release rates of the drug from the resin matrix, (3) the determination of drug levels in plasma, and, finally, (4) the correlation of plasma levels (bioavailability) with in vitro rates of drug release.

67 POLAR ORGANIC COMPOUND ANALYSIS -- HPLC OR IC?

Jack Korpi, Claudia Lincoln, Roy Rocklin, Leonard Henry, Rosanne Slingsby, William Edwards, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3 03, 408/737-0700.

During the past several years, Ion Chromatography has become widely used for the analysis of inorganic ions due to development of high performance ion exchange resins that allow mroe rapid separations and detectors that provide more sensitivity and specificity than previously possible. Chromatographic analysis of organic compounds has been mainly performed using HPLC techniques that, for the most part, utilize reversed phase rather than ion exchange columns. However, many organic compounds are also ionic, making them amenable to ion exchange separation. In fact, organic compounds with high or low pKa cannot be chromatographed very well using conventional HPLC columns and are much better suited to modern ion exchange techniques.

This paper will discuss new capabilities for the separation and analysis of organic compounds using Ion Chromatography separation and detection methods. Examples will be shown that illustrate ion exchange separation of amines, organic acids, and sulfonic acids using conductivity detection, carbohydrates using pulsed amperometric detection, and amino acids with post-column derivatization.

68 THE CLASS SEPARATION OF POLYCYCLIC AROMATIC HYDROCARBONS, NITROGEN HETEROCYCLES, AND HYDROXYL AROMATICS BY LIQUID CHROMATOGRAPHY.

S. C. Ruckmick and R. J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071.

Polycyclic aromatic hydrocarbons, nitrogen heterocycles, and hydroxyl aromatics, which are known to be in solvent refined coal-liquids, were separated into functional classes with high performance μ-Porasil and Nucleosil NO_2 columns. The separation was accomplished by utilizing n-heptane:chloroform, carbon tetrachloride:chloroform and carbon tetrachloride:dimethyl sulfoxide mobile phases. The retention data demonstrated that the μ-Porasil-carbon tetrachloride:chloroform system separated polycyclic aromatic hydrocarbons from nitrogen heterocycles more effectively than a Nucleosil NO_2-n-heptane:chloroform system. The μ-Porasil column with a carbon tetrachloride:dimethyl sulfoxide mobile phase also offered a better separation of nitrogen heterocycles from hydroxyl aromatics compared to the Nucleosil NO_2-n-heptane:chloroform system. It was found that carbon tetrachloride based mobile phases were advantageous due to the high solubility of certain coal liquid fractions in this solvent and the high degree of chromatographic selectivity that could be obtained.

69 SOLVENT SELECTION FOR METAL CHELATE SEPARATION BY LIQUID AND THIN LAYER CHROMATOGRAPHY. B. Wenclawiak and R.E. Sievers. Dept. of Chem., University of Colorado and Cooperative Institute for Research in Environmental Sciences, Campus Box 449, Boulder, CO, 80309.

Most approaches of finding the right solvent in liquid chromatography start with common solvents. This is based on similarities of compounds and chromatographic systems which have been used before.

Snyder [1] and Glajçh, Kirkland and others [2] developed and improved a classification system of solvents for LC.

The eluents for metal chelate separation, which is only a minor part of all LC work, are still being selected by empirical knowledge.

Based on suggestions mentioned in [2], a number of different metal chelates like 8-Hydroxyquinolinates and β-Diketonates have been investigated and tested by application of the solvent triangel in metal chelate separations.

[1] L.R.Snyder, J. of Chromatogr.Sci. 16, 223, 1978
[2] J.L.Glajch, J.J.Kirkland, K.M.Squire, J.M.Minor, J. of Chromatogr. 199, 57, 1980

70 QUANTITATIVE DETERMINATION OF COMPOUND CLASSES IN JET TURBINE FUELS BY HPLC/DIFFERENTIAL REFRACTIVE INDEX DETECTION. C.W. Sink, Department of Chemistry/Physics, Edinboro University of Pennsylvania, Edinboro, Pa. 16444, D.R. Hardy and R.N. Hazlett, Combustion and Fuels Branch, Code 6180, U.S. Naval Research Laboratory, Washington, D.C. 20375.

Fuel Compositions are known to affect significantly jet turbine engine performance. Turbine fuel specifications limit the total aromatics in JP-4 and JP-5 military fuels, but total aromatic content alone does not afford a completely reliable indication of combustion behavior. NRL has undertaken the development of improved methods to characterize jet fuels. One approach uses HPLC to separate hydrocarbon classes, and direct quantitation with a low sensitivity differatial refracture index detector. The detector is calibrated by using known blends of pure compounds or previously separated fuel fractions. The standards refractive index is matched to the fuel in each compound class. Each compound class is matched to that of the fuels analyzed. This method is found to be fast, precise and accurate when applied to test fuels and pure compound mixtures. The results are in general agreement with ASTM-D-13177, FIA method and HPLC/gravmetric determinations.

71 NO ABSTRACT

72 NO ABSTRACT

73 PACKED COLUMN SFC FOR THE SEPARATION OF METAL CHELATES. B. Wenclawiak Anorganisch Chemisches Institut der Westfälischen Wilhelmsuniversität, Correnstrasse 36, D-4400 Münster, W-Germany

Supercritical fluid chromatography (SFC) is becoming increasingly important as separation technique. SFC complements GC and LC and combines many advantages of the other two techniques. Changes in the density of the mobile phase strongly influence the separation and add another dimension to supercritical chromatography. Pressure programming in SFC can be used analogus to temperature programming in GC and gradient programming in LC. The separation of different metal chelates like 8-Hydroxyqinolinates and 8-Diketonates will be shown; the results will be compared to GC and LC.

74 RECENT DEVELOPMENTS AND APPLICATIONS OF THERMOSPRAY LC/MS, Marvin L. Vestal, Department of Chemistry, University of Houston-University Park, Houston, Texas 77004

Both the problems and the promise of the on-line combination of HPLC with mass spectrometry are well known. The thermospray technique has emerged from efforts to solve these problems and realize the enormous analytical potential of the combined techniques. Thermospray is particularly useful with conventional columns and aqueous mobile phases. The recent development of commercially available thermospray interfaces for many popular quadrupole and magnetic mass spectrometers appears to indicate that this effort has been successful. Instrumental features, fundamentals of the processes involved, and performance data are presented for some of these thermospray LC/MS interfaces. In addition to clearly defining thermospray and elucidating its range of applications, an attempt is made to provide a clear statement of its fundamental limitations as well as limitations imposed by particular solvent systems or MS ionization techniques. Prospects for further improvements and new directions are discussed. Recent applications are summarized.

75 KEITH L. CLAY and ROBERT C. MURPHY. Mass spectral characterization of platelet activating factor and other phospholipids by mass spectrometry.

Platelet-activating factor is a recently described phospholipid with wide range of important biological activities. Characterization an analysis of the molecular species of this 1-O-alkyl-2-O-acety phosphatidylcholine has been achieved with the combined use of fas atom bombardment mass spectrometry and gas chromatography/mass spectrometry. Complimentary information from both mass spectra techniques was used for unequivocal assignment of the structure of this phospholipid. In addition, general procedures for the isolatio and characterization of molecular species of phospholipid classes hav been developed. With the use of simple chromatographic procedures followed by fast atom bombardment mass spectrometry, rapid analysis of phospholipid moleculr species can be achieved. Specific hydrolyti procedures and the use of GC/MS is a very useful procedure for the specific analysis of fatty acids or diglycerides derived from the phospholipids. Stable isotope labelling of phospholipids has bee used for quantitative analysis of phospholipids and for the estimati of kinetic parameters relevant to the membrane biochemistry of phospholipids.

DOI: https://doi.org/10.56902/RMCMR.1985.27.1

76 SELECTIVE DETECTION OF ORGANOSULFUR COMPOUNDS IN HPLC VIA FLUORINE-INDUCED CHEMILUMINESCENCE REACTIONS. E.A. Mishalanie, J.W. Birks. Department of Chemistry and Cooperative Institute for Research in Environmental Science (CIRES), University of Colorado, Boulder, Colorado 80309

A sulfur-selective detector for microbore HPLC has been developed in our laboratory. The gas-phase chemiluminescent reaction of molecular fluorine with organosulfur compounds is the basis for this detector which was successfully demonstrated with packed-column GC in our laboratory in previous years. The gas-phase reaction of F_2 with most organosulfur compounds produces vibrationally-excited HF in levels up to v=6, resulting in the (6,2), (5,1), and (4,0) overtone emission bands between 650 and 750 nm. Reaction of F_2 with non-sulfur containing compounds typically yield HF ($v \leq 3$) at wavelengths greater than 850 nm. Selectivity for organosulfur compounds is achieved by monitoring HF emissions below 800 nm. The microbore LC effluent is vaporized prior to entering a detector cell which is maintained at low pressure (<2 torr) by a vacuum pump. The vaporized effluent mixes with a 10% F_2/He mixture in the cell in front of a cooled, red-sensitive photomultiplier tube and bandpass filter wihch monitors emissions between 650-750 nm. There is little or no emission observed from vaporized methanol, acetonitrile, or water, which are typically used as solvents for reversed-phase HPLC. Selectivity over hydrocarbons, alcohols, aldehydes, and ketones is greater than 10^3. The detector has a linear response to a number of sulfides, disulfides, and mercaptans over four orders of magnitude and detection limits ranging from 100 picograms to 5 nanograms of analyte. The theory of operation of the detector will be presented with examples of potential applications.

77 HPLC DETECTION OF SINGLET OXYGEN SENSITIZERS. Curtis Shellum and John W. Birks, Department of Chemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309.

Presented in this talk is an HPLC detection scheme involving the use of a highly fluorescent probe molecule. The goal is to utilize the inherent sensitivity of fluorescence to detect light absorbing but nonfluorescing analytes. The detection is based on the photochemical reaction sequence in which the photoexcited analyte molecules transfer their electronic excitation energy to oxygen which then reacts with a judciously chosen fluorescent reagent. Apon reaction with oxygen, the reagent ceases to fluoresce and the drop in fluorescence is seen by the fluorometric detector. The analytes are thus observed as negative peaks. The critical part of the reaction sequence is finding a molecule that reacts rapidly with singlet oxygen and exhibits the property of going from fluorescent to nonfluorescent via this photooxidation reaction. Also, self-photooxidation of the fluorescent reagent must be minimal or able to be made so by the use of light filters. Thus far, 2,5-diphenylfuran and 1,3-diphenylisobenzofuran have been utilized and have found to be very effective for analytes with chromophores above 300nm and 400nm respectively. The talk will discuss the photochemical reaction sequence and what has been learned thus far as to its utility in HPLC detection.

78 WHOLE COLUMN DETECTION: A MULTIDIMENSIONAL SEPARATION TECHNIQUE. PART I.

David G. Gelderloos, Kathy L. Rowlen, John W. Birks, James P. Avery, Christie G. Enke, Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309

The potential advantages of simultaneous detection along the entire length of a chromatography column have been explored using a computer model. In the technique of whole column detection (WCD) chromatography, the distribution of peaks as a function of column position is utilized as an additional dimension for the separation. In contrast to conventional chromatography where resolution is limited by the degree of separation at only one point on the column (i.e., the exit) WCD allows quantitation of any pair of peaks at the position on the column where maximum resolution occurs. Through the use of actual k' data and standard assumptions about the chromatographic elution process, the computer is able to generate "snapshots" of the peak distribution along the entire length of the column. Solute peaks can be observed as they separate, merge and cross, depending on the solvent program used. Model results demonstrate that solvent programs may be used to selectively separate a chosen set of peaks. Once these peaks are separated to the desired degree of resolution, the solvent program may be altered to separate additional sets of peaks without regard to any degradation of resolution of the earlier set. Early results show that WCD has both the ability to give superior separation in a shorter time than optimized exit chromatography as well as the ability to more accurately predict a possible optimization procedure.

79 WHOLE COLUMN DETECTION: A MULTIDIMENSIONAL SEPARATION TECHNIQUE PART II.

David Gelderloos, Kathy L. Rowlen, John W. Birks, James P. Avery, Christie G. Enke, Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309

Whole Column Detection (WCD) is the continuous detection of solute distribution along the entire length of a chromatography column. This visual observation technique provides realtime information about the elution process which can be utilized to achieve selective separations. Future development of WCD will include the use of an Expert System to monitor peak progress, decide upon the changes required to achieve a desired separation goal and execute those changes through parameter control. In WCD a peak need only be resolved at one point on the column in order to be quantitated. Therefore, the Expert System could systematically program for the maximum resolution of a succession of individual peaks without regard to the status of other peaks. Capacity factor data obtained at the position of maximum resolution would form a data base the Expert System could use to identify compounds during elution. There are a number of possible applications of WCD, three of which include 1) chemiluminescence, 2) fluorescence, and 3) thermal lensing. It is anticipated that WCD will also prove extremely useful in combination with a sensitive post column detector, such as a mass spectrometer, due to its ability to predict the exact moment of exit from the column.

80 THE ION CHROMATOGRAPHIC DETERMINATION OF OXALATE IN URANIUM RECOVERY SOLUTIONS.

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The recovery of enriched uranium from various waste streams is done by liquid-liquid column extraction. The extraction system consists of two stages: stage 1 - diethylene glycol dibutyl ether (DGBE) and concentrated nitric acid, and stage 2 - tributyl phosphate (TBP) and concentrated nitric acid. Under certain conditions, the DGBE is oxidized to oxalic acid which then reacts with the uranium-containing solution to form uranyl oxalate. Uranyl oxalate will precipitate under certain conditions and interfere with the column extraction. In the development of control techniques to prevent the extraction interference, it was necessary to develop a method to analyze for oxalate in the extremely acidic extraction media. Of several techniques that were tried, only ion chromatography proved to be successful, with the added benefit that it requires a minimum of sample preparation. Example chromatograms, the sample preparation scheme, and some proposed reactions will be discussed.

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*Operated for the U.S. Department of Energy by Martin Marietta Energy Systems, Inc under contract DE-AC05-840R21400.

81 The utility of High Performance Liquid Chromatography (HPLC) for the study of bacteria has been examined. E. coli grown on and harvested from Trypticase Soy Agar was used as the model bacterium for the study. The effect of experimental parameters (including choice of column and detector, column temperature, and mobile phase composition) on the diagnostic chromatogram of E. coli were found to be critical and will be discussed. Optimum isocratic operating conditions were found to be as follows: Column, C-18 reverse-phase; mobile phase, 10% methanol in a 0.005 M Phosphate buffer at pH 2.6; flow rate, 1.5 ml/min.

82 AN IMMUNOAFFINITY CHROMATOGRAPHIC ASSAY WITH AMPEROMETRIC DETECTION.

U.de Alwis and G.S. Wilson Department of Chemistry, University of Arizona, Tucson, AZ 85721

We have recently demonstrated (Anal. Chem. 55, 771,(1983)) the use of immunosorbents packed in miniature HPLC columns as the basis for an immunoassay. The immunosorbents are prepared by immobilization of the antibody (Ab) or it's fragments (Fab, $F(ab)'_2$) or the antigen (Ag) on silica spheres or cross linked agarose activated using different methods. The extent of the Ab - Ag reaction is determined by using enzyme labels. The label produces an electro- active product (H_2O_2) which can be determined electrochemically. The utility of this setup to carry out rapid (20 min or less) and sensitive (picomole- femtomole range) ELISA assays will be discussed together with kinetic and thermodynamic properties of the column immunological reaction.

83 APPLICATION OF MONOCLONAL ANTIBODIES TO ANALYTICAL DETERMINATIONS.

R. G. Nielsen and G. S. Wilson, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

Immunological reactions have found wide application in specific and sensitive determinations of analytes in complex biological matrices. We have previously demonstrated the use for immunoassays of a microbore HPLC column containing approximately 50 mg of packing material on which an antibody is immobilized(Sportsman et al., Anal. Chem., 1980). A site-displacement model has been developed which describes the interaction of a mobile phase antigen with the antibody stationary phase thus permitting estimation of the binding constant and the number of column binding sites. Much of the previous work was performed using polyclonal antibodies and it was accordingly difficult to decide whether the observed heterogeneous behavior was attributable to the immobilization or to the heterogeneity of the antibody population. Studies have been carried out using monoclonal antibodies to observe the amount of heterogeneous behavior due to the immobilization process. The homogeneous nature of monoclonal antibody reactions allows one to probe nonspecific interactions, the effect of the label attachment, and the orientation of immobilized antibodies.

DETERMINATION OF AVERMECTIN IN CITRUS BY REVERSED PHASE LIQUID CHROMATOGRAPHY WITH FLUORESCENCE DETECTION.

Jeffrey J. Jenkins and Janice Cobin, Merck Sharp & Dohme Research Laboratories, Three Bridges, NJ 08887.

The Avermectins are comprised of at least eight related macrocyclic lactones produced by the actinomycte Streptomyces Avermitilis. Of these compounds, Avermectin B_1 is currently being developed as a miticide against Citrus Rust Mite and Citrus Red Mite. To study field dissipation and to establish food tolerances, an analytical procedure has been developed for the isolation and determination of Avermectin B_1a in citrus peel, pulp, and processed fractions. The method is based upon detection of a flourescent derivative following reversed phase liquid chromatography employing column switching.

85

HPLC/EC DETERMINATION OF SELECTED VETERINARY DRUGS IN TISSUES AND FEEDS

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Food & Drug Administration, 500 U.S. Customhouse 721 19th St., Denver, CO 80202

High performance liquid chromatography with electrochemical detection has proven itsel 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 zeranol zearalenone, diethylstilbestrol, estradiol, and derivatized penicillins were investigated. They were separated under isocratic conditions using a reverse phase, C18, 5 micron column, and they were detected using an amperometric controller. Parameters such as HPLC/EC conditions, recoveries, and detection limits are reported.

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REVERSED-PHASE HPLC OF NUCLEOSIDES, NUCLEOTIDES, DI- AND TRINUCLEOTIDES.

Allen M. Schoffstall, Elizabeth Miller, Euton M. Laing and Nancy J. Getzinger, University of Colorado at Colorado Springs (UCCS), Colorado Springs, CO 80933-7150.

Reversed phase HPLC serves as an excellent method for separating nucleoside and nucleotide derivatives that are derived from a particular nucleic acid base. Triphosphates and diphosphates are eluted first, followed by the mononucleotides. The isomeric mononucleotides are separated readily for deoxynucleotides and nucleotides of purine bases. Pyrimidine nucleotide derivatives are eluted faster and are not fully resolved. Nucleosides and cyclic nucleotides are retained longer. A Novapak C_{18} column has been used to resolve short oligonucleotides. Nucleotide derivatives are eluted rapidly. Dinucleotides and trinucleotides are eluted by the Novapak C_{18} column, but not by an Ultrasphere ODS column. The method has been used to analyze reaction mixtures that contain nucleotide derivatives and short oligonucleotides.

87

HPLC STUDY OF NADH DEGRADATION PRODUCTS WITH ELECTROCHEMICAL DETECTION

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There has been considerable interest in the redox chemistry of pyridine bases such as the NAD+ (nicotinamide adenine dinucleotide)/NADH couple because of their importance in biochemistry. The electrochemical reduction of NAD+ has been well characterized. Also there have been numberous studies of the oxidation of NADH at solid electrodes. From the analytical point of view it is desirable to be able to determine NADH in aqueous solution Because of the well-known difficulties associated with use of solid electrodes, especially in aqueous solution, it would also be desirable to be able to determine NADH voltammetrically at mercury electrodes. The oxidation of NADH occurs at +0.8 V vs. SCE in neutral aqueous media, which is well positive of potentials at which mercury itself is oxidized in these media. We report here on the reduction of NADH at mercury electrodes in aqueous solution containing succinic acid. Moreover, separation of NADH degradation products was achieved by HPLC, followed by electrochemical detection.

88 PEPTIDE SEPARATIONS USING POLYMERIC ION-EXCHANGE COLUMNS.

Paula Mychack and James R. Benson. Interaction Chemicals Inc.
1615 Plymouth Street, Mountain View, CA 94043 415-969-2400

Interest in separating peptides using high performance liquid chromatography has grown in the last few years, and efforts to utilize various high efficiency packing materials with methods that would allow fast and sensitive separations have evolved. We report on the separation of several mixtures of peptides using recently developed high efficiency polymeric columns. Interaction BIO-10 and BIO-20 columns were used for cation-exchange chromatography. These 0.3 X 10 cm columns respectively contain relatively high and low capacity cation-exchange polymers, each exhibiting unique selectivity for the peptide mixtures studied.

Both fluorescent and UV detection were employed in this study. By monitoring fluorphores formed from the reaction of effluent peptides with o-phthalaldehyde in a post-column reaction, high sensitivity detection (picogram) was realized. Ultraviolet monitoring provided a simple method when sensitivity was not important. Tryptic peptides formed by digestion of various proteins were used as samples.

Our work has shown that polymeric columns exhibit several advantages over silica columns. The greater chemical stability permits separation of highly acidic and basic peptides, ionic compounds often difficult or impossible to chromatograph using silica.

89 BEVERAGE ANALYSIS USING POLYMERIC COLUMNS.

Dexter J. Woo, Bart Poulsen, and James R. Benson. Interaction Chemicals, Inc., 1615 Plymouth St., Mountain View, CA 94043.

Liquid chromatography can be useful in determining a variety of components in beverages. The use of polymeric columns can be instrumental in analyzing many components that are important in nutritional value, flavor enhancement and preservative ability.

The ION-300 is a column especially designed for analyzing short chained carboxylic acids and alcohols in the presence of sugars in fruit drinks, juices and wine. Many acidulants including citric and malic acids are added to these products. The amount of these acids in the formulation is important for calculating manufacturing cost and for tasting. The amount of alcohols such as glycerol and ethanol in fruit juices and wine are indicators of fungi growth and level of fermentation. The separation of these compounds in midst of the sugars sucrose, glucose and fructose is possible with the ION-300 due to its unique selectivity.

In some soft drinks and fruit juices and wines, sorbic acid, gallic acid, benzoic acid and its derivatives are used as preservatives. These compounds can be analyzed along with citric, ascorbic, tartaric and malic acids in a single chromatographic run using the ARH-601 column.

90 ELECTROCHEMISTRY, SPECTROCHEMISTRY AND PHOTOREDOX CHEMISTRY OF MIXED PHOTOCENTER/DONOR/ACCEPTOR COMPLEXES.

C. M. Elliott, R. A. Freitag and Jon Merkert. Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

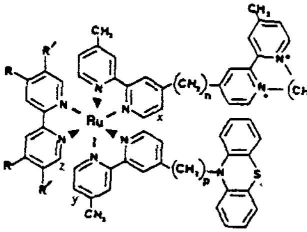
Intramolecular photoinduced electron transfers are of interest for many reasons. One major advantage of studying intramolecular reactions is the degree of structural control that can be exercised relative to that in bimolecular reactions. We have developed a series of such systems based on 1) a Ru(II) trisbipyridine photocenter; 2) a diquat acceptor; and 3) a phenothiazine donor. In these systems the various components are covalently linked together with alkyl chains.

P-D   P = $Ru(II)L_3$
P-A   D = Phenothiazine
D-P-A   A = Diquat

The significant feature of this system is the "tunability" of the structure.

Where each of the above parameters can be varied systematically.

Electrochemical, spectral, and photophysical studies will be presented.



$x + y + z = 3$
R & R′ $CH_3 \rightarrow COOR$

$m = 2,3\ldots\infty$
$n = 2,3\ldots\infty$
$p = 1,3\ldots\infty$

91 KINETICS AND THERMODYNAMICS OF ELECTRON TRANSFER REACTIONS INVESTIGATED BY SQUARE WAVE VOLTAMMETRY.

Cindy M. Reidsema and Carl A. Koval, Department of Chemistry, University of Colorado, Boulder, CO 80309.

There have been numerous experimental and theoretical studies conducted over the past 30 years which have led to a general understanding of the energetic factors that influence the rates of electron transfer processes. While these studies continue, new interests have focussed on another question. What are the effects of distance on the rates of charge transfer processes? The approaches to this question have been numerous. However, our approach has been to look at several series of sterically hindered transition metal complexes, such as those based on $Co(phen)_3$ and $Ru(NH_3)_5py$, and obtain electrochemical kinetic ($k°$, $E_{1/2}$, and α) and thermodynamic ($\Delta S°_{rc}$) data for each member of the series. Comparison of the kinetic and thermodynamic data gives information concerning how the steric effects manifest themselves in the electron transfer process. The data that has been collected suggests that nonadiabatic behavior is being exhibited by the $Co(phen)_3$ series. Square wave voltammetry and staircase voltammetry are two techniques used to obtain kinetic data; a non-isothermal cell arrangement is used for the thermodynamic data acquisition. The applicability of the two voltammetric techniques for obtaining kinetic information and several aspects of the actual experiment will be discussed.

92 ELECTROCHEMICAL STUDIES OF IRON PORPHYRINS AND HYDROPORPHYRINS.

Steven H. Strauss and Ronald G. Thompson, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

The discovery of iron chlorins and isobacteriochlorins in a number of heme proteins and enzymes has prompted us to investigate how and why these iron hydroporphyrins are different than iron porphyrins. We are studying structural, magnetic, thermodynamic, and kinetic properties of homologous series of iron porphyrins and hydroporphyrins. With respect to an electrochemical thermodynamic property, the chlorin macrocycle pi system is some 300 mV easier to oxidize than the porphyrin macrocycle, yet so far we have not found a significant difference in Fe(II)/Fe(III) potentials as a function of macrocycle.

We are continuing these cyclic voltammetric experiments using a variety of spin-states and ligation-states. Other thermodynamic properties, such as ligand binding, are macrocycle dependent when theligated complex is high-spin but not macrocycle dependent when the complex is low-spin. Our electrochemical experiments are designed to probe this discovery, to see if the spin-states of the Fe(II)/Fe(III) couple affects the thermodynamics or kinetics (studied by chronocoulometry) of electron transfer.

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93 ELECTROCHEMISTRY IN TOLUENE. L. Geng, J. Jernigan and Royce W. Murray, Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, N.C. 27514.

Using microelectrodes and tetra-hexylammonium perchlorate electrolyte, it is now possible to investigate a wide range of electrochemical phenomena in the low dielectric constant solvent toluene. From voltammetric $E^{1/2}$ values for a series of one electron couples, an approximate translation of reference electrode potentials between toluene and acetonitrile can be made. Some metallotetraphenyl porphyrins exhibit electrocatalytically interesting two electron oxidation waves in toluene, in contrast to the sequential one electron waves known in methylene chloride solvent. Electron transport rates through redox polymer films on microelectrodes are $\geq$ 10x slower in toluene as compared to acetonitrile.

94 ELECTROCHEMICAL STUDIES OF TWO-ELECTRON REDOX PROCESSES INVOLVING Ni AND Pd COMPLEXES, Daniel L. DuBois and Alex Miedaner, Solar Energy Research Institute, 1617 Cole Boulevard, Golden, CO 80401.

We have recently synthesized three classes of nickel and palladium complexes which are capable of undergoing reversible two-electron reductions, or two closely-spaced one-electron reductions. The factors important in determining the difference in half wave potentials, $\Delta E_{1/2}$, for the Ni(II/I) and Ni(I/0) couples will be discussed. For example, reaction of $[Ni(PP_2)(CH_3CN)](BF_4)_2$ (where PP_2 is $PhP(CH_2CH_2PPh_2)_2$) with monodentate phosphines, L, leads to the formation of $[Ni(PP_2)L](BF_4)_2$. When L is PEt_3 $\Delta E_{1/2}$ is 280 mV. When L is $P(OMe)_3$ $\Delta E_{1/2}$ is 0 mV. In nickel complexes of the type $[Ni(Ph_2P(CH_2)_nPPh_2](BF_4)_2$ (where n = 1, 2, or 3) $\Delta E_{1/2}$ ranges from 130 mV to 860 mV, depending on the value of n. In complexes of the type $[Ni(PP_3)L](BF_4)_2$ (where PP_3 is $P(CH_2CH_2PPh_2)_3$ and L is a monodentate phosphine) reversible two-electron reductions are observed in which the bond between nickel and the central phosphorus atom of PP_3 is is cleaved during the reduction. The electrochemical properties of $[Pd(PP_2)L](BF_4)_2$ and $[Pd(PH_2P(CH_2)_nPPh_2)](BF_4)_2$ will also be discussed as well as preliminary results on the behavior of these complexes as redox catalysts.

95 WEIGHING AN ELECTODE SURFACE - QUARTZ MICROBALANCE, J. G. Gordon II, K. K. Kanazawa, Owen Melroy, D. Buttry, T. Li and R. Schumacher, IBM Research Laboratory, 5600 Cottle Road, San Jose, California 95193.

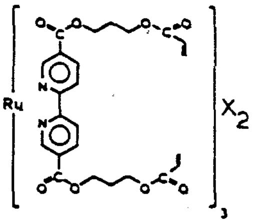
We have recently achieved stable oscillation of a quartz crystal in solution and have been exploring its use as a mass balance for studies of adsorption and deposition on metal surfaces. The sensitivity to thin solid films is the same in solution as it is in air or vacuum, namely less than an atomic monolayer. A technique has been developed to use one of the oscillator's electrodes as an active working electrode in an electrochemical cell. Direct, in situ, measurements of the mass of material deposited in the underpotential deposition or adsorption of Pb, I, and Cd on Au electrodes have been made. These coupled with simultaneous measurements of the charge passed, have permitted the first unambiguous calculations of the electrosorption valency of the adsorbed atoms. Mathematical analysis based on a simple physical model has resulted in a general analytical expression which permits quantitative interpretation of frequency shifts from three major sources: the overlayer film, the liquid, and the roughness of the crystal surface. The expressions commonly used in the vacuum and thin film communities are special cases of this general equation. A significant result is that the frequency change due to immersion is proportional to the square root of the viscosity times the density of the liquid. Quantitative agreement with experiment is obtained with no adjustable parameters In addition to the adsorption studies mentioned above, the microbalance has been applied to many other problems including ionic motion in conducting polymers, and the electrochemical oxidation of metals. Some results of these experiments will be presented.

96 ION TRANSPORT IN ELECTROACTIVE POLYMER FILMS. C. M. Elliott and J. G. Redepenning.

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

Relative to the parent ligand 2,2'-bipyridine, substitution in either the 4,4'- or 5,5'- positions with electron withdrawing groups such as COOR causes significant changes in the redox chemistry of the ligand and of metal complexes formed therefrom.[1-2] For example, tris ruthenum complexes of these ligands can exist in eight formal oxidation states (+3 to -4). Additionally, when substituted in 5,5'- positions with ester functions each oxidation state possess a distinctively different visible color.

We have extended this chemistry to prepare a thermally polymerizable monomer which when polymerized maintains both the electrochemical properties and spectral properties of the monomer[3].



The stability and response characteristics of this polymer coated on an optically transparent thin layer SnO_2 electrode will be discussed. Also, the details of ion transport within the polymer under electrochemical conditions will be considered.

1. C.M. Elliott, J.C.S., Chem. Commun., 261 (1980).
2. C.M. Elliott and E.J. Hershenhart, J. Am. Chem. Soc., 104 (1982) 7519.
3. Chemical and Engineering News, 61 (1983) p. 21

97 TRANSPORT NUMBERS IN 1-METHYL-3-ETHYLIMIDAZOLIUM CHLOROALUMINATE MOLTEN SALTS.

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Mixtures of 1-methyl-3-ethylimidazolium chloride (MEICl) and $AlCl_3$ form ionic liquids that melt well below room temperature. The transport numbers of the ions in these melts are of interest because of their impact on electrochemical cell design and on calculations of cell potentials. For certain cell designs based on the melts, theoretical specific energies vary over an order of magnitude depending on which ions transport charge through the cell separator. A moving boundary method and a modified Hittorf method were used to obtain transport numbers in basic (mole fraction, N, of $AlCl_3 < 0.5$) and neutral ($N = 0.5$) melts. The external transport numbers (relative to fritted glass barriers in the electrolytic cells used) were found to be 0.70 ± 0.02 for MEI^+, and from 0 to 0.30 for the Cl^- and $AlCl_4^-$ ions depending on their concentrations. These values appear to be independent of the type of barriers used, although some selectivity was observed in barriers made from MEI^+- selective NAFION and a Cl^--selective polymer. The internal transport number (relative to Cl in the melt) for the MEI^+ was found to be 1.00 ± 0.02.

98 KINETIC ASPECTS OF FACILITATED TRANSPORT THROUGH LIQUID MEMBRANES. C.A. Koval and Z. E. Reyes.

Dept. of Chemistry, University of Colorado, Boulder, CO 80309.

A variety of promising separation methods involve reversible chemical complexation, wherein a chemical carrier binds reversibly with the molecule to be separated (permeate). One separation method that uses reversible chemical complexation is facilitated transport in liquid membranes. The liquid membrane contains the mobile chemical carrier that remains in the membrane phase. At one interface, the membrane phase contacts the phase that is enriched with the permeate species. The carrier reacts with the permeate to form the complex. The complex diffuses to the opposite boundary where the reverse reaction takes place and frees the permeate into the permeate-lean phase. This method provides a very selective separation while also achieving high flux rates. Recently, Kemena et al (L.L. Kemena, R.D. Noble, N.J. Kemp, J. Member Sci(1983)15,259) developed an optimization model for facilitated transport resulting from the reversible chemical complexation. The optimization model allows the chemical factors (reaction rates, diffusion rates, solubility, etc.), which limit facilitated transport for a given system, to be identified. Once these limiting factors are known, facilitation can, in principle, be improved via molecular engineering. Results for the separation of CO using an Fe(II) macrocyclic complex as a carrier in a benzonitrile liquid membrane (C.A. Koval, R.D. Noble, J.D. Way, B. Louie, Z.E. Reyes, B.R. Batemen, G.M. Horn, D.L. Reed, Inorg. Chem.(1985) 24,0000) and the separation of CO_2 using ethylenediamine as a carrier in a Nafion membrane (J.D. Way et.al, unpublished results) will be presented. The application of these separation systems to electroanalytical chemistry will be discussed.

99 COMBINED ELLIPSOMETRIC AND ELECTROCHEMICAL MEASUREMENTS OF PtCr ALLOYS IN ACIDIC SOLUTION

Mark T. Paffett, Shimson Gottesfeld[1], Los Alamos National Laboratory, MS D429, Los Alamos, NM 87545.

The combined ellipsometric and electrochemical responses of a series of PtCr bulk alloy compositions (in atomic percent) studied were: $Pt_{0.90}Cr_{0.10}$, $Pt_{0.65}Cr_{0.}$ $Pt_{0.5}Cr_{0.5}$ and $Pt_{0.20}Cr_{0.80}$. In addition to the in-situ characterization of these alloy surfaces, pre- and post-mortem surface analyses using Auger electron spectroscopy, X-ray photoelectron spectroscopy, and Rutherford backscattering spectroscopy were performed. The electrocatalytic activity of these alloy surfaces toward oxygen reduction in acid will be discussed relative to the performance of pure Pt and pure Cr. The potential dependence on the stability of these alloy surfaces will be addressed, with particular reference to their use as supported electrocatalysts for oxygen reduction in an operating phosphoric acid fuel cell environment.

[1] On sabbatical leave from Tel Aviv University

100 A MODULAR MEMORY SYSTEM FOR RAPID DATA ACQUISITION IN MULTIWAVELENGTH SPECTROELECTROCHEMISTRY

David T. Rossi, Monsanto Industrial Chemicals Company, 800 N. Lindbergh, St. Louis, Missouri 63167; Harry L. Pardue, Department of Chemistry, Purdue University, W. Lafayette, Indiana 47906

This paper describes the design, construction, and performance of a modular memory system for rapid collection of digital data. The memory module can collect 64 kilobytes of data in as little as 64 ms, and has been used, in conjunction with a diode array spectrophotometer, to kinetically monitor the irreversible hydrolysis of p-aminophenol in a thin layer optically transparent electrochemical (OTTEL) cell.

101 CHEMICAL SEPARATION AND ANALYSIS OF OXYGENATED POLYNUCLEAR AROMATIC HYDROCARBONS FROM THE PHOTOCHEMICAL DEGRADATION OF WEATHERED CRUDE PETROLEUM.

R. E. Jordan, and D. A. Chatfield, Department of Chemistry, San Diego State University, San Diego, CA 92182

Crude petroleum and petroleum products introduced into the marine environment via accidental spills or routine discharges undergo a complex weathering process of evaporation, dissolution, photochemical and microbial degradation, emulsification, and sedimentation. This work has focused upon the photochemically-induced formation of oxygenated polynuclear aromatic hydrocarbon (OXPAH) species in a simulated oil spill experiment and in controlled laboratory photo-irradiation experiments. A multidimensional liquid chromatography isolation scheme has been developed which integrates preparative normal-phase liquid-solid chromatography with analytical reversed-phase and normal-phase high pressure liquid chromatography. The latter provides resolution of OXPAH components into nonpolar, aromatic and polar fractions for subsequent GC and GC-MS analysis. In the simulated spill experiment, Prudhoe Bay crude petroleum was added to natural seawater (~ 400 ℓ tanks) and exposed to natural sunlight for approximately four months. A series of laboratory photo-irradiation experiments has been under taken to examine the influence of initial oil composition and the presence of atmospheric ozone on OXPAH formation. In addition, isotope labelling (^{18}O) of OXPAH products has been attempted to help provide insight into formation mechanisms.

102 CADMIUM SPECIATION IN NATURAL WATERS AND THEIR EFFECT ON RAINBOW TROUT, W. C. Gorman, Jr. and R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523; P. W. Davies, Colorado Division of Wildlife, 317 West Prospect, Fort Collins, Colorado 80522.

Most water quality criteria for metals are based solely on the total metal concentrations. However, recent evidence has shown that toxicity is not related to the total metal but is related to the concentrations of the free metal and labile metal complexes. In this paper, DPASV was used to monitor the rate of formation of cadmium-ligand complexes in tap and well water. pH titrations were employed to estimate the stability constants of the various cadmium complexes from which the form of the complexes can be tentatively identified. Also, the toxicity of the different cadmium species on rainbow trout will be examined.

103 NEW NBS STANDARD REFERENCE MATERIALS FOR QUALITY ASSURANCE IN ENVIRONMENTAL ANALYSIS. T. E. Gills and S. B. Rasberry, Office of Standard Reference Materials, National Bureau of Standards, Gaithersburg, MD 20899.

Chemical pollution has created increased concern for the role of trace elements and/or toxic constituents in biological and environmental processes. In the United States this has resulted in cooperative efforts among the National Bureau of Standards (NBS), Environmental Protection Agency (EPA), Food and Drug Administration (FDA), and National Institute of Occupational Safety and Health (NIOSH), to produce standards by which a variety of trace elements and/or toxic constituents can be accurately monitored and measured. These Standard Reference Materials (SRM's) serve as a basis for the quality assurance of measurement and monitoring of trace elements that are considered toxic and/or essential. This paper will present recent data on NBS environmental SRM's and a summary of the methods employed in the analysis and certification. In addition, trends and projections for the technical aspects of SRM research and production will be discussed.

104 ASBESTOS IN THE BUILDING ENVIRONMENT - THE ANALYTICAL ALTERNATIVES, I.M. Stewart and D.A. Brooks, McCrone Environmental Services, 5500 Oakbrook Parkway, 200 Oakbrook Business Center, Norcross, GA 30093

Asbestos has been described as "the fiber that's panicking America". Recent publicity on asbestos-containing materials in buildings has produced a torrent of samples for analysis. Almost everyone with an analytical capability has touted his technique as the ultimate tool for these analyses. This paper discusses realistic asbestos analytical alternatives and their scope of application.

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105 "A CONTINUOUS FLOW ANALYZER FOR AMMONIA, NITRATE, AND TOTAL INORGANIC NITROGEN"

P.J.Barthel Jr., T.H. Jupille, D.W. Togami; Wescan Instruments Inc.,
3018 Scott Blvd., Santa Clara, CA 95054.

A continuous flow method for the determination of ammonia, nitrate, and total inorganic nitrogen using membrane distillation and conductivity quantitation will be described. It can be used to measure ammonium nitrogen continuously or in discrete samples.

A sample stream is mixed with potassium hydroxide and the combined stream passed over a porous teflon membrane which is permeable to ammonia gas but not to liquid. The ammonia is absorbed into a solution flowing past the other side of the membrane and the consequent change in conductance used to quantitate the ammonia.

Differential conductance detection permits the use of absorbents with inherently significantly conductance. A modified boric acid solution absorbs ammonia to give a solution in which conductance is linearly related to ammonia concentration from zero to 10 milliequivalents per liter. With such an absorber the instrument can be adjusted to read out directly in either parts per million or milliequivalents per liter on a panel meter or recorder.

106 MOLECULAR WEIGHTS OF AQUATIC FULVIC ACIDS BY VAPOR PRESSURE OSMOMETRY.

George R. Aiken, U.S. Geological Survey, Water Resources Division, Denver Federal Center, MS 407, Denver, CO 80225.

The molecular weights of eight fulvic acids, which were isolated from 5 rivers, were determined by vapor pressure osmometry (VPO) with water (H_2O) and tetrahydrofuran (THF) as solvents. Small angle x-ray scattering measurements of the fulvic acids indicate that they are relatively monodisperse, and that VPO is a suitable method for molecular weight determination. THF is shown to be an excellent solvent for the measurement of molecular weights by VPO of aquatic fulvic acids. Dissociation of organic acids is suppressed in THF and no correction of the molecular weight data for dissociation is required. Data from measurements made in water were mathematically corrected for dissociation using solution pH and the apparatus constant. Results from determinations made in each solvent are in close agreement with each other and with estimates of molecular weight from the small angle x-ray scattering measurements. The measured molecular weights of the fulvic acids ranged from 550 to 900 daltons. These results contain important implications concerning the distribution of molecular weights of dissolved organic carbon (DOC) in natural waters. Results of size distribution studies of DOC by ultrafiltration reported in the literature indicate that a major fraction of the DOC of rivers and lakes is of molecular weight greater than 10,000 daltons. Aquatic fulvic acid accounts for approximately 40% of the DOC of most surface waters. The remainder of the DOC can be accounted for by low-molecular-weight hydrophilic acids (30%), humic acid (10%), and identifiable organic compounds (20%), such as amino acids and carbohydrates. The results of this work suggest that the DOC of rivers and lakes is much lower in molecular weight than would be estimated by size distribution studies.

107 MAJOR AND TRACE ELEMENT DETERMINATIONS IN ACID MINE WATERS:

J. W. Ball and D. K. Nordstrom, U.S. Geological Survey, 345 Middlefield Road, MS-421, Menlo Park, CA 94025

Acid mine waters from Iron Mountain mine, Shasta Co., and Leviathan mine, Alpine Co., California, have been analyzed for 38 dissolved major and trace constituents. Concentrations range from the ng L^{-1} range to the g L^{-1} range. These waters contain up to tens of mg L^{-1} concentrations of As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Tl, V and Zn, and up to hundreds or thousands of mg L^{-1} concentrations of Al, Cu, Fe, Zn and SO_4 at pH values as low as 0.8. Other elements, including Au, B, Ba, Be, Bi, Mo, Sb, Se and Te are elevated above background concentrations, and usually fall in the μg L^{-1} concentration range. Extraordinarily high concentrations of As (40 mg L^{-1}), Au (33 ng L^{-1}), Cd (15 mg L^{-1}), Tl (1 mg L^{-1}) and Zn (1500 mg L^{-1}) were found at one site. The determinations were performed using several techniques, including d.c. argon plasma, multielement emission spectrometry, flame, graphite furnace, hydride-generation and cold-vapor atomic absorption spectrophotometry, ion chromatography and uv-visible spectrophotometry. Quality of analyses was checked by: 1) comparing determinations using two or more techniques; 2) calculating solution charge balance before and after chemical speciation calculations; 3) comparing conductance measured on site to conductance calculated from analytical concentrations of major solute species; 4) examining the relationship of the predominant anion, SO_4, to the measured conductance; 5) comparing measured Eh to Eh calculated from the activity ratio of Fe^{2+}/Fe^{3+}; and 6) mass-balance calculations for conservative constituents at stream confluence points.

108 SOIL SORPTION OF ORGANIC CONTAMINANTS IN RELATION TO SOIL COMPOSITION AND MOISTURE CONTENT, Cary T. Chiou, U.S. Geological Survey, Denver Federal Center, P.O. Box 25046, MS 407, Denver, CO 80225

Because sorption by soil/sediment plays a major role in the transport of organic contaminants in hydrogeological systems, the effects of soil composition and water content on sorption have been investigated. Both partition into soil organic matter and adsorption onto soil minerals can be important, depending on the soil-water content. The uptake by soil/sediment of (nonionic) organic compounds in aqueous systems consists primarily of solute partition (dissolution), rather than surface adsorption, into the humic phase, in keeping with (i) a linear correlation between soil uptake and humic content; (ii) a high linearity of sorption iostherms over a wide range of concentration relative to solute solubility; (iii) low heats of sorption of solutes in soil-water equilibria; and (iv) a lack of solute competition in uptake. Adsorptive contribution by the soil mineral fraction is relatively insignificant in wet soils presumably because of its preferred dipole interaction with water, excluding these solutes from this portion of the soil. By contrast, the soil uptake from hexane and from vapor phase on dry and partially hydrated soils is controlled mainly by adsorption on soil minerals, as is consistent with nonlinearity of the isotherm, high heat effect, and solute competition in sorption. The sorptive capacity of the water-unsaturated soil is markedly greater than that of the water-saturated soil. Transport of organic contaminants through the unsaturated soil zone therefore would be affected to a varying extent by the degree of water saturation in soil in addition to variations in soil composition.

109 DIEL CHANGES IN IRON CONCENTRATION IN AN ACIDIC ROCKY MOUNTAIN STREAM. Ken Bencala, USGS-WRD, MS 496, 3475 Deer Creek Rd., Palo Alto, CA 94304; Diane McKnight, USGS-WRD, Box 25046, MS 407, Denver Federal Center, Denver, CO 80225

Dissolved iron concentrations and other chemical, physical and biological parameters were measured over a 24 hour period in September and a 48 hour period in November in the Snake River, a small Rocky Mountain stream that is naturally acidic (pH 4.0) from weathering of disseminated pyrite. On both dates, the iron concentration was positively correlated with light intensity, with maximum iron concentrations of about 1.2 mg/L at midday and minimum concentrations of about 0.5 mg/L at night. This pattern was not observed for other chemical constituents or for discharge; and benthic invertebrate and bacterial activity followed the opposite pattern with increased activity at night. We hypothesize that the daytime peak in iron concentration results from photoreduction involving hydrous iron oxides on the stream bed. Further, this implies that under these acidic conditions, within stream chemical processes are the primary controls on iron concentration rather than processes occurring within the watershed, which explains the differences between seasonal trends for iron concentration and for other inorganic constituents.

110 MASKING, CHELATION, AND SOLVENT EXTRACTION TO IMPROVE THE DETERMINATION OF SUB-PPM LEVELS OF TRACE ELEMENTS IN HIGH IRON AND SALT MATRICES. Mary Carol Williams, Los Alamos National Laboratory, P.O. Box 1663, MS-E518, Los Alamos, New Mexico 87544.

The ammonium pyrrolidine-N-carbodithioate (APCD or APDC) and 4-methyl- 2-pentanone (methyl isobutyl ketone of MIBK) system for the chelation and extraction of transition metals was investigated over pH ranges of 0-12 units. This system reduced the troublesome interferences associated with high total dissolved solids. The addition of a masking agent precluded the extraction of iron through complexation. The masking effects of ammonium citrate and tiron (4,5-dihydroxybenzene-1, 3-disulfonic acid) were investigated for Cd^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, Cr^{6+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Tl^{1+}, and Zn^{2+}. Fe^{3+} was effectively masked by citrate and tiron above pH 7.5 and 6.5, respectively. All the metals, except Cr^{3+} and Cr^{6+}, were efficiently extracted by the APCD-MIBK system. The solubility of MIBK in water limits the degree of concentration attainable. The use of NaCl as a salting-out agent allowed a concentration ratio of 20 aqueous to 1 organic to be used. This enabled Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} to be analyzed at the ppb level by flame atomic spectroscopy.

111 ION CHROMATOGRAPHY AND EPA EQUIVALENCY. Robert J. Joyce, Denise Eubanks, Leonard Henry, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3 03, 408/737-0700.

Early environmental applications of Ion Chromatography focused on the determination of anions in airborne particulates. Since then, the use of this analytical technique has spread to nearly all aspects of environmental monitoring. Of particular interest is the suitability of Ion Chromatography for EPA-regulated analysis of drinking water and wastewater.

This report will summarize an extensive comparison of EPA Method 300.0, entitled "The Determination of Inorganic Ions in Water By Ion Chromatography" with currently approved methodology. It will also show a comparison of Ion Chromatography methods for transition metals and cyanides in wastewater with accepted EPA methods. Finally, this report will present a new method for chlorite and chlorate in drinking water disinfected with chlorine dioxide.

112 A RAPID, FIELD PRECONCENTRATION/PRESERVATION SYSTEM FOR ROUTINE MONITORING OF TRACE METALS IN NATURAL WATERS, Dana Heimbecker and R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523; Sam H. Kunkle, Water Resources Field Support Lab, National Park Service, 107C Natural Resources, Colorado State University, Fort Collins, Colorado 80523.

Field preconcentration and preservation of trace metals from natural waters in conjunction with laboratory analysis by inductively coupled argon plasma emission spectroscopy can significantly reduce the cost of a routine monitoring program. Preconcentration of the trace metals in the field can lower transportation costs, improve sample integrity and is particularly important for monitoring inaccessible water systems. In this paper, a rapid field preconcentration and preservation system will be described. The system, consisting of a hand-operated pump, a cartridge type filter, and an ion exchange column is capable of concentration factors of 200 with sampling times of 10 minutes. The performance of the system over a wide range of sample conditions including pH, temperature, conductivities, and hardness, will also be discussed.

113 PPB DETECTION OF CHROME (VI) IN DRINKING WATER AND GROUND WATER. Leonard Henry, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3 03.

Government regulations restricting the allowable levels of hexavalent chrome discharged into waste streams have necessitated the development of a specific, highly sensitive method for determining low part-per-billion levels of hexavalent chrome. The comparatively high molar extinction coefficient of hexavalent chrome as chromate in neutral or alkaline medium at 372 nm, combined with the concentration of trace amounts of chromate as a solute band by ion chromatography provides an extremely sensitive and specific method for determining trace levels of hexavalent chrome. The UV detection method for the discrete solute band eliminates interferences from common anions which are weakly UV absorbing or non-UV absorbing such that high concentrations of these anions can be tolerated in the matrix. Detection of chromate as low as 1 ppb has been demonstrated and quantitation of 10 ppb levels are possible without preconcentration using a 700 ul injection volume. Chromate may also be preconcentrated by anion exchange with good linearity, allowing determination in many matrices well below 1 ppb.

114 CHARACTERIZATION OF HUMIN ISOLATED FROM DIFFERENT SOURCES. James A. Rice and Patrick MacCarthy, Colorado School of Mines, Chemistry and Geochemistry Dept., Golden, CO 80401.

Humin samples isolated from five different organic materials by a liquid-liquid partitioning procedure are characterized by elemental analysis, carboxyl group content using a modified acetate method, total acidity using a baryta titration and infrared spectroscopy. The characteristics of the humin samples are compared. In addition, the characteristics of the humin samples are contrasted to those of the corresponding humic acid and fulvic acid. The humic and fulvic acids were obtained from the same source by the same isolation procedure and were characterized by the same methods.

115 CORROSION TESTING BY THE POLARIZATION RESISTANCE METHOD. M. Umaña, D. Whitaker, E.D. Pellizzari, Analytical and Chemical Sciences, Research Triangle Institute, P.O. Box 12194, Research Triangle Park, NC 27709; P. Fedkiw, R. Chapman, Department of Chemical Engineering, N.C. State University, Raleigh, NC.

The purpose of this research project was to evaluate and assess the equivalency of two selected methods for the measurement of the corrosivity of samples of significance to solid and hazardous waste studies.

The two methods selected for this research evaluation were Number 1110, "Corrosivity Toward Steel" and Number 1120, "Electrochemical Corrosion Method." Both methods are described in the solid waste manual, "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods," SW 846 (1982). These methods were evaluated by comparing the precision, accuracy, analysis time, advantages, disadvantages and other pertinent methodological parameters. A comprehensive literature review was performed and the sample matrices were obtained. The samples included hazardous wastes classified as F006 to F016. An evaluation and comparison of methods was performed. Seven replicates were run by each method using SAE 1020 steel coupons. In addition, standard controls were run with each set of replicates. An ICP analysis was performed on the waste samples and a SEM/EDX analysis was performed on some of the steel coupons. Statistical analysis was used to compare the results. Although the research described has been funded by US EPA through Contract Number 68-03-3099 to RTI, it has not been subjected to the Agency's required peer and administrative review and therefore do not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

116 A DISCUSSION OF THE X-RAY FLUORESCENCE DATA FROM PM-10 MONITORING. Margaret J. Zimmerman, Jenks, J. Maxine, Anselmo, Vincent C., Vallarino, Hazel C., and Denniston, Virginia J., Texas Air Control Board, 6330 Hwy. 290 East, Austin, Texas 78723.

In conjunction with the Environmental Protection Agency (EPA) the Texas Air Control Board (TACB) will have established a network of size-selective inlet (SSI) and dichotomous monitors with a particulate cut-off of 10 microns. This network will be fully operational by April 1985. The SSI monitors will collect particulate on quartz filters and the dichotomous samplers will collect on fluorocarbon filters. All valid samples will be analyzed by x-ray fluorescence spectrometry (XRF) for 31 different elements. This paper will discuss the results of these analyses. At sites where PM-10 are colocated with high volume monitors, the XRF will be compared.

117 MIGRATION OF FONOFOS FROM MUCK SOIL INTO SURFACE AND GROUNDWATER. T. D. Spittler and R. W. Straub. New York State Experiment Station, Cornell University, Geneva, NY 14456.

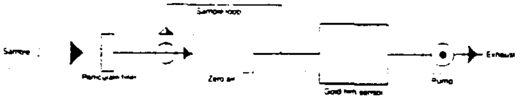
Fonofos (Dyphonate) is used extensively in muckland onion cultivation for root maggot control. Several pet deaths in Orange County, New York, were blamed upon the presence of leached material in open ditches draining these treated fields. Water and waterborne silt from drainage tiles, drainage ditches, and lateral ditches were monitored for fonophos in 1984-85. No large scale movement of material was detected, however, unusual weather condition may have disrupted the usual drainage patterns. There is indirect evidence of this from efficacy data on insect control which suggest that high water volume may have removed much material before the 1984 monitoring program was in place. Monitoring is continuing through the 1985 season.

118 QUANTITATIVE ANALYSIS OF PART PER BILLION CONCENTRATION OF HYDROGEN SULFIDE IN AIR USING A GOLD FILM SENSOR; Richard T. McNerney, John J. McNerney
Jerome Instrument Corporation, PO Box 336, Jerome, Arizona 86331.

A thin Gold Film sensor has been developed and patented by the Jerome Instrument Corporation; this sensor allows for the direct determination of hydrogen sulfide in air. Range of analysis is from 1 to 500ppb H_2S. There is minimal response to SO_2, CO, CO_2, hydrocarbons, and water vapor.

Referring to the diagram below, a sample is analyzed in a 30 second automated sequence. By pressing "SAMPLE", a fixed volume of air is drawn into the instrument by an internal pump. The air passes through a zero air filter to ensure no carryover from the preceding sample. A solenoid valve is then actuated which allows a precise volume of sample air to pass over the Gold Film sensor. The sensor adsorbs and integrates the H_2S present in the sample, registering this as a proportional change in resistance and displaying the resulting signal on the digital meter in parts per billion. This value is displayed until the next sample is initiated. At the start of each sample the instrument is automatically rezeroed, eliminating zero drift.

GAS FLOW SCHEMATIC



119 CHEMISTRY AND MICROPHYSICS OF FOGS AND CLOUDS IN CALIFORNIA. Michael R. Hoffmann, 137-78 Caltech, Pasadena, CA 91125.

Fogwater was sampled at a number of sites with either a rotating arm collector or a flow-through vertical string collector. Field investigations in the Los Angeles basin, San Francisco, San Diego, Santa Barbara, the San Gabriel Mountains, and the San Joaquin Valley revealed very high ionic concentrations in polluted fogs, often coupled with very high acidities. Fogs and stratus clouds in the Los Angeles basin typically had pH values ranging from 2 to 4. Acidities were not as high in the San Joaquin Valley, because of scavenging of and subsequent neutralization by ammonia from agricultural sources. Fogwater is efficiently deposited on surfaces during fog events; this deposition was observed to be an important atmospheric pollutant sink during stagnation episodes in the San Joaquin Valley, but at the same time it may be an important source of acid input to surfaces. Extreme acidities observed in fogs (below pH 3) require condensation on preexistent acidic nuclei (haze aerosol) and scavenging of gaseous nitric acid. Stabilization of aquated sulfur dioxide in fogs and clouds has been observed. This has been attributed to the formation of bisulfite-aldehyde adducts. Hydroxyalkylsulfonates have been isolated, identified, and quantified by mobile phase ion chromatography.

120 AN AUTOMATIC-MULTICYLINDER SPLITTER FOR THE COLLECTION OF WET-ATMOSPHERIC DEPOSITION.

LeRoy J. Schroder, U.S. Geological Survey, Lakewood, Colorado, Bernard A. Malo, U.S. Geological Survey, Reston, Virginia, and Carl T. Scott, U.S. Geological Survey, Bay St. Louis, Mississippi.

The wet-collection side of a wet-dry atmospheric-deposition collector, has been modified to accept four separate sampling containers which provide for real-time preservation of precipitation samples. Each sampling container is a cylinder that is 13.2 centimeters in diameter and 27.9 centimeters in length. Each cylinder has a 13.2 centimeter diameter funnel inserted 8.9 centimeters from the cylinder base. Three of the funnels are connected to sample bottles by silicone tubing and one to an automatically-activated filtration system. The modification has produced individual receiver-sampling areas that are 15 percent of the original wet-sample container collection area. This feature requires 0.2 centimeter of wet deposition for 20 milliliters of sample to be collected in each of the four cylinders.

This sampling unit has been operated for 20 weeks at a collection site near Bay St. Louis, Mississippi, resulting in 14 sample-sets collected. Each sample set consists of an untreated sample, a mercuric chloride treated sample, a nitric acid treated sample, and a filtered sample.

Six of these samplers will be installed in April, 1985, as a part of the National Trends Network's trace-metal sampling program. The automatically-filtered samples will be analyzed for selected trace metals using graphite-furnace, atomic absorption spectrometry. The untreated sample will be filtered at the laboratory and analyzed for five cations and four anions. The mercuric chloride treated sample will be analyzed for nitrogen species; and the acid treated sample will be stored for subsequent trace metal determinations.

121 ACID RAIN EFFECTS ON LIMESTONE AND MARBLE,

Michael M. Reddy and Marilyn Werner, U.S. Geological Survey, Water Resources Division, Denver Federal Center, Denver, Colorado 80225

As a part of the U.S. National Acid Precipitation Assessment Program, Task Group G -- Effects on Materials and Cultural Resources -- has begun a 10 year program to measure and document acid rain effects on two types of stone, Shelbourn Marble and Indiana Limestone, which are commonly used in buildings and historical monuments. Reference specimens of limestone and marble (0.19 square meters) were exposed at four sites in the Eastern United States to measure acid deposition effects on these materials and to separate these effects from air pollution damage. Rainfall-runoff solution was collected from each reference stone and from an unused polypropylene stone holder. Runoff volume, specific conductance, and pH were determined on site as soon as possible after collection. Filtered samples, runoff and blank, were sent to the USGS labarataory in Denver, Colorado, for chemical analysis. Marble and limestone surface recession at Research Triangle Park, North Carolina were strongly correlated with rainfall amount. Acid rain damage to both limestone and marble can be expressed as a function of the hydrogen ion deposition to the stone surface. Sulfate concentration in stone runoff is significantly greater than that observed in rainfall for marble and for limestone.

122 A COMPARISON OF ION CHROMATOGRAPHY AND AUTOMATED COLORIMETRY FOR THE DETERMINATION OF MAJOR ANIONS IN PRECIPITATION SAMPLES

Susan R. Bachman, Illinois State Water Survey, Box 5050, Station A
Champaign, Illinois 61820

The two most common methods being utilized for the determination of sulfate, chloride, and nitrate in precipitation samples are ion chromatography and automated colorimetry. A methods intercomparison using 200 precipitation samples has been conducted to obtain data on the comparability of both methods in terms of bias, precision, detection limits, interferences, and analytical throughput. Samples selected for this intercomparison study were obtained from National Atmospheric Deposition Program (NADP)/ National Trends Network (NTN) collection sites from throughout the United States and consequently represented several climatic and geographic regions of the country. Data from analyte spikes and performance evaluation samples were pooled to calculate bias and precision for each of the three parameters investigated. Results from this study indicated that both methods yielded statistically equivalent data for all three anions examined. Interferences in the colorimetric methods due to the presence of nitrite, flouride, and bromide were also evaluated and found to be insignificant at the concentration levels found in precipitation.

123 CONTROLS ON SULFATE RETENTION AND MOBILIZATION IN FORESTED WATERSHED SOILS - SURFACE CHEMISTRY APPROACH

Afifa A. Afifi, U.S. Geological Survey, 432 National Center, Reston, Virginia 22092

Soils from a forested watershed in the Shenandoah Valley, Virginia, were leached with simulated rain of various pH values. The experiment simulated the infiltration of rain through different soil horizons. The surface chemistry of the soil minerals was studied by the XPS, FTIR, pH titration, and BET techniques. The chemistry of this soil leachate also was analyzed. Soil horizons desorbed sulfate and adsorbed organics when leached with the solution that passed through organic soil horizons; this solution simulated rain with pH values higher than that of the zero point of charge (ZPC) of the soil minerals. When the soils were leached by simulated rain of the same pH but not containing dissolved organics, the soils released some adsorbed organic matter. Sulfate in the simulated rain was not adsorbed by the soils. At a lower pH than the ZPC of the soil minerals, sulfate adsorption occurred regardless of whether dissolved soil organics were present, and soil organics generally desorbed; however, minor adsorption occurred in some cases. In this study, the results suggest that the ZPC of the soil minerals, relative to the pH of the soil solutions, controls sulfate sorption in soils. Organic matter, which is adsorbed on mineral surfaces or within clay interlayers and mineralogy of the soil horizons, affect the ZPC of soil minerals. The pK of the adsorbate (organic acids or HSO_4^-) and the ZPC of the mineral surfaces relative to the pH of the leaching solution, explain the present results. Results suggest that competition of soil organics for adsorption sites is not necessarily the only reason for desorption or low adsorption of sulfate by soils.

124 THEORY VERSUS PRACTICE IN THE DETERMINATION OF pH IN PRECIPITATION

Carla Jo Brennan, Mark E. Peden, Illinois State Water Survey, Box 5050, Station A, Champaign, Illinois 61820.

Basic theory and laboratory investigations have been applied to the determination of pH in precipitation samples in an effort to improve the reliability of the results obtained from these low ionic strength samples. The theoretical problems inherent in the measurement of pH in rain have been examined using natural precipitation samples with varying ionic strengths and pH values. The importance of electrode design and construction has been stressed. The proper choice of electrode can minimize or eliminate problems arising from residual liquid junction potentials, streaming potentials, and temperature differences. The use of calibration buffers specifically formulated for the measurement of pH in pure waters has also been examined. Reliable pH measurements can be made in precipitation samples using commercially available calibration buffers providing low ionic strength check solutions are routinely used to verify electrode performance.

125 A HOMOGENEOUS GAS PHASE MECHANISM FOR USE IN A REGIONAL ACID DEPOSITION MODEL

William R. Stockwell, National Center for Atmospheric Research, P.O. Box 3000, Boulder, Colorado 80307

The homogeneous gas phase mechanism for the EPA/NCAR regional acid deposition model will be described. This mechanism has been compared with more complex mechanisms: the explicit mechanism of Leone and Seinfeld and the carbon bond mechanism of Whitten, Killus, and Johnson. These two mechanisms were designed for the modeling of oxidant generation in urban atmospheres and have to be adapted to the modeling of acid formation. It will be shown that a mechanism with 80 reactions and 44 species can give homogeneous gas phase SO_2 and NO_x oxidation rates which are comparable for all three mechanisms. These gas phase oxidation rates are on the order of a few percent per hour. However, the integrated concentrations of HO_2 radicals which are produced by the three mechanisms can be different by a factor of three or more which gives even greater differences in the rate of H_2O_2 production because this rate depends upon the square of the HO_2 concentration. Since H_2O_2 is believed to be the most important oxidant of SO_2 in cloud water (where the rates of oxidation are on the order of 100% per hour), the choice of the gas phase chemical mechanism for a regional acid deposition model can have important effects upon the total amount of acid produced in the model simulations. The results of evaluating these mechanisms against smog chamber data will be reported.

126 A THEORETICAL METHOD FOR COMPUTING VERTICAL DISTRIBUTIONS OF ACIDITY AND SULFATE PRODUCTION WITHIN GROWING CUMULUS CLOUDS

Chris J. Walcek, National Center for Atmospheric Research, P.O. Box 3000, Boulder, Colorado 80307

An equilibrium aqueous chemistry model has been combined with a vertically entraining cloud model to predict distributions of pH within clouds. The cloud model predicts vertical variations of temperature, pressure, entrainment, and liquid water content, each of which will affect the composition of the cloud water. The model assumes that a cloud is composed of polluted boundary layer air into which clean cloud top air has been entrained. The aqueous chemistry model incorporates the effects of soluble aerosols and trace gases on cloud water pH levels. Vertical distributions of pH were predicted within the same cloud for three mixtures of polluted boundary layer air. In the first case, the aqueous composition was dominated by dissolved acidic sulfate. For this case, pH was found to increase with height above cloud base, primarily due to dilution by higher liquid water content. For the second case, acidity levels were determined by dissolved SO_2, formic acid, and HNO_3 gases in the boundary layer air. In this simulation, pH variations with height were not so clearly defined, with the diluting effects of entrainment, liquid water content, and pressure being compensated by the increased solubility of these trace gases at lower temperatures. In the final simulation, neutralizing agents were added to the air from which the cloud forms. It was found that acidity could increase with height above cloud base. These vertical variations in cloud water composition will affect aqueous oxidation of SO_2. Under typical cloudy conditions, it appears that aqueous sulfate production could maximize in middle or upper cloud levels.

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EFFECT OF STORAGE TIME AND COMPARISON OF ANALYTICAL METHODS FOR THE DETERMINATION OF ALKALINITY IN STREAM WATERS OF VARYING IONIC STRENGTHS

Margaret M. Kennedy and Owen P. Bricker, U.S. Geological Survey, 432 National Center, Reston, Virginia 22092

During the investigation of the geochemistry of several small Appalachian watersheds, a two-part study on alkalinity measurements of stream water was conducted. Sample storage times and analytical methods were compared. The effect of storage time on the alkalinity of stream water in the 8 micromole HCO_3^- to 500 micromole HCO_3^- range was determined by monthly measurements of a sample for a period of one year. The maximum storage time for samples greater than 250 micromoles HCO_3^- was five months. Samples with lower ionic strength were more labile and showed significant change within two months. In the second part of the study, replicate samples were measured by three different methods including the EPA Protocol of 15 February 1984, an incremental titration with a Gran Plot calculation of resulting data and an automatic titration with equivalence points determined by the second derivative method. The later two methods show excellent comparability of results. However, the method for auto titration requires a minimum of training and allows routine analysis to be completed quickly without sacrificing accuracy and precision.

128 RAINFALL pH MEASUREMENT VARIATIONS FOR VARIOUS PROTOCOLS AT RESEARCH TRIANGLE PARK, NORTH CAROLINA:

Michael M. Reddy, Randolph B. See, U.S. Geological Survey, WRD, P.O. Box 25046, MS-407, Denver Federal Center, Denver, CO 80225; and Cary Eaton, Research Triangle Institute, P.O. Box 12194, Research Triangle Park, NC 27709

Precipitation acidity was measured from July 2, 1984 to February 1, 1985 at Research Triangle Park, North Carolina as part of the national Acidic Precipitation Assessment Program, Task Force G, Effects on Materials. Specific conductance and pH measurements were determined one to two days after collection for: 1) monthly samples obtained using a wet-only Aerochem collector; and 2) event samples obtained with a wet-plus-dry collector. In addition, rainfall specific conductance and pH were continuously monitored using a microprocessor-controlled data logging system with a modified wet-only Geotech collector. Event samples from the event sampler were shipped in plastic and glass bottles to Denver, CO where specific conductance and pH were remeasured, two weeks after collection. Precipitation totaled 66.47 centimeters during the monitored period. pH values from the monthly wet-only samples were slightly lower than the combined average pH from the event samples. Field and laboratory pH measurements generally exhibited good agreement when samples were shipped in either glass or plastic bottles. Calibration checks of pH meters were made at the time of analysis for laboratory determinations and monthly for the continuous pH monitor. pH values of dilute sulfuric acid solutions and distilled water were monitored to assure that pH electrodes performed properly in low ionic strength solutions.

129 QUALITY ASSURANCE OF PRECIPITATION CHEMISTRY ANALYSES USING ION BALANCE CALCULATIONS

Jacqueline M. Lockard, Illinois State Water Survey, Box 5050, Station A,
Champaign, Illinois 61820.

The National Atmospheric Deposition Program (NADP) was initiated in 1978 to measure the quantity and quality of precipitation within the United States. Organized under the auspices of the State Agricultural Experiment Stations, the NADP network was designed to assess both the deleterious and beneficial effects of atmospheric deposition on a national scale. Since the beginning of the program, one Central Analytical Laboratory (CAL) has been responsible for the chemical analyses of precipitation and dry deposition samples. Over 30,000 wet deposition samples representing 180 sites have already been processed by the CAL facility. A rigorous internal quality assurance program has been developed to ensure that the laboratory measurements are of the highest quality. As a part of this program, each sample analysis is verified by the use of ion balance calculations. The ion balance data have been used in part to develop objective criteria for the reanalysis of samples on a routine basis. A closer examination of these data has revealed patterns in the ion ratios that are a function of sample pH, site location, and collection season. These patterns are discussed in terms of how to most effectively utilize ion balance data to verify the accuracy of laboratory measurements.

130 SOIL CHEMISTRY IN AN ALPINE WATERSHED, COLORADO FRONT RANGE,

Michael Z. Litaor, Geological Sciences Department, Campus Box 250, University of Colorado, Boulder, CO 80309 and E. Michael Thurman, National Water Quality Laboratory, U.S. Geological Survey, 5293 Ward Road, Mail Stop 407, Arvada, CO 80002.

Soil solutions were sampled by 12 lysimeters installed in the alpine and forest-tundra ecotone of the Green Lakes Valley, Colorado Front Range during the summers of 1983 and 1984. Comprehensive chemical analyses were performed. Soil interstitial waters have similar concentrations of H^+, Ca^{++}, HCO_3^-, and dissolved organic carbon (DOC) between years and similar seasonal trends within years. The mean values of Ca^{++}, HCO_3^-, and DOC were 5.2, 22, 33 mg/liter, respectively. The mean pH was 6.0. Although the precipitation acidity has increased in the last decade, no significant increase of $SO_4^{=}$, NO_3^-, or Al was observed in the alpine terrestrial system. The elemental composition of the soils from which the soil solutions were collected was determined by XRF spectroscopy. Eolian dust was collected and its elemental composition and mineralogical suite was determined by electron microprobe and XRD spectroscopy. Topsoil horizons and eolian dust have similar amounts of CaO ($\bar{x} = 3.0\%$) due to eolian-derived calcite. Bottom soils have significantly less CaO ($\bar{x} = 0.90\%$) which is derived mainly from the parent material and topsoil leachates. The buffering capacity of the terrestrial system is due mainly to the combination of eolian calcite and humic substances.

131 ACID DEPOSITION STUDIES IN THE SAN JUAN NATIONAL FOREST.

D. M. Mehs, Fort Lewis College, Durango, CO 81301, M. Story, San Juan National Forest, Durango, CO 81301, and M. Japhet, Colorado Division of Wildlife, Durango, CO 81301.

The presumed fragility of high elevation western lakes and the potential increase in regional sources of air pollution, particularly sources related to energy development, have led to increased concern with potential acid deposition problems. A cooperative study of selected lakes in the Weminuche Wilderness area has been undertaken by the U.S. Forest Service, the Colorado Division of Wildlife, and Fort Lewis College to address this concern. Samples from approximately eighty lakes were collected during the summer of 1984. Field values of alkalinity and pH were obtained at the time of collection using a field test kit. The samples were returned to the laboratory and titrated for alkalinity. The pH was measured with a pH meter. Geological and biological information on the lakes was also tabulated and attempts were made to relate the chemical nature of these lakes to their environmental context.

132 THE APPLICATION OF A CONCEPTUAL LANDSCAPE ACID PRECIPITATION ENVIRONMENTAL MODEL TO ASSESSING THE IMPACT OF ACID RAIN ON DRINKING WATER QUALITY. J. C. Méranger, National Health and Welfare, Ottawa, Ontario, K1A 0L2 and D. R. Gladwell, Barringer Research Ltd., Toronto, Ontario, M9W 5G2, Canada.

Studies have shown that the deposition of acid rain can produce a variety of significant physico-chemical changes in aquatic environments including a marked reduction in surface water pH and an increase in levels of dissolved nitrate, sulphate and aluminum.

Although chemical changes attributable to abnormal acid precipitation can generally be detected in surface waters, the impact on subsurface water is much less evident due to a variety of complex buffering reactions with overburden and bedrock. In order to establish the degree of acid rain impact on potential drinking water sources in acid sensitive areas in Canada, a theoretical conceptual model has been developed and applied to the interpretation of water chemistry data obtained from three communities in central and eastern Canada. This paper describes the model and the general strategy employed in the study. Preliminary analysis of the data is also presented along with a comparison of water chemistry for each of the three areas studied.

133 MANAGEMENT OF ENVIRONMENTAL DATA ON A PERSONAL COMPUTER, R. Roger Johnson, Solutech Corporation, 11011 W. 6th Ave., Suite 307, Lakewood, CO 80215

The concern for toxic substances in our environment has resulted in an increasing volume of data that is being produced by laboratories. Personal computers can be very productive and efficient in the management of environmental data. The design and application of software for the environmental professional should address the professional's needs to use the computer as a tool to accomplish his/her objectives of achieving, maintaining, and reporting compliance with environmental regulations. A commercially available product, ECOTRAC, is a database management system used for permit tracking, groundwater data management, RCRA manifesting and reporting requirements, emission inventories, TSCA substance management and reporting and environmental events reporting. The product is programmed in dBASE III a top selling relational data base system provided by the Ashton-Tate Corporation for IBM personal computers.

The design of the database, quality control checks, standard reports, and a means to select data from the database for further analysis are presented to demonstrate an approach to increase the productivity of environmental professionals. The relationship of information among files and recommended quality assurance practices to assure auditable data trail is also discussed.

134 APPLICATION OF RAPID SAMPLING AND ANALYSIS OF THE VOLATILE CONSTITUENTS OF AIRBORNE PARTICULATE MATTER, R. C. Greaves, R. M. Barkley, and R. E. Sievers. Department of Chemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), Campus Box 449, University of Colorado, Boulder, CO 80309.

A method has been developed for the rapid analysis of the volatile organic compounds in airborne particulate matter. The entire procedure, from sample collection to analysis, can be performed in less than 1.5 hours with minimal sample handling. The technique is based on low volume air sampling (40 to 2000 liters of air) coupled with direct thermal desorption of organic compounds from the collected particulate matter into a cryogenically cooled fused silica capillary chromatography column. As the column temperature is raised, chromatography proceeds, with detection of the desorbed organic compounds by flame ionization or mass spectrometry. Experimental evidence will be presented that shows this method to be a faster and simpler technique for obtaining much of the same qualitative and quantitative information that can be obtained by the traditional high volume sampling coupled with solvent extraction procedure. The simplicity of the technique makes it ideal for rapid routine determinations of specific organic compounds, such as benzo(a)pyrene. Results will be presented which show the advantages of this technique for studying rapid changes in the composition of airborne particulate matter. All of the chromatograms obtained using low volume sampling with thermal desorption exhibit a surprisingly large number of early eluting volatile organic compounds, such as 3-methyl furan. The possible origin and significance of these compounds will be discussed.

135 TRACE ORGANIC COMPOUNDS IN A SEWAGE CONTAMINATED GROUND WATER. Larry B. Barber, II, National Water Quality Laboratory, U.S. Geological Survey, 5293 Ward Road, Mail Stop 407, Arvada, CO 80002.

Specific organic compounds in contaminated ground waters with low dissolved organic carbon (DOC) generally occur at <µg/L concentrations. Thus, sensitive analytical techniques are required. In this investigation, gaseous closed-loop stripping (CLS) combined with capillary gas chromatography/mass spectrometry (GC/MS) was used to evaluate an extensive plume of contaminated ground water on Cape Cod, Massachusetts. The plume is the result of 40 years of disposal of secondary treated sewage into sand and gravel infiltration beds. CLS is capable of concentrating semi-volatile compounds from water by a factor of 250,000 to 500,000 which allows the identification and quantification of substances present at low ng/L concentrations. The CLS method isolates a minor but environmentally important fraction of the dissolved organic load. Although the DOC of the contaminated ground water at the Cape Cod site was only 4.0 mg/L, the organic matrix was quite complex and over 40 organic compounds were tentatively identified. Chlorinated aliphatic hydrocarbons, alkylated benzenes, chlorinated benzenes, alkylated phenols and an alkylated benzoquinone were the most common substances that could be directly related to the sewage effluent. Although the concentration of these compounds may be reduced by as much as 50% to 80% during rapid infiltration, once they reach the saturated zone they are quite persistent as is evidence by their extensive distribution with the aquifer. Discrete plumes of the above compounds extend at least 10,000 feet downgradient from the infiltration beds.

136 COMPOSITION AND ENVIRONMENTAL FATE OF HAZARDOUS ORGANIC COMPOUNDS IN WASTES GENERATED THROUGH PRODUCTION, PROCESSING AND DISTRIBUTION OF NATURAL GAS. B. Davani and G.A. Eiceman. Department of Chemistry, New Mexico State University, Las Cruces, NM 88003.

Large volumes of liquid and solid wastes are generated during all aspects of natural gas development from initial drilling of well to condensate formation in gas pipelines. These wastes are disposed usually with limited or no treatment into earthen waste pits or through re-injection in wells. Samples of such wastes have been collected and characterized for hazardous organic compounds including polycyclic aromatic hydrocarbons (PAH) and benzene. Sites sampled included drilling mud pits, brine water pits, dehydrator pits, pipeline drip pits, discharge water from hydrostatic testing, pipeline condensate, and natural gas at consumer distribution lines. A comprehensive view of presence of organic compounds throughout natural gas operations has been developed and in-field studies have been used to assess potential threat to groundwater in vulnerable aquifers.

At all sites for waste generation, aliphatic and aromatic hydrocarbons from C10 to C30 were detected as complex mixtures of as many as 200 organic compounds which were resolved using capillary GC and GC/MS techniques. Concentrations of PAH were especially large in certain samples. For example, over 50 PAH and alkylated PAH were found in brine waste pits at total concentrations of 130 to 24,500 µg/L in aqueous phases and 1055 to 13,500 mg/kg of non-aqueous phases. Since over 6.6 billion gallons of brine wastes alone are generated each year in New Mexico, potential for groundwater contamination must be addressed particularly when unlined earthen waste pits are used for waste disposal.

137 STATISTICAL STUDIES ON THE ELEMENTAL COMPOSITION OF HUMIC SUBSTANCES. James A. Rice and Patrick MacCarthy, Colorado School of Mines, Chemistry and Geochemistry Dept., Golden, CO 80401.

Elemental data for humic acids, fulvic acids and humin were collected from the literature. Data for 250 humic acid samples, 100 fulvic acid samples and 13 humin samples were found. Prior to the statistical analysis, the humic substances were grouped according to the environment from which they were obtained; terrestrial, aquatic (i.e. river, lake or swamp water) marine, peat or synthetic. These data sets were subjected to a basic statistical summary in which the mean, standard deviation, range, distribution and t-statistic were determined. Humic acid, fulvic acid and humin were compared as were aquatic, marine, terrestrial and synthetic humic substances. Statistically significant ($P \leq .01$) differences existed between the average elemental compositions of humic acids, fulvic acids and humin. Statistically significant differences were also observed between the average elemental compositions of humic acids from aquatic, marine, terrestrial and synthetic sources and, similarly, between fulvic acids of aquatic, marine and terrestrial origin.

138 SELECTIVE DETECTION OF ORGANOSULFUR COMPOUNDS IN CAPILLARY GC VIA FLUORINE-INDUCED CHEMILUMINESCENCE REACTIONS.

J.E. Tavernier, J.W. Birks. Department of Chemistry and Cooperative Institute for Research in Environmental Science (CIRES), University of Colorado, Boulder, Colorado 80309

A sulfur-selective detector for capillary GC has been developed in our laboratory. The gas-phase chemiluminescent reaction of molecular fluorine with organosulfur compounds is the basis for this detector which was successfully demonstrated with packed-column GC in our laboratory in previous years. The gas-phase reaction of F_2 with most organosulfur compounds produces vibrationally excited HF in levels up to v=6, resulting in the (6,2), (5,1), and (4,0) overtone emission bands between 650-750 nm. Reaction of F_2 with nonsulfur-containing compounds typically yields HF (v=3) at wavelengths greater than 850 nm. Selectivity for organosulfur compounds is achieved by monitoring HF emissions below 800 nm. Selectivity over hydrocarbons, alcohols, aldehydes, and ketones is greater than 10^3. The detector has a linear response to a number of sulfides, disulfides, and mercaptans over four orders of magnitude and detection limits ranging from 100 picograms to 5 nanograms of analyte. The detector is currently being used to quantify biogenically produced reduced sulfur compounds. The link between sulfur and the nitrogen cycle is also being investigated at the microcosm level. The preliminary results of these studies, as well as the design and advantages of the detector will be presented.

139 AN EFFECTIVE QUALITY ASSURANCE PROGRAM FOR NPDES DATA.

James A. Nelson, The Standard Oil Company (Ohio), Research Center, Cleveland, OH 44128

Beginning in April, 1982, The Standard Oil Company (Ohio) began a program to streamline and upgrade its quality assurance efforts for reportable environmental data. This formalized program focuses on NPDES and RCRA data generated at company or contract laboratories. It is operated from SOHIO's Research and Development Center in Cleveland and is the responsibility of the Environmental Testing and Research Group. This paper describes the principles on which it was founded, the concepts it has emphasized, and specific efforts which have made this program successful.

A unique aspect of the SOHIO approach is the use of a fully-equipped mobile laboratory. This mobile lab allows a team of highly-trained water chemists to work in the field at company facilities. There they perform quality assessment audits of laboratory testing and related activities. These audits involve a critical review of sampling techniques, test methods, quality control procedures, data handling, etc. The mobile laboratory allows parallel sampling and analysis of the site's wastewater. The test results from these analyses, along with data from analytical standards, etc. are reviewed statistically to establish the acceptability of the facility laboratory data. Recommendations for improvements are provided promptly.

140 GC-NCI MASS SPECTRAL STUDIES OF THERMAL CONVERSION OF NONCOMBUSTIBLE POLYMERS.

H. Collazo, J. de Kanel, C. Rappe, and R.C. Dougherty, Department of Chemistry, Florida State University, Tallahassee, FL 32306.

The world-wide production of noncombustible polymers is approximately 10^{11} kg per year. Poly-2-chloro-1,3-butadiene, polyvinylchloride, polyvinylidenechloride, polychlorotrifluoroethylene and polytetrafluoroethylene, all will not sustain combustion in an ordinary atmosphere. In the course of normal human activities, substantial quantities of these polymers are subjected to thermal conversion through accidental fires, combustion of municipal wastes and incineration of hazardous waste. The organic products of these thermal conversions include numerous polyhalogenated organic compounds which are easily detected by NCI mass spectrometry.

We will report the results of laboratory studies of thermal conversion of noncombustible polymers in a tube furnace as a function of temperature and air flow rate. Polychlorinated polymers gave ppb to ppm quantities of polychlorodioxins and polychlorodibenzofuransunder all pyrolysis conditions. The amount of chlorine in the pyrolysis products appeared to reflect the amount of chlorine in the starting polymers.

141 QUANTITATIVE ANALYTICAL SCREEN FOR THE DETERMINATION OF THE APPENDIX VIII HAZARDOUS CONSTITUENTS. J. L. Parr and Dr. M. J. Carter. Rocky Mountain Analytical Laboratory, 5530 Marshall Street, Arvada, Colorado 80002.

On October 1, 1984 the Environmental Protection Agency proposed new Subtitle C testing requirements under RCRA. As part of these testing requirements many companies will be required to analyze groundwater and waste samples for the 375 Hazardous Constituents listed in Appendix VIII of 40 CFR Part 261 using methods in SW-846, "Test Methods for Evaluating Solid Waste."

Due to a number of complex issues both in the proposed rule and in SW-846, RMAL prepared a report entitled "Evaluation of the Applicability of the SW-846 Manual to Support All RCRA Subtitle C Testing." As part of this effort, RMAL identified, developed and proposed an analytical strategy to effectively determine Appendix VIII constituents using the methods in SW-846.

This analytical strategy, designated as a Quantitative Analytical Screen (QAS), utilizes 17 different methods based on ICP, AA, GC, GC/MS and HPLC technology. The methods, constituents measured by each method and the general approach of the QAS will be discussed.

142 APPLICATION OF N-OCTANOL/WATER PARTITION COEFFICIENTS IN THE EVALUATION OF A COAL-TAR CONTAMINATED, TWO-PHASE GROUND-WATER SYSTEM. Colleen E. Rostad and Wilfred E. Pereira. U.S. Geological Survey, Box 25046, Mail Stop 407, Federal Center, Denver, Colorado 80225.

Coal tar contains numerous polycyclic aromatic compounds, many of which are suspected carcinogens or mutagens. Ground-water contamination by these toxic compounds occurred in St. Louis Park, Minnesota, creating a possible environmental health hazard in nearby public water-supply wells. Fluid samples from this aquifer developed two phases upon settling: an upper aqueous phase, and a lower oily-tar phase. After separating the phases, polycyclic aromatic compounds in each phase were isolated using complexation with N-methyl-2-pyrrolidone and identified by fused-silica capillary gas chromatography/mass spectrometry. Thirty-one of the polycyclic aromatic compounds from 4 different classes were chosen for further study: 12 polycyclic aromatic hydrocarbons, 10 nitrogen heterocycles, 5 sulfur heterocycles, and 4 oxygen heterocycles. The tar/water partition coefficient of these compounds averaged 89 percent of the respective n-octanol/water partition coefficient. The n-octanol/water partition coefficient is applicable as an indication of coal-tar compound partitioning in a two-phase, coal-tar contaminated ground-water system.

143 A MUMPS (DMS-11) DATA BASE FOR POLYCYCLIC AROMATIC HYDROCARBON MIXTURE DETERMINATION. T. R. Schwartz, C. J. Yeager, and J. D. Petty. Columbia National Fisheries Research Laboratory, U. S. Fish and Wildlife Service, Rt. 1, Columbia, MO 65201.

The successful analysis of individual components in complex multicomponent mixtures requires an analytical system with sufficient resolving capabilities. Chromatographic separation are commonly employed for the analysis of complex mixtures to reduce the complexity of the sample before it is subjected to the detection system. Capillary column gas chromatography is a technique commonly used for the analysis of complex mixtures such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons (PAH), and Toxaphene, just to mention a few. Identification and quantitation of the single components which are represented in a complex gas chromatogram is a difficult task. The problem is compounded by the massive amount of data generated when analyzing complex mixtures for differences in component distribution and relating these data to the compound distribution after the mixture has been exposed first to abiotic degradation and then to metabolic processes. Assessment of the biological effects of potentially toxic PAH's ultimately may require correlation of the toxicological effects to the internal composition of the PAH mixture. A laboratory data base system was developed to aid in editing and quantitation of data generated from environmental samples being analyzed. Data base management was provided by programs written in DSM-11 (Digital Standard Mumps) for the PDP-11 family of computers. DSM-11 is a multi-user, time sharing operating system that also functions as a programming language. As an operating system, DSM-11 provides utilities for maintenance and backup as well as supporting a variety of peripheral devices, and as a language it is high level, self-documenting, and interpretively executed. This data base system will be discussed.

144 APPLICATION OF THE EP OILY WASTE TOXICITY PROCEDURE TO PETROLEUM REFINERY WASTES. C. Wibby, and Dr. M. J. Bollinger, Rocky Mountain Analytical Laboratory, 5530 Marshall Street, Arvada, Colorado 80002.

The Environmental Protection Agency has indicated that the EP Toxicity Procedure currently used (Method 1310, SW-846) is inappropriate for the preparation of samples containing oil or grease. The Agency stated that oil or grease in a sample would effecftively coat any solids present and prevent the extraction of toxicants of concern. A new procedure has been proposed, Method 1330, that includes an extraction of the oil and grease prior to the leaching step. Rocky Mountain Analytical Laboratory has applied the new procedure to over 100 refinery waste samples. Problems which were encountered during the application of the procedure and the ability of the data generated to reliably assess environmental problems associated with the disposal of these wastes will be discussed.

145 EVOLUTION OF GAS CHROMATOGRAPHY-MASS SPECTROMETRY ANALYTICAL METHODS FOR ANALYSIS OF POLLUTANTS IN WATER. William A. Telliard, Industrial Technology Division WH-552, U.S. Environmental Protection Agency, Washington, DC 20460 and D. R. Rushneck, Interface, Inc., P.O. Box 297, Fort Collins, CO 80522-0297.

In 1976, the United States Supreme Court mandated the analysis of 65 compounds and classes of compounds in the nation's wastewaters. The list of 65 was refined by EPA's Industrial Technology Division (ITD--formerly Effluent Guidelines Division) into 129 specific parameters, termed the "priority pollutants." Of these 129 parameters, 114 are organic compounds or mixtures of organic homologs. Of the 114, 25 are pesticides and PCB's. The remaining 89 are volatile and semi-volatile organic compounds. The technology chosen by ITD for analysis of the pesticides and PCB's was gas chromatography with electron capture detection (GC/ECD), and for analysis of the remaining compounds was gas chromatography combined with mass spectrometry (GCMS). Initial GCMS analytical protocols used for analysis of the organic parameters were derived from methods developed in EPA laboratories in Cincinnati, Ohio and Athens, Georgia. These protocols were directed at screening for the compounds of interest in wastewater. Subsequent protocols developed by EGD included requirements for rigorous quality assurance of results, isotope dilution, and specifications based on inter-laboratory validation. This paper describes the evolution of analytical methods for analysis of pollutants in water and presents details of the validation of EPA's latest isotope dilution GCMS methods.

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RECOVERY AND DETECTION LIMITS OF ORGANIC COMPOUNDS IN PETROLEUM REFINERY WASTES. M. P. Phillips, O. J. Logsdon, and J. Lowry. Rocky Mountain Analytical Laboratory, 5530 Marshall Street, Arvada, CO 80002.

In April, 1983, EPA initiated a Petroleum Refinery Waste Characterization Study to evaluate the basis for listing the five currently regulated waste streams and to evaluate other refinery waste streams for possible inclusion as listed wastes. The methods used to analyze these types of samples are contained in the "Handbook for the Analysis of Petroleum Refinery Residuals and Waste", U.S. Environmental Protection Agency, originally issued in April, 1984 and revised in October, 1984. Because of the widespread use of these methods by the EPA in delisting, Part B and land treatment studies, a limited study of the effectiveness of the GC/MS methods contained in the Handbook was conducted by Rocky Mountain Analytical Laboratory (RMAL) under contract to the American Petroleum Institute RCRA Refinery Waste Characterization Task Force. Recovery data for the target organic compounds of interest in this program spiked into representative sample matricies were collected. Detection limit data were also collected by spiking the target compounds into a representative sample matrix at levels near the expected detection limits estimated from the recovery data. The data from the recovery and detection limit studies will be presented and the implications of the results will be discussed.

147 THE GENERATION OF CHROMATOGRAPHIC PROFILES OF WATER AND WASTEWATER SAMPLES USING A COMMERCIALLY AVAILABLE, MICRO COMPUTER BASED, DBMS/ GRAPHICS SOFTWARE PACKAGE

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The results of chromatographic survey analyses of water and wastewater samples from an advanced water treatment plant are necessary for plant performance evaluation and for process optimization. The amount of time required for sample preparation and GC/MS analysis, although considerable, is often dwarfed by data evaluation time requirements. We have found it necessary to develop sample screening and chromatographic profiling procedures in order to provide useful information in a reasonable period of time. Once dat has been transported to the DBMS it can be manipulated in a variety of ways.

The microcomputer software industry currently offers a smorgasbord of integrated Data Base Management/Graphics software packages. Unfortunately, the most attention has been placed on the business applications of this software. For the small laboratory, commercial business software can serve as a versatile and inexpensive alternative to customized laboratory systems. We will discuss how our laboratory has taken advantage of the user programmable features of one successful business package to aid in the reduction, integration, evaluation and presentation of GC and GC/MS data.

148 SEASONAL VARIATIONS IN THE CHEMICAL AND MUTAGENIC ACTIVITY OF A DRINKING WATER SOURCE,

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, Illinois 61455.

Samples were collected periodically from a midwestern surface impoundment drinking water source and subjected to chemical and biological examination. The samples from Spring Lake, Macomb, Illinois were analyzed for fifteen chemical parameters including manganese, phosphate, nitrate, nitrite and ammonia. In addition, the Tradescantia-Micronucleus (Trad-MCN) test, a sensitive bioassay, was performed for each of the samples analyzed chemically. Both the chemical activity for some constituents and mutagenic activity exhibited seasonal variations. Periods of increased chemical and mutagenic activity occurred in both summer and fall. Meteorological records reveal that periods of heavy rainfall preceded the periods of elevated chemical and mutagenic activity by approximately a month. (Research partially supported by US EPA Grant R80-7947-01 and the Research Council of Western Illinois University).

149 **THE FREQUENCY OPTION IN EPR,**

R. Linn Belford, Department of Chemistry, University of Illinois, 505 S. Mathews Ave., Urbana, IL 61801

Although it is not easy to adjust source frequencies in EPR spectroscopy, there are often substantial benefits to be realized in using substantially lower or higher frequencies than the customary X band (9 Ghz). Therefore, despite the difficulties, several systems have been assembled over the years in various laboratories to operate at nonstandard frequencies, from radiofrequency to far infrared. Selected examples and applications will be reviewed. Special problems encountered in interpreting spectra at such frequencies will be discussed.

150 **MULTIFREQUENCY ESR SPECTROSCOPY** James S. Hyde, National Biomedical ESR Center, The Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, Wisconsin 53226.

Multifrequency ESR involves the examination of a sample at two or more microwave frequencies in order to increase the available information. In this definition, selection of an optimum microwave frequency for a particular sample simply to obtain an improved signal-to-noise ratio is excluded. One can create a three dimensional grid of experimental situations for which multifrequency ESR is applicable, as follows: on one axis the type of sample (eg. fast tumbling, slow tumbling, powder, or crystal), on one axis the physical phenomenon (eq. nuclear state mixing, electron state mixing, interplay of electron zeeman and hyperfine interactions, interplay of zeeman interactions of different nuclei) and on the third the experimental observable (eg. spectral shape, spectral signal intensity, and the various relaxation times). Within this conceptual framework recent applications from our laboratory of multifrequency ESR spectroscopy will be presented. Available microwave frequencies are 0.5 to 1, 1 to 2, 2 to 4, 10 and 35 GHz. Particular attention will be paid to results obtained with the recently completed 0.5 to 1 GHz microwave bridge.

151 **ESR-ENDOR SPECTROSCOPY AT V BAND, Harold C. Box and Harold G. Freund, Biophysics Department, Roswell Park Memorial Institute, Buffalo, New York 14623**

ESR-ENDOR spectroscopy at a microwave frequency of 70 GHz (V band) was first accomplished in this laboratory in 1973 (1). The spectrometer uses superheterodyne detection and a cylindrical transmission cavity (TE011 mode). Periodically improvements in performance have been realized through various instrumental changes. In the main, improvements in signal-to-noise ratio have been the result of advances in high frequency microwave technology which have made lower noise sources and detectors commercially available. Concomitantly the frequency range accessible for ENDOR measurements has been extended. For example, the ENDOR resonances of atomic hydrogen have been observed. In view of the mounting interest in higher frequency ESR-ENDOR spectroscopy, a brief review of our experience with this technology will be presented.

The principal application of V band ESR-ENDOR spectroscopy has been to the study of radiation damage in single crystals of nucleic acid constituents. The improved separation at V band of the ESR absorptions arising from different products of irradiation is a considerable advantage in this work and depends, of course, upon there being at least some differences in g values among the various products. Recently attention has focused on radiation damage to the carbohydrate components of nucleic acid consitutents. V band ENDOR measurements have provided a complete specification of proton hyperfine coupling tensors of radiation-induced oxidation products. From these data a structural relationship could be established among a variety of oxidation products which belies the diversity of their ESR spectra.

(1) H.C. Box and H.G. Freund, Annals N. Y. Acad. Sci 222, 446 (1973).

152 NO ABSTRACT

153 NO ABSTRACT

154 MULTIFREQUENCY ESR OF CU(II)-(HISTIDINE)$_n$. R. Basosi, W. Froncisz, W.E. Antholine, and J.S. Hyde, National Biomedical ESR Center, The medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, WI 53226.

ESR studies at three microwave frequencies of ^{63}Cu(histidine)$_n$ frozen in excess histidine were undertaken to further demonstrate the multifrequency approach and to support either the glycine-like or histamine-like complexes. Low frequency, S-band data are well resolved for the $M_I = -1/2$ line in the $g_{\parallel}$ region and the number of lines is attributed to four approximately equivalent nitrogen donor atoms. Upon increasing the pH from 56.8 to 7.3 a second form is detected from the $M_I = -1/2$ in the $g_{\parallel}$ region but not in other portions of the spectrum. The change in ESR parameters does not appear to be large enough to account for a change from four nitrogen donor atoms to three nitrogen donor atoms in the square planar configuration. This small change is more consistent with a change in axial coordination. It is most likely that these same two forms are also observed for the $M_I = +3/2$ line in solution. Further analysis of Cu(histidine)$_n$ frozen in excess histidine with the ^{14}N atoms replaced with ^{15}N atoms in the imidazole ring suggests either that four imidazole nitrogens are bound to cupric ion or that the spectra are not readily subject to simple interpretation. Supported by NIH Grant RR-01008.

155 STUDIES OF THE INTERACTION OF Pd^{3+} and Pd^+ WITH ORGANIC ADSORBATES, WATER AND MOLECULAR OXYGEN IN Pd-CaX ZEOLITE BY ELECTRON SPIN RESONANCE AND ELECTRON SPIN ECHO MODULATION SPECTROSCOPY. J. Michalik, M. Narayana and Larry Kevan. Univeristy of Houston Department of Chemistry, Houston, Texas 77004.

Electron spin resonance and electron spin echo modulation (ESEM) spectroscopic studies have been carried out for several paramagnetic palladium species in CaX zeolite. Oxidation at 773 K of the CaX zeolite exchanged with $Pd(NH_3)_4^{2}$ resulted in the formation of Pd^{3+} which on prolonged evacuation at 773 K partly converts into Pd^+. Subsequent hydrogen reduction at temperatures of 295 to 500 K substantially increases the concentration of Pd^+ at the cost of Pd^{3+}. Adsorption of water or oxygen on activated Pd-CaX zeolite results in almost identical oxygen based paramagnetic radicals indicating decomposition of water molecules by Pd^3 cations. The interaction of Pd^+ with various organic adsorbates as studied by ESEM is discussed in terms of possible locations and coordination geometries of Pd^+ in CaX zeolite.

156 NO ABSTRACT

157 MAGNETIC RESONANCE IN THE ORDERED STATES OF $(NH_3(CH_2)_nNH_3)CuBr_4$ FOR HIGH n.

Stuart L. Hutton, G. V. Rubenacker, and John E. Drumheller. Department of Physics, Montana State University, Bozeman, MT 59717

The so-called 'eclipsed' magnetic compounds with the title formula, abbreviated $nDACuBr_4$, have the interesting property that as n increases above n=4, the magnetic behavior switches back and forth from antiferromagnetic (AF) to ferromagnetic. The magnetic characteristics for each particular compound represented by the different n are unique but because of the quasi-two-dimensional magnetic character of all of them, interesting features of both ferro- and antiferromagnetic resonances obtain. We report our resonance results which yield in- and out-of-plane anisotropies and discuss cases of high anisotropy where the magnetization does not follow the field. In addition, for the AF compounds, we present results for the interplanar exchange which, because the values are so small, cannot be derived from the usual high-temperature expansion methods. In order to explain the temperature behavior of the resonances, we will present our attempt to apply energy minimization techniques with critical behavior included.

158 ESR STUDY OF MN(II) IN SPIN-CROSSOVER FE(II) COMPLEXES.

P.E. Doan and B.R. McGarvey; Department of Chemistry, University of Windsor, Windsor, ON N9B 3P4.

The ESR of Mn^{2+} can be detected in both the diamagnetic and paramagnetic phases of solid Fe(II) spin-crossover complexes. We report on studies of $Fe(phen)_2(SCN)_2$, $[Fe(pic)_3]Cl_2.EtOH$, and $[Fe(isoxazole)_6](ClO_4)_2$. Powder studies were done in $[Fe(phen)_2(SCN)_2]$ and $[Fe(isoxazole)_6](ClO_4)_2$ and a single crystal study in the case of $[Fe(pic)_3]Cl_2.EtOH$. Results will be compared to NMR studies done earlier on the same systems.

159 NATURAL ABUNDANCE ^{13}C AND ^{29}Si ENDOR STUDIES OF CYCLOPOLYSILANE RADICAL ANIONS.

B. Kirste, R. West*, and H. Kurreck, Freie Universität Berlin, Inst. f. Org. Chem., Takustr. 3, D-1000 Berlin 33, West Germany, and *University of Wisconsin, Madison, Wisconsin 53706.

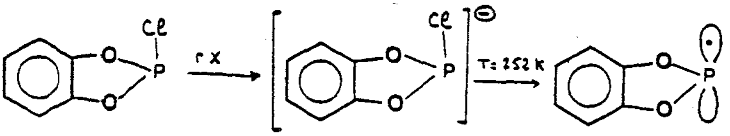
Nonproton ENDOR spectroscopy of radicals in solution has developed rapidly during recent years, and the conditions for obtaining an optimum ENDOR response are now well understood. When dealing with isotopes occurring in low natural abundance (e.g. ^2H, ^{13}C, ^{15}N, ^{29}Si), isotopic enrichment is usually necessary. Recently we have demonstrated that in favorable cases ^{13}C ENDOR can be performed successfully without isotopic labeling. It was beneficial for these studies that the low-abundance nuclei exhibited fairly large isotropic hyperfine splittings but small anisotropic hyperfine interactions. Moreover, the presence of several equivalent nuclei is helpful. Only one ^{29}Si ENDOR study has been reported so far, dealing with radical ions containing trialkylsilyl groups attached to a carbon π system (H. Bock et al., Angew. Chem. Int. Ed. Engl. 22, 787 (1983)).

Here we report on the first successful ^{29}Si ENDOR study of silicon-centered radicals, namely the radical anions of peralkylcyclosilanes. ^1H, ^{13}C, and ^{29}Si ENDOR and TRIPLE experiments yield detailed information about hyperfine coupling constants, their signs and temperature dependences, and the relaxation behavior of the nuclei. The results show only a small hyperfine anisotropy for ^{29}Si, consistent with Si-Si σ^* or 3d spin population but not with π type delocalization. The spectra provide evidence of dynamic processes due to a flexible structure of the molecules.

160 AN ESR STUDY OF X-IRRADIATED SINGLE CRYSTALS OF 1-2 PHENYLENE PHOSOPHOCHLORIDITE.

M. Geoffroy and M.-A. Lorente, Department of Physical Chemistry, University of Geneva, Geneva, Switzerland.

Single crystals of 1-2 phenylenephosphochloridite are obtained by slow cooling of the melted compound. X-irradiation at 77 K gave rise to an unstable radical which is investigated by ESR. This radical exhibits hyperfine structure with ^{31}P and ^{35}Cl. These two coupling tensors and the g tensor are obtained by studying the angular dependence of the spectrum at 77 K. These results lead us to identify this species as being the radical anion (I). A variable température study shows that this radical disappears at 252 K, the decrease of the corresponding lines is accompanied by the formation of a new species (II) which exhibits hyperfine coupling with ^{31}P only. This hyperfine tensor is consistent with an unpaired electron which is strongly localized in a phosphorus 3p-orbital. These results indicate that the formation of a radical (II) is due to a dissociative electron attachment process in accord with the following mechanism:



(I) (II)

161 THE SIMULATION OF ELECTRON PARAMAGNETIC RESONANCE SPECTRA USING RATIONAL FUNCTION APPROXIMATIONS FOR SPECTROSCOPIC LINE SHAPES.

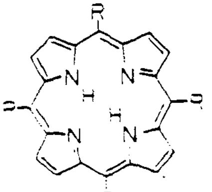
Martin M. Maltempo, Physics Department, University of Colorado at Denver, 1100 Fourteenth Street, Denver, Colorado 80202.

In order to simulate an Electron Paramagnetic Resonance spectrum one must evaluate an integral involving the transition probability, the line shape, and the orientation of paramagnetic sites with respect to the external magnetic field. Due to the difficulty of dealing with the commonly used Gaussian line shape, as well as other complications, the integrals are commonly evaluated on a computer by numerical integration. This paper presents a derivation of a rational function approximation for a generalized, spectroscopic line shape and its derivative. The rational function can generate an exact Lorentzian line shape, a very close approximation to a Gaussian line shape, or a wide range of hybrid line shapes, depending upon the value of a single function parameter. One can then evaluate the integral for the simulated absorption or derivative spectrum as a closed-form, analytic function for the case of an axially symmetric paramagnetic species in a powder distribution, for different mechanisms of line broadening, and a wide range of line shapes (in both H-domain and ν - domain), without the usual necessity of computer-assisted numerical integration.

162 ENDOR STUDY OF VO(II) AND Cu(II) PORPHYRIN DIMERS WITH TRIPLET GROUND STATES,

Hans van Willigen and T. K. Chandrashekar, Department of Chemistry, University of Massachusetts at Boston, Boston, MA 02125

Vanadyl and copper substituted crown porphyrins (VOTCP, CuTCP) can be made to dimerize by addition of alkali ions to solutions in chloroform-methanol. The dimers have a triplet ground state and frozen solutions give the usual triplet ESR powder spectrum. Using these two compounds as models it will be shown that ENDOR spectra from triplet state transition metal complexes randomly oriented in frozen solution can give detailed information on hyperfine interactions between electron spins and ligand nuclear spins as well as quadrupole interactions.. The ENDOR data give an insight into the effect of dimerization on the electron spin distribution over the ring systems, on quadrupole interactions, and on the relative signs of hyperfine interactions and zero field splittings.



R = benzo-15-crown-5

163 EPR OF PARTIALLY ORDERED COPPER PHTHALOCYANINE MONOLAYERS. M. D. Pace, A. W. Snow, and W. R. Barger. Naval Research Laboratory, Code 6120, 4555 Overlook Avenue, S. W., Washington, D. C. 20375-5000

Copper phthalocyanine [$Cu^{2+}C_{32}N_8H_{16}$] is a square planar complex with Cu^{2+} located between the four central nitrogens of the phthalocyanine molecule. By using the Langmuir-Blodgett technique and a soluble copper phthalocyanine compound, molecular layers having an approximate thickness of a single molecule (monolayers) and a specific orientation can be deposited onto a substrate such as quartz. When the ratio of uncomplexed phthalocyanine to copper complexed phthalocyanine molecules is ca. 10 to 1 by weight, the exchange and dipolar effects are small and the nitrogen superhyperfine couplings of the four magnetically equivalent central nitrogens are resolved. The nitrogen-14 (I=1) superhyperfine coupling has a maximum anisotropic component of 4.5 MHz. The Cu^{2+} ion has an unpaired electron spin, I=3/2 and a maximum anisotropic hyperfine coupling component of 239 MHz. The g-value components vary from 2.050 to 2.179. The angular dependence of the epr spectra from monolayer samples of copper phthalocyanine is compared to the known values of the Cu^{2+} hyperfine coupling, the nitrogen-14 superhyperfine coupling and g-value. This comparison indicates an estimate of the molecular disorder within the monolayer and the propagation of disorder through stacks of monolayers. Experimental spectra and computer simulated spectra will be presented.

164 AN EPR STUDY OF NITROXIDE SPIN LABEL DOPED HIGH VOLATILE BITUMINOUS COAL: EXAMINATION OF PORE DISTRIBUTION. S-K. Wuu and L. D. Kispert, Department of Chemistry, University of Alabama, Tuscaloosa, AL 35486.

A recently developed technique in our lab has made it possible to estimate the average relative pore (accessibility) size and number distribution in high volatile bituminous Alabama coal from the Mary Lee and Black Creek seams as well as samples of Illinois #5. Such information is of importance in designing an optimum catalyst system for the economical conversion of coal to liquid fuels since catalysis must occur from within, in addition to the normal surface catalysis. Different sized nitroxide spin probes are diffused into coal swollen by an appropriate solvent, the coal matrix is collapsed around the coal by pumping off the solvent, spin probes adhering to the surface of the coal are removed by a nonswelling solvent and the concentration of the spin probe remaining in the coal measured by EPR techniques. The resulting EPR powder spectra resemble that of an immobilized spin probe with a temperature dependent nitrogen coupling, A_{zz}. The temperature dependence near room temperature appears to be due to a librational motion presumably of the nitroxide moiety about a N-C bond. Below 200 K, the temperature dependence resembles that observed when hydrogen-bond formation occurs. The effect of grinding in air and nitrogen, swelling solvent (xylene, toluene, quinoline or acetic acid) and temperature conditions on the pore distribution as well as ELDOR and ENDOR measurements of the spin probe doped coal samples will be discussed.

165 ESR STUDY OF BONDING AND DYNAMICS OF PARAMAGNETIC CATIONS IN CROSSLINKED POLYACRYLAMIDE GELS. G. C. Rex and S. Schlick. Department of Chemistry, University of Detroit, Detroit, MI 48221.

Electron spin resonance spectra of Cu^{2+} and VO^{2+} ions in crosslinked polyacrylamide (PAA) gels were studied as a function of crosslinking method and degree of crosslinking. Chemically crosslinked PAA was obtained by polymerization of acrylamide in the presence of N,N'-methylenebis(acrylamide) (BIS). Linear PAA was also crosslinked by γ-irradiation. For VO^{2+} at ambient and higher temperatures (46°C) an isotropic spectrum was observed. The correlation time for tumbling of VO^{2+} was found to increase as pore size of the gel decreased. At lower temperatures and in pore size less than 17 Å in diameter spectra consist of a superposition of rigid and mobile species. ESR spectra of Cu^{2+} at 77 K in chemically crosslinked gels have been simulated by assuming a correlated distribution of $g_{\parallel}$ and $A_{\parallel}$ values. ESR spectra of Cu^{2+} in γ-irradiated PAA indicates ligation to nitrogen.

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DOI: https://doi.org/10.56902/RMCMR.1985.27.1

166 FIELDS AND GRADIENTS FOR E.S.R. IMAGING. A. Sotgiu* and J. S. Hyde, Department of Radiology, The Medical College of Wisconsin, 8701 Watertown Plank Rd., Milwaukee, WI 53226, On leave from the Biological Institute, University of L'Aquila, 30100-L'Aquila, Italy.

In the context of E.S.R. imaging of living samples, an air core magnet has been designed that generates a uniform two-dimensional magnetic field and a linear gradient. Field and gradient extend over a cylindrical region of 20 cm in height and 8 cm in diameter and are obtained by 24 current lines flowing on the walls of a cylinder and parallel to its axis. By individually controlling these currents, the intensity and the direction of the field and the intensity of the gradient can be changed thus permitting a two-dimensional representation of the spin density. Four axial coils are used to produce the third gradient. Also in this case by individually controlling the currents a linear gradient of the total field along the cylinder axis is obtained. The magnet is interfaced to an IBM 9000 microcomputer which sets the current values and samples the signal for each current setting. The complete spectrometer is intended for frequencies up to 0.8-1.0 GHz and permits the observation of living samples up to a weight of the order of 30 grams. The maximum gradient is of the order of 30 gauss/cm.

167 NOVEL DETECTION AND EXCITATION TECHNIQUES IN PULSED ESR
A. Schweiger, J.M. Fauth, J. Forrer, L. Braunschweiler and R.R. Ernst, Laboratory for Physical Chemistry, ETH-Zentrum, CH-8092 Zurich, Switzerland.

Pulsed ESR techniques have become very powerful tools to study relaxation times, small hyperfine and quadrupole interactions and shortlived paramagnetic species. In this contribution we present novel detection and excitation methods which are able to improve the applicability of ESR spectroscopy in the time domain. The presented subjects include

- elimination of all unwanted echoes and FID's in three-pulse experiments
- introduction of a new detection technique
- revision of the widespread view that nonselective pulses ($\gamma_e B_1$ > nuclear frequencies) are a prerequisite for the observation of echo modulations.

The experiments are performed on a home-made electron spin echo spectrometer equipped with a high resolution (1 ns) pulse programmer which generates up to 96 pulses with programmable delays (0 to 1 ms) and variable pulse widths (3 ns to 1 μs). The spectrometer comprises three independent microwave channels with variable phases and amplitudes and a pulse power up to 1 kW.

168 ANALYSIS OF NUCLEAR QUADRUPOLE INTERACTION EFFECTS IN ELECTRON SPIN ECHO MODULATION SPECTRA BY SECOND ORDER PERTURBATION METHODS. M. Heming, M. Narayana and Larry Kevan University of Houston, Department of Chemistry, Houston, Texas 77004.

The incorporation of nuclear quadrupole interaction into electron spin echo modulation spectra by second order perturbation methods has been developed for both two pulse and three pulse echo sequences. The results have been compared with exact numerical diagonalization of the Hamiltonian and with a first order perturbation treatment. Model calculations have been carried out for deuterium (I = 1) and aluminum (I = 5/2) nuclei. It is shown that the second order expressions can be used to obtain relatively accurate values for the number and distance of interacting nuclei at electron-nuclear distances greater than 0.26 nm. The procedure is more limited when the quadrupolar interaction exceeds the dipolar interaction when neither can be neglected.

169 ELECTRON SPIN RESONANCE AND ELECTRON SPIN ECHO MODULATION STUDIES OF N,N,N',N'-TETRAMETHYLBENZIDINE PHOTOIONIZATION IN FROZEN MICELLAR SOLUTIONS: STRUCTURAL EFFECT OF n-BUTANOL ADDITION TO SODIUM- AND TETRAMETHYLAMMONIUM DODECYLSULFATE AND DODECYLTRIMETHYLAMMONIUM CHLORIDE MICELLES.

E. Pietek, Rene Maldonado, Larry Kevan and Richard R.M. Jones, University of Houston, Department of Chemistry, Houston, Texas 77004. Department of Chemistry, Wake Forest University, Winston Salem, N.C. 27109.

The electron spin echo modulation (ESEM) and electron spin resonance (ESR) spectra of the photogenerated N,N,N',N'-tetramethylbenzidine cation radical (TMB^+) in frozen micellar solutions of sodium- and tetramethylammonium dodecylsulfate (SDS and TMADS respectively) as well as dodecyltrimethylammonium chloride (DTAC) have been studied as a function of n-butanol (n-BuOH) concentration from 0 to 200 mM. 5-Doxylstearic acid spin probe has also been used in ESEM experiments. The efficiency of TMB photoionization has been determined from ESR data, while ESEM analysis has given information about micelle hydration and aqueous interactions of TMB^+. The variations observed with BuOH addition depend on the micellar charge and the nature of the counterion in dodecylsulfate micelles. The main findings are that (1) hydration of TMADS micelles decreases with BuOH concentration, while that of SDS and DTAC micelles increases slightly on going from 0 to 100 mM n-BuOH, and (2) the efficiency of charge separation upon photoionization of TMB can be increased by alcohol addition in SDS micelles, but not in TMADS and DTAC micelles. The results are interpreted in terms of the effect of added alcohol on the surfactant head-group density and on the degree of micelle ionization.

170 ENDOR AND ESE OF DISORDERED SOLIDS.

R. L. Belford, R. B. Clarkson, J. B. Cornelius, and P. A. Snetsinger. Department of Chemistry, University of Illinois, Urbana, Illinois 61801.

ENDOR and ESE spectroscopy techniques have been used to study weak hyperfine interactions in disordered solids with broad EPR lines having unresolved hyperfine coupling. Model systems were examined in order to develop data reduction techniques for ESE time domain spectra. The narrow modulation depth of the envelope and complex decay of this modulation complicated analysis. ENDOR experiments were employed to corroborate results. Both techniques have been applied to understanding the molecular structure of coal macerals and ultimately, whole coal.

Work performed under the auspices of U.S. Dept. of Energy, University Advanced Coal Research Program, grant no. DEFG84PC70782 and with the assistance of M. K. Bowman, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.

171 DEPENDENCE OF THE IRON(III) - NITROXYL SPIN-SPIN INTERACTION ON THE LINKAGE BETWEEN THE TWO CENTERS.

Kundalika M. More, Lee Fielding, Gareth R. Eaton, and Sandra S. Eaton, Departments of Chemistry, University of Denver, Denver, CO 80208 and University of Colorado at Denver, Denver, CO 80210.

A series of substituted iron(III) tetraphenylporphyrins has been prepared with nitroxyl radicals attached to the ortho position of one phenyl ring. The linkage between the phenyl ring and the nitroxyl ring was varied from two to seven atoms. EPR spectra were obtained in fluid solution and frozen solution for both high-spin and low-spin states of the iron. Spectra in frozen solution were simulated by diagonalization for one value of the magnetic field followed by use of Belford's fourth order frequency shift perturbation method to give the field-dependent spectrum. The magnitude of the spin-spin interaction was strongly dependent on the linkage between the porphyrin and the nitroxyl.

172 ELECTRON SPIN ECHOES WITH A LOOP-GAP RESONATOR. Joseph P. Hornak and Jack H. Freed. Rochester Institute of Technology, Rochester, NY, and Baker Laboratory of Chemistry Cornell University, Ithaca, NY.

The split-ring or loop-gap microwave resonator has several features which make i more advantageous than the traditional overcoupled TE_{102} microwave cavity in electro spin echo (ESE) experiments. Among these are the large uniform microwave magnetic fiel H_1 per incident microwave power, broad band (low Q), small sample volume, high fillin factor, and high field homogeneity over the sample. We have compared a two slit loop-ga resonator with a TE_{102} cavity under various conditions in ESE spectroscopy. The efficiency of producing H_1 (H_1 per (incident microwave power)$^{1/2}$) and signal to noise ratio of the two resonators were determined. For volume limited samples the LG resonator wa fifteen times as efficient and gave an eight fold improvement in signal to noise ratio over the TE_{102} cavity. These results show that conventional ESE experiments could b performed with a one Watt klystron and low power microwave devices, thus making ESE mor attractive to the low-budget researcher. With slightly larger power sources (100 W TWTA and pulses of approximately 2 nsec, it should be possible to rotate the entire nitroxid spin probe spectrum with a pi/2 pulse, thus making routine Fourier transform ESR spectroscopy more plausible.

173 STRUCTURAL AND MAGNETIC PROPERTIES OF NOVEL ONE DIMENSIONAL COPPER OXALATES - PYRIDINIUM BIS(OXALATO) CUPRATE(II) OXALIC ACID AND BIS(2-METHYL IMIDAZOLE) COPPER(I OXALATE. B. L. Ramakrishna. Urs Geiser and Roger D. Willett, Department of Chemistr Washington State University, Pullman, WA 99164-4630.

The crystal structures of the title compounds were determined by x-ray diffractio The pyridinium salt consists of stacked planar bis(oxalato) Cuprate(II) complexes givi rise to a 4+2 coordination. The interaction pathway is through two oxygen bridges. T 2-methylimidazole compound forms polar zig-zag chains of 5 coordinate copper complexe The bridging oxalate ion coordinates in a bidentate fashion on one side and as monodenta to an adjacent copper on the other side. Magnetic susceptibility measurements are co sistent with chain-like structure. Single crystal EPR linewidth analysis yields detail information of the spin dynamics - magnitude and dimensionality of exchange interacti and the effect of dipolar and hyperfine interactions on the linewidth.

174 SPIN-LATTICE RELAXATION RATES OF TRANS-POLYACETYLENE DETERMINED BY SATURATION RECOVERY EPR. R. St. Denis, and B. H. Robinson, Department of Chemistry, BG-10, University of Washington, Seattle, WA 98195; C. Mailer, Department of Physics, University of New Brunswick, Fredericton, Canada.

Trans-polyacetylene (tPA) is the prototypical organicsemiconductor, which, even in its pristine form, contains a paramagnetic defect. This defect, described as a soliton, is capable of migration along the polymer. To characterize the nature of solitonmigration in tPA we have measured the spin-lattice relaxation rate, R1, of pristine (CH)x, (CD)x and (13CH)x as a function of temperature using the time domain EPR technique of Saturation Recovery (SR) The experiments were performed on our newly completed, computer controlled EPR/SR spectrometer, employing the standard " 3 arm" bridge A variety of pulse lengths and amplitudes, and observer amplitudes were used to insure that neither spectral diffusion nor finite observer power influenced the results.

Spin-lattice relaxation rates measured by SR on (CH)x and (CD)x were identical to those previously obtained using Electron Spin Echo (ESE) techniques. However ESE could not be used to measure R1 on samples of (13CH)x because the phase memory times were too short, and the 13C modulation too severe to permit accurate determination of R1 by this technique We have analyzed R1 of (CH)x and (CD)x assuming the standard one-dimensional diffusion model. The temperature dependence of R1 over the range from 35 mK to 400 K indicates that R1 obeys a simple power law dependence on temperature. We have interpreted this dependence to be indicative of a spin-phonon interaction. The R1 as a function of temperature of (13CH)x follows the same temperature dependence as (CH)x and (CD)x for temperatures less than 150K In the 150 to 300K range, the data clearly indicates a second dynamic process with the opposite temperature dependence, which is indicative of activated diffusion. Such an activated process may be indicative of migration of the mean position of the defect either along the chain or from one chain to another.

175 PHASE MEMORY TIME OF TRANS-POLYACETYLENE; EVIDENCE FOR SOLITON DIFFUSION.

Eric J. Hustedt and Bruce H. Robinson, Department of Chemistry, University of Washington, Seattle, WA 98195; Hans Thomann, Exxon Research and Engineering, Annandale, NJ 08801.

Interest in organic semiconductors has led us to consider the nature of soliton dynamics in pristine trans-polyacetylene as observed by 2-pulse electron spin-echo experiments. From these experiments, the phase memory time, Tm, is given by the time constant obtained from an exponential fit to the echo decay. In an attempt to simulate the experimental results, the motion of the electron is modeled as random jumping along a 1-d lattice of nuclei (with jumping rate, k). The interaction of the electron with the nuclei (^{13}C or ^{1}H) is described by the simplified Hamiltonian, $H = h(w_e Sz + AIzSz)$, where A is the spin-spin contact term. In the calculations, the full set of all possible Iz = ± 1/2 nuclear states is taken into account. Analytical results for a 2-site model and numerical results for lattices with up to 15 nuclei have been obtained. In the slow motion limit, k<< A/2, the simulated echo decay is a single exponential with a small amplitude modulation (1/Tm = 2k for the 2-site model). In the fast motion limit, k>> A/2, a single exponential curve is obtained for the 2-site model, which is the well-known Redfield result. In the intermediary region, the fit to a single exponential is not good (the departure from single exponential behavior indicative of 1-d diffusion), but it is clear that 1/Tm increases until k ~ A/2 and then decreases. When k ≤ A/2, the phase memory time is independent of the number of nuclei, N, for N > 10. When k > A/2, 1/Tm increases nearly linearly with N. The simulations correctly predict the observed single exponential echo decays for trans-polyacetylene at high and low temperatures, as well as the observed temperature dependence of 1/Tm, and provide a means of estimating N.

176 DESIGN AND SYNTHESIS OF ISOTOPIC SPIN LABELS. S. D. Venkataramu

and D. E. Pearson, Departments of Chemistry and Physiology, Vanderbilt University, Nashville, TN 37235

Our research focuses on the design and chemical synthesis of new and potentially useful spin labels for EPR investigations of biomedical problems. We have previously shown that deuteration and incorporation of ^{15}N in the paramagnetic group of the maleimide spin label resulted in marked increases in spectral sensitivity and resolution. These isotopic substituted spin labels enabled the first computerized simulations of complex EPR and ST-EPR spectra of proteins and membrane-bound enzymes. In order to improve motional characterization of lipids in model and biological membranes, we have now developed a general procedure, starting from ^{15}N-glycine, for the synthesis of ^{15}N-substituted stearic acid and cholestane spin labels with a "doxyl" group. The method is readily applicable for deuteration as well as incorporation of radiolabels in the spin label group. These new probes offer important advantages for studying the dominant interactions of membrane components. Our recent work on novel probes will also be discussed. (Supported by U.S. Public Health Service, Muscular Dystrophy Association and Biomedical Research Support Grant).

177 SYNTHESIS AND APPLICATION OF SPIN-LABELED AND PHOTOAFFINITY SPIN-LABELED NUCLEOTIDES: THE ADVANTAGE OF ISOTOPIC SUBSTITUTION.

Wolfgang E. Trommer
Fachbereich Chemie der Universität, D-6750 Kaiserslautern, F.R.G.

Spin-labeled (SL) derivatives of NAD and of its structural components have been applied in studies of structure-function relationships in lactate dehydrogenase (LDH), glyceraldehyde-3-phosphate dehydrogenase (GAPDH), glutamate dehydrogenase and ß-hydroxybutyrate dehydrogenase (BDH). The enhanced spectral resolution provided by isotopic substitution of the spin-label with either ^{2}H or ^{2}H and ^{15}N allowed, e.g., for the identification of distinct nucleotide binding sites in membrane-bound BDH. ESR spectra of BDH/SL-NAD complexes in oriented multi-layers are dependent on the H_o field direction indicating a non-statistical incorporation into the membrane. Binding of SL-NAD to GAPDH was consistent with the ligand-induced sequential model as proposed by D.E. Koshland. Complex formation of the cofactor with remote and/or adjacent active sites in the enzyme tetramer was revealed by dipolar splitting in spectra when adjacent sites were occupied. ATP derivatives spin-labeled at N^6 or C_8 of the adenine ring or in the ribose moiety were utilized for studies of the Ca-ATPase from sarcoplasmic reticulum and F_1-ATPase from M. luteus. In order to allow for investigations under conditions where the spin-label is poorly bound, various photoaffinity SL-derivatives of ATP and NAD carrying the photoaffinity group either in the nicotinamide or adenine moiety were employed.

178 THE USE OF MOLECULAR GRAPHICS AND X-RAY CRYSTALLOGRAPHIC STRUCTURAL DATA IN THE INTERPRETATION OF EPR DATA OBTAINED FROM BIOLOGICAL MACROMOLECULES.

J.J. Birktoft and J.H. Park. Dept. of Biochemistry, Washington University, St. Louis, MO 61110, USA and Dept. of Physiology, Vanderbilt University, Nashville, TN 37232, USA.

The conformational space available to a ligand bound to a biological macromolecule can be explored in a rational manner when molecular models of the structures are available from high resolution X-ray crystallographic analysis. Recent advances in interactive molecular graphics have now made this a most convenient tool for the analysis of interaction of proteins with their ligands. When combined with information obtained from EPR, meaningful conclusions can be reached about possible modes of protein:ligand interactions. We investigated glyceraldehyde 3-phosphate dehydrogenase and the coenzyme NAD^+, spin labeled on the adenine ring at the N6 or C8 position with a nitroxide radical. EPR signals were dependent upon binding stoichiometries and juxtapositioning of the four binding sites on the tetramer. Both N6-SL-NAD^+ and C8-SL-NAD^+ derivatives located on adjacent subunits resulted in resolved dipolar interactions. Molecular modeling based on known X-ray crystallographic data showed that the spin moieties were separated by 11-13 A and 8-10 A for N6-SL-NAD^+ and C8-SL-NAD^+, respectively. Molecular modeling also indicated that the spin-moiety of N6-SL-NAD^+ was in a highly restricted conformational space, whereas C8-SL-NAD^+ was in a less restricted environment. These conclusions were fully supported by the experimental EPR spectra. Upon substrate binding, separation of adjacent spin labels was shown to decrease. Molecular modeling suggested a narrowing of the cleft into whic the substrate binds, thereby moving spin labels on adjacent subunits closer together. Supported by NSF grant PCM 7921864 and NIH grants GM-13925 and GM-07884.

179 EPR AND ST-EPR STUDIES OF MEMBRANE BOUND PROTEINS.

A. H. Beth, Department of Physiology, Vanderbilt University, Nashville, TN 37232.

We have employed a ^{15}N, ^{2}H spin labeled derivative of coenzyme NAD to examine the solution and crystal structure of the tetrameric enzyme glyceraldehyde-3 phosphate dehydrogenase (J. Biol. Chem. 259, 9717, 1984). These studies have provided a well characterized spin labeled enzyme which has now been employed to probe the structure a flexibility of the cytoplasmic domain of the erythrocyte anion transport protein (band in various membrane preparations. Studies have indicated that the cytoplasmic domains adjacent band 3 monomers in the membrane oligomer are unable to bind simultaneously to single GAPDH tetramer. Removal of the cytoplasmic membrane skeleton, a procedure which leads to clustering of band 3 monomers, does not promote binding to additional subunit of the GAPDH tetramer although a significant increase in mobility of membrane bound enzyme is observed. Consideration of these data in concert with ST-EPR measurements o the rotational motions of different segments of band 3 leads to a dynamic model for th intrinsic membrane protein which compliments a variety of other structural data from protein crosslinking and proteolytic cleavage experiments.

180 THE DYNAMICS OF THE MEMBRANE BOUND PROTEIN D-β-HYDROXYBUTYRATE DEHYDROGENASE (BDH) AS STUDIED EPR AND STEPR.

B.H. Robinson, Dept. of Chemistry, University of Washington, Seattle, WA 98195, O.J. McIntyre and S. Fleischer, Dept. of Molecular Biology, Vanderbilt University, Nashville, TN 37235.

The molecular dynamics of BDH, a lecithin requiring enzyme, inserted into mitochondrial phospholipid vesicles has been studied by both the EPR and STEPR techniques. The study of BDH has been accomplished using both a maleimide-spin-label (msl) attached to the essential sulfhydryl, and two spin-labeled derivates of the cofactor (NAD). We have examined the experimental spectra for characteristics which are indicative of the effect of the lipid on the protein's dynamics: anisotropic rotational motion. The anisotropic character is clearly delineated using EPR and STEPR spectra together. The EPR spectra are used to quantitatively evaluate the faster motional processes. The STEPR spectra ar then sensitive to the slow processes. A series of simulated spectra exploring the effects of widely anisotropic molecular motion was calculated to characterize the sensitivity of spectra to motion. The results indicate that STEPR spectra of msl-BDH clearly show anisotropic character with one time component is around 50 nanoseconds and another around 10 microseconds. Furthermore, the relative spectral changes indicate differences in local mobility among the different labels. Determination of the orientation of the labels relative to the bilayer is in progress. Preliminary results indicate that the msl-BDH is tilted (60 to 90) with respect to the normal to the bilayer.

181 ELDOR STUDIES OF INTERACTIONS BETWEEN ^{14}N:^{15}N SPIN-LABEL PAIRS.

J. B. Feix, J-J Yin, S. D. Venkataramu, A. H. Beth, J. H. Park, and J. S. Hyde
National Biomedical ESR Center, Medical Coll. of Wisconsin, Milwaukee, WI 53226 and
Departments of Physiology and Chemistry, Vanderbilt Medical School, Nashville, TN 37232

Electron-electron double resonsance (ELDOR) methodology has been employed to study the interaction between ^{14}N and ^{15}N nitroxide spin-label pairs. Utilization of ^{14}N:^{15}N pairs eliminates neuclear relaxation as an ELDOR-active mechanism, allowing direct study of Heisenberg exchange. The use of two spin label populations also allows study of interactions between probes on dissimilar carrier molecules - for example lipid and protein, different classes of lipids, or probes in predominantly different regions of a lipid bilayer. Using this methodology interactions are readily observed between stearic acid spin labels with the nitroxide moiety lacated at carbons 5, 12, and 16 (C5, C12, and C16), as are interactions between C5, C12, or C16 and the cholestane spin label (CSL). A phospholipid head-group spin label, tempo-PE, also interacts with CSL, however tempo-PE and the stearic acid spin labels do not interact. Interaction between C5 and C16 indicate strong vertical fluctuation of the terminal methyl group of C16 toward the membrane surface. By utilizing the $^{14}NC16$:$^{15}NC16$ spin-label pair to determine lateral diffusion constants and the $^{14}NC16$:$^{15}NC5$ pair to study vertical fluctuation; we have examined the influence of lipid composition on the physical properties of model membranes. The effects of cholesterol, alkyl chain-length matching, and host lipid unsaturation will be discussed. Supported by NIH Grants RR01008, GM22923 and the Muscular Dystrophy Association.

182 NUCLEAR MAGNETIC RESONANCE OF A MONOCLONAL ANTI SPIN LABEL ANTIBODY.

J. Anglister, T. Frey, M. Whittaker, and H. M. McConnell, Department of Chemistry, Stanford, University, Stanford, CA 94305.

The structure of the combining site of a monoclonal antibody against dinitrobenzene conjugated to Tempo is being studied by nuclear magnetic resonance techniques. The broadening effect of the unpaired electron on the NMR spectrum of the complex of the Fab fragment and the spin labeled hapten is used to simplify the NMR spectrum. The difference spectrum between the proton NMR spectrum of the Fab and the NMR spectrum of the Fab complex with the hapten shows only the contributions to the spectrum from amino acids which are in the combining site region. Selective in vitro incorporations of deuterated amino acids have been used to assign the contributions of the aromatic and the aliphatic amino acids.

Difference spectra were calculated for different occupancies of the combining site. The peak heights in these spectra have been simulated by computer calculations and from the best fit, distances of amino acid protons from the unpaired electron have been calculated.

Specific labeling of the chains has been made possible by selective deuteration of the whole Fab, separation of the light and the heavy chains, and recombination of chains from different preparations of Fab fragments that differ in their labeling. The difference spectra that were measured for the different recombinant Fab fragments show the contributions of each chain to the combining site.

NOE measurements using selectively deuterated Fab fragments and diamagnetic analogs of the hapten are being used to deduce short range proximities between amino acids in the combining site region and to deduce short distances between them and the paramagnetic hapten.

183 SPIN LABELING OF PLASMA MEMBRANES IN DISEASES.

D. Allan Butterfield, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055

The electron spin resonance techniques of spin labeling provide valuable information on the molecular interactions which occur in protein, bilayer lipid, and cell-surface carbohydrate components in plasma membranes. The sensitivity of the spin labeling method to the local polarity, molecular motion, and chemical interactions in the microenvironment of the paramagnetic center of the spin label has allowed new insight into the molecular alterations in plasma cell membranes in several disease states. As examples of these kinds of studies, this lecture will present a brief review of spin labeling studies in the muscle disorders, Duchenne muscular dystrophy and myotonia (prolonged contraction upon stimulation) and the degenerative memory disorder, Alzheimer's disease. In addition, some newer specific spin labeling techniques and important factors in the treatment of cell membranes will be discussed. Finally, some thoughts of future directions of spin labeling in disease will be presented. Supported in part by grants from NIH (AG-00084), the Alzheimer's Disease and Related Disorders Association, and the Dreyfus Medical Foundation.

184 DISORDERS IN LEUKOCYTE FUNCTION AS DETERMINED BY EPR AND SPIN TRAPPING.

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The major function of polymorphonuclear leukocytes (PMNL) is to serve as the first line of host defense against invading bacteria. To carry out this role PMNL must find, recognize, ingest and kill the pathogens. During these cellular responses, changes occur in membrane fluidity, surface potential and hydroxyl radical production. These parameters can be monitored by EPR, and therefore, leukocyte disorders with abnormal values can be readily detected. For example, the average membrane fluidity of resting PMNL can be compared with 5-doxyl stearic acid. PMNL from patients with Chediak-Higashi Syndrome, a disorder characterized by recurrent infections, have an abnormally high resting membrane fluidity. During the ingestion phase of phagocytosis, normal PMNL membranes become less fluid. Chronic granulomatous disease (CGD) patients' PMNL, which fail to kill ingested bacteria, do not show this change. The surface potential of PMNL can be compared using fatty alkyl ammonium spin labels. Normal PMNL decrease their surface charge in response to chemotactic signals, aiding their sticking to tissues during migration to find invading pathogens. A patient with a lactoferrin deficiency (LD) failed to show altered PMNL surface potential. Hydroxyl radicals are lethal to many bacteria and are generated by PMNL to aid in killing invaders. OH production can be compared using the spin trap DMPO. Normal PMNL exhibit a characteristic burst of OH production following stimulation. PMNL from CGD patients totally lack such a response while PMNL from the LD patient were intermediate in OH production.

185 EPR SPECTROSCOPIC STUDIES OF A HIGHER PLANT CELL WALL PARAMAGNETIC ION LATTICE

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EPR studies have provided strong evidence that divalent cations sequentially bind to intact cell wall polyuronides. From second moment theory, we calculate that the dimer-only nearest neighbor Cu^{2+} and Mn^{2+} distance parameters are ca. 11 and 14Å, respectively. The lattice constant was 2.45 ± 0.21, indicating that approximately 5-7 spin-spin interactions occur per paramagnetic ion in the filled lattice. Hydrated cell wall-bound Mn^{2+} spin-spin coupling had an unusual temperature dependency whereby linewidths increased as the EPR sample temperature was lowered from 20°C to T_{max}, where maximum linewidths occurred; thereafter linewidths decreased. T_{max} was inversely proportional to the degree of lattice hydration and was above 0° in certain samples; this is evidence that the temperature dependency was not associated with the freezing of bound water. Other data indicate that the temperature effect is due to changes in the relative positions of point dipoles in the lattice and is controlled by intact cell wall polyuronide orientation and structure.

186 SPIN-LABEL STUDIES OF THE CUTICLE OF THE SCORPION CENTRUROIDES SCULPTURATUS

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Electron paramagnetic resonance measurements of spin-labeled cuticle of C. sculpturatus were used to investigate the phase behavior and molecular dynamics of epicuticular lipids. It was found that polar lipids at the cuticulin-wax layer interface undergo two order transitions in the temperature range -20°C to 90°C. The low-temperature transition at 25°C was assigned to a chain-melting transition upon heating. The high-temperature transition at 55°C was assigned to the formation of a isotropic liquid or isotropic liquid crystal in the high-temperature phase. The results for extracted epicuticular lipids in which a spin label had been introduced confirmed the existence of the two order transitions. Also, it was found that the interaction of the polar epicuticular lipids with the citiculin had an ordering effect on these lipids. The temperatures of the two transitions correlate with temperatures of permeability transitions reported previously. The assignment of the low-temperature transition to a chain-melting process is consistent with the monolayer model for the temperature dependence of cuticular permeability.

187 INVESTIGATION OF THE MOLECULAR MECHANISM OF MUSCLE CONTRACTION BY EPR SPECTROSCOPY

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Conventional and saturation transfer EPR spectroscopy of spin labeled muscle fibers have proven to be valuable techniques for investigating the molecular processes of muscle contraction. Muscle contraction involves a cyclic interaction between two proteins, myosin and actin, and we have specifically attached spin labels to myosin. Myosin, in muscle fibers, was labeled by reacting the spin label (iodacetamide and maleimide derivitives) directly with myosin (SH-1 site) or using spin-labeled nucleotides which bind to the nucleotide binding site of myosin. ST-EPR has shown that the spin label is rigidly bound to myosin and can be used to monitor the motion of myosin in the muscle. We detect a high degree of spin label anisotropy and EPR is a very sensitive monitor of any change in orientation of myosin during muscle contraction. Popular theories of muscle contraction involve a change in the orientation of myosin during muscle contraction. However, ST-EPR and EPR analysis of contracting muscle fibers detect no change in the orientation of the spin label. These results indicate that a model for myosin action during muscle contraction must include a domain of fixed orientation.

188 BIS-HISTIDINE COMPLEXES IN HEMOGLOBIN: A PROBE OF THE PROTEIN CONFIGURATION IN THE HEME POCKET.

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We have recently found that in the temperature range of 210 - 250 K a thermally available conformation of the heme pocket permits reversible coordination of the distal histidine in both methemoglobin and deoxyhemoglobin. Low temperature electron spin resonance (ESR) spectra of these methemoglobin complexes indicate distinct spectra for the α and β subunits. An assignment of the different chains was made using valency hybrids where only one chain was oxidized. The sensitivity of the ESR parameters for this complex were also shown to depend on conformational perturbation on both the proximal and distal sides of the heme. Comparison of ESR parameters of these reversible bis-histidine complexes, with those obtained for hemichromes produced by the addition of denaturants, suggests a denaturant induced perturbation of the protein structure which alters the geometry of the bis-histidine complex producing a more stable complex. The sensitivity of the ESR spectra of these complexes to even subtle differences in protein configuration, which are not detected for other low spin Fe(III) hemoglobin complexes can be attributed to the added constraints placed on the geometry of the complex by coordination to two indigenous ligands.

189 ELECTRON SPIN ECHO STUDIES OF PHOTOSYNTHETIC OXYGEN EVOLUTION. R. D. Britt, K. Sauer and M. P. Klein. Laboratory of Chemical Biodynamics, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

We have recently completed construction of a new 1 kw pulsed EPR spectrometer. We are beginning electron spin echo studies on the light induced multiline EPR signal associated with photosynthetic oxygen evolution (1). We hope to measure hyperfine couplings to associated paramagnetic nuclei via electron spin echo nuclear envelope modulation and both pulsed and conventional ENDOR. We are employing waveguide-mounted loop-gap resonators (2) in acquiring spin-echo data. We have found these to be excellent for cryogenic applications. Work supported by the U. S. Department of Energy under Contract No. DE-AC03-F00098.

(1) Dismukes, G.C. and Siderer, Y. (1980) FEBS Lett. 121, 78-80.
(2) Froncisz, W. and Hyde, J.S. (1982) J. Mag. Res. 47, 515-521.

190 Ca^{2+} ACTIVATION OF SPIN-LABELED SARCOPLASMIC RETICULUM ATPase: EFFECT OF HISTIDINE MODIFICATION. Carol Coan, Dept. of Physiology, U. of the Pacific, 2155 Webster St., San Francisco, Ca. 94115.

An iodoacetamide spin label (ISL) can be placed at the active site of sarcoplasmic reticulum (SR) ATPase without causing inhibition. The EPR spectrum is sensitive to the formation of an activated enzyme complex which is precursory to utilization of ATP by the enzyme for active Ca^{2+} transport. Both ATP and Ca^{2+} binding are required for the proper structural integrity of the complex. Thus, the ISL·SR spectrum provides a means of monitoring conditions which affect enzyme activation through alterations in the structure of the active site. This has been particularly useful in defining the role of Ca^{2+} in activating the forward transport mode of the enzymatic cycle, and in the backward inhibition which follows high levels of Ca^{2+} accumulation. We are now pursuing chemical modification studies to further delineate the coupling between enzyme structure and chemical mechanism. Here it is demonstrated that modification of a histidyl residue by ethoxyformic anhydride decreases the Ca^{2+} binding affinity, and the degree of binding cooperativity, concomitantly with loss of the enzyme's ability to utilize ATP.

191 IRON AND OXYGEN FREE RADICAL INVOLVEMENT IN OXIDATIVE DAMAGE IN BRAIN, R.A. Floyd, M.M. Zaleska and K. Nagy, Okla. Med. Res. Fnd.,825 N.E. 13th St., OK OK, 73104, USA

Oxidative damage in brain may be important etiologically during aging, ischemic damage, as well as epilepsy, resulting from head trauma. Our studies have shown that iron is crucial in initiation of peroxidative damage in brain and that the focal point of the initiation appears to be in the electron transport chain of brain mitochondria. Studies of dopamine synthesis in striatum synaptosomes have demonstrated that small levels of peroxidation initiated by ADP-Fe(11) causes a large decrease in the amount of dopamine synthesized from tyrosine. Peroxidation of striatum synaptosomes causes significant changes in membrane fluidity assessed by 5-nitroxyl stearate and 16-nitroxyl stearate. Peroxidation caused drastic changes in the membrane protein sulfhydryls as assessed by maleimide nitroxyl spin-label with a significant loss in the weakly immobilized component. Studies with model membranes have revealed the effect of several factors, including surface charge, antioxidant and protective enzymes on membrane peroxidation as assessed by oxygen consumption and malondialdhyde formation.

192 REDUCTION OF THE METALLOCHROMIC INDICATORS MUREXIDE AND TETRAMETHYLMUREXIDE TO THEIR FREE RADICAL METABOLITES BY CYTOPLASMIC ENZYMES AND REDUCING AGENTS.

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Murexide underwent a one-electron reduction by rat liver cytosolic fraction or a hypoxanthine-xanthine oxidase system to produce a free radical metabolite. Reduction of murexide by the freshly prepared cytosolic fraction depended upon the presence of ascorbic acid. N^1-methylnicotinamide, xanthine or hypoxanthine, in that order, could also serve as a source of reducing equivalents for the production of that free radical by the cytosolic fraction. Several thiol compounds (GSH, cysteine, and cysteamine), pyridine nucleotides (NADH, NADPH) and ascorbic acid were also effective in generating the murexide-derived free radical. Tetramethyl murexide was also reduced to its free radical derivative by a hypoxanthine-xanthine oxidase system.

193 ENDOR OF SEMIQUINONES IN VITRO AND IN BACTERIAL REACTION CENTERS,

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Ubisemiquinone-10 and other related semiquinones have been studied with different solvents/counterions by ENDOR/TRIPLE resonance spectroscopy in liquid and frozen solutions. The hyperfine couplings (hfc's) were compared with those from advanced MO calculations in order to obtain information about the inflnence of the molecular environment on the spin density distribution. These results are relevant for the structure and function of (semi)quinones involved in biological electron transfer reactions, e.g. the first and second electron acceptor quinone (Q_A and Q_B) in bacterial reaction centers. In the phototropic bacterium Rps. sphaeroides both acceptors are protein-bound ubiquinones with different redox potential; Q_A functions as a one-, Q_B as a two electron gate. The semiquinone forms can therefore be created via one ($Q_AQ_B^-$) or three ($Q_A^-Q_B^{2-}$) saturating LASER flashes in the presence of cyt c^{2+} followed by rapid freezing. EPR/ENDOR detection of these species is hampered by the presence of a high spin Fe^{2+} coupled to both quinones. This Fe^{2+} was replaced by the diamagnetic metal ion Zn^{2+}. Under these conditions narrow EPR signals and ENDOR resonances could be observed for Q_A^- and Q_B^-. Replacement of the natural ubiquinones by other quinones, deuteration of the protein quinones, and D_2O exchange experiments, helped to assign the observed hfc's to specific positions in the system. The result is that the spin density distribution in Q_A^- is different from Q_B^-. Both are bound to the protein via hydrogen bonds of different strength. They are in a very hydrophobic environment and in close contact with protons and nitrogen of the protein. The binding sites are different for Q_A and Q_B. These differences could explain the different properties of the ubiquinones in vivo, leading to the vectorial electron transport in photosynthesis.

194 ESR, ENDOR, and TRIPLE RESONANCE OF IMIDAZOLE, 1-VINYLIMIDAZOLE AND 2-METHYL-1-VINYLIMIDAZOLE RADICALS IN SOLUTION,

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Imidazole is proving to be very important in biological systems where it is found in the amino acid histidine. ESR spectroscopic data of imidazole and alkyl- or vinyl-substituted imidazole radicals in solution are sparse because of the instability in solution.

The preparation and spectra of imidazole, 1-vinylimidazole and 2-methyl-1-vinylimidazole are described. MO calculations by the INDO method were used for theoretical interpretation of the experimental results and evaluation of coupling constants and their signs.

195 ELECTRON SPIN RESONANCE AND ELECTRON SPIN ECHO STUDIES OF CHLOROPHYLL-a CATION RADICAL IN FROZEN VESICLE SOLUTIONS.

Larry Kevan and Nobuaki Ohta. University of Houston, Department of Chemistry, Houston, Texas 77004.

Electron spin resonance (ESR) studies of chlorophyll-a (Chla) cation radical ($Chla^+$) produced by photoirradiation have been carried out in frozen Dl-α-dipalmitoylphosphatidylcholine (DPPC) vesicle solutions with and without electron scavengers. Photoinduced $Chla^+$ was observed by ESR in DPPC vesicle solutions with no electron scavenger at 77 K for the first time. In the presence of an electron scavenger, simultaneous photoinduced formation of $Chla^+$ and some scavenger anions was observed.

ESR and electron spin echo (ESE) studies of $Chla^+$ produced by photoirradiation and chemical oxidation have been carried out in frozen DPPC vesicular solutions and in methylene chloride-methanol glassy solutions. The Fourier transformation of the ESR modulation spectra of $Chla^+$ shows several modulation frequencies of nitrogen nuclei in the pyrrole rings of $Chla^+$ which differ somewhat between the two types of frozen solutions. Such differences are interpreted by different quadrupole interactions of the nitrogen nuclei.

196 MICROENVIRONMENT AROUND THE ESSENTIAL CYSTEINE RESIDUES IN CHICKEN LIVER FRUCTOSE 1,6-BISPHOSPHATASE AS ANALYZED BY ESR.

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Chemical modification and Electron Spin Resonance Spectroscopy (ESR) spin labelling techniques have been employed to investigate the local environment of the essential sulfhydryl groups of chicken liver fructose-1,6 bisphosphatase. The results demonstrate the presence of two distinct classes of sulfhydryl groups in this enzyme. The first class of sulfhydryl groups react preferentially with iodoacetate and its spin labelled derivative and results in an increase in catalytic activity, while the second class of sulfhydryl groups react preferentially with N-ethylmaleimide and its spin labelled derivative and leads to a decrease in catalytic activity. The ESR spectral data strongly suggest that the first class of sulfhydryl groups is located in a deep cleft of the enzyme molecule, while the second class of sulfhydryl groups is located in a shallow crevice. The environment of the second class of sulfhydryl groups appears to undergo a significant change after the modification of the first class of sulfhydryl groups by iodoacetate.

197 MULTIPLE, OVERLAPPING SPECTRA FOR NON-HEME IRON OXYGENASES: BIOCHEMICAL BASIS.

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Phenylalanine hydroxylase and lipoxygenase are enzymes catalyzing reactions of dioxygen with substrates. Both enzymes have one iron atom per subunit and iron is required for catalysis. The ESR spectra at 4-20 K for these enzymes are those of high-spin iron in environments ranging from axial to rhombic, depending on experimental conditions. Experiments have been done to correlate ESR line shapes with the biochemical states of these enzymes. Phenylalanine hydroxylase is ferric in the resting state and has ESR spectra for two different types of iron. The iron component associated with active enzyme has $g_{yy} = 6.8$, $g_{xx} = 5.2$ and $g_{zz} = 2.0$. In the presence of catechol inhibitors, the low-field feature shifts to $g = 7.1$. In the presence of substrate (phenylalanine), the iron geometry changes to rhombic and the dominant signal is from a middle Kramer's doublet at $g = 4.3$. Lipoxygenase in the resting state is not ESR visible. Ferric enzyme results when lipoxygenase is treated with its hydroperoxy fatty acid product. The immediate product of this oxidation resembles the spectrum of phenylalanine hydroxylase with catechol inhibitors. Decomposition of the hydroperoxide yields multiple lipoxygenase spectra with low-field features from $g = 7.4$ to 6.0.

198 RELAXATION MEASUREMENTS OF LIPOXYGENASE FERRIC ESR SIGNALS.

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Lipoxygenases are non-heme, non-iron-sulfur proteins that catalyze the oxidation by molecular oxygen of polyunsaturated fatty acids to hydroperoxides. Soybean lipoxygenase is the most studied, but lipoxygenases have also been isolated from other sources such as rabbit reticulocytes. We have used ESR to examine the multiple iron environments in oxidized soybean lipoxygenase. Native soybean lipoxygenase contains 1 atom of ferrous non-heme iron per mole of enzyme. Under several sets of conditions, soybean lipoxygenase can be oxidized with hydroperoxide to yield one, two and three component spectra. The single component spectrum appears to be of most significance, since the other two can be obtained from this spectrum with time or with addition of contaminants. In order to quantitate the amount of iron represented in these spectra, zero-field splittings are being determined from temperature dependence of T_1. The temperature dependence of T_1 has been examined by several techniques including progressive saturation and rapid adiabatic passage conditions where the dispersion spectra yield T_1 using the equation $\tan(\phi-90) = \omega_m T_1$. T_1's for lipoxygenase are on the order of microseconds for 5-15 K. In addition to accounting for the iron in the different overlapping lipoxygenase spectra, T_1 data are used to compare the lipoxygenase iron site with that of other non-heme, non-iron-sulfur proteins such as phenylalanine hydroxylase.

199 COMPUTER SIMULATION OF HIGH SPIN FE(III) ESR SPECTRA OF NON-HEME IRON PROTEINS

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The spin Hamiltonian usually used to fit high spin Fe(III) ESR spectra is

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + D\,\{[S_z^2 - \frac{1}{3}S(S+1)] + \lambda(S_x^2 - S_y^2)\}$$

For several non-heme ferric proteins, experimental ESR spectra of frozen samples are described by this Hamiltonian in which the two terms are of comparable magnitude. Under this circumstance, the only method of determining the frozen solution pattern is to diagonalize the entire secular determinant.

A FORTRAN computer program was constructed using the routines from IMSL to calculate resonance magnetic fields and transition probabilities and then generate simulated patterns on a plotter. ESR spectra of two high spin Fe(III) non-heme iron proteins, transferrin and phenylalanine hydroxylase, have been simulated. The parameters used for the transferrin ESR simulation are $D = 0.325\ \text{cm}^{-1}$, $\lambda = 0.225$. The phenylalanine hydroxylase ESR spectrum is composed of three species of high spin Fe(III) with different D and λ, which are shown below.

	I	II	III
λ	0.03	0.333	0.28
$D(\text{cm}^{-1})$	0.302	0.28	0.28

The relative concentrations of these three species of Fe(III) can also be evaluated from simulated spectra.

200 ESR STUDIES OF FREE RADICAL METABOLITES IN PERFUSED LIVERS.

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Electron spin resonance (ESR) spectroscopy has been used to monitor the response of perfused rat livers to the xenobiotics, bromotrichloromethane and carbon tetrachloride. The spin trap, N-t-butyl-α-phenylnitrone (PBN), has been perfused into the liver with the halocarbon in order to capture short-lived free radicals. ESR analyses of aqueous perfusates and organic extracts of perfusates and livers have indicated the presence of PBN adducts of trichloromethyl radical and other halocarbon mediated free radicals. Characterization of the structures of the PBN adducts has utilized C-13 substituted compounds and model reactions.

201 HYDRALAZINE FREE RADICALS PRODUCED IN RAT LIVER MITOCHONDRAL,

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Hydralazine is used in the treatment of hypertension. As a side affect it has been found to induce systemic lupus erythematosus, and is mutagenic, as well as carcinogenic in experimental animals. Incubation of hydralazine with rat liver mitochondria, at PH 7.4, with the spin traps DMPO (5,5-dimethyl-1-pyrroline-1-oxide) and PBN (α-phenyl-tert-butylnitrone) yielded a carbon centered radical adduct as detected by electron spin resonance. Malate/glutamate, as well as molecular oxygen, were essential for producing hydralazine free radicals by mitochondria. Rotenone, antimycin A and boiling of the mitochondral, on the other hand, caused inhibition. Another Kreb cycle substrate, succinate, was not effective. Superoxide dismutase had no inhibitory effect, and, in addition, the xanthine/xanthine oxidase system did not produce carbon centered radicals of hydralazine. These experiments ruled out the involvement of O_2^- in the activation process. Among the hydrazine derivatives tested, namely, dimethylhydrazine, isoniazid, ipromiazid, p-toluene sulfonhydride and phenylhydrazine, only the latter yielded carbon centered free radicals. Free radical intermediates of the hydrazines may play a role in their toxicity as well as their carcinogenicity. This research was supported in part by an NIH grant (CA18591).

202 MOLECULAR DYNAMICS IN PROTEIN - SINGLE STRANDED DNA COMPLEXES.

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Enzymatically spin labeled polyribo- and polydeoxyribonucleotides have been used to derive local base motion and local structural base information in the absence and presence of poly-L-lysine and gene 5 protein. We conclude from a systematic lineshape analysis of these systems that the correlation time of the spin labels for rotations perpendicular to the principal axis of diffusion ($\tau_\perp$), which according to a simple motional model reflects nucleoside motion, is of the order of 1 ns for single stranded RNA, DNA or base paired bases in duplexes, and of the order of 4 ns in duplexes. In a single stranded nucleic acid - protein complex two distinct motions are discernible, one with a $\tau_\perp$ of the order of 8 to 10 ns, and a second one with a $\tau_\perp$ larger than 100 ns (reflecting strong immobilization). The % of strong immobilization does not depend on the percentage of sping labels present in poly dT for either poly-L-lysine or gene 5 protein, but is a function of the polypeptide present in the complex. With poly-L-lysine about 70% of the nucleosides are immobilized, whereas with gene 5 protein only about 25% of the bases show strong immobilization (Supported in part with NIH GM-27002).

203 INTERACTION BETWEEN CUPRIC ION AND SPIN-LABELLED CYSTEINE 93ß IN FETAL HEMOGLOBIN.

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ESR studies have identified a high affinity site as well as several low affinity sites of cupric ions in human and animal hemoglobins. Cupric ion bound to the high affinity site in frozen solutions is in a type 2, square planar configuration. Two of the donor atoms appear to be the nitrogens at the amino-terminal residue and the imidazole group of ß2 histidine. The nature of the remaining two donor atoms are less certain but involvement of a peptide nitrogen as a third donor atom is considered likely since it would permit formation of a favorable tridendate copper complex.

The γ chains of fetal hemoglobin (HbF) differ by 39 amino acid residues from the ß chains of adult hemoglobin. Among these, two histidines (His 143 and His 116) in the latter are replaced by ser and ileu respectively in the former. Previous work with human adult hemoglobin demonstrated strong interaction between copper bound to the high affinity site and a maleimide-TEMPO spin label attached to cysteine 93ß. This result suggested the possibility that the imidazole group of His 143ß may be involved as the fourth donor atom at the high affinity site. Since the γ chains of fetal hemoglobin lack a histidine at this position in its sequence (His ⟶ Ser), the interaction between tightly bound copper and the spin lable at cysteine 93ß was examined. It was found to be similar to the interaction between cupric ion and spin labeled adult hemoglobin for frozen samples. At room temperature, the high affinity copper site appears to be closer to the spin labeled 93ß cysteine in both fetal hemoglobin and in adult hemoglobin assuming the theory of Leigh is valid. It is concluded that the substitution for ß143 histidine in fetal hemoglobin does not substantially alter the interaction between spin-labeled ß93 cysteine and the tight copper binding site. Supported by NIH Grants AM15770 and RR01008.

204 SPIN-MEMBRANE IMMUNOASSAY STUDIES OF ANTI-GANGLIOSIDE IMMUNITY IN MULTIPLE SCLEROSIS. J.B. Feix, B. Khatri, M.P. McQuillen and S.M. Koethe, The National Biomedical ESR Center and Departments of Neurology and Pathology, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, Wisconsin 53226.

Multiple Sclerosis (MS) is a severe neurological disorder characterized by the destruction and loss of central nervous system myelin, and is the leading neurological disorder in the United States. Although thought to be an autoimmune disease, the precise aetiology of MS is unknown.

We have employed a spin-membrane immunoassay (SMIA) to examine the immune reactivity of serum from patients with MS against liposomes containing ganglioside GM$_1$ (Immunol. Comm. 13, 465 (1984). Exposure to serum results in a rapid lysis of GM$_1$-liposomes. No lysis occurs if the liposomes lack ganglioside, or if serum complement is heat-inactivated. The mean (± S.E.M.) lysis values were 52.3 (± 9.8) percent for twenty MS patients and 33.2 (± 4.5) percent for eleven controls. There was little overlap between the two groups. The difference between the means is highly significant (student's t-test, $P < 0.0001$), indicating increased anti-ganglioside immunity in patients with MS.

205 NEUTROPHILL METABOLIC BURST PROFILE VIA ESR. F.W. Kleinhans, S.T. Barefoot, and R.A. Haak, Department of Physics, IUPUI, 46223, Department of Medical Research, Methodist Hospital, Inc. 46202, and Department of Micro. and Immun., I.U. School of Medicine, 46202, Indianapolis, IN.

Hydroxyl radicals produced during the metabolic burst of stimulated neutrophils may be readily detected by trapping the OH· with DMPO to produce a moderately stable spin adduct which is detectable via ESR. A curve of ESR signal strength, A, vs. time, t, is readily obtained but there are problems of interpretation. The metabolic burst lasts 2' to 5' with typical stimuli, e.g. opsonized zymosan. If the spin adduct lifetime were long compared with this time, >10', the ESR signal would be the net OH· production and if the adduct lifetime were short, ~ seconds, the ESR signal would reflect the rate of OH· production. The actual situation is intermediate and greatly complicates the analysis. The tail end of A vs. t exhibits simple exponential decay with a time constant, tc, of 300 to 500 S. If this tc is assumed constant during the metabolic burst, A vs. t is readily deconvoluted to yield the true OH· production rate vs. t. To test for constant tc, ascorbic acid is used to measure tc during peak metabolic activity. When ascorbic acid is added (35 to 140 μM), the decay time is shortened according to (1/tc)obs. = (1/tc)natural + (1/tc)ascorbic acid. By varying the ascorbic acid concentrationa and measuring the reduction in ESR amplitude and shift of the A vs t peak to earlier times, and estimate of tc during the peak of metabolic activity may be obtained. We find a preliminary value of 20 to 30 S. These results are obtained under conditions of progressive oxygen depletion in the sample.

206 PULSED EPR STUDIES ON AXIAL LIGATION IN LOW-SPIN HEME COMPLEXES. J. McCracken, R.S. Magliozzo, and J. Peisach, Department of Molecular Pharmacology, Albert Einstein College of Medicine, 1300 Morris Park Ave., Bronx, NY 10461.

The electron spin echo envelope modulation technique has been used to study weak superhyperfine interactions between Fe(III) and axial ligands in low spin bis-cyano and bis-imidazole heme complexes. In both cases, one observes echo envelope modulations due to N-14 nuclei weakly coupled to the Fe. Using N-15 substitution, echo envelope modulations due to the axial ligands can be distinguished from those due to the heme nitrogens. Analysis of these modulation patterns yields hyperfine and nuclear quadrupole coupling parameters for the weakly coupled N-14 nuclei. The use of these magnetic coupling parameters to characterize the axial bonding in low spin heme complexes will be discussed. Also, the application of the electron spin echo envelope modulation technique to studies of axial bonding in heme proteins will be addressed.

207 SPIN-LABEL OF MEMBRANE-SKELETAL PROTEIN INTERACTIONS IN HUMAN ERYTHROCYTES,

D. Allan Butterfield, Troy M. Harmon, and Bennett T. Farmer, II, University of Kentucky, Lexington, KY 40506-0055

Spectrin, the predominant protein of the erythrocyte membrane skeleton, normally exists i the tetrameric state of aggregation. Increased amounts of dimeric spectrin results in decreased membrane skeleton stability. The polyamine, spermine, and the polyphosphate, 2,3-diphosphoglycerate 2,3-DPG retards or accelerates respectively, the lateral diffusio of transmembrane proteins. The effects of increasing the amount of dimeric spectrin in membranes and separate investigations of the effects of spermine and 2,3-DPG on the physical state of erythrocyte membrane skeletal proteins were studies by protein, lipid, and carbohydrate-specific spin labeling methods. Increasing the proportion of dimeric spectrin and disruption of the skeletal protein interactions by 2,3-DPG greatly alters t physical state of skeletal proteins ($P<0.002$ and $P<0.01$, respectively), but does not alt the physical state of membrane phospholipids or cell surface carbohydrates. In contrast spermine significantly decreases the mean ESR parameter reflective of protein segmental motion by nearly 40% ($P<0.005$), slightly increases the order of membrane phospholipids (P 0.05), and increases the rotational rate of cell surface sialic acid, most of what is on glycophorin A ($P<0.002$). These findings demonstrate the usefulness of ESR to membran skeletal protein interactions and provide new insight into the spatial relationship of the major transmembrane sialoglycoprotein with respect to the membrane skeletal network. Supported by NIH (AG-00084), the Alzheimer's Disease and Related Disorders Association, and the Dreyfus Medical Foundation.

208 ESR STUDIES OF THE EFFECTS OF Al^{+3},Cd^{+2}, AND Hg^{+2} ON HUMAN ERYTHROCYTE MEMBRANES.

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Considerable interest in determining the molecular effects of toxic metal ions on human physiology has been reported. ESR studies employing spin labels specific for membrane lipids, protein, or carbohydrates were performed to monitor the effects of 0.1 mM Al^{+3}, Cd^{+2}, or Hg^{+2} on the physical state of human erythrocyte (RBC) ghosts. A highly significant change in lipid motion was monitored by the stearic acid spin label employed in erythrocytes treated with Cd^{+2} or Hg^{+2} but not Al^{+3}. In contrast, the physical state of membrane proteins monitored by a protein S-H group specific spin label was altered by Al^{+3} but not by Cd^{+2} or Hg^{+2}. Additional studies employing either extracted lipids or RBC membranes pretreated with N-ethylmaleimide (protein S-H group specific) showed no change in lipid motion with any ion suggesting that these toxic metal ions affect membrane proteins and only secondarily membrane lipids. Results of studies employing carbohydrate specific spin labels to help determine the interaction site(s) of these ions will also be reported. Al^{+3}, Cd^{+2}, and Hg^{+2} may impart their physiological effect in various tissues by alteration of proteins in cell membranes. Support: NIH (Ag-0008 and the Alzheimer's Disease and Related Disorders Association.

209 THE MECHANISM OF RADIOLYSIS PROBED BY ESR.

Martyn C. R. Symons, Department of Chemistry, The University, Leicester, LE1 7RH, U. K.

A simple model of radiolysis will be presented which seems to account satisfactorily for most ESR results. This comprises electron ejection, either followed by electron capture to give radical-cations and radical-anions or followed by electron return, giving excited-states which may undergo bond homolysis. Examples of these processes will be illustrated and methods for inducing specific electron-capture or electron-loss will be described, together with several recent examples. Finally, some applications to biological systems will be outlined.

210 EPR OF CYCLOSILANE ANION-RADICALS. Robert West and Cynthia L. Wadsworth, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.

Cyclosilanes $(RR'Si)_n$, where R and R' are alkyl or aryl groups and n = 4-6, undergo chemical or electrolytic reduction to anion-radicals in which the unpaired electron is delocalized over the ring. Small hfsc values are found for ^{1}H (<1G) and ^{29}Si (~5G). Larger hfsc, 13-25G, are found for ^{13}C, indicating participation of the carbon 2s orbitals in the SOMO. An orbital model is developed in which the SOMO is represented as a linear combination of Si-C σ^* and symmetry adapted Si-Si σ^* orbitals. A simple perturbational approach is used to account for the values of ^{13}C hfsc observed for substituted cyclopentasilanes, $[Me_9Si_5R]^{\cdot-}$, in terms of altered mixing between Si-Si and Si-C σ^* orbitals.

211 EPR INVESTIGATIONS OF THE EARLY STAGES OF TNT DECOMPOSITION, J. T. Swanson, R. W. Carper, and J. A. Zirrolli, Frank J. Seiler Research Laboratory, USAF Academy, Colorado Springs, CO 80840-6528

Trinitrotoluene (TNT) in the neat liquid phase produces a radical signal in the EPR when heated above 200°C. The identity and kinetics of this radical have been examined to ascertain its role in the overall decomposition mechanism of TNT. Isotope labelling with deuterium and ^{15}N indicate a nitroxide radical formed by trapping of a benzyl radical by the nitro group of another molecule. Kinetic studies of TNT mixed with hexamethyl benzene (HMB) and semi-empirical molecular orbital calculations indicate that earlier radical forming reactions produce the unobserved benzyl radical. The kinetic isotope effect for the deuterated compounds indicate C-H bonding is important on the mechanism, consistent with the calculations. The rate of formation of the radical correlates well with the formation of products isolated by high pressure liquid chromatography.

212
A STUDY OF THE BOND HOMOLYSIS OF BI(3,5,5-TRIMETHYL-2-OXOMORPHOLIN-3-YL)
Tad H. Koch and John B. Olson
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In solution, bi(3,5,5-trimethyl-2-oxomorpholin-3-yl) (TM-3 dimer) exists in equilibrium with its persistent, stabilized free radical, 3,5,5-trimethyl-2-oxomorpholin-3-yl (TM-3 radical).

$$\text{TM-3 Dimer} \rightleftharpoons 2\ (\text{TM-3 Radical})$$

The equilibrium constant is a function of solvent, as are the rates of bond homolysis and radical recombination. TM-3 dimer has beeen proposed for use in high dose rescue chemotherapy. The reaction of TM-3 with adriamycin is a function of the rate of dimer bond homolysis. The technique of quantitative EPR was used to measure the equilibrium constants for bond homolysis of TM-3 dimer in ethanol, 1,2-dimethoxyethane, benzene, 0.1 M magnesium perchlorate in ethanol and 0.1 M sodium perchlorate in ethanol. The equilibrium constants ranged from 5.8×10^{-16} to 1.3×10^{-9}, being larger in the more polar solvents. Magnesium ion greatly increased the equilibrium constant. 2,2-Diphenyl-1-picrylhydrazyl was used as a scavenger of TM-3 radical to measure the rate constants of bond homolysis of TM-3 dimer. Visible spectroscopy was used to monitor the kinetics of reduction of 2,2-diphenyl-1-picrylhydrazyl in ethanol, 1,2-dimethoxyethane and benzene. The primary cause of the solvent effect is most likely due to hydrogen bonding. Capto-dative stabilization of the radical and steric crowding in the dimer are also important factors in understanding this system.

213 EXTENDED-TIME EXCITATION ELECTRON SPIN ECHO SPECTROSCOPY

A. Schweiger, L. Braunschweiler, J.M. Fauth and R.R. Ernst, Laboratory for Physical Chemistry, ETH-Zentrum, CH-8092 Zurich, Switzerland.

Electron spin echo (ESE) spectroscopy is extensively used to investigate paramagnetic systems. In the solid state, structural information may be obtained via the modulation of the ESE envelope originating from hyperfine interactions of the unpaired electron with surrounding nuclei. To record an ESE modulation in the conventional way the time between the microwave pulses is incremented from experiment to experiment, each providing one point of the trace. The measurement of a full echo envelope may therefore be time-consuming. In this contribution an alternative approach to record the ESE modulation is presented. Instead of applying an initial $\pi/2$ pulse followed by a π refocusing pulse, we excite the spin system by a low level irradiation for an extended time τ_0 prior to the π pulse which consists of a coherent, stochastic or burst stimulation. With an extended-time excitation the entire echo modulation can be obtained in a single experiment. Since with this novel technique the full ESE trace is recorded in each experiment the time for data acquisition may considerably be reduced.

214 EPR STUDY OF PHASE TRANSITIONS IN Cu^{2+}-DOPED $CaCd(CH_3COO)_4.6H_2O$.

S.K. Misra and K. Kumar, Physics Department, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal,Quebec, H3G 1M8 Canada.

Detailed X-band EPR study of a single crystal of $CaCd(CH_3COO)_4.6H_2O$ doped with Cu^{2+} has been made from room down to liquid helium temperature.The crystal has only one reversible structural phase transition over this temperature range; this occurs at 141±.5K. As the temperature is lowered the single set of four hyperfine lines at room temperature split into four sets of four hyperfine lines each at 141±.5K, indicating the presence of four magnetically inequivalent ions below this temperature. The principal values and direction cosines of the g- and A- tensors at different temperatures, and for different Cu^{2+} sites, are rigorously evaluated using a recently developed computer technique , based on the method of least-square fitting, employing all resonant line positions obtained for several orientations of the external magnetic field in three mutually perpendicular plans.

215 EFFECTS OF COMBUSTION ON 9 and 34 GHz EPR OF COLD LAKE OIL SANDS.

V. M. Malhotra* and H. A. Buckmaster,** Physics Department, Southern Illinois University, Carbondale Illinois 62901,* Physics Department, University of Calgary, Calgary, Canada.**

Cold Lake Oil Sands were subjected to air flow thermal conditions encountered under dry forward combustion (DFC). Samples were withdrawn from the combustion tube assembly at 80K intervals and their 9.5 and 33.92 GHz EPR Spectra recorded. The following results have been obtained and conclusions can be drawn: 1) If $290 \leq T \leq 508K$, then the free radical g-values of the bitumen are larger at 9 GHz than at 34 GHz. This g-value shift vanishes as the coke formation progresses. It is suggested that EPR measurements at two microwave frequencies could be used to predict coke formation in an oil-sand reservoir. 2) At $590 \leq T \leq 663K$, the viscosity of the oxidized bitumen is sufficiently reduced so that a fraction of it moves ahead and crystallizes as a black shiny material in the colder region of the oil sand. This fraction is rich in carboxylic acids, anhydrides, oxygen and free of V^{4+} complexes. FTIR measurements show that the water and CO_2 were trapped within this fraction. This fraction reduces the permeability of the reservoir, and it is suggested that to obtain relief from the formation damage, CO_2 should be injected into the hot formation. 3) The effects of partial combustion on the free radical and vanadium spectra will be discussed.

216 TOPOLOGIES OF THE LOOP-GAP RESONATOR.

W. Froncisz* and J. S. Hyde. National Biomedical ESR Center, Dept. of Radiology, Medical College of Wisconsin, 8701 Watertown Plank Rd., Milwaukee, WI 53226. *On leave from Jagiellonian University Krakow, Poland.

Since the very first loop-gap resonator was made for EPR spectroscopy (1), many different structures based on the loop-gap resonator principle have been proposed, built and tested for both EPR and NMR spectroscopy in the very broad frequency range of 25 MHz to 36 GHz. These different resonators can be classified according to their geometrical properties into linear, planar and three-dimensional arrays of n-loops and m-gaps. Different topologies of the loop-gap resonator within each of these three classes can be proposed giving the spectroscopist flexibility in designing suitable resonators for particular experiments. Scaling of dimensions of loop-gap resonators over this broad frequency range is straightforward. At higher microwave frequencies, shields are required to reduce radiation losses. Over the full range that has been tested, resonator unloaded Q's fall between 500 and 2000.

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217 APPLICATION OF HELICAL RESONATORS TO ENERGETIC MATERIALS RESEARCH.

M. D. Pace, Naval Research Laboratory, Code 6120, Washington, D.C. 20375-5000.

A special research project to detect thermal decomposition products from energetic materials (explosives) created a need for innovative epr hardware that is both inexpensive and disposable. One choice is the helical resonator (or helix) which is a coiled wire that can be operated either as a resonator or radiating antenna. A helix which operates at x-band frequency (9.5 GHz) was constructed based upon design specifications described by other researchers. The typical quality factor (Q) of this helix is 500. This is much lower than a cavity resonator and results in a reduction in signal-to-noise of 1/40 for a helix versus a cavity. For concentrated paramagnetic samples this is not a problem. A system for using the helix in a remotely controlled epr spectrometer was designed and tested. This required overcoming problems such as the helix-to-waveguide coupling and interchangeability of samples. In certain decomposition experiments the use of an electron-beam was required and special hardware in addition to the helix was developed to meet the needs of this experiment. The x-band helix will be described and epr spectra recorded with this helix will be presented.

18 RE-ENTRANT CAVITIES FOR E.S.R. SPECTROSCOPY.

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On the basis of lumped-constant equivalent circuits the expressions for the
resonant frequencies and Q factors of re-entrant cavities are derived. Many prototype
of different shapes and configurations have been built, ranging from 0.78 to 9.5 GH
showing a good agreement with the theory. They are characterized by one or more r
entrances that act as lumped capacitances and by inductive arms one of which is used
sample arm. The variable coupling between the resonator and the coaxial line is obtai
by means of a loop whose plane can be externally rotated. To a certain extent the dim
sions of the sample arm are determined by the operating frequency but there is the p
sibility of designing specific resonators to optimize the ηQ product for partic
experiments. The diameters of the sample arm of the present prototypes range from
cm for an X-band resonator to 5.0 cm for a two re-entrances prototype working at
GHz. This last resonator has been used to perform experiments on living mice up
weight of 25 grams.

219 CONSTRUCTION OF A COMPACT X-BAND MICROWAVE RESONATOR FOR USE WITH LIQUID HELIUM FLOW SYSTEMS.

R. LoBrutto and J. S. Leigh, Dept. of Biochemistry and Biophysics/G4, University of Pennsylvania, Philadelphia, PA 19104.

Our desire to make pulsed X-band EPR (electron spin echo) measurements on protein solutions at liquid helium temperatures has led to a narrowly-defined set of requirements for a microwave resonator. Since protein concentrations are limited, sensitivity is an important consideration, so the filling factor must be maximized. On the other hand, substantial total quantities of sample are often available, so th resonator should be able to accomodate a 3-4 mm O.D. sample tube. The structure must be compatible with a flow-type liquid helium cryostat.

We have developed a resonator that meets these specifications, and that is very easy and inexpensive to construct. It consists of two conducting rectangular strips mounted on a quartz tube, which is inserted between the sample tube and the quartz flow dewar. Coupling through the flow dewar walls is accomplished by a loop at the end of a coaxial feed line. Easy coupling adjustment and a tuning range of about 100 MHz have been achieved. Q values of about 800 at room temperature and 2200 at cryogenic temperatures have been measured.

The mode of operation, construction details, and calculation of electronic characteristics of the resonator will be discussed.

220 MICROWAVE RESONATOR PERFORMANCE IN PHOTOSYNTHETIC PULSED EPR EXPERIMENTS.*

C. P. Lin, R. J. Massoth, J. R. Norris and M. K. Bowman. Chemistry Division, Argonne National Laboratory, Argonne, Illinois, 60439.

The performance characteristics of a microwave resonator, which are important for pulsed EPR experiments, differ from those for CW EPR experiments. Important parameters concern: (1) maximizing the conversion of transmitter power into H_1; (2) efficiency of converting sample magnetization into signal power; and (3) total ringing time. We have used several published x-band resonator designs in pulsed EPR experiments on photosynthetic systems and will present the results here. The resonators include a conventional cavity, a bimodal cavity, several loop-gap and slotted-line resonators, and a folded half-wave resonator. In general, the smaller the effective volume of the resonator the better, and the lumped element resonators perform better than the distributed element resonators. The smaller resonators should make possible high performance pulsed spectrometers with up to 12 db better sensitivity and 14 db lower power requirements than with conventional designs. There is a substantial improvement in spectra of photosynthetic reaction centers taken with the folded half-wave resonator as compared with those taken with a conventional cavity.

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221 NO ABSTRACT

222 FLOW INJECTION ANALYSIS: AN OVERVIEW. L.C. LeGros, Lachat Instruments

Flow injection analysis has been demonstrated to be an extremely versatile technique for sample processing and ion determination where automated wet chemistry is required. With the capability of being interfaced with a variety of detectors, FIA serves as a mechanism for precise dilution, dialysis, distillation, extraction, and development of reactions to determine a wide range of analytes in diverse sample matrices. The basic flow injection technique involves injection of reproducible sample volumes into a continuously flowing unsegmented analytical stream. The sample is then carried into a reaction manifold where it can be introduced to one or more reagents. While on the manifold, the sample and reagents can be incubated, diluted, and/or run through a column to produce the desired reaction product. This product flows to an appropriate detector to generate an electrical signal which is measured by a data station.

The flow of sample from the sample tray to detector occurs very rapidly. Typically samples can be analyzed in less than 60 seconds at rates of 90-120 per hour. Along with high sample throughput, FIA gives the user startup and shutdown times of less than five minutes and chemistry changeover requires less than ten minutes. These performance characteristics of FIA give users a fast, precise, accurate, and easy to operate instrument for automated wet chemical analysis.

223 DETERMINATION OF NITRATE AND AMMONIUM IN SOILS USING FLOW INJECTION ANALYSIS. S.M. Workman, Colorado State University

A method for the measurement of ammonium in 2 M KCl extracts will be presented. Ammonia reacts with sodium salicylate and sodium hypochlorite forming a colored complex, which is detected at 630 nm. Interference caused by the precipitation of metal hydroxides is overcome by complexation with tartrate and citrate. The manifold is simple allowing for rapid start-up and shut-down of the system. Wide concentration ranges can be accommodated by changing the volume of injected sample. The sampling rate for ammonium analysis is 106/hour.

A method will be described for the determination of nitrate in various types of soil extracts. A column filled with granular zinc is included in the manifold to reduce the nitrate to nitrite and nitrite is measured colorimetrically. The zinc column is easily prepared and after conditioning shows minimal drifting due to changes in reduction efficiency. The sampling rate for nitrate analysis is 100/hour.

224 AUTOMATED STANDARD ADDITION TECHNIQUES FOR ATOMIC SPECTROSCOPY UTILIZING FLOW INJECTION ANALYSIS. K.G. Schick, FIAtron Systems, Inc.

With the introduction of the generalized standard addition method (GSAM) by Kowalski (1) and Zagatto (2) and the development of a FIA standard addition procedure by Tyson (3), new techniques have become available for dealing with spectral and matrix interference problems commonly encountered in atomic spectroscopy.

FIAtron has developed a solution handling system capable of automating these new standard addition techniques for routine use by the spectroscopist in ICP, DCP, and AA applications. A review of recent developments as well as specific applications will be discussed in detail.

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225 DETERMINATION OF PHOSPHORUS AND NITROGEN IN WATER USING FLOW INJECTION ANALYSIS IN AN ENVIRONMENTAL LABORATORY. K. Kringlie, North Dakota State Department of Health Public Health Laboratory

In the early 1970's a new concept in continuous flow analysis was introduced. This concept is referred to as flow injection analysis. This paper describes the use of a Lachat Flow Injection Analysis System for the determination of ammonia, total Kjeldahl nitrogen, orthophosphate, and total phosphorus in our laboratory.

The distinct advantages of unsegmented continuous flow analysis are faster determinations and less consumption of reagents. It accomplishes this while also producing accurate and precise results. These are attractive features when work load is heavy and the reliability of data is also of high concern. These are pressures faced in the environmental laboratory today.

This paper will provide data to show that flow injection analysis has significantly increased the number of determinations per unit of time in our laboratory. It accomplishes this while also featuring instrumentation that is easy to operate and maintain. Results of the analysis of actual samples received in our laboratory will be presented and the accuracy and precision of these results will be demonstrated.

226 FLOW INJECTION ANALYSIS OF PHOSPHORUS IN $NaHCO_3$ SOIL EXTRACTS. J.L. Havlin, University of Nebraska

Soil extraction with 0.5 M $NaHCO_3$ provides an index of plant available phosphorus in neutral and calcareous soils. Phosphorus in the extracts is routinely determined by the colorimetric molybdate-ascorbic acid "blue" method, which is sensitive to pH. Optimum pH range for color development is pH 2 to 4. After extraction the solution pH is about 9.0 and slightly less than 0.5 M in HCO_3^-. Therefore, extracts must be neutralized prior to color development and detection. In an automated analysis system "in-line" neutralization is difficult because of CO_2 evolution. Flow injection analysis of phosphorus in $NaHCO_3$ extracts is described, wherein 0.6 mmole·ml^{-1} HCl is added to 1.0 ml of extract for neutralization prior to sample loading and injection into the FIA system. Forty samples can be run in 15 minutes. Detection limit is 0.01 mg P·kg^{-1}. Chemistry, instrument parameters, and general analysis procedures are described.

227 SURVEY OF FIA METHODS FOR FEEDS AND FERTILIZERS. D. Diamond, Lachat Instruments

The paper will discuss colorimetric methods for nitrogen and phosphorus in fertilizers and protein and phosphorus in feeds. It will address techniques which can be used to vary sensitivity eliminating off-line dilutions. Typical RSD's are 0.3 - 0.5%.

Nitrogen in fertilizers is done using the salicylate method. Cycle time is 50 seconds, (72 samples per hour), with no carryover and complete baseline resolution. Concentrations range from 0.1 to 300 ppm NH_4-N in Kjeldahl digest. Sample preparation is per AOAC or by using a modification that uses $CuSO_4$ as a catalyst.

Phosphorus determinations using both total and direct available methods will be discussed. Ranges are 0 - 50% P_2O_5 and sampling rate is 72 samples per hour, using the molybdovanadate method.

Protein in feeds uses the salicylate method with a range of 0.1 to 300 ppm in Kjeldahl digest.

Phosphorus in feeds uses either the molybdenum blue method, or the molybdovanadate method. Ranges of 0.1 to 150 ppm phosphorus can be accommodated at 80 samples per hour.

228 MULTI-CHANNEL ANALYSIS, EXPECTATIONS VS. REALITY AND INTERFACING THE FIA TO LIMS, M.L. Daniel and H.M. Rutchey, South Florida Water Management District.

The District Laboratory has been routinely operating a Lachat FIA for about 18 months. The instrument is configured for four channel operation with a data station as supplied by Lachat. The parameters determined are ammonia, nitrate + nitrite, orthophosphate, chloride, methyl orange alkalinity, and silicate in surface and ground water. The nutrients are analyzed simultaneously and the anions are analyzed simultaneously due to the nature of the samples submitted. This paper will discuss the problems found with multi-channel analysis and the solutions found for some of the problems. The FIA data station has been interfaced to a Perkin-Elmer 3230 LIMS 2000 minicomputer for the integration of the results of analysis into the District database.

229 AUTOMATED LOW LEVEL DETERMINATIONS OF NITROGEN AND PHOSPHORUS IN ACID DIGESTS OF WATER USING FLOW INJECTION ANALYSIS WITH IN-LINE NEUTRALIZATION. R. Gill, California Water Quality Control Board

The methods for chemical analysis of water and wastes published by the U.S. Environmental Protection Agency prescribes methods, approved for NPDES, for the automated determinations of total Kjeldahl nitrogen (Storet 00625) and total phosphorus (Storet 00065) from a single acid digest. These exact methods have been adapted to flow injection analysis resulting in increased sample throughput (90+ samples per hour) and decreased analysis time (45 seconds) with accuracy, precision, sensitivity and ranges equivalent to those obtained by the Storet methods. The pH of each standard and sample is adjusted in-line as required for each chemistry.

230 MATRIX EFFECTS IN INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY. G.Horlick and S.H. Tan, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2.

Inductively-coupled plasma-mass spectrometry is one of the newest techniques for trace element analysis. As with almost any new such technique initial reports tend to de-emphasize problem areas and acentuate the new key features. Certainly such was the case with both flame AAS and ICP-AES. In the case of the ICP-MS significantly superior detection limits, spectral simplicity when compared to AES and inherent isotope information are key advantages features. However, matrix effects affecting analyte ion intensities are also present. While de-emphasized in some early reports, they, not unexpectedly, do exist and only failure to recognize and understand them constitutes a problem. In this report, results are presented from a study of the effect of the so called easily ionizable elements on analyte signals. At the level of 1000 ppm matrix element (K, Na, Ca) to 0.1 ppm analyte, signal depressions of 50% to 80% are observed and there are, as of yet, no readily apparent set of operating conditions to alleviate this suppression, outside of dilution. Interestingly for species having significant oxide levels, say Sc^+ and ScO^+, the degree of signal suppression is about the same for both species. This effect and those for several other analytes and matrix elements will be illustrated and ways of managing and minimizing these matrix effects will be outlined.

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231 ICP-MS: HIGH SPEED ISOTOPE GEOCHEMISTRY. A.R. Date and Yuk Ying Cheung, British Geological Survey, 64 Gray's Inn Road, London WC1X 8NG, U.K.

Natural variations in isotopes and isotope ratios provide the geochemist with a wealth of information about geological processes. The field of isotope geochemistry has been well served by conventional techniques for atomic mass spectrometry, using spark, thermal, and secondary ion sources. However, these conventional techniques may suffer from one or more of the following limitations: (a) the necessity to separate isotopes of interest from the matrix, (b) time-consuming analysis, (c) limited element coverage, and (d) complex spectra. The recent development of the inductively coupled plasma (ICP) as an ion source for atomic mass spectrometry provides yet another analytical technique, but a method offering certain advantages over the existing techniques.

The first papers describing the use of the ICP as an ion source were published in 1980 (1) and 1981 (2), but a viable form of the ICP-MS technique did not appear until 1982 (3). The British Geological Survey (BGS) has ben actively involved in the development of ICP-MS since 1979 (2,3,4,5,6,7,.8) with a contract from the Commission of the European Communities. Since the beginning of 1983, two instruments have been operated by BGS. The prototype system at the University of Surrey is used for further instrument development and the application of a laser ablation stage for the analysis of solids. The second instrument installed at the BGS laboratories in central London is used for a more detailed applications study, with sample introduction by conventional solution nebulization, principally for geochemical research.

The BGS interest in ICP-MS was aroused by its potential for rapid isotope ration determination in geochemical prospecting. Preliminary data have been reported for the determination of lead isotope ratios in minerals (3,4). The characteristics of ICP-MS in terms of isotope ratio determination are summarized below:

1. Separation of the isotopes of interest may be unnecessary, unless pre-concentration is required
2. Samples may be processed at a rate of one every few minutes
3. Simple specra are produced
4. Wide element coverage is possible
5. Precision in the range 0.1 to 1% is possible

The work on lead isotope rations in mineral samples is now extended to cover a wider range of elements in different sample types. The potential of the ICP-MS method will be illustrated with several examples.

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232 Os ISOTOPIC RATIONS FOR NANOGRAM-SIZED SAMPLES. G.P. Russ, J.M. BAZAN, D.A. Leich, Lawrence Livermore Natl. Lab., Livermore, CA 94550 and A. Date, British Geologic Survey, London, England.

As part of a project to measure the half-life of ^{187}RE and to develop Re-Os chronology, and ICP/MS technique has been developed for determining the isotopic composition of 1-10 nanogram-szied osmium samples. In this technique OsO_4 is generated by adding sample to aqueous H_5IO_6 and heating. The solution is then sparged with Ar, which is introduced into the ICP torch. The enhancement in sensitivity over that of solution nebulization is approximately a factor of 100. Ions from a single sample of Os are collected over a period of 20-30 minutes. Mass fractionation is constant for a given set of operating conditions. When normalized to a constant 188/192, the 186/192, 189/192, and 190/182 ratios (nominally 0.038, 0.39, and 0.64) agree from sample to sample withing counting statistics. For 10 ng samples the 1σ uncertainties are ~ ± 2%, 1%, and 1%, and 1%, respectively for 1 ng samples the uncertainties are roughly a factor of two larger. One sample of "natural" Os showed a 50% higher 187/192 than another reflecting natural variations due to ^{187}Re decay. Difficulties associated with variable ion yields/ng and contamination will be discussed. Preliminary data on isotope ratios for other elements will be presented.

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233 AN IMPROVED INTERFACE FOR INDUCTIVELY-COUPLED PLASMA-MASS SPECTROMETRY.

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A critical feature of any ICP-MS system is the differentially pumped interface between the ICP and the vacuum system housing the mass spectrometer. Early attempts to construct these interfaces encountered an unexpected problem - the ICP tended to arc to the sampling orifice and this was termed a "pinch" effect. In work carried out here it was found that the "pinch" was simply an electrical breakdown at the sampler caused by a high RF potential difference between the ICP and the sampler. A unique (patented) means of reducing this voltage has been found. The result is the complete elimination of any secondary discharge effects. The advantages include: (1) the complete absence of any ions in the background derived from sputtering of the sampler and skimmer material, (2) low levels of doubly charged ions and (3) a greatly increased sampler lifetime. The development of this unique interface will be described. The accompanying improvements in ICP-MS operation, as shown by the SCIEX ELAN 250 ICP-MS system, will be summarized.

234 INDUCTIVELY-COUPLED PLASMA-MASS SPECTROMETRY FOR THE QUANTITATIVE ANALYSIS OF NATURAL WATERS.

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The inductively-coupled argon plasma is an efficient ionization source capable of ionizing the vast majority of elements. Coupling multielement analytical technique capable of not only measuring isotope ratios but also determining sub-ppb analyte concentrations. Modified simplex optimization studies were conducted using factors significant to both quadrupole and plasma operation maximize analyte response. Optimized parameter values obtained through this study were confirmed through the generation of response curves for each factor. Compromize factor settings were employed for multielement determinations based on these findings. Background spectra for various matrices are described and representative calibration curves are shown to have a linear working range over at least 5 orders of magnitude. Interferences resulting from overlapping isobars, oxide formation, and multiply charged ions are identified. Short- and long-term drift of analyte intensity is outlined. Sensitivities and detection limits are presented and the utility of this method is supported with accuracy and precision data obtained for a series of reference standards and spiked natural water samples using the technique of standard additions.

235 SOLIDS MASS SPECTROMETRY USING SAMPLE INTRODUCTION BY LASER ABLATION INTO THE ICP ION SOURCE.

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Although sample introduction to the ICP Ion Source is usually by means of solution nebulisation, other methods used for ICP-AES are also applicable in principle. Solids may be introduced by laser ablation and a number of users have reported this for AES (1,2,3). This method has now been applied to an ICP Ion Source and some of the results are reported here. Samples are prepared in the form of discs 3mm thick by 32 mm dia. and may be metal or powder compacts made from mineral samples and a binder. A ruby laser of nominal Q-switched pulse energy 1.5J with a repetition rate up to 1H$_z$ is used. Up to 200 shots may be accommodated on each disc. Ablated material is carried to the ICP torch by the injector argon flow through a tube 1.5m long. The response has a peak about 5 secs. long followed by a decaying tail of about 30 secs. The mass analyser is scanned over the selected mass range, up to 250 daltons, at 10 scans sec.$^{-1}$ so that a representative spectrum may be stored in up to 2000 memory channels. High sensitivity is obtained with detection limits down to 10 ng.g.$^{-1}$ and isotope ratios may be determined (4).

Recent developments of this technique are described and the performance obtained is discussed.

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236 OPTIMIZATION OF ICP-MS FOR THE ANALYSIS OF SILICATE MATERIALS.

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The ICP-MS technique offers extremely high sensitivities for elements in single element solution Limits of detection for most elements can be obtained at 10 pg/mL or better. However these detection limits deteriorate in the presence of high concentration of other elements: especiall refractory elements.

Silicate rocks contain approximately 10 percent aluminum plus lower concentrations of titanium an other refractory elements. Even though a digestion of rock using only acids, and dilution factors o 5000 to 1 will yield a low total salt content and theoretically offer detection limits of 0.1 ppm or lower for most trace elements in the sample, the practical contribution from contamination from the reagents, glassware, and handling renders the high sensitivity feature to be useless. Thus, with consideration of the effects of contamination, the ICP-MS system must be optimized for solution containing at least 5 mg/mL total salt. This represents a dilution of the original rock o approximatley 200 to 1. Using this dilution factor, a 0.1 ppm limit of detection for an element in the rock can be attained using a limit of detection of 0.5 mg/mL in a solution containing a 5 mg/ml total salt.

The performance of the ICP-MS system for silicate rock analysis following an acid dissolution will be discussed.

237 SOME OBSERVATIONS OF PERFORMANCE CRITERIA IN ICP-MS.

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Much of the comparative discussion to date about the technique of ICP-MS has revolved around detection limits of elements in matrices which are traditionally problematical when analyzed using optical spectrometry. This paper discusses a wider range of analytical performance criteria of the ICP Mass Spectrometer and consequently the extent of usefulness of the technique in real problem solving.

Results obtained under multi-element compromise conditions are reported and the effects of changing instrument parameters are discussed, e.g. trade-offs in abundance sensitivity with analytical sensitivity. The long and short term reproducibility of the technique is quantified and the major sources of irreproducibility are considered. The effects of peristaltic pumps and mass flow controllers are discussed.

The ICP as an ion source is, of course, not completely free from interferences. Doubly charged ions, oxides and a variety of other molecular species can limit performance in some specific applications. These difficulties are considered together with strategies for minimizing their effects.

238 MEASUREMENT OF TRACE ELEMENTS AND ISOTOPE RATIOS IN PETROGEOLOGICAL SAMPLE BY ICP/MS: A PRELIMINARY REPORT.

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A variety of petroleum crudes, related reservoir rock and source rock samples were examined for trace element distributions. Sample sources included Arabian crudes, North Sea crudes (United Kingdom and Norwegian sectors), on-shore and off-shore Californian crudes, and Alaskan North Slope crude. Uranium and thorium ratios for some drill stem samples ranges from 0.59 to 0.85 which are consistent with literature references for carbonate structures. Lead isotope ratios were measured for all of the samples. The lead isotope ratios showed deviations from normal isotopic distributions ranging from deltas of -0.09 to 0.3, where delta were equal to the accepted values minus the corrected measured value. All samples were digested using acid dissolution techniques. National Bureau of Standards SRMs were used for correction of instrumental bias in the measurement of isotope ratios.

239 THE DETERMINATION OF TRANSITION ELEMENTS, V, Cr, Mn, Co, Ni, Cu, and Zn, IN GEOLOGIC REFERENCE MATERIALS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY. A.E. Meier and F.E. Lichte, U.S. Geological Survey, Box 25046, MS 928, Denver, CO 80225.

The determination of elemental constituents in geologic materials is complicated by variable matrix and the necessity to determine trace quantities of some elements in the presence of major concentrations of other elements. The application of inductively-coupled plasma-mass spectrometry to the determination of some of the major and trace elements in geologic material was studied. The first row transition elements (V, Cr, Mn, Co, Ni, Cu, and Zn) were selected for this study because the concentrations of these elements in standard reference materials are well documented and most of the interferences and high salt content of the solutions likely to be encountered in rock analysis can be demonstrated with this group of elements.

Several USGS standard reference materials were analyzed by inductively-coupled plasma-mass spectrometry. The accuracy of the technique is demonstrated by comparing values obtained to reference values. Data on the precision and the linear range of these elements will be presented.

Interference effects of rock matrix materials, isobaric and oxide interferences, and drift were studied. It was found that adequate correction for these interferences can be made by proper choice of dilution, plasma parameters, interference correction equations, and use of an internal standard.

240 THE EFFECT OF PLASMA OPERATING PARAMETERS ON ANALYTE SIGNALS IN INDUCTIVELY-COUPLED PLASMA-MASS SPECTROMETRY. G. Horlick, S.H. Tan, M.A. Vaughan and C.A. Rose, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2.

Utilizing the SCIEX ELAN an extensive study of the effects that plasma operating parameters have on analyte ion signals in ICP-MS has been carried out. Parameters studied included aerosol flow rate (Nebulizer pressure), auxiliary flow rate, power and sampling depth (sampling position from the load coil). The two key parameters are aerosol flow rate (nebulizer pressure) and power. Elements can be grouped into characteristic behavior patterns based on the overall dependence of their ion count signal on these two parameters. The nebulizer pressure-power behavior patterns allow a sensible selection of compromise operating conditions and significantly clarify single parameter observations which often indicate confusing trends in behavior. In addition to characterizing analyte ion signals the parameter behavior plots have also been used to study oxide species and plus two ions in ICP-MS. While aerosol flow rate and power appear to be the key ICP parameters in ICP-MS, ion signals are dependent on sampling depth and auxiliary flow rate and some data are also presented illustrating the signal dependence on these two parameters.

241 LUMINESCENCE SPECTROSCOPY USING A PERSONAL COMPUTER

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My project involves the systematic cataloging and analysis of the luminescence properties of rocks, minerals, and other natural and man-made materials so that data from luminescence remote-sensing devices can be evaluated with greater specificity. A fluorescence spectrometer, modified and integrated with a personal computer, is used to produce luminescence data which is combined with chemical and mineralogical information to determine the probable physical and/or chemical causes of the luminescence of these materials. Software, written in-house, guides the acquisition of data, provides for the manipulation of that data, and displays it in several different forms. For the analysis of the visible and near-visible excitation and emission properties, a data array is produced by repeatedly scanning the emission monochrometer with luminescence intensity read at 10 nanometer intervals and with the excitation monochrometer stepped at 10 nanometer intervals. Using a co-processor, plots of 3-D perspective views of these emission/excitation arrays are generated at speeds approaching that of mini-computers. In addition, luminescence is measured with the emission monochrometer set at the wavelengths of various Fraunhofer lines to assess whether the intensity is within the sensitivity limits of the Fraunhofer line discriminator (an airborne electro-optical device for detecting and/or imaging materials that have been stimulated to luminesce by the sun). This information is also used with chemical and mineralogical data for statistical analysis. These tasks might have been accomplished using a mini-computer except for the availability of hardware and software interfacing techniques for personal computers and the increasing speed, power and versatility of these smaller and less expensive tools.

242 TOTAL NITROGEN DETERMINATION IN PETROLEUM USING A CHEMILUMINESCENT METHOD

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An improved chemiluminescent method for nitrogen determination has been developed for the heavy ends of petroleum using programmed pyrolysis to 850° C. A small amount nitrogen attached to low molecular weight compounds is detected when the pyrolysis temperature is around 400° C. The remaining carbonaceous compounds contain nitrogen whic is bonded to more stable molecules. These compounds include ring-systems which are highly incorporated into the coke during pyrolysis. Two main peaks for this type of nitrogen appear at 550°C and 700° C on the thermogram. A final pyroreactor temperatur of 850° C is optimum to break down these nitrogen containing compounds. Variables whic affect chemiluminescent response are: the flow rates of helium and oxygen carrier gase pyro-oxygen, and ozone generator oxygen; pyrolysis tube temperature; isothermal period; temperature program rate; and oxidation catalyst (V_2O_5). The standard deviation in thi study for 0.3% and 0.15% nitrogen in hydrocarbon standard residual oils (Alpha Resource Inc.) is ±0.013% and ±0.006%, respectively. Research was funded by the U.S. Department of Energy under contract number DE-AC03-84BC99880.

243 FLOW INJECTION ANALYSIS WITH CHEMILUMINESCENCE DETECTION USING THE RUTHENIUM TR BIPYRIDINE COMPLEX

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The ruthenium tris(2,2'-bipyridine) complex in its oxidized 3+ state has been show to chemiluminesce in the presence of hydrazine [1], hydralazine [2], and oxalate [3]. Hercules predicts that the $Ru(bipy)_3^{3+}$ is reduced to the 2+ state by means of an exicte 2+* route in the presence of hydrazine, which generates ammonia and nitrogen gas [1]. is the relaxation of the 2+* state to the 2+ state which generates the observed visible light. However, other reducing agents have not been investigated analytically using th chemiluminescence system. We have investigated other reducing compounds with some emphasis being made to nitrogen heterocycles. Among these include hypoxanthine, indole reserpine, pyridine, and terpyridine. Flow injection analysis provided high sample throughput with good reproducibility for reaction timing. This enabled linear range an detection limit data to be easily generated.

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244 FLUOROMETRIC DETERMINATION OF DANTHRON BY REDUCTION IN A FLOW INJECTION ANALYSIS SYSTEM

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Danthron (1,8 dihydroxyanthraquinone) is a common active constituent of cathartic laxatives. With the use of a flow injection analysis (FIA) system, the detection of danthron in pharmaceutical samples can be done rapidly. The reduction of danthron in 100% methanol to the highly fluorescent hydroxyl compound can be carried out in an FIA system using sodium dithionite in a 50/50 water/methanol mixture with tetraborate buffer. A linear range of 0.1 to 30.0 ug/ml has been established for danthron standards. Initial work with commercial laxative tablets gave a slight positive deviation compared to the direct UV method. The placement of a C-18 cartridge into the injection loop can be used to strip danthron out of aqueous solutions and separate it from possible interferences. Because of the aqueous-organic mobile phase employed in this method, extension of this work to on-column derivatization of danthron in a high-performance liquid chromatography system should be feasible.

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TEMPERATURE DEPENDENCE OF THE LUMINESCENCE OF BIACETYL VAPOR, C. Weiser, Grumman Aerospace Corporation, R&D Center, M/S A-08-35, Bethpage, New York 11714

Measurements of the temperature dependence of the laser induced luminescence from biacetyl vapor have been made. The experiments have been carried out in an evacuable test cell which is enclosed within a small oven. A pulsed, nitrogen pumped, tunable dye laser operating at 4200 Å is used to excite the biacetyl. The biacetyl fluorescence intensity in the 4600 Å region and the phosphorescent radiation at 5150 Å were concurrently measured between 20°C and 400°C. In addition the variation of the transmission of biacetyl at 4200 Å was measured over the same temperature range.

246 THE ROOM TEMPERATURE PHOSPHORESCENCE BEHAVIOR OF SELECTED PESTICIDES AND PRIORITY POLLUTANTS. Nelson Herron, M. J. Zabik, and S. R. Crouch, Pesticide Research Center, Room 204, Michigan State University, East Lansing, MI 48824.

The Room Temperature Phosphorescence (RTP) behavior of selected compounds in both micellar and cyclodextrin solutions will be examined. These spectra will be evaluated as to their selectivity and sensitivity as analytical tools. They will also be examined as to their analytical value for certain non-luminescent compounds such as ethylene dibromide (EDB) which may be selectively concentrated by the micelle of cyclodextrin and which may then act as a heavy-atom spin donor to promote the RTP of the co-entrained probe molecule. The lifetimes of these spectra will be examined to gain some insights into some anomalous quenching behavior.

247 INFLUENCE OF FORSTER ENERGY TRANSFER ON FLUORESCENT LIFETIMES. Eugene R. Weiner and Marvin C. Goldberg. U.S. Geological Survey, P.O. Box 25046, MS 424, Denver Federal Center, Lakewood, CO 80225.

Fluorescent lifetime measurements permit detailed examination of several different processes for molecular electronic energy deexcitation. Excited state lifetimes of spontaneous emission and internal conversion. Observed lifetimes are modified by the presence of neighboring molecules that stimulate additional deexcitation processes, resulting in energy transfer to neighboring recievers. When lifetime measurements are correlated with energy reciever concentrations, solvent viscosity, and absorbtion and emission spectra, it is possible to identify which of several energy transfer mechanisms is dominant. These include collisional encounters, complex formation, emission-reabsorbtion, and the Forster energy transfer (long range dipole-diploe interaction). When deexcitation occurs by the Forster mechanism, lifetimes are shortened with a very characteristic dependence on reciever concentration and spatial distribution. There is no dependence on solution viscosity, or influence on the donor absorbtion or emission spectra, and, in certain cases, there is a modification to the emission polarization. In systems where Forster energy is dominant, measured fluorescence lifetimes are a sensitive measure of the average donor-reciever separation distance, and a probe for determining donor-reciever spatial distributions.

248 OXYGEN QUENCHING OF HUMIC SUBSTANCE LUMINESCENCE AND ITS CONSEQUENCES FOR TERPENES IN AQUATIC ENVIRONMENTS. Kirkwood M. Cunningham and Marvin C. Goldberg, U. S. Geological Survey, P.O. Box 25046 MS 424, Denver Federal Center, Lakewood, CO 80225.

Light-excited humic substances in aqueous solution are known to dissipate their excitation energy by several routes. Some routes, like luminescence, yield no net chemical change. Other routes, which can quench luminescence, give rise to very reactive organic and inorganic species. An example of the latter type is the transfer of excitation energy to oxygen to yield singlet oxygen, $^1O_2$. Singlet oxygen is capable of attacking double bonds, with epoxides and hydroperoxides the proximate products.

The terpene alpha-pinene is emitted in quantity by certain land and aquatic plants. Despite the presence of the oxidation products of alpha-pinene in aquatic systems in small quantities, the parent hydrocarbon is generally undetectable. A reason for this may be its light-sensitized oxidation by $^1O_2$. To test the possibility, we have photolyzed humic substance (NaOH extracted "Florida Muck") in a $CH_3CN:H_2O$ mixture with near UV light (300-400 nm) in the presence of alpha-pinene and O_2 at pH 5-7. Using GC-MS and HPLC, the formation of a major photoproduct was followed, and could be identified as pinocarvyl hydroperoxide by comparison with the known product formed by photolysis of the methylene blue - pinene - $CH_3CN:H_2O$ system. The overall quantum efficiency of the humic-sensitized pinene oxidation is about .01.

249 FLUORESCENCE PROPERTIES OF SYNTHETIC MELANIN. David L. Bolton, Department of Chemistry, University of Denver, Denver, CO 80208.

Melanins are biological polymers that are largely responsible for pigmentation in animals. They are found in the hair, skin, eye, brain, and inner ear. With the possible exception of photoprotection, the function of these polymers remains unclear. The structure of melanin remains incompletely identified ; however, the physical and chemical properties render the study of melanin especially difficult. It is opaque, insoluble in most solvents, amorphous, and without a well defined molecular weight. The addition of certain species to water has been found to increase the solubility of melanin. Although the UV absorbance does not change significantly, the use of modified solvents has reduced the amount of light scattering resulting in the observation of fluorescence emanating from fluorophores within the melanin polymer. Fluorescence of melanin/water suspensions occurs with a peak emission at ca. 400 nm ; however, addition of a solubilizing agent (e.g., carbonate) results in greatly reduced light scattering and a red shift in emission of ca. 50 nm. In addition, the influence of pH, metal ion complexation, and quenching by inorganic species has been examined on the basis of observed spectral changes.

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LASER INDUCED FLUORESCENCE OF LIGNINS FROM WOOD DIGESTION

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Lignin is a complex polyphenolic molecule which in the course of wood digestion (pulping) is known to undergo cleavage and condensation reactions. We are interested in monitoring changes in the condensation during the course of pulping and have utilized a modified Low Angle Laser Light Scattering instrument and an argon-ion laser/dye laser coupled with a Raman Spectrometer to monitor fluorescence of lignins as a number of wavelengths. Samples studied were chosen to be representative of a range of kraft lignin to be able to assess fluorescence changes as a function of pulping conditions.

251 DEPOLARIZATION MEASUREMENTS USED TO DETERMINE THE MOLECULAR PROPERTIES OF FULVIC ACID. Marvin C. Goldberg, U.S. Geological Survey, P.O. Box 25046, MS 424, Denver Federal Center, Lakewood, CO 80225.

Interest in the molecular bonding properties of fulvic acid has prompted a need to understand its molecular structure. Fluorescence measurements provide insights into the molecular structure of the fulvic acid molecule in the following way. By measuring the polarization of the fulvic acid and its fluorescent lifetime, one can calculate the molecular rotation of the molecule. Lifetime measurements on fulvic acid produce 2 lifetimes (τ) that are 2 and 8 nanoseconds (ns), respectively. A measurement of the depolarization value (p) at 455 nanometers (nm) gave a value of .04. Solving the Perrin equation $\{(1/p + 1/3) = (1/p_o - 1/3)(1 + 3\tau/\rho)\}$ for τ of 2×10^{-9} ns, ρ (the total relaxation time) is 4.5×10^{-10} sec. The equation $\rho = 3V\eta/RT$, where η is the solution viscosity, R is the gas constant and T is the temperature is solved for V (the molar volume). Substituting the expression $4/3\pi r^3$ (spherical geometry) for V, one obtains the molecular radius (r) which is 4.5×10^{-8} cm.

252 THE USE OF AN INTENSIFIED DIODE ARRAY TO DETERMINE PHOSPHORESCENCE LIFETIMES. Nelson R. Herron, M. J. Zabik and S. R. Crouch, Pesticide Research Center, Room 204, Michigan State University, East Lansing, MI 48824.

In this study we set out to investigate the possibility of determining phosphorescence lifetimes and the complete phosphorescence spectrum in the same real time experiment. We were interested in the development of this technology as a possible HPLC detection system using Room Temperature Phosphorescence. We were also interested in investigating the limits of available technology.

We will describe the special restrictions placed on the Intensified Diode Array by this sort of experiment and those steps taken to satisfy those restrictions. A brief description of the special data acquisition electronics will be presented as well as the pertinent features of an Intel 8085 based microcomputer used to drive the system.

Some preliminary applications will be presented and some of the data reduction problems inherent to using a diode array at this clock frequency will be addressed. Attempts to apply this research to Room Temperature Phosphorescence in both micellar and cyclodextrin solutions will be considered.

253 INFRARED MONITORING OF CONDENSED PHASE PYROLYSATES PRODUCED BY CO_2 LASER PROCESSING OF PLASTICS. J.M. Kokosa and D.J. Doyle. Department of Science and Mathematics, GMI Engineering & Management Institute, Flint, MI 48502.

The CO_2 laser is finding increasing industrial application for the machining of polymeric materials such as polyethylene (PE), polymethylmethacrylate (PMMA) and nylon. While the vapor and condensed phase products produced by standard pyrolysis techniques are well characterized by infrared, at present no studies have been published characterizing the condensed phase pyrolysates produced by CO_2 laser irradiation. Characterization of these products by IR might lead to useful techniques for the monitoring of potentially hazardous products produced in the workplace. The following study entailed the pyrolysis of several of the more common polymers, including PE, PMMA, polypropylene (PP) and polyvinylchloride (PVC) at reduced pressure in argon or air utilizing a Sylania model 973 CO_2 laser and a diffuse beam at 1.6 kw power for 0.1 to 0.5 sec. The condensed pyrolysates were extracted into $CDCl_3$ (for pmr studies) and cast onto a NaCl plate for IR. The extracts were also examined with pmr, HPLC, UV, and GC/MS techniques. The IR for PE, PP and PMMA were similar to standard pyrolysis IR except that PE and PP pyrolysates contain significant amounts of olefinic fragments. The PMMA to a small extent and PVC to a large extent contained polycyclic aromatic products.

254 THERMAL SHOCK OF HEAVY OIL FORMATIONS: FTIR STUDY.* V.M. Malhotra and R.D. Moore,
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High viscosity is a major constraint in the production and processing of heavy oils and oil sand bitumen. Thermal recovery processes such as dry forward combustion (DFC) are used to lower oil viscosity and enhance its production. DFC processes subjects the oil bearing formation to a thermal shock at $625 K \leq T \leq 1125K$. Under these conditions, the reservoir minerals undergo structural changes, new mineral phases are synthesized and their grain sizes are altered. These reactions control the porosity and the permeability of the reservoir. In our experiments the oil saturated cores and oil stripped cores of heavy oil formations were subjected to air flow thermal conditions encountered under DFC. Samples were withdrawn at 40K intervals and their FTIR, EPR and XRD spectra were recorded. These results show that combustion produces a significant amount of Fe_2O_3 and reduces the quantity of various clays. In addition, new mineral phases are synthesized which may adversely effect the porosity of the formation.

*Work supported by Coal Research Center, SIU.

255 FTIR ANALYSIS OF ROSIN FLUX - METAL OXIDE INTERACTIONS. Randy W. Snyder, 1701 North Street, Dept. T43/014-3, Endicott, NY, 13760.

Metal surfaces must be clean and free of oxide layers prior to soldering operations or the solder will not wet the surface properly and good joints cannot br formed. Rosin based flux, whose major constituent is abietic acid, is a good material for removing these oxides when using high temperature solders. However, it removes them at different rates which depend on the metal and the oxidation state. FTIR diffuse reflectance (DRIFT) and total reflection techniques will be described for studying interactions between several metal oxides and the flux. The activity of the flux towards the different metal oxides will be described as the degree of ionization of the abietic acid.

256 QUANTIFICATION OF BENZOYL PEROXIDE IN SILICONE ADHESIVES. Susan E. Stemporzewski, Kendall Company, 17 Hartwell Avenue, Lexington, MA, 02173.

Silicone adhesives can be cured with the use of benzoyl peroxide. The benzoyl peroxide forms free radicals which allow crosslinking of the silicone polymer. Determination of the amount of benzoyl peroxide in the polymer can be a useful tool for monitoring the cure of an adhesive. An infrared spectroscopic method is described for the quantification of benzoyl peroxide in silicone adhesives.

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QUALITY AND THICKNESS ANALYSIS OF THERMOPLASTIC COATINGS BY DIFFUSE REFLECTANCE IR SPECTROMETRY. Michael E. Hawkins and Howard C. Price, Zimmer, Inc., P. O. Box 708, Warsaw, IN 46580.

The utility of Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectrometry for the analysis of polymers is now widely appreciated. We have developed a DRIFT method for the evaluation of thin (20-150 micron) transparent coatings on metal substrates. With this technique, the assessment of coating composition, thickness, uniformity, and solvent residues is achieved on individual intact specimens. Our discussion will compare DRIFT with other IR reflectance methods as well as with nonspectrometric methods such as eddy current and gravimetric analysis. The DRIFT approach will be compared to these other techniques in terms of reliability, precision, versatility, and resource requirements.

258 THE APPLICATION OF FT-IR PHOTOACOUSTIC SPECTROSCOPY AS A SURFACE ANALYSIS TECHNIQUE. C. Q. Yang and W. G. Fateley. Department of Chemistry, Kansas State University, Manhattan, Kansas, 66506.

The application of FT-IR photoacoustic spectroscopy to the characterization of solid materials has attracted considerable interests since late 1970's. One of the major advantages of FT-IR/PAS over conventional spectroscopic techniques is it's ability to obtain absorbtion spectra of solid samples without sample preparation. This is because the photoacoustic signal is generated by the sample and directly detected by a microphone without employing any photodetector. FT-IR/PAS is very useful as a surface technique because only the materials within the thermal diffusion length can be measured by photoacoustic detection. In our FT-IR/PAS studies, thin ploymer films on the metal surface, sized and desized fibers and the finish on the surface of fabric were investigated. The application of PAS depth profiling technique in the studies of finish on fiber surface will also be reported. The reported data will demonstrate that FT-IR/PAS has good surface sensitivity and is well suited for surface studies of a variety of solid samples.

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IN VIVO FTIR STUDIES ON SKIN SURFACES
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In vivo or in vitro surface FTIR studies on biological systems, such as skin, are accomplished with a multiple internal reflectance accessory called a "skin analyzer". Penetration rates of topically applied materials are readily determined by fitting reference spectra to a multiple linear regression least squares algorithn. Although human in vivo penetration rates are most important, the guinea pig model is also used in cases where materials of unknown properties are being evaluated. The penetration rate of propylene glycol into the human forearm is much faster than into guinea pig stratum corneum. The reason(s) for this difference is being investigated. Interactions between skin (and/or lipids) and propylene glycol have been observed which are consistent with an α-helix to an antiparallel β-pleated sheet protein conformational change. These interactions were also monitored with time. The behavior of a lipophilic penetration enhancer (Azone®) on skin was found to be different than the hydrophilic proylene glycol. Surface lipids were rapidly carried into the stratum corneum by this compound. Although resolvable, a relatively simple system (neet Azone on skin) became complicated by multiple physicochemical interactions.

260 THE 1600 CM^{-1} AND 700-800 CM^{-1} BANDS OF SOOT AS A FUNCTION OF SOURCE. J.A. Jassim, Hsay-Ping Lu, A.R. Chughtai, and D.M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208.

The model proposed for carbon soot surface functionalities and of this material have been subjected to further study in this laboratory. Soot generated from more than twenty-five different fuel sources revealed the same carbon-oxygen functionalities as observed from the combustion of n-hexane studied earlier by this group. Acetone-D_6 soot showed an isotopic shift for surface hydroxyl groups absorbing at 3500 cm^{-1} as well as for the aromatic =CH groups at 3100 cm^{-1} and 1400 cm^{-1}. The isotopic shift also was observed for the three bands in the 800 cm^{-1} region. Assignment of the IR bands in this region has been made through several experiments performed either by the study of the reaction products of the hexane soot with SO_2 and NO_2 gases, ozone or by labeling soot with O^{18} and deuterium. They result from the out-of-plane C-H deformation ring-substitution bands: the 760 cm^{-1} and 880 cm^{-1} bands to be due to aromatic 1:3 substitution while the 840 cm^{-1} and 880 cm^{-1} bands to be due to 1:2:4 substitution.

261 PHOTODEGRADATION PATHWAYS OF SILVER BACKED POLYACRYLONITRILE (PAN) FILMS AS DETERMINED BY FOURIER TRANSFORM INFRARED REFLECTION ABSORBANCE SPECTROSCOPY. C.A. Sergides, A.R. Chughtai and D.M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208.

Ultraviolet radiation in the regions $266 \leq \lambda \leq 400$ nm and $250 \leq \lambda \leq 400$ nm has been employed to study oxidative photodegradation pathways for silver-backed polyacrylonitrile (PAN/Ag) films. Measurements were based on Fourier transform infrared reflection absorbance (FTIR-RA) spectroscopy and supported by electron paramagnetic resonance (EPR) studies. Isotopic PAN (^{13}CN) was used to confirm some photodegradation products. Upon irradiation at wavelengths down to 266 nm, the polymer turns yellowish brown with an increase in its electrical conductivity. The species responsible for this color and the increase in conductivity appears to be a chromophore system of the type $(-\overset{|}{C}=N-)_n$.

262 PHOTODEGRADATION INHIBITORS FOR POLYACRYLONITRILE/Ag (PAN/Ag) FILMS. C.A. Sergides, A.R. Chughtai and D.M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208.

Three types of UV stabilizers have been utilized for the photostabilization of PAN/Ag films. First, the effect of UV-absorber stabilizers, such as hydroxybenzophenone derivatives (UVINUL SERIES, BASF) absorbing UV radiation in the same region as PAN, was studied. Such stabilizers generally have little effect while, in some cases, photodegradation of PAN was enhanced because of photosensitization. Second, the effect of quencher stabilizers like Nickel chelate complexes (Irgastab 2002, CIBA-GEIGY) on the photodegradation of PAN/Ag film was examined, and showed decreases in the photodegradation of the polymer. Thirdly, antioxidant stabilizers, such as 2,6-di-tert-butyl-4-methylphenol derivatives (Irganox 1010, CIBA-GEIGY), were studied and found to have a significant inhibiting effect on the photodegradation of PAN. Increasing the concentration of the stabilizer increases the inhibition. However, to maintain specularity, the stabilizer concentration was kept as low as possible. A combination of 1% w/w antioxidant and 0.5% w/w quencher proved to be optimum.

263 The red coloration of the highly magnetic Martian surface is presumably due to the presence of ferric iron. We have investigated the two major possibilities: 1) the magnetism is carried by superparamagnetic particles in "metanontronite" (1,2,3) or 2) the magnetism is caused by a thin red magnetic ferric oxide or hydroxide coating on otherwise nonmagnetic silicates (or other mineral particles) (1,2). During our investigation of the second theory, we found that mineral substrates strongly influence the phase precipitated from aqueous solution. IR absorption spectroscopy coupled with thermomagnetic measurements unambiguously determines the mineralogy of the micron and sub-micron sized coatings on these grains which are otherwise impossible to identify by conventional X-ray techniques.

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2. Hargraves, R.B., Collinson, D.R., Avidson, R.E. and Cates, P.M., 1979, J. Geophys. Res., v. 84, p. 8379-8384.
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264 SIMULTANEOUS MULTICOMPONENT DETERMINATIONS BY VIBRATIONAL SPECTROSCOPY.

Thomas J. Vickers and Charles K. Mann, Department of Chemistry, Florida State University, Tallahassee, FL 32306.

Work in this laboratory has for some time been directed to the development of approaches for simultaneous multicomponent determinations without prior sample treatment. Use has been made of both infrared and Raman spectroscopy; the latter technique has proven to be remarkably versatile for the kinds of analyses encountered. Recent reports have described work in which the Raman method has been applied to the determination of low levels of phenols in water and the simultaneous determination of two major components, phenylpropanolamine hydrochloride and acetaminophen, in pharmaceutical preparations. Further work has extended the examination of the determination of phenols in aqueous samples to some nitrophenols. Detection limits of 0.03, 0.4, 0.07 and 0.2 mg/l have been found for the determination of 2-nitro-, 3-nitro-, 4-nitro- and 2-chloro-4-nitrophenol, respectively. Results will be described for the simultaneous determination of the 2-, 3-, and 4-nitrophenols using correlation and least squares data treatments. Some recent preliminary work on the determination of organics adsorbed on solid surfaces and metabolites in fermentation broths will also be described.

265 CALCULATED INFRARED TRANSITIONS FOR SOLUTION MACROMOLECULES MODELED AS ASYMMETRIC ROTOR ELLIPSOIDS.

John R. Riter, Jr. and Marvin C. Goldberg. U.S. Geological Survey, P.O. Box 25046, MS 424, Denver Federal Center, Lakewood, CO 80225.

By modeling solution macromolecules as constant-density continuous asymmetric rotor ellipsoids, we have computed the range of moments of inertia and hence rotational constants expected, given only the experimentally determined radius of gyration (R_g) and the quotient of molecular weight and density (M/ρ), or the molar volume (V_m). The pure rotation transition frequencies are calculated to be the order of a few MHz for the prolate, oblate and skew limits of the asymmetric rotor ellipsoid model for naturally occuring fulvic acids. For example, using our best estimates of R_g and V_m for aquatic Suwannee River fulvic acid, we compute the molecular rotational constant B to be 17, 33 and 25 MHz for the prolate(p), oblate(o) and skew(s) respectively. The general result for the rotational constants (A B C) is:

$$A_p > A_s > A_o = B_o > B_s > B_p = C_p > C_s > C_o$$

These macromolecular transition energies at the absorbtion edges are much less than those of the lowest energy rotational transitions of the solvent.

266 QUANTITATIVE ANALYSIS BY FTIR AND DIFFUSE REFLECTANCE OF METHYL METHACRYLATE-BUTADIENE-STYRENE POLYMER BLENDS.

H. Lee Mc Peters, Rohm and Haas Company, P.O. Bo
219, Bristol, PA 19007.

Methyl methacrylate-butadiene-styrene (MBS) polymer blends are frequently used to modify the impact properties of various polymer matrices. We are studying the feasibility of using transmission and diffuse reflectance FTIR spectroscopy to routinely determine the overall MBS composition and butadiene isomer content of these compounds. We will discuss the effects of sample preparation and different data analysis techniques upon the quanitative analysis of MBS blends.

267 PRESENCE OF THE ACID SALT OF CALCIUM BILIRUBINATE IN CHOLESTEROL GALLSTONES SUGGESTS THAT AN ACID MICROENVIRONMENT OCCURS DURING STONE NIDATION AND GROWTH.

J.M. Berman, M.A. Dabezies, P.F. Malet, R.D. Soloway. Gastrointestinal Section, University of Pennsylvania School of Medicine, Philadelphia, PA 19104.

Cholesterol gallstones contain pigmented rings which are associated with a diminished response to dissolution with chenodeoxycholic acid. In order to characterize the composition of these pigmented areas, we analyzed portions of 6 cholesterol stones using Fourier transform infrared spectroscopy to quantify the acid and neutral salts of calcium bilirubinate (CaBR), protonated bilirubin, cholesterol, inorganic calcium salts, and fatty acids. Results were expressed as percent composition by weight. There was a significant difference in composition between pigmented areas and whole stones in content of CaBR (5.62 ± 1.50% SEM vs 1.72 ± 1.01, $p<.05$), cholesterol (73.24 ± 6.24 vs 90.20 ± 2.85, $p<.05$), and unmeasured residue including protein, (19.98 ± 4.45 vs 6.90 ± 2.85, $p<.025$). The CaBR in these areas was always the acid salt. Conclusions: 1) The pigmented areas of cholesterol stones are chemically distinct from pigment stones becaus of their high cholesterol content and lack of inorganic calcium salts and fatty acids; therefore, cholesterol stones do not contain a pigment stone nidus. 2) The presence of both the acid salt of CaBR and cholesterol in the same region of cholesterol stones suggests precipitation together from bile in a microenvironment with a pH between 6.3 and 7.3, the range in which the acid salt is formed. Conditions favoring concomitant precipitation of the acid salt of CaBR and cholesterol appear to occur frequently during nidation and periodically thereafter during stone growth.

268 RECENT STUDIES ON MITOMYCIN C.

G. L. Verdine and K. Nakanishi, Department of Chemistry, Columbia University, New York, N.Y. 10027.

Mitomycin C (MC) is a clinically used antitumor antibiotic which has been termed the prototype of the "bioreductive alkylating agents." It has been conclusively demonstrated that MC aklylates specific DNA residues in the presence of reducing agents. We have recently shown that the alkylating capacity of MC toward DNA can also be unmasked by acidic catalysis. The structural studies on these various MC-DNA adducts will be discussed with a particular focus on spectroscopic techniques, e.g. difference FTIR, difference UV (normal and second derivative), and circular dichroism (CD).

269 PROTEIN STRUCTURE BY DECONVOLVED FTIR SPECTROSCOPY. Heino Susi and D. Michael Byler, U.S. Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, Philadelphia, Pennsylvania 19118.

The infrared spectrum of a protein usually exhibits a very broad, unresolved carbonyl stretching band. The observed band can be resolved into five to nine components by means of Fourier self-deconvolution. The components are assigned to *different classes of secondary structure, such as alpha-helices and extended chains,* by comparison with the spectra of model compounds and with the frequencies determined by normal coordinate calculations. The areas of the components were measured by means of a computer program based on Gauss-Newton iteration. The band areas were found to be approximately proportional to the fractional substructure content (helix, extended chains) as determined by a reinterpretation of protein X-ray data by Levitt and Greer. Deconvolved FTIR spectra thus offer a relatively fast way to estimate the secondary structure of globular proteins in the solid state as well as in deuterium oxide solution.

270 "A MODIFIED "QUICK" MULL TECHNIQUE,AN INNOVATION IN IR SPECTROSCOPY", Donald O. Woolf, Jr., Innovative Spectroscopy, 5426 Marilyn Road, Indianapolis, IN, 46226

The "Quick" technique used plates ground in a circular manner on frosted glass. Recently, the silicon carbide grit papers were found to provide optimally "cell pathed" pairs of salt plates. The scouring is performed by pressing the plate while drawing it first in one direction and then at right angle. Samples of 1, 2 mg. and oil volumes of 3, 4 microliters provide excellent mulls, even on 25 mm round plates. The spectroscopist must experiment to determine the proper grit paper to use. Two pairs of plates greatly simplify the preparation of "split" mulls, allowing the concentrations to be adjusted at a common band. Those samples, which as pellets, exhibit excessive scatter, poorly resolved bands or broad hydrogen bonded envelopes should be rescanned as mulls. Improved spectra will be the reward; flatter baselines, improved resolution of adjacent bands and well-defined OH and NH bands have been obtained.(Very possibly the relationship of refractive indicies of the oil and crystals may be the determining factor.)

Error Propragation As A Criterion For Optimal Spectrophotometric Multicomponent Analysis

John H. Kalivas

271 For analytical results, it is necessary to determine the optimum set of operating parameters influencing a chemical analysis. This is usually performed by experimental optimization or by using mathematical models. Regardless of the method of optimization the analyst is usually trying to obtain the maximum objective function (i.e. sensitivity or signal to noise ratio) for the response surface of a chemical analysis scheme. Another consideration in determining the optimal experimental conditions is error propagation. As with any analytical calibration system, there is a possibility for error magnification resulting in the relative errors for the estimated analyte concentrations being larger than the relative response errors. This error magnification can be represented by the condition number of the calibration matrix. Therefore, an attempt should be made to minimize the condition number of the calibration matrix with respect to the operating parameters affecting the chemical analysis. For UV-vis spectrophotometry there are several variables that can be varied which will influence the absorbtion spectrum. Varying the pH or the type of solvent can shift the absorbtion spectrum thereby altering the calibration matrix and correspondingly change the condition number of this matrix. Thus the analyst should not only be concerned about adjusting the pH or the solvent to obtain the maximum objective function but also the minimum condition number of the calibration matrix. The methodology and applicability of using error propagation, the condition number of the calibration matrix, for optimal multicomponent analysis using UV-vis spectrophotometry will be discussed.

272 MODERN ION CHROMATOGRAPHY. James R. Benson, Dexter J. Woo, Douglas MacBlane and Naotaka Kitagawa. Interaction Chemicals Inc., 1615 Plymouth Street, Mountain View, CA 94043 415-969-2400

In the last few years, numerous reports have appeared describing "single column" methods of ion chromatography that do not require use of suppression devices, but detection limits have not been as high as obtained using post-column eluent modification. We describe newly developed procedures for high sensitivity (ppb) determination of anions and cations.

When polymeric columns are coupled to ultraviolet detectors, any liquid chromatograph can determine inorganic anions at the ppb level. Using "vacancy chromatography", these columns permit analyses of a wide range of samples without specialized apparatus. Analyses of a variety of anion containing samples were performed using Interaction ION-100 and ION-110 anion columns. ION-200 and ION-210 cation chromatography columns were used for cation and transition metal determination. A Kratos model 773 variable wave length ultraviolet detector and a Wescan model 213A Conductivity detector were employed for detection.

Analyses can be performed for most ions in the low ppb range without sample concentration. Routine analyses at the ppm level is easily accomplished. For example, fluoride in drinking water was easily determined with only a 20 uL injection.

273 ADVANCES IN HIGH PERFORMANCE IC TRANSITION AND POST-TRANSITION METALS. Shawn Heberling, John Riviello, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

High performance Ion Chromatography with post column derivatization (IC-PCD) has been shown to be a versatile and powerful method for the multi-elemental determination of transition and post-transition metals. Recent advances in the chromatography and the post column chemistry have enhanced the versatility as well as the capabilities of this powerful method.

The chemistry of the post column system and how an understanding of it can be used in order to achieve flexible detection selectivity will be discussed. Applications involving plating baths, environmental monitoring and process streams will be presented.

Improvements in column technology have expanded the number of elements which can be simultaneously separated and determined. Multi-element determinations of greater than eight transition metal ions will be presented. Anionic separation of the lanthinide series metals will be shown.

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DETECTOR OPTIMIZATION FOR TRANSITION METAL ANALYSIS IN ION CHROMATOGRAPHY

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Two techniques may be used for the detection of transition metal cations in Ion Chromatography:

- -- direct detection by electrical conductivity.
- -- post column derivitization with spectrophotometric detection.

Both detection techniques can be coupled with cation exchange separation using complexing eluants.

The relative merits of each approach depends on the sensitivity required and on the complexity of the matrix. As a general rule, simplicity and ease of operation dictate direct conductivity detection whenever possible. Samples containing a high electrolyte concentration, or low level analysis may requires an analyte specific approach to detection such as post-column reaction for greater selectivity and sensitivity.

275 THE DETERMINATION OF TELLURIUM IN GEOLOGIC SAMPLES USING ION CHROMATOGRAPHY AND HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROSCOPY. D. B. Hatfield and S. A. Wilson, U.S. Geological Survey, Box 25046, DFC, MS 928, Denver, Colorado 80225.

The determination of tellurium in geologic samples is considered significant due to its promise as a pathfinder element for a variety of polymetallic ores. Tellurium is generally associated with other chalcophile elements such as arsenic, antimony, and selenium; and with silver and gold in epithermal precious metal deposits. A variety of analytical methods have been developed for the quantification of tellurium though their suitability for geologic analysis is limited due to their poor sensitivity or interference problems. Hydride generation atomic absorption spectroscopy has been used for the determination of tellurium analysis in nongeologic applications and has demonstrated excellent sensitivity. The principal limitation of hydride generation in geologic applications is the severe interference encountered from copper, arsenic or selenium. In an attempt to minimize these interference problems, a method has been developed for the determination of tellurium in geologic materials using a combination of hydride generation atomic absorption spectroscopy and ion chromatography (HGIC).

The method utilizes an acid decomposition of the sample followed by a preconcentration of the hydride elements (As, Se, and Te) using coprecipitation with iron or lanthanum hydroxide. The hydride elements are then separated from each other using a combination of anion and cation chromatography. The procedure is capable of quantifying tellurium at the 50 ppb level in sample. At the 100 ppb level, observed precision is ±5% rsd.

276 EXAMPLES OF TRACE ANALYSIS IN COMPLEX MATRICES. Steve Stone, Mark McKay, Shawn Heberling, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

Methods for the determination of trace levels of iodide in glacial acetic acid and the determination of trace Fe (III) in concentrated sulfuric acid have been developed.

Due to the nature of the matrix, previous attempts at quantifying iodide have not been possible. Separation is achieved by concentrating iodide on a Dionex Trace anion concentrator column. Reproducible separation and quantitation was obtained utilizing a standard addition calibration method. Dilution of the glacial acetic acid was not required, and the method was reproducible in the 10 ppb range.

Another application of importance is the determination of trace levels of metal contaminants in concentrated sulfuric acid. Detection limits were determined for Fe (III) by this method to be 0.1 ppm in the concentrated matrix. Linearity was excellent in the range of 0.2 to 0.8 ppm, utilizing a standard addition calibration method.

277 RECENT DEVELOPMENTS USING IC FOR PETROCHEMICAL PROCESS AND WASTEWATER ANALYSIS. R. Rubin, P. Lanier, and D. Eubanks, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

Current methods for ethanolamines, alkylamines, sulfur species, and phenols are time-consuming, labor-intensive, and plagued by interferences. A variety of apparatus is required and methods are frequently operator-dependent and difficult to automate. Simple Ion Chromatographic methods for those analytes have been developed.

Ethanalamines and other alkylamines are separated on a polystyrene-divinylbenzene resin with hexanesulfonic acid/water/acetonitrile eluants and detected by continuous, chemically-suppressed conductivity.

Sulfur speciation of sulfide, sulfite, sulfate, and thiosulfate can be detected in a single injection with a combination of amperometric and continuous, chemically suppressed conductivity following anion exchange separation.

Phenols are separated by polymer reverse-phase followed by pulsed amperometric or UV-Vis detection.

A single Ion Chromatograph can be automated to perform these analyses sequentially, which simplifies operation, minimizes operator dependence, and maximizes sample throughput.

278 DYNAMIC ION EXCHANGE CHROMATOGRAPHIC SEPARATION OF RARE EARTHS AND THORIUM IN SAMPLES FROM PROCESSING OF URANIUM ORES

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The energy program at CANMET is concerned with the development of new and improved solvent extraction (S.X.) processes to maximize the recovery of uranium and all valuable by-products such as thorium and the rare earths from low-grade and complex ores. Analytical methods for these metals have included X-ray fluorescence, multi-chemical separations, and classical column ion-exchange techniques. These méthods can require tedious sample preparation and can be time-consuming.
Recent studies (1) were carried out on development of dynamic ion exchangers for the rapid determination of lanthanides fission products. This paper describes the investigation to apply this technique to the determination of rare earths and thorium in samples from the various stages of S.X. processing circuits. The metals were separated on a reverse phase dynamically modified with 1-octanesulfonate and the eluted metal ions detected with a postcolumn reaction using Arsenazo III. Examples are given and the results compared with those obtained by XRF.
(1) C.H. Knight, R.M. Cassidy, B.M. Recoskie, and L.W. Green, Anal. Chem. 1984, 56, 474.

279 IMPROVEMENTS IN THE ANALYSIS OF CHROME PLATING BATHS.

Steve Stone, Mark McKay, Lani Angers, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

The improvement of the analysis of chrome plating solutions via ion chromatography is discussed in detail. The analysis of chrome plating solution is becoming increasingly more important as the cost for these baths continue to rise. This, as well as tightening regulations on the waste streams, necessitate that these baths perform better and longer. When the levels of SiF_6^{2-}, Cl^-, SO_4^{2-} and CrO_4^{2-} are not maintained, the plating process loses efficiency and the end products may not be to specification. The Ion Chromatograph utilizes a diluter to pretreat the samples as well as dilute them to specification. The system is controlle via the Auto Ion 300 which not only controls, but does the data reduction.

280 DETERMINATION OF ARSENIC(III) AND ARSENIC(V) IN ACIDIC FERRIC CHLORIDE OR FERRIC SULFATE LEACHING MEDIA BY ION CHROMATOGRAPHY.

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Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Ontario, Canada K1A 0G1.

Dissolved As(III) and As(V) are frequently formed during the ferric chloride or ferric sulphate leaching of base metal sulfide concentrates. The oxidation state is of concern both for the processing operations and the environmentally acceptable impoundment of the leach residues. Direct analysis of arsenic by ion chromatography (IC) gives unreliable results due to the formation of arsenic-bearing precipitates during dilution of the leaching sample. Column overloading is also encountered because of the overwhelming amounts of the anion from the ferric salt used for leaching An analytical method based on IC that involves a preseparation of Fe(III) by cationic exchange and evaporation of the HCl is quantitative and effectively eliminates the difficulties associated with the dilution method. IC with conductivity detection is used for the measurement of arsenate, and the effects of acidity, arsenic concentration solution composition, etc. on the method have been determined. Arsenite is determined by difference after oxidation of the initial solution by aqua regia. Simultaneous IC measurement of arsenate and arsenite using conductivity and electrochemical detections, respectively, has also been attempted and the results of the combined technique are are discussed.

281 ION-CHROMATOGRAPHIC DETERMINATION OF BROMIDE IN GROUNDWATER AND SEAWATER.

G. Schmuckler; Department of Chemistry, Technion - Israel Institute of Technology, Haifa 32 000, Israel. M. Magaritz and A. Nadler; Isotope Dept., The Weizmann Institute of Science, Rehovoth 76 100, Israel.

The intrusion of seawater into groundwater aquifers, wells, ect. is frequently indicated by Br$^-$ in the water supply based on these sources. In seawater the ratio between Cl$^-$ and Br$^-$ is as high as 296:1, and Br$^-$ determination requires a sensitive analytical method (below 1 ppm), which is undisturbed by the presence of large amounts of Cl$^-$.

In the present work IC was applied to this problem. To make the determination of Br$^-$ sensitive, two improvements were introduced:

1. Fumaric acid was used as eluant for improved Cl$^-$/Br$^-$ separation.
2. Potentiometric detection with silver indicator electrode was used for increased Br$^-$ sensitivity relative to Cl$^-$.

A Vydac anion-exchange column was used; the fumaric acid eluant concentration was 1.5X10^{-3} M and pH 3.15. Under these conditions the retention time of Cl$^-$ is 13.2 mins. and that of Br$^-$ is 16.8 mins. The method works well for concentration ranges as low as .5 - .1 ppm Br$^-$ in the presence of 35 - 50 ppm Cl$^-$. It was applied to seawater, diluted 1:500, giving a Cl$^-$ concentration of about 40ppm and a Br$^-$ concentration of about 0.13ppm. The Br$^-$ peak can be correctly measured, but no peak can be traced with a comductivity detector at this low Br$^-$ concentration.

282 DETERMINATION OF METAL CYANIDE COMPLEX BY ION CHROMATOGRAPHY.

John Salois, Joel Gannotti, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

The determination of metal cyanide complexes is of interest to a wide variety of analysts. In the plating industry, the determination of precious metal cyanide complexes of gold, silver, platinum and palladiums are necessary. Determination of other metal cyanide complexes, such as iron, nickel, copper, ect. are of interest in plating, metallurgy, mining, and environmental analysis.

The determination of metal cyanide complexes has suffered from the instability of many of these complexes in solutions, precluding the analysis of the intact complex. A new approach using a cyanide-based eluant system eliminates many of the problems typically encountered with a metal cyanide complex analysis.

This paper will detail the new methodology as well as discuss some of the unique environmental and toxicity problems associated with this type of eluant system.

283 REPORT ON ALBUQUERQUE EXPERIENCES IN USING ION CHROMATOGRAPHY FOR THE ANALYSIS OF WATER AND WASTES.

David C. Kersey and Emory W. Moore. Albuquerque Water Resources Laboratory, P.O. Box 1001, Albuquerque, New Mexico, 87103.

The Albuquerque Water Resources Laboratory began using ion chromatography in October, 1983 to explore the analysis of various water and waste samples for common anion and cations. Intent was to implement a regular analytical regimen with minimal research and development effort by using existing technology for these analyses. In addition, it was hoped that certain trace constituents (bromide, iodide, sulfide, cyanide) in ground water and waste water samples might prove to be acceptably determined by this method. To date the laboratory has had mixed successes in using techniques of ion chromatography for the intended purposes and the laboratory is now re-evaluating analytical techniques over all as well as our analytical goals for the method. No major research and development activity has been implemented using the instrument because of its heavy analytical load. Analytical problems encountered along with other related problems are discussed as they relate to analytical requirements. To date the laboratory has analyzed both waste water and surface water, as well as ground water for both anions and cations. Specific innovations to accomplish these determinations are discussed as well as specific difficulties with the principle methods. A list of needs to enhance the technique are also discussed.

284 ION CHROMATOGRAPHIC ANALYSIS OF GAS SAMPLES FROM VOLCANOES AND FUMAROLES.* R. M. Merrill, Sandia National Laboratories, Albuquerque, NM 87185.

Samples of gases collected from volcano and fumarole sites in Hawaii, California, and Mexico have been analyzed using ion chromatography. The samples were collected in sodium hydroxide solutions and transported to the laboratory for analysis. The samples have been analyzed for fluoride in the 30 to 600 micromole range, chloride from 6 to 2500 micromoles, sulfide from 10 to 5000 micromoles, and total sulfur (as the sulfate ion) in the range of 0.002 to 0.055 moles. A series of experiments was carried out in the laboratory to validate the sampling techniques and the results will be discussed. The analyses were done using commercially available columns and instrumentation and ions were detected using both conductivity and electrochemical devices.

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FACTORS AFFECTING THE PERFORMANCE OF SAMPLE PRECONCENTRATION FOR HIGH SENSITIVITY ANALYSIS

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Chromatographic sensitivity is most conveniently expressed as a minimum detectable quantity of sample. Unfortunately, however, analytical chemists are typically interested in the minimum detectable concentration in a particular matrix. The latter can often be improved by simply increasing the volume of sample taken. In practice, SCIC allows direct injections of samples as large as a milliliter or so without problems. Larger samples, however, are best handled by sample preconcentration or trace enrichment techniques.

A number of factors must be taken into account when "scaling up" sample injection by sample preconcentration:

-- concentrator cartridge capacity.
-- total ion concentration of the sample.
-- differences in concentration efficiency among ions.
-- sources of contamination.

Each of these factors will be discussed as a potential contribution to errors in quantitation.

286 AUTOMATIC TRACE ENRICHMENT METHOD UTILIZING SINGLE COLUMN ION CHROMATOGRAPHY. W.R. Jones, G. Harrison, and W.T. Robinson, Waters Chromatography Division, 34 Maple St., Milford, MA. 01757.

Ion chromatography has been used in the semiconductor and power industry to routinely analyze trace ionic impurities. The single column approach presented achieves parts per trillion sensitivity of anions and cations. This technique allows usage of various eluents to vary selectivity and sensitivity giving trace enrichment greater flexibility. Sample chromatograms from each industry will be shown.

287 PRE-COLUMN CONCENTRATION OF IONS, Tim Schlabach and Ron Majors, Varian Instrument Group, Walnut Creek Division, 2700 Mitchell Drive, Walnut Creek, CA 94598.

Quantitative determination of ions at the ppb level requires sample concentration to improve measurements. The analytical column can provide "on-column" concentration, but requires injection of large sample volumes (greater than 500$\mu\ell$) which causes massive "solvent" peaks. The preferred method is pre-column concentration. This can be accomplished with a separate column and solvent delivery system (off-line) or with a small column in the injection apparatus of an ion-chromatograph (on-line).

Disposable ion-exchange columns have proven to be useful for the concentration of ions in water samples. We have achieved about a 50-fold concentration using syringe-type columns containing about 1cc of a silica-based ion exchanger. Furthermore, the method is transferrable to "on-line" concentration using the same materials and methods, but on a smaller scale. The ion-exchange material (40mg) is packed into a series of cartridges that are first loaded with sample and then placed into a special injection apparatus (AASP) connected to an ion chromatograph. The sample ions are eluted from the cartridge onto the analytical column by the mobile phase. The cartridges are subjected to the full column head pressure during elution. Unlike column switching techniques which re-use the same concentrator column, the single-use cartridges exhibit no carry-over or sample matrix bleed.

We shall discuss the properties of ion-exchange materials for concentration of sample ions and solvents for rapid elution. The "on-line" method will be applied to the analysis of process water and rain water.

288 ADVANCES IN AUTOMATION: SAMPLE PRETREATMENT AND DELIVERY. Dennis Gillen, Shawn Heberling, Denise Eubanks, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

Ion Chromatography has matured to the point where automation is becoming increasingly more important and a standard part of the system. Data acquisition and instrument control is routine, improving the quality and precision of the data. With the addition of an Autosampler, sample throughput can be increased dramatically, further raising the efficiency of the lab.

Sample preparation and handling is becoming one of the major limitations to productivity. There are a number of standard sample handling steps that are involved with any method. Each method has its own set of steps. This could include dilution, concentration, extraction, filtration, neutralization, clean-up or separation. This paper will describe procedures that have been developed at Dionex to solve a number of problems associated with sample preparation and delivery unique to Ion Chromatography, but which are broadly applicable to other chromatographic techniques as well.

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A GENERAL ANALYTICAL PROCEDURE FOR THE DETERMINATION OF COMMON INORGANIC ANIONS BY SINGLE-COLUMN ION CHROMATOGRAPHY (SCIC)

T.H. Jupille, P.J. Barthel, and D.W. Togami
Wescan Instruments, Inc., 3018 Scott Blvd., Santa Clara, CA 95054

Early work on Ion Chromatography described an analytical procedure for common anions which have become a de facto standard: fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate. Most recently, a procedure for six of these ions (all the above except bromide) has been proposed by the EPA (Method 300.0).

Because SCIC allows a great deal of flexibility in eluant pH and composition, a large number of anion separations have been developed in which the elution order differs from that encountered in the "standard" chemical suppression IC method. Appropriate choice of eluant ion, pH, and concentration, however, allows an analysis for the seven standard anions with the same elution order observed in EPA method 300.0

290 ON-LINE ANALYSIS, A PROGRESS REPORT. L. Angers, E. Johnson, E. Gavin, K. Haak, and G. Lee, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

The analytical capabilities of the 8000 on-line analyzer were initially focused on monitoring high purity deionized water (DI) for trace anions (primarily chloride and sulfate) and monovalent cations (primarily sodium and ammonium) providing necessary information for monitoring performance of the DI plant as well as the levels of corrosives/additives/contaminants circulating throughout the plant system.

Since that time, the 8000's applications have expanded to include transition metals (primarily iron, nickel, and copper), soluble silica, and hydrazine in DI water in order to provide the plant operator with as much information as possible on the plant water quality. On-line ion chromatography has also been successful in monitoring more complex matrices including high levels of a catalyst (transition metals and anions) in an acid stream providing the necessary information for optimization of the production processes.

This presentation will briefly discuss some of the specific strategies for developing methods for continuous operation as well as show preliminary results from a number of different test locations.

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ELIMINATION OF MATRIX INTERFERENCES IN INDIRECT PHOTOMETRIC CHROMATOGRAPHY. Dennis Jenke, David Brown and Robert Payton, Travenol Laboratories, 6301 Lincoln Avenue., Morton Grove, IL 60053.

The removal of UV absorbing matrix interferences in the title technique can be accomplished either by exploiting differences in the UV spectral profiles of the interferant and the mobile phase or by using post column, fiber suppressor eluant modification. In the former case, the presence of the interferant is masked spectroscopically while in the latter case the suppressor chemistry is such that the interferant is removed from the mobile phase prior to detection. The utilizaation of both techniques is demonstrated by the removal of amino acid type interferants from pharmaceutical type matrices.

292 SIMULTANEOUS DETERMINATION OF ANIONS AND CATIONS VIA INDIRECT ION CHROMATOGRAPHY. J.M. Riviello, C.A. Pohl, and M.S. Taylor, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

Of the single column ion analysis methods currently practiced, indirect Ion Chromatography (I^2C) is one of the most novel. One of the unique capabilities of I^2C is the simultaneous determination of anions and cations. For simultaneous anion and cation determination, the displacing anion and cation are light-absorbing. When a transparent solute anion or cation is eluted, a trough in the baseline absorbance results which corresponds to the absence of the light-absorbing displacing ions.

Simultaneous anion and cation determinations via I^2C have been accomplished using a variety of low capacity ion exchange columns. Eluant concentration, pH, sample concentration, and the monitoring wavelength(s) will be discussed in terms of chromatographic and detector selectivity. A discussion of single and dual wavelength detection will be presented. A comparison of indirect ion detection and conductivity detection will be made for simultaneous anion and cation determinations.

Small, H.; Miller, T.E. Anal. Chem., 1982, 54, 462.

293 ION CHROMATOGRAPHY OF SOME PHOSPHONIC-PHOSPHINIC ACIDS, E. L. Grove, IIT Research Institute, 10 West 35th Street, Chicago, Illinois 60616

Some ion-chromatography properties for sixteen phosphonic and phosphinic acids and halides were studied. Alkyl substituents on the phosphorus atom provided some unexpected influences on retention time, relative response and shape of the elution peak. Less basic eluents yielded longer retention times and smaller relative responses. The elution peaks for methylfluophosphonic acid, fluoride, isopropylmethylphosphinic and isopropylethylphosphinic acids are not resolved with 0.003M HCO_3^- - 0.0024M $CO_3^{=}$ eluent and type AS-3 column. More weakly basic eluents were studied to resolve such peaks for quantitative measurements.

294 INDIRECT DETERMINATION OF HYDROGEN PEROXIDE BY ION CHROMATOGRAPHY. Dennis Jenke, Travenol Laboratories, 6301 Lincoln Avenue., Morton Grove, IL 60053.

Hydrogen peroxide is determined indirectly in organic samples after preliminary reaction with the bisulfite ion by quantitating post reaction changes in bisulfite and sulfate concentrations via ion chromatography. Sensitivity, precision and total analysis time of the assay can be controlled through the use of various chromatographic methodologies. While suppressed methods exhibit a superior sensitivity in water matrices, the presence of organic related interferants dictates the use of indirect photometric detection. Detections limits range from 10 ppb as H_2O_2 for the suppressed system in a water matrix to 300 ppb for the indirect photometric method in the drug matrix. The latter technique can be used to characterize the rate of peroxide degradation in both the water and organic matrices.

295 FLUORESCENCE DETECTION WITH FLUOROGENIC ION INTERACTION REAGENTS IN TRANSITION METAL IC. P.K. Dasgupta and K. Saroka, Department Of Chemistry, Texas Tech University, Lubbock, TX. 79409-4206

Sulfoxine (oxine-5-sulfonic) acid is a unique fluorogenic complexing agent that functions as an anionic IIR for generation of cation exchange sites. Sulfoxine forms a wide variety of soluble fluorescent metal complexes with a number of transition metals. These properties were exploited for transition metal IC on different stationary phases.

DOI: https://doi.org/10.56902/RMCMR.1985.27.1

296 ION EXCHANGE RESIN PACKED ANNULAR DUAL MEMBRANE SUPPRESSORS IN IC.

P.K. Dasgupta and M. Mercurio-Cason, Department of Chemistry, Texas Tech University, Lubbock, TX. 79409-4260

A linear dual annular membrane suppressor is described. The inside of the inner membrane tube is packed with ion exchange resin beads. The space between the outer membrane and the external jacket tube, constructed of stainless steel, is also packed with ion exchange beads. The device is capable of operating under considerable back pressure and capable of exchanging high fluxes e.g., 0.1 M NaOH at 2 mL/min. Dead volume and band dispersion characteristics are addressed.

297 ION-CHROMATOGRAPHIC DATA REDUCTION USING A COMPUTER.

A.G. Hedley and H.E. Taylor, U.S. Geological Survey, Denver, Colorado

A previous paper[1] describes the automation of an ion chromatograph for the determination of anionic constituents in water. A computing integrator is used to collect, store, and reduce the acquired data. The limited memory of the computing integrator, and the inconvenience of audio-cassette magnetic tape used by the integrator for mass data storage, creates a need for a more powerful computer to reduce the acquired data.

This paper describes how the ion-chromatographic data stored by the computing integrator can be transferred to and reduced by a MINC-11[2] computer. The computer has a graphics video-display terminal by which the user interacts with the computer; the computer also has dual, 8-inch, floppy-disk drives for mass data storage. User-friendly, menu-driven, computer programs are available for rapidly and conveniently reducing ion-chromatographic data.

[1] Hedley, A.G., and Fishman, M.J., 1982, Automation of An Ion Chromatograph for Precipitation Analysis with Computerized Data Reduction: U.S. Geological Survey Water-Resuources Investigations 81-78, 33p.

[2] The use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

298 EVOLVING APPLICATIONS OF ION CHROMATOGRAPHY: ORGANICS, METALS, AND INORGANIC ANIONS.

J. Korpi, and G. Franklin, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

Ion Chromatography (IC), through continuing improvements in columns and detectors, is being applied to analyses of increasingly diverse types of ionic species. Use of pellicular ion exchange resins that can be readily synthesized to perform a specific separation has resulted in development of columns tailored to specific analyses. In addition to conductivity detection usually associated with IC, there have been new developments in post-column reaction and amperometric techniques. Conductivity has also become a more versatile technique through evolution of chemical suppression from columns to fibers to a new membrane that allows use of more concentrated eluants and greater convenience of use.

Organic compounds that are ionic or can be made so, are very amenable to analysis by IC, since columns and detectors that are suitable for analysis of inorganic ions can be easily adapted to organic ions.

Analysis of metals is another area where improvements in IC capabilities have been evident. New columns and detectors for analysis of transition metals will be described as well as a new method for single column analysis of alkali metals and alkali earths.

Application of IC for analysis of inorganic anions has progressed from chloride and sulfite to inclusion of arsenite and selenite as well.

299 IMPROVEMENTS IN SELECTIVITY AND SENSITIVITY VIA CHEMICAL SUPPRESSION.

R. Rocklin, C. Pohl, and E. Johnson, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

Sensitivity and selectivity are two important qualities of successful analytical techniques. Sensitivity is the ability to distinguish the signal from noise, which can be defined as random variations in the background level. Selectivity is the ability of the technique to distinguish the signal from systematic interferences. In ion chromatography, chemical suppression offers major improvements in both sensitivity and selectivity.

Changes in background conductivity are caused by changes in temperature, ionic strength, flow rate, pressure, and turbulence within the cell. Since the magnitude of the noise is directly dependent on the magnitude of the background conductivity, reductions in noise can only be obtained through attenuation. It is important to distinguish between attenuation and offset. Attenuation is the opposite of amplification, that is, a reduction in both the background level and in the magnitude of changes in the background level (noise). An offset has absolutely no effect on noise. "Electronic Suppression" is a term commonly used in single column ion chromatography. Since there is only an offset in the background without attenuation, the term is misleading. Without causing a corresponding attenuation in the signal, the background can only be reduced by selective chemical changes in the eluant.

300 NEW AMPEROMETRIC DETECTOR FOR SINGLE COLUMN ION CHROMATOGRAPHY.

P. Jandik, D. Cox, and W.T. Robinson, Waters Chromatography Div., Maple St., Milford, MA. 01757.

Application of the new amperometric detector for the determination of anions in different environmental and industrial samples will be described.

Using silver electrode as a working electrode cyanide, sulfide, thiosulfate, and thiocyanate were analyzed in soil, river waters as well as in mining process waters. Trace amounts of sulfite were measured in a variety of food samples.

The electrochemical detection method presented can also be successfully applied to the analysis of iodide in different pharmaceutical formulations.

301 ANALYSIS OF SOIL AND PLANT EXTRACTS.

Denise Eubanks, R.J. Joyce, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

To increase crop yield, essential nutrients for plant growth are monitored and replenished through land management programs. Until recently, agriculture has relied solely on wet chemical methods to determine these ionic constituents in soil as well as plant extracts. Steam distillation and reduction followed by colorimetric methods were used to determine such anions as nitrate and sulfate. These methods are complex and subject to many interferences.

Today, scientists in analytical, agronomy and soil labs are becoming more familiar with Ion Chromatography (IC) and its ability to provide such information with less interference and with higher throughput. IC can also be adapted to most of the extraction solutions and procedures currently in use and, in many cases, requires smaller sample amounts. This paper will present ion chromatographic procedures used for the determination of common anions (Cl^-, NO_3^-, HPO_4^{2-}, SO_4^{2-}) and cations (NH_4^+, K^+, Ca^{2+}, Mg^{2+}) in soil and plant extracts.

302 HETERO-ATOM MICROANALYSIS USING ION CHROMATOGRAPHY. G.T. Louthan, F. Block, and J. DeZwaan. The Upjohn Company, Kalamazoo, Michigan 4900.

Ion chromatography has become recognized as an excellent means of separating and quantitating common anions. Based on this, ion chromatography may be combined with the Schoniger combustion flask technique to determine the levels of heteroatoms in organic samples. This talk will describe the results obtained for heteroatom microanalysis (S, Cl, Br, and P) by ion chromatography on a wide range of samples submitted for routine elemental analysis. These results will be compared with results obtained with some classical procedures on the same samples and the relative merits of the techniques will be discussed.

303 NEW DEVELOPMENTS IN ORGANIC ANALYSIS. Jack Korpi, Claudia Lincoln, William Edwards, Leonard Henry, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

Ion Chromatography (IC), originally developed for analysis of inorganic ions, has expanded in scope to include organic ions as well.

This paper will discuss new developments in the analysis of organic acids, amino acids, polar amines and carbohydrates. Separation techniques employed include ion exchange, novel ion exclusion, mobile phase IC, and reversed phase. Detection by enhanced conductivity with a new membrane suppressor, post-column reaction, amperometric, and UV/Visible methods will be examined.

In particular, breakthroughs in analysis of organic and amino acids using optimized anion and cation exchange resins will be included.

304 DETERMINATION OF ALCOHOLAMINES AND SUBSTITUTED SACCHARIDES BY IC/EC. J.M. Frye and J.L. Buteyn, The Standard Oil Company (Ohio), 4440 Warrensville Center Road, Cleveland, Ohio 44128

Alcoholamines and substituted saccharides were determined by ion chromatographic separation with electrochemical detection in sodium hydroxide. Two different electrochemical detectors were explored: a gold anode with a pulsed applied potential, and a nickel oxide potentiostatic anode. Both were optimized for sensitive response to amine-substituted hydroxy compounds. The merits of each will be presented. Such detection was important in the development of a rapid separation method for glucose and glucosamine and for ethanolamine, diethanolamine, and methyldiethanolamine.

305 PERCENT LEVEL ANALYSIS OF COMPONENTS IN INDUSTRIAL LIQUORS: MIXED ACID ETCHANTS AND PICKLING LIQUORS. Roy Rocklin, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

Mixed acid etchants and pickling liquors are mixes of concentrated acids such as hydrochloric, hydrofluoric, nitric, sulfuric, phosphoric, and acetic. Mixed acid etchants are designed to selectively etch certain materials on semiconductor devices during their manufacture. Pickling liquors are used to passivate metals. The rate at which these reactions occur is dependent on the concentrations of the constituent acids in the mix. For this reason, it is necessary to accurately assay the concentrations of these acids. Traditionally, wet chemical methods have been used to perform these assays. In this presentation, results from both ion chromatographic and wet chemical analysis will be compared.

Wet chemical methods suffer from two problems. First, they are generally far more time-consuming than instrumental methods. Second, the interferences caused by the major components can interfere with the determination of the lower concentration species. As an instrumental method, ion chromatography offers speed of analysis, and as an analytical technique based on separation, freedom from interferences.

306 APPLICATION OF ION CHROMATOGRAPHY IN SOFT DRINK BEVERAGES. K. Giryluk, C. Kehoe, A. A. Khan, PepsiCo Research & Technical Center, 100 Stevens Avenue, Valhalla, New York, 10595.

In recent years, Ion Chromatography (IC) has become an important tool for monitoring anions, cations, and organic acids on a routine basis for a variety of ingredients commonly used in Pepsi-Cola products. One of the key ingredients of PepsiCo brand products is water. On an on-going basis, the chemist evaluates the composition of anions and cations in raw and treated water. The specifications for treated water are stringent to assure the high quality of the beverages. IC has replaced conventional EDTA titration for hardness, sodium, potassium, and the time-consuming colorimetric procedure for Cl-, NO_3, SO_4, and PO_4. The reproducibility of IC is between ±3 percent for most common anions and cations and is a rapid analysis. The IC unit is used to evaluate HFCS-55, sucrose, MIS, and juices. On a regular basis, chemists are evaluating levels of oxalic, citric, tartaric, and phosphoric acids in the laboratory. Finally, IC can be fully automated. The conventional cation analysis done by A.A. requires a chemist in attendance, while IC can be automated to handle 50 samples at a time. Current research for the evaluation of fruit juice quality using IC will also be discussed.

307 ANALYSIS OF FERMENTATION BROTHS. C.R. Lincoln, J. Korpi, and C. Pohl, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA. 94088-3603, 408/737-0700.

Rapid analysis of multiple components in complex fermentation media requires highly efficient and selective chromatographic columns coupled to sensitive and specific detectors. This paper describes the analysis of four classes of compounds important to fermentation processes: (1) amino acids; (2) carbohydrates; (3) organic acids; (4) inorganic ions.

Amino acids are separated on a unique pellicular cation exchange resin, which provides faster analyses and utilizes simpler instrumentation than previously possible. Detection is by post-column reaction to form either fluorescent or UV-absorbing derivatives.

Carbohydrates are separated by anion exchange chromatography and detected by highly sensitive and specific pulsed amperometry. Organic acids are resolved by an ion exclusion technique that separates them from mineral acids and allows for conductimetric detection. Inorganic components are analyzed using appropriate cation and anion exchange columns and either conductimetric or UV detection.

Examples will be shown of how information from all four analytical methods can be used to monitor existing fermentation processes, develop new processes, and determine the quality of raw materials.

308 THE ANALYSIS OF FREE ORGANIC ACID AS A DEGRADATION PRODUCT OF ITS SALT IN SUPPORT OF STABILITY STUDIES. T. Catalano, S. Dugar, and R. Faulstich, Searle Research and Development, Skokie, Illinois

Many pharmaceutical products are developed as the salts of their free acids. In many instances, the solid state degradation of the acid salts results in the formation of the free acid as a degradation product. Thus, the analysis of the free acid in the presence of its salt is essential to support solid state stability studies. Classical liquid chromatography (HPLC) procedures, with UV detection, are not suitable for this analysis. Analytical techniques such as IR, AA, and Ion Chromatography may be applicable to this type of analysis. This paper will discuss the use of Ion Chromatography with conductivity detection for the analysis of the free acid in the solid state degraded sample. The results obtained by this technique will be compared to other analytical techniques.

309 SAMPLE PREPARATION TECHNIQUES IN ION CHROMATOGRAPHY.* R. M. Merrill, Sandia National Laboratories, Albuquerque, NM 87185.

Routine ion chromatographic analyses can now be conducted on aqueous samples with relatively low total ionic strengths, and a wide variety of both cations and anions can be determined in less than one hour. The most difficult problems associated with ion chromatography often arise in the sample preparation steps. Over the past several years a variety of techniques to analyze concentrated brines, non-aqueous solutions, organic materials, glasses, and other insoluble inorganic materials using ion chromatography have been developed. Sample preparation techniques such as fusion with basic fluxes, solution matrix modification, solvent exchange, water extraction, and combustion have been used and the procedures will be discussed. The use of ion exchange resins to remove interfering ions without the addition of other ionic species will also be presented.

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The Analysis of Trace Elements in Metals and Semiconductors by Glow Discharge Mass Spectrometry P.J. Goddard, P.J. Turner, VG Isotopes Ltd., Ion Path, Road Three, Winsford, Cheshire CW7 3BX, United Kingdom and J. E. Cantle VG Instruments Inc., Inorganic Div., 300 Broad St., Stamford, CT 06901

Mass Spectrometry is increasingly finding important applications for elemental analysis. Glow Discharge Mass Spectrometry is a new analytical technique which shows some quite dramatic performance advantages over conventional methods. The source is similar to those seen on a variety of optical instruments but, by using mass spectrometric detection, improvements in both sensitivity and selectivity are observed and good operational characteristics are retained. Samples may be analyzed directly as solids and detection limits can be put conservatively at around 10ppba for most elements in most conducting or semiconducting samples. Results are reported on steels, high purity aluminum and semiconductors. Calibration curves are plotted for a range of elements in this matrices. Linearity is demonstrated down to ppb levels for U in aluminum. Reproducibility is good for a solids analytical technique and typically precision of a few percent can be obtained at ppm levels provided sample homogeneity is good. Even elements which are considered to be difficult to determine can be quantified. C, N, Si and P in steel samples are discussed.

311 "THERMAL DECOMPOSITION OF TRINITROTOLUENE: A COMBINED ELECTRON PARAMAGNETIC RESONANCE AND MASS SPECTROSCOPIC APPROACH", J.T. Swanson, J.L. Pflug, R.W. Carper and J.A. Zirrolli, Frank J. Seiler Research Laboratory, USAF Academy, CO 80840-6528.

The analysis of the thermal decomposition of trinitrotoluene (TNT) has been performed with many different techniques: differential scanning calorimetry (DSC), gas chromatography (GC), infrared (IR) and mass spectroscopy (MS). These techniques have monitored either general properties of TNT or the final decomposition products. Our interest in this reaction is directed toward understanding the kinetics of the initial and intermediate products. Since thermal decomposition reactions are believed to proceed via free radical mechanisms, we have developed electron paramagnetic resonance (EPR) spectroscopic techniques to analyze these processes. TNT when heated in the neat liquid phase above 200°C produces a radical signal in the EPR. Isotopic labelling of TNT with deuterium and nitrogen - 15 indicate that this radical may be formed by the interaction of an initial benzyl radical with the nitro group of another TNT molecule. To aid in the identification of other intermediate products the thermal decomposition is quenched at appropriate times, the reaction mixture separated by ODS-HPLC and products analyzed by mass spectrometry. Initial identification attempts using electron ionization direct insertion probe or gas chromatography - mass spectrometry were unsuccessful, perhaps due to non-volatility or thermal lability of the intermediate products. Subsequently chemical ionization, in both positive and negative ion modes, was used. The identities and kinetics of these intermediates have been examined to define the decomposition mechanism of TNT.

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RECENT FLOWING AFTERGLOW STUDIES OF ORGANOSILICON COMPOUNDS
R. Damrauer, C.H. DePuy, and V.M. Bierbaum, Chemistry
Departments, University of Colorado at Denver and Boulder,
1100 14th Street, Denver, Colorado 80202

In previous work we have demonstrated that organosilicon compounds undergo a variety of interesting reactions. In particular, we have been interested in the formation of pentacoordinate silicon anions, determinations of the acidity of weakly acidic hydrocarbons, and the anionic reactions of reactive organosilicon intermediates. We will discuss in this paper our most recent activities in these areas.

313 STRUCTURAL DETERMINATION OF COMPLEX CARBOHYDRATES BY MASS SPECTROMETRY. Michael McNeil, Alan G. Darvill, Peter Albersheim, James M. Lau, Thomas T. Stevenson and William S. York. Dept. of Chemistry, Campus Box 215, University of Colorado, Boulder, CO 80309, and Anne Dell, Dept. of Biochemistry, Imperial College of Science and Technology, London SW7, Great Britain.

Complex carbohydrates have many biological functions. These functions include being major structural components of bacterial and plant cell walls; being antigenic determinants; being recognition factors in cell/cell, glycoprotein/cell, and microbial/cell interactions; and being regulatory molecules. Determining the complete structure of a complex carbohydrate requires technically sophisticated procedures. Methods for determining the structures of complex carbohydrates based on l.c.-m.s., g.c.-m.s., f.a.b.-m.s., and n.m.r. will be presented. Application of the methods to structurally characterize Rhizobium and plant cell wall polysaccharides will be discussed.

ION TRAP DETECTOR^{TM}(ITD^{TM}): A NEW APPROACH TO ENVIRONMENTAL SCREENI

Frank LeMunyon
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314 The development of advanced techniques for the determination of target compounds within a biological or environmental matrix continues to be of high interest in the analytical community. Today, the complexity of many sample matrices presented to the analytical laboratory often exceeds the selectivity of standard analytical procedures and requires extensive clean-up schemes. High resolution capillary column gas chromatography (GC) with conventional GC detection is often not sufficient to routinely characterize environmental samples which may contain unusual industrial products or by-products,or their photolysis or metabolic products. For these analytical problems, mass spectrometric(MS)detection has become an established technique, providing the required qualitative information as well as quantitative accuracy. The introduction of the ITD, a small scale MS detector for capillary column GC, has significantly broadened the scope of many analytical laboratories.

The technique of capillary column GC/MS with an Ion Trap Detector(ITD) has been investigated for environmental applications,highlighting the powerful qualitative and quantitative ability provided by this analytical system. The instrumental theory and operation of the ITD, using its advanced data system, will be discussed. Many examples of the trace-level sensitivity and interference-free quantitation made possible with the ITD will be shown.

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Residual Gas Analysis of TO-5 Relays Jim Davis, Hewlett Packard, P. O. Box 2197, Colorado Springs, CO 80901-2197

One of several customers of the Materials Analysis and Applications Lab in the Hewlett Packard Colorado Springs Division is Cathode Ray Tube Manufacturing. Because of this customer, the Lab has developed an RGA system with software to analyze the residual gases in the CRT production operation. When we were asked to help one of our other Divisions with a problem involving the failure of some new designed relays, we easily modified our existing equipment to analyze the fill gas in the TO-5 envelope. The analysis was performed on three different groups of Relays after modifications completed by the Relay vendor. The handling of the data was optimized by using existing hardware and software within access of the Lab. This included the HP3000 Computer, HP150 Personel Computer with Lotus 123, and an HP9825 Computer. In this paper I will describe the procedure for preparing the sample, collecting the data, manipulating the data, and transmitting the data to a customer over electronic mail.

316 PERSPECTIVES OF MASS SPECTROMETRY IN CANCER RESEARCH AND THERAPY.

John Roboz, Dept. Neoplastic Diseases,
Mount Sinai School of Medicine, New York, NY, 10029.

The use of modern mass spectrometric techniques will be reviewed with respect to applications in cancer research and therapy. Emphasis will be on methodological approaches to obtain profiles of groups of structurally or metabolically related compounds, to identify unknowns, to confirm the identity of expected constituents, and to quantify selected compounds in complex biological matrices. The role of analytical performance measures, including sensitivity, specificity, and sample preparation requirements will be discussed. Realized and potential applications will be illustrated in the areas of carcinogenesis, environmental toxicology, pharmacokinetics, drug metabolism and toxicity, of antineoplastic agents, cancer biomarkers, and the diagnosis of infections in immunosuppressed patients.

317 QUANTITATION OF METHYLMALONIC ACID AND OTHER DICARBOXYLIC ACIDS IN NORMAL SERUM AND URINE USING CAPILLARY GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Paul D. Marcell, Sally P. Stabler, Elaine R. Podell and Robert H. Allen UCHSC, Denver, CO 80262

Urinary excretion of methylmalonic acid (MMA) is increased in most patients with cobalamin (Cbl) deficiency. This condition may be the result of inborn errors of metabolism involving the adenosylcobalamin-dependent enzyme, L-methylmalonyl-CoA mutase, or the synthesis of adenosylcobalamin. MMA has been quantitated previously in human urine using colorimetric techniques, thin layer chromatography, gas chromatography and gas chromatography-mass spectrometry. MMA has not been reliably quantitated in human serum with the exception of a few sera from patients with severe inborn errors of Cbl metabolism. We have developed a highly specific method for quantitating MMA in normal human serum. A stable isotope internal standard (trideuterated MMA, 200 ng) is added to 0.5 ml serum followed by ether extraction and anion exchange HPLC. The TBDMS derivatives of the acids are formed and analyzed by capillary gas chromatography-mass spectrometry using selected ion monitoring. The assay has a detection limit of 5 ng of MMA and is linear from 5 to 5000 ng. Values obtained with serum from 50 normal blood donors ranged from 18-78 ng/ml with a mean of 41 ng/ml and gave a normal range of 19-76 ng/ml (mean ± 2 S.D. after log normalization). Elevated values for serum MMA were found in 69 of 73 patients with clinically confirmed Cbl deficiency (mean 2880 ng/ml, range 55-23,000 ng/ml). The utilization of other internal standards makes it possible to quantitate succinic acid and would make it possible to quantitate malonic acid, dimethylmalonic, ethylmalonic acid, methylsuccinic acid, glutaric acid and other dicarboxylic acids.

318 COMPARISON OF SULFONAMIDE DERIVATIVES FOR CAPILLARY GC/MS ANALYSES AT 0.1 PPM RESIDUE LEVELS.

William J. Morris, Gene J. Nandrea, Hank R. Skinner, Food and Drug Administration, 500 U.S. Customhouse, Denver, Colorado 80202.

Problems with sulfonamide confirmations by capillary GC/MS as methyl derivatives at legal tolerance levels of 0.1 ppm in animal feeds and tissues have been caused by a combination of inadequate cleanup procedures and inadequate chromatographic separations. Recent publications in the Federal Register, have mandated the development of a mulrisulfonamide residue procedure providing GC/MS confirmations at tolerance levels for a) sulfanilamide, b) sulfpyridine, c) sulfathiazole, d) sulfamerazine, e) sulfamethazine, and f) sulfaquinoxaline. In our laboratory current regulatory work mandated including g) sulfadimethoxine. As a first step this paper discusses a series of derivatives that were prepared: h) monomethyl, i) methylacetyls, j) methyl-fluoroacetyls, k) methyltrimethylsilyl and l) methyl-t-butyldimethylsilyl. These were analyzed on different polarity 12m capillary columns such as DB-1, DB-5 and DB-1701. Examples of each will be shown and discussed with regards to optimum derivatization for chromatographic separation and low level detectability in sample matrices. Criteria for evaluating mass spectra for regulatory analyses will be discussed and used to eliminate several otherwise acceptable derivatives. Examples of the use of better derivatives to enhance current levels of detection will be discussed.

319 SYNTHESIS OF DEUTERIUM-LABELED ALPHA AND BETA ISOMERS OF 7OH-CHOLESTEROL: INCORPORATION OF DEUTERIUM FROM THE ALPHA ISOMER INTO NEWLY-SYNTHESIZED CHENODEOXYCHOLIC ACID (CDCA), BY A HUMAN HEPATOBLASTOMA CELL LINE, HEP G2. Antal Nemeth, Barbara M. Miles, Mark A. Polokoff, Paul V. Fennessey, Gregory T. Everson. Departments of Medicine and Pharmacology, University of Colorado Medical School, Denver, Colorado 80262.

The objectives of this study were 1) to synthesize and purify the alpha and beta isomers of deuterium-labeled 7OH-cholesterol, and 2) to measure the incorporation of deuterium from this compound into bile acid by Hep G2. Methods: The alpha and beta isomers of deuterium-labeled 7OH-cholesterol were synthesized by $LiAl(^2H)_4$ reduction of 7-ketocholesterol and purified by thin layer chromatography. Both isomers were monodeuterated and 99% pure by subsequent TLC, capillary gas chromatography, and mass spectrometry. These compounds were dissolved in ethanol and added to the culture media of dishes containing Hep G2. Media was removed after 4, 8, and 24 hours of incubation, CDCA and cholic acid (CA) were isolated, and the conversion of each isomer to CDCA or CA was determined by GC/MS using selected ion monitoring. Results: There was a linear increase in the M+1/M isotope ratio of CDCA after administration of 7β2H, 7αOH-cholesterol: t=0, IR=.3137; t=4h, IR=.3188; t=8h, IR=.3261; t=24h, IR=.3433. However, there was no change in the M+1/M IR of CA. In addition, the conversion to CDCA was stereospecific since the deuterium label from the beta isomer was not incorporated into either CDCA or CA. Conclusion: Hep G2 can synthesize CDCA but not CA from the known bile acid precursor, 7αOH-cholesterol. These data suggest that although Hep G2 can synthesize bile acid, it is specifically deficient in pathways of cholic acid synthesis.

320

THE ANALYSIS OF STABLE ISOTOPE ENRICHMENT OF TRACE METALS USING FAST ATOM BOMBARDMENT MASS SPECTROMETRY

Paula Peirce, K. Michael Hambidge, Leland Miller and Paul Fennessey, Departments of Pediatrics and Pharmacology, School of Medicine, University of Colorado Health Sciences Center, 4200 East Ninth Avenue, Box C232, Denver, CO 80262

The use of stable isotopes for the study of net and true absorption of trace metals in Pediatric populations has been a goal of many research groups. A major impediment to the use of stable isotopes has been the method of analysis. Both mass spectrometry and neutron activation have been successfully used but both methods have, to date, been labor intensive. We would like to report on the results obtained using a mass spectrometer as the isotope detector by means of surface ionization of the metal using a fast atom bombardment gun. The method has the following advantages. a) Direct ionization of the metal of interest at nanogram concentrations on the target. b) Direct measurement of all the stable isotopes of the metal of interest. c) A relatively long measurement lifetime (10 min.) which provides for multiple measurement on each isotope. d) Isotope ratios that are representative of the natural metal abundance (i.e. no additional carrier organics needed). Using this method $zinc^{67}$ and $zinc^{70}$ isotope enrichment have been measured for standard solutions and in a biochemical matrix (feces, milk). Data from both will be presented showing the precision and accuracy of this technique as well as its use in measuring absorptions.

321 MULTIPHOTON IONIZATION MASS SPECTROMETRY OF METAL CHELATES: APPLICATIONS TO TRACE METAL DETERMINATIONS. Jeffrey B. Morris and Murray V. Johnston, Department of Chemistry and CIRES, University of Colorado, Boulder, Colorado, 80309.

Multiphoton ionization is a technique where two or more ultraviolet or visible photons are absorbed by a molecule to cause ionization. This process is wavelength selective since only those molecules which absorb strongly at the excitation wavelength are efficiently ionized.

Fragmentation studies have been performed upon various metal chelates by directing a high power laser into the ionization region of a mass spectrometer. The primary factors which affect the specific fragmentation mechanisms of these compounds are (1) ligand binding energies and (2) steric factors which constrain the ligand to the vicinity of the metal center.

Applications of this method to trace metal ion determinations will be discussed.

322 QUANTITATION OF LYSO-PAF BY GC/S AND FAB/MS: PE Haroldsen, KL Clay, RC Murphy, Dept. of Pharmacology, Univ. of Colorado Med. Sch., Denver, CO 80262 Platelet activating factor (PAF) has been identified as 1-0-alkyl-2-acetyl-sn-glycero-3-phosphocholine and has been implicated as being an important mediator of inflammatory reactions. This substance is known to be synthesized by various cells including neutrophils, aveolar macrophages and endothelial cells. PAF is rapidly hydrolyzed by tissue and plasma esterases to form the inactive deacetylated lyso-PAF. Currently, there are only indirect ways to measure this phospholipid based upon reconverting the lyso compound into PAF by various chemical means followed by bioassay. We would like to report here a physical chemical method for the quantitative analysis of lyso-PAF based on GC/MS as well as FAB/MS using stable isotope dilution. The internal standards used were a mixture of C16 and C18 alkyl ether lyso PC molecular species synthesized from beef heart plasmalogen. This internal standard contained deuterium in the alkyl chain with the following atom% excess: d0(5.8%), d1(8.8%), d2 (48%), d3(26.2%), d4(7.8%), d5(1.7%), d6(1.1%) and d7(0.4%). The GC/MS assay is based on the HF hydrolysis of the phosphocholine head group to yield the ether monoglyceride. Condensation of this with acetone is then carried out to yield the 1-0-alkyl isopropylidine cyclic ether suitable for GC analysis. The ions monitored are the M-15 fragments in the unlabeled and labeled derivatives. The limit of detection is well below 1 ng injected onto the GC column and standard curves were found to be linear over the range tested up to 2 ug. For the FAB assay, the internal standard contains deuterium in the choline moiety made by methylation of lyso-PE using CD_3I. The unmodified lyso-PAF is well suited for direct analysis for FAB/MS. The limit of detection using glycerol matrix was found to be 20 ng using 500 ng internal standard. We have found that human PMNs contain 20-40 ng lyso-PAF (per 50 million cells) which is increased two-fold following challenge with A23187.

323 FRAGMENTATION MECHANISMS OF ORGANIC MOLECULES BY RESONANTLY ENHANCED MULTIPHOTON IONIZATION. S. W. Stiller and M. V. Johnston, Department of Chemistry, University of Colorado, Boulder, Colorado 80309.

The analytical application of electron impact fragmentation mechanisms to organic structure elucidation has been studied and utilized extensively by the scientific community. Multiphoton Ionization (MPI) is a highly selective and efficient ionization technique. MPI, when used with a time-of-flight mass spectrometer, is a useful tool that is only beginning to be studied by the analytical community. The utility of MPI fragmentation mechanisms has not previously been examined. In many cases, MPI and electron impact ionization can give qualitatively similar fragmentation patterns. Situations exist, however, where marked differences occur between electron impact and MPI. In this talk we will discuss these differences and how they relate to the unique aspects of energy deposition into the molecule by multiphoton absorption.

324 MULTIPLE-QUANTUM NMR IN DIPOLAR SOLIDS, M.G. Munowitz, J. Baum, A.N. Garroway,
and A. Pines, Dept. of Chemistry & Materials & Molecular Research Division,
Lawrence Berkeley Laboratory, Univ. of Calif., Berkeley, CA 94720.
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Multiple-quantum NMR methods are applied to extended coupling networks in solids, where direct dipole-dipole interactions can be used to create spin coherences of very high order (~100). The progressive development of these coherences over time depends upon the formation of multiple-spin correlations, as does the more familiar free induction decay. We have monitored the buildup of coherence experimentally, and accounted for the process theoretically with a statistical model in which the apparent size of the spin system is allowed to expand. Since multiple-quantum statistics are highly sensitive to the spatial arrangement of the nuclei, the time development of the spectra varies significantly depending on whether the spins are distributed regularly or randomly, or grouped into dilute isolated clusters. In addition, the order-specific response of multiple-quantum coherence to a resonance offset greatly facilitates spin imaging in protonated solids. We demonstrate the potential of multiple-quantum NMR as a tool for materials characterization in a series of experiments on model systems containing ^1H.

325 TIME DOMAIN ZERO FIELD NMR AND NQR, A. Bielecki, J. M. Millar, A. M. Thayer,
D. B. Zax, and A. Pines, Department of Chemistry and Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

Time domain zero field NMR and NQR spectra have been shown to offer higher resolution than comparable high field spectra for polycrystalline and amorphous samples. This advantage comes about because in the absence of applied fields, one may probe the effects of the local dipolar and quadrupolar interactions directly and not as perturbations on the Zeeman energy. We have continued in the development of zero field techniques, with emphasis in the areas of analysis of spectra of dipolar coupled multi-spin systems, and the employment of pulsed DC fields to coherently manipulate spin systems in zero field.

326 ECHO OF THE PAST, AND AN ECHO OF THE FUTURE. B.C. Gerstein, Ames Laboratory, Energy and Minerals Resources Research Institute and Department of Chemistry, Iowa State University, Ames, Iowa 50011.

The second order quadrupolar echo, demonstrating refocusing of the second order quadrupolar interaction in the 1/2 - 1/2 central transition of spin (2n +1)/2 quadrupolar nuclei, is presented. The applications of the use of re-focusing this interaction to high resolution solid state NMR of quadrupolar nuclei, while retaining the chemical shift interaction, are discussed.

327 SECOND GENERATION CP/MAS TECHNIQUES: APPLICATION AND EXPERIMENTAL ASPECTS. K.W. Zilm, and G.G. Webb, Department of Chemistry, Yale University, 225 Prospect Street, New Haven, CT 06511

The combination of multiple pulse homonuclear decoupling with CP/MAS makes a number of 2-D techniques feasible in solids. The increased resolution in carbon-13 and proton solid state MAS spectra made possible by 2-D techniques is especially useful for disentangling complex polymer and fossil fuel spectra. Unfortunately, the combination of CP/MAS and multiple pulse decoupling creates several experimental difficulties for the spectroscopist, especially when applied to rigid, strongly coupled systems. This paper will describe an experimental set-up and procedure that we have found to give reliable, reproducible results. Special attention will be given to carbon-13/proton heteronuclear shift correlations, J-resolved spectroscopy, and to the related problem of decoupling protons from carbon-13 in CP/MAS spectra. Model compound and fossil fuel examples will be presented. This work was supported by the Department of Energy under Grant Number DE-FG22-83PC60791.

328 NO ABSTRACT

329 NO ABSTRACT

330 VARIABLE TEMPERATURE C-13 CP/MAS STUDIES. J.F. Haw, R.A. Crook, S.W. Hanna, R.A. Crosby and G.C. Campbell, Department of Chemistry, Texas A&M University, College Station, Texas 77843.

Using an improved apparatus for cooling the spinner gas, we have been able to obtain MAS spectra at temperatures between 81 K and 330 K. The convenience of this apparatus allows us to operate for several hours with minimal attendance. We have used this capability to characterize solid-solid phase transitions, molecular motion in solid polymers, molecules adsorbed on catalytic surfaces and paramagnetic solids. We will illustrate our work with examples from each area and demonstrate that variable temperature MAS operation can be a routine experiment if approached properly.

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331 TRITIUM NMR - NEW PROSPECTS, PROBLEMS AND SOME RESULTS. Sun Un, G.S. Karczmar, F. Tang, H. Morimoto and M.P. Klein. Chemical Biodynamics Div. and National Tritium Labelling Facility, Lawrence Berkeley Lab., Univ. of Calif., Berkeley, CA 94720.

The Triton has $I=1/2$ and nuclear moment some 7% greater than that of the proton. Aside from some small and useful isotope shifts, the chemical shifts, on a ppm scale, are the same for both isotopes. There are numerous interesting potential applications of tritium as an NMR probe, especially in the biological arena. Developments and trials in this direction have been limited by the constant concern for the health hazards associated with the radioactive tritium especially at the concentrations presumed necessary for an NMR experiment, and for the availability of highly enriched specifically tritiated molecules. The establishment of the NTLF at LBL under the sponsorship of NIH has provided a setting where these concerns can be addressed. Using a dowager but highly versatile homebuilt 270 MHz spectrometer we routinely observe tritium spectra at 288 MHz. A typical S/N for a 200 uL 150 mCi sample is about 50:1 (normalized to one pulse). We employ capped teflon liners within screw-top 5 mm NMR tubes to insure containment of the sample should the tube break. This precaution degrades the spectral resolution and hence the sensitivity. We will present spectra obtained from a variety of samples that have provided some new insights into reaction mechanism and demonstrate a true biological experiment. Work supported by the U.S. Dept. of Energy under Contract DE-AC03-765-F00098 and NIH Grant RR01237.

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332 DEUTERIUM RELAXATION AND LINESHAPES IN CLATHRATES. Regitze R. Vold, Robert L. Vold, Michael S. Greenfield and Alan D. Ronemus. Department of Chemistry, University of California, San Diego, La Jolla, California 92093.

Small hydrocarbons trapped in channel clathrates are often free to rotate about an axis parallel to the channel axis, while simultaneously undergoing a variety of more restricted internal rotations and librations. When such motions are slow, on the order of $10^4\ s^{-1}$ to $10^6\ s^{-1}$, it is possible to distinguish among different motional models on the basis of deuterium quadrupolar echo lineshapes. Faster processes contribute to spin lattice relaxation and if single crystal samples can be obtained, recently developed methods for determining individual spectral densities of motion can be applied in conjunction with sample rotation experiments to provide information about details of the motion. Illustrative data will be presented and discussed for single crystal samples of perdeuterated nonadecane in urea and for perdeuterated biphenyl in β-cyclodextrin. In both these systems the motion is fast at room temperature, but is effectively frozen out at ca. 100 K.

333 DNP-HRNMR INSTRUMENTATION: A QUASI-OPTICAL APPROACH. C.S. Yannoni, R.D Kendrick, IBM Research Laboratory, San Jose, California 95193, and D. Singel, Chemistry Department, Harvard University, 12 Oxford Street, Cambridge, MA 02138.

Dynamical Nuclear Polarization has been utilized in NMR spectroscopy to elucidate the magnitude and dynamics of electron-nucleus interactions, as well as to enhance markedly the amplitude of NMR signals.

In order to prove fruitful in such applications, an apparatus which allows for significant DNP without grossly sacrificing NMR sensitivity is necessary. The microwave apparatus itself should additionally be uncomplicated in its application and be able to perform, at least moderately well, as a spectrometer for locating the electron spin resonance.

We will discuss the considerations and the compromises which, in our experience, enter into the development of a DNP spectrometer useful for high resolution NMR.

Our design incorporates a tuneable, spherical mirror, Fabry-Perot resonator for the microwave irradiation.

The use of this resonator compels only modest alterations in NMR probe design. The DNP experiement itself does necessitate at least a 1 percent tuning range in decoupling, locking, etc. We have, furthermore, incorporated multinuclear capability into the NMR spectrometer and probe.

334 NO ABSTRACT

335 NO ABSTRACT

Solid State NMR of Surface Adsorbed Species: Results from Some Model Systems

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In our studies of H_2 and CO adsorbed on supported metal catalysts, we have found a number of solid state NMR techniques very useful. Broadline proton NMR, MAS, and static spin echo carbon-13 NMR and zero field NMR have helped us in understanding binding of these small molecules to surfaces. A number of model compounds have been especially helpful in understanding what to expect from surface adsorbed species. For CO, we have studied several platinum carbonyl complexes as models for CO adsorbed on Pt. An especially interesting complex that we have studied for H_2 adsorption is $(PCy_3)2(CO)_3W$-H_2. This complex reversibly binds molecular hydrogen as a ligand. Results on the system and related catalysts will be discussed in terms of the geometries and electronic stucture of the surface species. In addition, we will descrie an MAS probe and rotor system that routinely spins samples in evacuated 7mm glass ampules up to 3.5 KHz.

337 STUDY OF DYNAMICS OF SMALL MOLECULES SORBED BY ZEOLITES

R. R. Eckman, Exxon Chemical Company, 5200 Bayway Drive, Baytown, Texas 77520 and A. J. Vega, Central Research, E. I. DuPont de Nemours, Wilmington, DE 19898

An important application of solid state NMR has been the study of molecular motion and dynamics. In solids or other systems where motion is restricted, the NMR resonance lines are broad due to interactions of the nuclei with local fields. The lineshapes observed are directly related to the motion or reorientation of molecules or groups within molecules. In this work, solid state deuterium NMR has been used for the first time to probe the dynamics of organic molecules adsorbed within the internal channels of a zeolite molecular sieve. In zeolites and other microporous solids, the organic adsorbate can have highly restricted reorientational motion and slow translational diffusion. Deuterium NMR offers new and direct information on the dynamics of organic molecules within zeolitic materials. These results provide direct spectroscopic evidence of the molecular sieve effect. This can shed light on size and shape phenomena observed in heterogeneous catalysis and other applications. For instance, a preferred diffusion of p-xylene in the straight channels of ZSM-5 has been found. Also, information can be obtained about surface and intermolecular interactions, adsorption phenomena, and exchange and diffusion dynamics.

338 SOLID-STATE OXYGEN-17 NMR STUDIES OF ZEOLITES

Hye Kyung C. Timken, Gary L. Turner, Eric Oldfield, School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, Illinois 61801, L. B. Welsh and Jeane-Pierre Gilson, Signal UOP Research Center, 50 UOP Plaza, Des Plaines, Illinois 60016-6187.

Oxygen-17 enriched zeolites were prepared and studied by solid state ^{17}O NMR to determine zeolitic structure and condition information obtainable by ^{17}O NMR techniques. As-synthesized, dealuminated and ion-exchanged zeolites were studied with various degrees of hydration. Static, magic-angle and variable-angle sample-spinning (MASS and VASS) ^{17}O NMR spectra at 8.45 and 11.8 Tesla were obtained on the zeolites. In all cases the ^{17}O NMR lineshapes were dominated by the effects of quadrupole interactions. For faujasites, the chemically distinct Si-^{17}O-Si and Si-^{17}O-Al configurations were resolved, and spectral simulations yield values of the ^{17}O quadrupole coupling constant, asymmetry parameter, and the isotropic chemical shift. The dependence of these ^{17}O NMR parameters on the ionic nature of the T-O-T bond will be discussed. This work was supported by DOE grant 83PC60779.

339 NO ABSTRACT

340 NO ABSTRACT

341 THE TWO-DIMENSIONAL J-CORRELATED AND NOE-CORRELATED PROTON NMR SPECTROSCOPY OF POLY (METHYL METHACRYLATE). R.C. Schilling, F.A. Bovey, and S.A. Kozlowski, AT&T Bell Laboratories, Murray Hill, NJ 07974, and M.D. Bruch, E.I. du Pont de Nemours and Co., Inc., Experimental Station, Wilmington, DE 19898.

Two-dimensional (2D) NMR techniques have been applied extensively to biological macromolecules. However, only recently have these techniques been employed in the analyses of vinyl and related polymers. We have used the proton 2D J correlated and the nuclear Overhauser effect correlated (NOESY) experiments at 500 MHz in a detailed analysis of poly (methyl methacrylate). The 2D spectra permit unambiguous association of the nonequivalent methylene protons, which aids in the assignment of resonances of configurational sequences. Correlations of a α-methyl and methylene protons through the weak (1-2 Hz) four bond coupling are observed in the COSY spectra of the isotactic and atactic polymers. From the 2D data a consistent set of assignments for the methyl and methylene protons is obtained. The use of the 2D NMR techniques as probes in the determination of polymer microstructure will be discussed.

342 CORRELATION OF NMR MEASURED STRUCTURAL PARAMETERS WITH PHYSICAL AND ELECTRONIC PROPERTIES OF AMORPHOUS CARBON FILMS. S. Kaplan, F. Jansen, M. Machonkin, Xerox Webster Research Center, Webster, N.Y. 14580.

The structure and properties of thin amorphous carbon films deposited from the gas phase depend markedly upon the preparatory conditions. Solid state ^{13}C magic angle spinning NMR measurements of the sp^2 and sp^3 bonding sites, as well as proton NMR spin counting and C:H combustion analysis, have been applied to investigate the structure of a number of hydrogenated amorphous carbons prepared by both ion beam and dc and rf glow discharge techniques. Film hardness and density correlate with the extent of hydrogen incorporation, which is dependent upon the electron and ion energies present at the substrate during the deposition process. Optical bandgap, on the other hand, depends upon electronic states and is controlled by the fraction of tetrahedral (sp^3) vs graphitic (sp^2) bonding sites. It is shown that structural tradeoffs prevent the formation of so-called amorphous diamond, a material with simultaneous extreme hardness and wide optical bandgap.

343 SOLID-STATE NMR STUDIES OF ^{13}C-^{15}N CROSSLINKS.

J.R. Garbow, J. Schjaefer, E.O. Stejskal, and G.S. Jacob, Monsanto Company, St. Louis, MO 63167, and Karl L. Kramer, United States Department of Agriculture, Manhattan, KS 66502.

Carbon-nitrogen crosslinks provide structural stability in a variety of polymeric and biopolymeric systems. By its ability to detect quantitatively ^{13}C-^{15}N bonds, double-cross-polarization (DCP) NMR is ideally suited to the study of crosslinked materials. This talk will describe the use of cross-polarization magic-angle spinning NMR and DCP NMR to study the chemistry of exo-skelton (cuticle) hardening in tobacco hornworm (Manduca sexta), a process thought to involve the formation of carbon-nitrogen crosslinks.

Cuticle hardening is an essential function in the life cycle of many insects. The hardened cuticle seals moisture in and protects the insect from a variety of predators during development. Because of the cuticle's isolubility, the process of cuticle hardening has resisted characterization by traditional chemical means, which have required partial or complete degradation. By contrast, solid-state NMR permits the metabolism of ^{13}C- and/or ^{15}N-labeled amino acids to be examined directly in intact, lyophilized insect tissue. Our studies indicate that carbon-nitrogen crosslinking is indeed involved in the hardening process, with the ring nitrogens of histidine playing a central role. Correlation of the degree of crosslinking with the intensity of specific resonances in the ^{13}C spectra of the cuticle points to the involvement of particular aromatic carbons in the crosslinks to histidine.

344 APPLICATIONS OF DYNAMIC NUCLEAR POLARIZATION IN COAL RESEARCH

Robert A.Wind, Dept. of Applied Physics, Delft University of Technology.
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In this paper results are shown of ESR, ^{1}H NMR and ^{13}C NMR experiments on a series of 60 coal samples of different rank and origin. It is shown that for higher rank coals the application of Dynamic Nuclear Polarization (DNP) leads to a considerable reduction in measuring time of especially ^{13}C experiments, and opens the possibility to perform new experiments from which a more detailed information about the coal structure can be obtained. Next the use of various parameters which can be measured by means of MR as a means of coal characterization is discussed. It is shown that the proton Zeeman relaxation time can be used to determine the oxygen content, provided that the oxygen content is larger than 10%. Furthermore the ^{13}C aromaticity has been determined both from (DNP)-CP and (DNP)-CPMAS experiments. Systematic differences were found, and possible explanations of this phenomenon are given. Finally special experiments are shown from which the detected percentage of ^{13}C atoms can be obtained. It is found that in a number of coals only 50 to 60% of the aromatic carbon content is detected.

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345 FRACTIONATION AND MAGNETIC RESONANCE CHARACTERIZATION OF COAL-LIQUEFACTION RESIDUUM.

H. L. Retcofsky, R. F. Sprecher, M. B. Perry, R. P. Warzinski, and R. G. Lett, U. S. Department of Energy, Pittsburgh Energy Technology Center, P. O. Box 10940, Pittsburgh, PA 15236.

The Pittsburgh Energy Technology Center is actively involved in the separation and subsequent characterization of residuum from coal liquefaction. Using a novel method that employs fractional destraction with continuous supercritical fluid flow (R.P. Warzinski and J.A. Ruether, FUEL, 63, 1619, 1984), fractions are generated in a manner analogous to conventional distillation of lower boiling materials. Fractions are collected with respect to the temperature of a "hot finger" that is an integral part of the unit, with the more intractable material being collected at the lower temperature. Among the most useful analytical tools for characterizing the fractions are nuclear magnetic and electron spin resonance spectrometries. An investigation of destraction fractions from residuum from the Wilsonville Coal Liquefaction Facility showed increases in carbon aromaticity, number of unpaired spins per gram, and the average molecular weight as the temperature of the "hot finger" is reduced. Accompanying these changes are decreases in the ESR g value and the atomic H/C ratio. These results will be discussed in terms of changes in mean structural units and possible intermolecular interactions between functionality-enriched fractions.

346 INVESTIGATION OF THE FREE SWELLING BEHAVIOR OF COAL BY IR AND NRM. T. E. Hammond,
W. M. Ritchey, Research and Development, The Standard Oil Company,
4440 Warrensville Center Road, Cleveland, Ohio 44128.

Free swelling index measurements have been found to be useful for predicting the coking behavior of bituminous coals. In this study, coals were analyzed by NMR and IR, and it was demonstrated that the free swelling behavior appears to be dependent on the amount of organic oxygen functionalities. Both the ^{1}H and ^{13}C spin-lattice relaxation times can be correlated to free swelling index values. It was determined that the NMR T_1 values are mostly dependent on the oxygen content and not on the unpaired electron content in coals containing up to 85% carbon. Therefore, free swelling measurements also appear to be dependent on the level of oxygen functionalities. FT-IR examination of coals heated to 350°C shows that ester groups are formed in coals which have low free swelling index values. The ester groups are believed to originate from the reaction of phenolic hydroxyls and aromatic carboxylic acids. The ester groups are believed to be cross-linking sites which prevent fluidity and swelling as coals are heated. Higher levels of phenols and acids, therefore, would increase the chances for this reaction to occur and reduce the free swelling index values.

347 SPARK TESTING STEELS. F. Xavier Spiegel, Loyola College, Baltimore, MD 21210.

Spark testing has been used in the scrap metal industry for many years to identify and sort metals and alloys. A brief description of the equipment and methodology for conducting the spark test including information on the photographic technique for obtaining useful photographs of the generated spark patterns. Photographs and descriptions of the spark patterns are presented for selected stainless steels and tool steels.

348 AN EVALUATION OF HAMMETT RELATIONSHIPS DERIVED FROM INFRARED C=N STRETCHING DATA FOR AROMATIC SCHIFF BASES, J. J. Rafalko and E. W. Choe
Celanese Research Company, 86 Morris Ave. Summit, N.J. 07901

Infrared spectra of benzylidene aniline, p-nitrobenzylidene aniline p-N-dimethylaminobenzylidene aniline and their ^{15}N labelled azomethine analogs were obtained to assess the reliability of C=N stretching assignments and Hammett relationships based on these results. The isotopic data indicate that there is extensive mixing of internal coordinates in bands near 1600 cm^{-1}. Bands possessing the greatest C=N stretching character are not always readily distinguishable from aromatic ring breathing modes due to variations in relative intensities and band overlap. Problems related to using frequency and intensity data of highly coupled normal modes in Hammett correlations are discussed.

349NATURAL GOLD SOLUBILITY AND THE FORMATION OF CRYSTALLINE GOLD IN PLACERS.

By J. G. Crock, R. C. Severson, and B. M. McConnell, U.S. Geological Survey, Box 25046, DFC, MS 928, Denver, Colorado 80225.

Crystalline gold can sometimes occur in placer-type gold deposits. A placer deposit is an accumulation of a clastic geological material by mechanical means, such as stream transport and deposition. Sharp projections of a delicate crystal of gold should not survive this transport and concentration process.

To test the hypothesis that the crystalline gold was formed in place, two gold placer operations and a regional background area in Alaska were examined. At these sites, soil profiles, native vegetation, and outcropping rocks were sampled. At one sampling site, the soil was panned and yielded crystalline gold as well as with the more common rounded nuggets.

The soils were analyzed for a variety of total constituents including major elements, trace elements, total carbon, and total sulfur. Several soil extractions were also analyzed. The plants and rocks were analyzed for their total major elements and select traces. Dissolved gold in the extracted soil solutions range from <0.5 µg/L to 15 µg/L in solution. This concentration represents a gold enrichment of as much as 10^4 in soil solution relative to an average river water concentration of 0.002 µg/L gold. This indicates that gold is being taken into solution in the soil. An explanation of this solubility and the presence of gold crystals and nuggets will be offered based on the correlation between the extraction and total elemental concentrations of the soils and plants.

350 AN ANALYTICAL CHEMICAL APPROACH TO PROBLEMS IN ANASAZI ARCHEOLOGY.

M. Schwindt, and D.M. Mehs, Fort Lewis College, Durango, CO 81301, and S.E.E. Schwindt, Edge of the Cedars Museum, Blanding, Utah 84511.

Traces of Anasazi civilization abound in the Four Corners region. One of the most often seen artifacts is broken pieces of pottery. Pot sherds are more than just pretty artifacts; they are surviving pieces of a material culture from which information about their age and place of manufacture may give crucial inferential evidence about the Anasazi culture itself. In an attempt to develop an analytical chemical method to supplement dates and proveniences for Anasazi pot sherds, a large number of samples was selected from the collection at Edge of the Cedars Museum, a Utah State park in Blanding, Utah. Small sections of these sherds were analyzed for trace concentrations of heavy metals using Atomic Absorption Spectroscopy. The results of the analyses provided a heavy metal profile for each sample which was compared to the profiles for the entire set of samples using cluster analysis. Similarities between the heavy metal profiles for sherds from similar sources were apparent. A discussion of the utility of this method of approaching problems of time and space will be presented.

351 A STREAM SURVEY IN WESTERN COLORADO.

S. Krening and D. Mehs, Fort Lewis College, Durango, CO 81301.

Mountain streams in western Colorado are often considered to pristine. However, this region has been the site of extensive mining activity, and the present growing population centers offer the potential for anthropogenic degradation of water quality. To gain an insight into the present character of western Colorado streams, a survey was conducted in late 1984. Water samples were collected and analyzed for pH, and a number of Group I, Group II, and heavy metals. The streams were than compared to each other on the basis of their analytical profiles using cluster analysis. Correlations between the analytical profiles and the stream environment will be discussed.

352 A POWERFUL KJELDAHL NITROGEN METHOD USING PEROXYMONOSULFURIC ACID

by Clifford C. Hach, Scott V. Brayton, and Alan B. Kopelove
Hach Technical Center, Hach Company, Loveland, Colorado 80539

A method for the determination of Kjeldahl nitrogen uses peroxymonosulfuric acid (Caro's acid) as a strong oxidant for rapid sample decomposition without added salts or metal catalysts. Peroxymonosulfuric acid is formed in a hydrogen peroxide-sulfuric acid mixture, and flows at 2 mL/min into a sample carbonized in concentrated sulfuric acid. The peroxy method obtains full recovery of nitrogen from nicotinic acid in 17.5 minutes. Most amino acids are digested in less than 10 minutes. Decomposition occurs about 10 times faster in the peroxy method than with the standard AOAC method. The digestion is followed by rapid colorimetric determination by an improved Nesslerization. A Digestion Index rates the difficulty of digestion of compounds, and enables the digestion time and reagent to be minimized. Results with this method are accurate, fast, and comparable to standard Kjeldahl methods. The digest is not contaminated by salts or metal catalysts, and can be further analyzed for other elements.

353 CONTAMINATION OF A SURFICIAL AQUIFER BY POLYCHLORINATED DIBENZO-P-DIOXINS.

W. E. Pereira and C. E. Rostad. U.S. Geological Survey, Box 25046, Mail Stop 407, Federal Center, Denver, Colorado 80225.

Contamination of ground water in industrialized areas of the United States is rapidly becoming a national problem. Many toxic organic compounds have been identified in ground water, and relatively few studies concerning the fate and movement of these compounds in subsurface environments have been reported. Polychlorinated dibenzo-p-dioxins (PCDD) belong to a class of hazardous organic compounds that are of environmental concern. Fate and movement of dioxins in subsurface environments are poorly understood due to difficulties encountered in the analytical determination of trace quantities of these compounds in complex matrices, such as those found in environmental samples.

A geochemical study was initiated to understand better the fate and movement of PCDD in a sand and gravel aquifer, contaminated by wood-treatment wastes containing creosote and pentachlorophenol. Samples of ground water, pond sludge, and porous media from the unsaturated and saturated zones were collected and analyzed for chlorinated dioxins by capillary gas chromatography-tandem mass spectrometry. These samples were found to contain isomers of hexachlorodibenzo-p-dioxin (HXCDD), heptachlorodibenzo-p-dioxin (HPCDD), and octachlorodibenzo-p-dioxin (OCDD). This study clearly demonstrated that the PCDD were mobile in the subsurface, and are found at considerable distances from the source of contamination. Concentrations of chlorinated dioxins in ground water were several orders of magnitude less than in porous-media samples. Ratios of the various isomers remained relatively constant in the most highly contaminated areas. In less-contaminated areas, isomer ratios changed dramatically; at certain locations, one HXCDD isomer predominated. Abiotic or biological processes may explain the differences in isomer-distribution patterns.

354 USE OF WIDE BORE CAPILLARY COLUMNS IN GAS CHROMATOGRAPHS DESIGNED FOR PACKED COLUMNS

James Brown and Paul Silvis, Supelco, Inc., Supelco Park, Bellefont, PA 16823-0048

Wide bore (0.75mm ID), wall coated open tubular capillary columns have the large sample capacity of packed columns and the great efficiency of 0.20 - 0.25mm ID capillary columns. Wide bore capillary columns can be used in packed column gas chromatographs, with sample injectors and carrier gas flow regulators designed for packed columns. Specially designed but simple hardware kits enable an analyst to quickly interconvert the injector and detector connections of a packed column gas chromatograph for installing a 0.75mm ID column or a packed column. A 0.75mm ID column can also be used in instruments designed for capillary columns. In a capillary column system, 0.75mm ID columns are compatible with split, splitless, and direct injection techniques. Typical analyses obtained from 0.75mm ID capillary columns in packed column systems will be discussed, and the conversion kits will be described.

355 ENERGY TRANSPORT AND ANALYTE EXCITATION IN THE ICP.

Gary M. Hieftje, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

Despite its many strengths, the ICP still suffers from interferences, particularly those caused by easily ionized elements (EIE). Interestingly, EIE interferences appear, although in somewhat different form, in both emission and mass spectrometric measurements. It is important, therefore, to detail the underlying cause of such problems. In this presentation, methods for measuring energy transport and analyte excitation in the ICP will be described and the observations used in an attempt to explain how EIE effects are generated.

356 THE ANALYSIS OF GEOLOGIC MATERIALS FOR SELECTED VOLATILE TRACE ELEMENTS BY SOLID SAMPLE ICP-OPTICAL EMISSION SPECTROGRAPHY.

D.E. Detra and J.A. Domenico, U.S. Geological Survey, Denver Federal Center, Box 25046, MS 973, Denver, CO 80225.

Analytical parameters have been established for the analysis of geologic materials for As, Au, Bi, Cd, Hg, Pb, Sb, Te, and Tl by solid sample ICP-optical emission spectrography. Excitation is attained by inserting a preformed graphite electrode containing a minus-100-mesh rock, soils, and stream-sediment sample directly into the argon plasma and recording the spectra on photographic plates using a 3.4 Ebert mounted grating spectrograph. Analytical parameters were studied and optimized for maximum instrument sensitivity and for reduction or elimination of matrix effects and line interferences produced from the characteristically complex matrices of geologic materials.

Significant parameters for rapid simultaneous analyses are determined to allow for maximum line intensity and for sustaining the plasma while inserting and withdrawing the sample electrode. Parameters include torch design, electrode type, plate emulsion, carrier compound, and instrument operating conditions of forward R.F. power, argon gas flow rates, and optics.

357 ^{15}N-NMR INVESTIGATION OF HYDROXYLAMINE DERIVATIZED HUMIC SUBSTANCES.

K.A. Thorn, U.S. Geological Survey, Water Quality Laboratory, 5293 Ward Road, MS 407, Arvada, CO 80002; J.B. Arterburn and M.A. Mikita, Department of Chemistry, University of Colorado at Denver, Denver, CO 80202.

Humic substances comprise the most abundant form of organic carbon in soils and waters. In an effort to investigate the carbonyl functionality of humic substances, representative humic and fulvic acids were derivatized, using ^{15}N-labeled hydroxylamine. A series of model compounds representing a variety of carbonyl functionalities was similarly reacted. Subsequent ^{15}N-NMR analyses suggest hydroxamic-acid formation as the major reaction product with humic materials. Confirmatory evidence is provided by ^{13}C-NMR analyses. These results suggest lactones or esters as significant components of the structures of the humic materials examined.

358 EXPERIENCES WITH MS/MS AT THE TEXAS AIR CONTROL BOARD, James L. Lindgren, J. Maxine Jenks, Ph.D., Texas Air Control Board, 6330 Highway 290 East, Austin, Texas 78723.

Mass spectroscopy has become a routine tool for qualitative identification and quantitation of compounds, when combined with gas chromatography and a dedicated data system. The coupling of two mass spectrometers in series has introduced a rapid means of qualitatively screening complex matrices for specific compounds. MS/MS can allow the identification and quantification of trace amounts of compounds in matrices which would need further processing if other analytical instruments were used. Experiences of the Texas Air Control Board laboratory in applying MS/MS techniques to the analysis samples containing pesticides and organic chlorides will be presented. The benefits and speed of the MS/MS technique will be emphasized.

359 ION CHROMATOGRAPHY WITH POTENTIOMETRIC DETECTION USING A METALLIC COPPER ELECTRODE, P.R.Haddad, P.W.Alexander, Dept of Analytical Chemistry, University of NSW, Kensing-on 2033 NSW Australia; and M.Trojanowicz, Dept of Chemistry, University of Warsaw, Poland.

large variety of inorganic anions and cations can be detected with a metallic copper electrode after chromatographic separation. The following mechanisms of electrode response ay apply:

(a) direct sensitivity toward species which complex copper ions;
(b) vacancy detection of noncomplexing copper species when copper complexing agents are used as eluents;
(c) oxidation of metallic copper by solutes which are strong oxidants;
(d) reduction of copper ions at the electrode surface by solutes which are strong reductants.

These response mechanisms are discussed in detail. Direct detection of amino acids, organic acids, chloride, bromide, iodide, chlorate bromate and iodate is illustrated. Indirect detection is shown to be applicable to species such as nitrite, nitrate, acetate, formate, succinate, benzoate, alkaline earth ions and transition metal ions. Detection of ascorbic acid, dehydroascorbic acid, hydrazine and hydroxylamine is also illustrated.

In most cases the heights of the chromatographic peak is linearly related to the amount of injected solute, and this behavior is consistent with theoretical prediction of the electrode response. Generally, direct detection is the most sensitive mode, with detection limits typically falling in the sub nanomole range, compared to the indirect detection mode with which detection limits are usually in the sub micromole range.

The construction and operation of the detector will be discussed and samples given of its application to ion chromatography.

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Cover Photograph

Peak 1 near Dillon, Colorado

Photographed by Dawn Reed, Wheat Ridge, Colorado

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