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29th Rocky Mountain Conference

Abstract

Program and abstracts from the 29th annual meeting of the Rocky Mountain Conference, co-sponsored by the Rocky Mountain Section of the Society for Applied Spectroscopy and the Rocky Mountain Chromatography Discussion Group. Held in Denver, Colorado, August 2-6, 1987.

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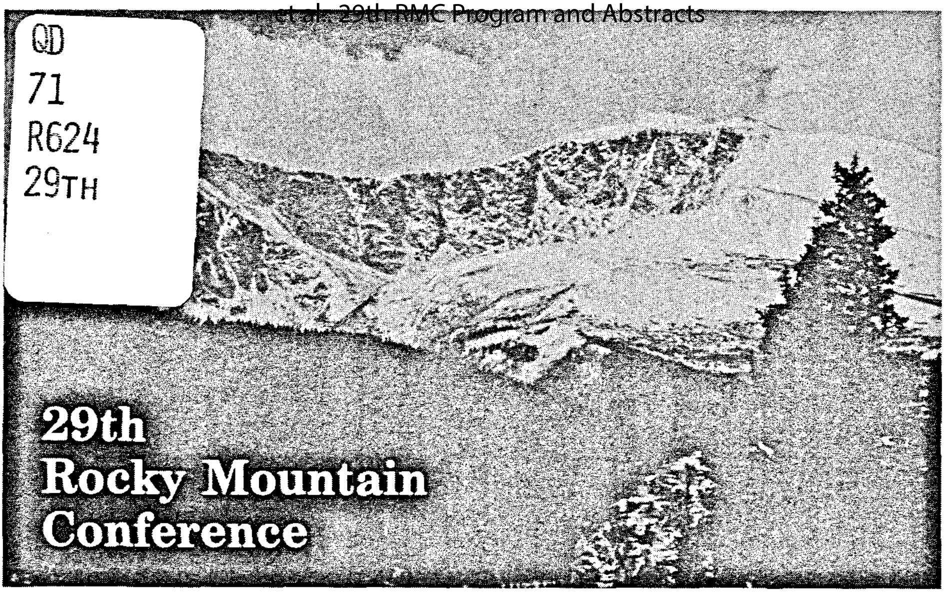

29th
Rocky Mountain Conference

PROGRAM
AND
ABSTRACTS

AUGUST 2-6, 1987

RADISSON HOTEL DENVER
1550 COURT PLACE
DENVER, COLORADO

SPONSORED BY

ROCKY MOUNTAIN SECTION
SOCIETY FOR
APPLIED SPECTROSCOPY

ROCKY MOUNTAIN
CHROMATOGRAPHY
DISCUSSION GROUP

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Map of Downtown Denver IBC

Symposia Schedule
(Page Number in Program)

	Monday August 3		Tuesday August 4		Wednesday August 5		Thursday August 6
	AM	PM	AM	PM	AM	PM	AM
Atomic Spectroscopy Spruce Room	8	8					
Chemiluminescence Gold Room					9	10	
Chromatography Colorado Room			10	11	12	12	
Computer Applications Cedar Room	13	13					
Environmental Chemistry Denver Room	14	15	15	16	16	17	
EPR Silver Room	18	18	19	20	21	22	24
General Posters Convention Lobby		37					
ICP/MS Cedar Room			25	26			
IR Cedar Room					26		
Ion Chromatography Gold Room	27	27	28	28			
Mass Spectrometry Cedar Room						29	
NMR Century Room	30	31	31	32	32	32	
Supercritical Fluid Chromatography Colorado Room	33	34					
Quality Assurance Spruce Room			35	35	36	36	

PROGRAM CHANGES
29th ROCKY MOUNTAIN CONFERENCE

Paper No.	Title/Changes
82	The Determination of Water Soluble Boron at Nine Irrigation Study Sites in the Western United States. Date and Time Changed to Wednesday 10:40 a.m. (Denver Room)
90	Total and Water Soluble Arsenic and Selenium Associated with Drainage Sediments Collected from Nine Irrigation Sites in the Western United States. Date and Time Changed to Tuesday 2:50 a.m. (Denver Room)
93	Halide Determination in Used Oils and Non-Aromatic Organics for Recycle or Disposal by Bomb Combustion and Ion Chromatography. Withdrawn
Addition	Three presentations have been added to the Wednesday Session of the NMR symposium. Titles, abstracts, and times are available in the NMR and EPR symposia.
268	Packed Capillary Column in Supercritical Fluid Chromatography. Withdrawn
Addition	Partition of N-Pentane Supercritical Fluid into 5% Phenyl Methyl Silicone Stationary Phase. Mustasa I. Selim, Joseph Strubinger. Poster. Author will be present 1:00-2:30 p.m. Wednesday.
Addition	Capillary Supercritical Fluid Chromatography with Electron Ionization Mass Spectrometry. Steven Zaugg, Stephan Deluca, G. U. Holzer, and Kent J. Voorhees, Colorado School of Mines. The application of capillary column supercritical fluid chromatography (SFC) for the separation of several high molecular weight compounds is described. Samples of intermediate complexity, such as polymers, biological lipids, solvent refined coals (SRC) and petroporphyrins were amenable to SFC analysis. THe development of a simple interface for SFC with EI/MS enabled PNA's and model compounds to be detected in the 1-5 ng range using total ion monitoring. Wednesday 2:25 p.m., Denver Room

290 Deterioration of Coquina by Acid Rain at Castillo De San Marcos National Monument.

Withdrawn

Addition Wear Indices by Atomic Absorption Spectroscopy - A new Approach to Spectroscopic Analysis of Wear Debris in Used Lubricating Oils. Graham M. Kimber, Queensland Institute of Technology, Neville A. Glover, Queensland Goverment Lab, Brisbane Australia.

General Poster

301 Solution of the ^{14}N-^{15}N Spectral Overlap Problem Using Pulse EPR.

Will be presented in EPR Poster Session A.

302 Recent EPR Studies of Indian Coals.

Will be presented in EPR Poster Session D.

303 A 9 GHz Loop-Gap ENDOR Spectrometer.

Will be presented in EPR Poster Session C.

304 An ESR Study of the Conformation of the Transient Germanium-Centered Tris- (2-Phenyl-2-Methlpropyl) Germyl Radical.

Will be presented in EPR Poster Session D.

Workshop Quality Control Functions in LIMS, Art Ambrose, Perkin-Elmer Corporation.

A limited attendance workshop with Perkin-Elmer's LIMS/2000. Register at the P-E booth the first day of the conference to reserve a space.

The workshop will demonstrate how a LIMS system can streamline laboratory operations and how new QC functions will insure the integrity of lab data. Historically, LIMS has kept track of samle status and all analytical data associated with the samles. With the latest revision of Perkin-Elmer's LIMS/2000, it is now possible to track data quality as well.

There will be an actual LIMS system at the workshop and the emphasis will be on realistic examples. Some of the standard functions that will be illustrated include: sample log in; test assignment; generation of worklists of varying complexity, including the automatic insertion of QC samles such as blanks, duplicates, and triplicates; spreadsheet-like results entry, with automatic QC and results, calculations, and multiple specification checking; tabular and graphic reports.

WELCOME

On behalf of the conference committee I am pleased to welcome you to the 29th Rocky Mountain Conference. Our meeting has grown into one of the most prominent summer analytical meetings in the United States. Two special events mark this year's conference: the 10th International Symposium on Electron Paramagnetic Resonance Spectroscopy and the Walton Symposium. The Rocky Mountain Conference EPR Symposium includes presentations by representatives of major research centers from around the world. Our symposium honoring Professor Harold Walton has attracted colleagues worldwide. We join with them in congratulating Professor Walton on his long and distinguished career as a researcher and teacher.

Thanks to all the exhibitors whose displays are as important to the scientific content of the conference as their booth fees are to our financial viability. I encourage all attendees to pay careful attention to the exhibits. You'll find exciting new products and ideas this year.

For our out-of-state visitors we welcome you to Denver and Colorado. We hope you have time to enjoy our many recreational and scenic opportunities and to plan more activities around your visit to the 30th Rocky Mountain Conference in 1988!

Sincerely,

Carol Eifling Gies
Conference Chair

FUTURE CONFERENCES

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

General Chair - Michael Reddy
U.S. Geological Survey
5293 Ward Road
Arvada, CO 80002
(303) 236-3617

31st Rocky Mountain Conference - July 30-August 3, 1989

32nd Rocky Mountain Conference - July 29-August 2, 1990

33rd Rocky Mountain Conference - July 28-August 1, 1991

REGISTRATION

Admission to all technical sessions and the exhibition is by a name badge for the 29th Rocky Mountain Conference. Conference fees are payable by check (dominated in $US, only) made payable to the Rocky Mountain Conference.

Registration Fees - 1987

Registration - on site	50.00
Registration - one specified day	30.00
Student registration	10.00
Additional Vendor registration	35.00
Unemployed or retired registration	No charge
Film Festival only	No charge
Exhibition only (non-vendor)	No charge

Times

Registration for the 29th Rocky Mountain Conference will be held in the Convention Lobby of the Radisson Hotel Denver during these times:

Sunday, August 2	5:00 pm - 9:00 pm
Monday, August 3	7:30 am - 3:30 pm
Tuesday, August 4	7:30 am - 3:30 pm
Wednesday, August 5	7:30 am - 3:30 pm
Thursday, August 6	8:00 am -10:00 am

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

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EXHIBITION

The Rocky Mountain Conference exhibition provides an opportunity to see and discuss the latest in analytical instrumentation, apparatus, supplies, and services. The exhibitors support the Rocky Mountain Conference - please support them!

Hours

Monday, August 3	9:30 a.m. - 5:00 p.m.
Tuesday, August 4	9:30 a.m. - 5:30 p.m.
Wednesday, August 5	9:30 a.m. - 2:00 p.m.

Beverages will be served in the exhibit area during symposium breaks.

The following exhibitors have reserved space as of June 1, 1987:

Applied Technical Products
Biorad, Digilab Division
Brownlee Labs
Bruker Instruments, Inc.
CEM Corporation
Chemagnetics, Inc.
Coulometrics, Inc.
Dionex Corp.
Doty Scientific
Dynamic Solutions
EG&G Labs
  Princeton Applied Research
Finnigan MAT
Harris Analytical
JEOL U.S.A., Inc.
Lee Scientific
Leeman Labs
Mettler Instrument Corp.
Micro-Now
Nicolet Instruments
Pacific Scientific - Instrument Division
Perkin-Elmer Co.
Rainin Instrument Co.
Sadtler Research Laboratories
Sievers, Inc.
Spectral Data Services, Inc.
Supelco, Inc.
Telecation Associates
Technicon
Tegal Scientific
Thermo Jarrell Ash
VG Instruments
Varian Instrument Group
Waters
Wilmad Glass Co., Inc.
Zymark Corporation

SOCIAL PROGRAM

Registration Night Mixer

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

Conference Mixer

All conferees and spouses are invited to attend this lively affair on Monday, August 3. This year's mixer will be held in the Exhibition area from 5:00 to 7:30 p.m.

Evening at Coors

On Tuesday, August 4, Coors Brewery will host an evening consisting of a plant tour, late night snacks, and dancing. Coors beer, soft drinks, cheese and crackers, cold cuts, a movie, music, dancing, and door prizes are included in the evening's entertainment. Bus transportation will be provided from the Radisson Hotel. We will leave the Radisson Hotel at 6:30 p.m. and return around midnight. Continuing transportation to the Denver University Housing will be provided on the return. Cost per person is $15 including bus transportation. Tickets are limited for this popular event, so register early!

Conference Banquet

The Conference Banquet will be Wednesday, August 5, at 7:00 p.m. in the Majestic Ballroom of the Radisson. Tickets are $18.00 each. There will be a cash bar in the Majestic Lounge at 6:00 p.m.

This year's banquet honors Sandra and Gareth Eaton on the occasion of the 10th International Symposium on Electron Paramagnetic Resonance. The Eatons have built their symposium into a primary medium for information interchange in EPR. Join us in recognition of their efforts.

Pete Smythe, our banquet speaker, is a well-known part of the Rocky Mountain scene. Pete has been entertaining Westerners since 1928 when he toured with his dance band, the Whiz Bang Four. Since then he has won national awards for writing and directing commercial and public service radio shows. He has written for top radio network shows (including the Bing Crosby Show) and for local television shows. For many years Smythe's General Store aired on KOA radio and TV in Denver. During this time 'Hizzoner' Smythe became mayor of the legendary East Tincup, Colorado. Pete has authored three books and produced one record album. His presentation, "Springs for the Wagon and Grease for the Wheels" is based on his lifelong collection of Western humor and music.

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ADDITIONAL ACTIVITIES

Visitor Information

Although no specific program is planned for the guests and families of conferees, Denver and the surrounding area boast a large number of activities that are enjoyable for both young and old. For additional information contact the Denver Metro Convention and Visitors Bureau, 225 W. Colfax Ave., Denver CO 80202. (303) 892-1112. For information about statewide attractions contact the Colorado Tourism Board, 1625 Broadway, Suite 1700, Denver CO 80202. (303) 592-5410.

Film Festival

Several films of scientific interest will be shown throughout the Rocky Mountain Conference. Admission to the film festival is by a paid or complimentary conference badge. Titles and a schedule will be posted in the registration area.

Employment Clearing House

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

Message Center

Incoming telephone messages for conferees will be posted at the message center in the registration area. The telephone number is (303) 893-3333, ext. 337. Ask for the Rocky Mountain Conference message center. This service will be available from 8:00 a.m. to 3:30 p.m. Monday-Wednesday and from 8:00-10:00 a.m. on Thursday.

Speaker Preparation Room

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

ORGANIZERS OF THE 29th ROCKY MOUNTAIN CONFERENCE

Conference Chairperson - Carol Gies, Rockwell International, General Lab Bldg. 881, P.O. Box 464, Golden, CO 80401, (303) 966-7380.

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

Exhibits - Glenda Brown, PSL Bldg. 559, Rockwell International, P.O. Box 464, Golden, CO 80401, (303) 966-7817.

Registration - Wendy Sticka, CPSD Bldg. 881, Rockwell International, P.O. Box 464, Golden, CO 80401, (303) 966-4724.

Treasurer - Rik Getty, Rockwell International, PSL Bldg. 559, P.O. Box 464, Golden, CO 80401, (303) 966-4791.

Social Events - Greg Johnson, Adolph Coors, Mail # BC600, Golden, CO 80401, (303) 277-5961.

Staff - David Ordeman, Adolph Coors Co., Mail No. BC600, Golden, CO 80401, (303) 277-2590.

Publicity - Jan Gurnsey, 5531 Bitterbush Way, Loveland, CO 80537, (303) 669-9216.

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

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

Mailing List - Sandy Grande, Manville Service Corp., R&D Center, P.O. Box 5108, Denver, CO 80217, (303) 978-5386.

SYMPOSIA CHAIRPERSONS

Atomic Spectroscopy - Thomas Niemczyk, Dept. of Chemistry, University of New Mexico, Albuquerque, NM 87131, (505) 277-5319 and Larry Layman, G740, Los Alamos National Lab, Los Alamos, NM 87545, (505) 667-0686.

Chemiluminescence - John Birks, CIRES, Campus Box 449, University of Colorado, Boulder, CO 80309-0449, (303) 492-7018.

Chromatography - Kenneth Brooks, University of Illinois, 107 Chemistry Annex, 601 S. Mathews, Urbana, IL 61801, (217) 333-6353.

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

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

Environmental Chemistry - Marvin Fishman, U.S. Geological Survey, 5293 Ward Rd., Arvada, CO 80002, (303) 236-3604.

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

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

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

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

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

NMR - James Haw, Dept. of Chemistry, Texas A&M University, College Station, TX 77843, (409) 845-1966.

Supercritical Fluid Chromatography - Bernd Wenclawiak, Dept. of Chemistry, University of Toledo, 2801 W. Bancroft St., Toledo, OH 43606, (419) 537-2664.

Quality Assurance - Victor Janzer, U.S. Geological Survey, 5293 Ward Rd., Arvada, CO 80002, (303) 236-3612.

SYMPOSIUM ON ATOMIC SPECTROSCOPY

Organized by Thomas Niemczyk and Larry Layman

Monday Morning, August 3 - Spruce Room

T. M. Niemczyk, Presiding

8:30 **KEYNOTE SPEAKER**

1. LASER-ASSISTED IONIZATION OF ATOMS IN FLAMES AND PLASMAS. S. R. Crouch, Department of Chemistry, Michigan State University.

9:10 2. A COMPARISON OF ATOMIC ABSORPTION AND PLASMA EMISSION TECHNIQUES FOR THE DETERMINATION OF WATER AND WASTE. Bettina D. Oelke, Mike W. Routh, Applied Research Laboratories, Inc.

9:30 3. BACKGROUND CORRECTION IN GRAPHITE FURNACE AAS. D. E. Shrader, L. M. Beach, T. M. Rettberg, Varian Instrument Group.

9:50 4. THE CHARRING EFFICIENCY OF BIOLOGICAL MATRICES IN THE GRAPHITE FURNACE. Thomas W. Brueggemeyer and Fred L. Fricke, Elemental Analysis Research Center, U.S. Food and Drug Administration.

10:10 **BREAK**

10:40 5. GETTING THE MOST OUT OF YOUR GRAPHITE FURNACE. G. R. Carnrick, W. Slavin, Perkin-Elmer Corp.

11:00 6. GRAPHITE FURNACE DETERMINATION OF MOLYBDENUM BY PALLADIUM-HYDROXYLAMINE HYDROCHLORIDE MATRIX MODIFICATION. Ernest W. Loya, U.S. Bureau of Reclamation.

11:20 7. ANALYSIS BY ICP-AES AND AAS OF RESISTANT GEOLOGICAL MATERIALS WITH A SODIUM PEROXIDE SINTER DIGESTION. Paul H. Briggs, James G. Crock, and E. E. Foord, U.S. Geological Survey.

11:40 8. TRANSFER AND MANIPULATION OF ATOMIC ABSORPTION DATA USING REPORT MANAGER AND LOTUS 123. F. Delles, J. Douglass, R. Matters, S. Skujins, Varian Instrument Group.

Monday Afternoon, August 3 - Spruce Room

T. M. Niemczyk, Presiding

1:30 **KEYNOTE SPEAKER**

9. NEW DIRECTIONS AND NEW SOURCES IN PLASMA FUNDAMENTAL STUDIES. M. W. Blades, L. L. Burton, and D. Liang, Dept. of Chemistry, University of British Columbia.

2:10 10. THE ROLE OF ELECTRONS IN ATOMIC AND IONIC EXCITATION LOW IN THE INDUCTIVELY COUPLED PLASMA (ICP). Laurie J. Prell and S. Roy Koirtyohann, Chemistry Department, University of Missouri-Columbia.

2:30 11. PRECONCENTRATION, MATRIX NORMALIZATION, AND SIGNAL ENHANCEMENT FOR ATOMIC SPECTROMETRY VIA ON-LINE DONNAN DIALYSIS. John A. Koropchak, Ewa Dabek-Zlotorzynska, Department of Chemistry and Biochemistry, Southern Illinois University.

2:50 12. REVERSE OSMOSIS PRECONCENTRATOR FOR AQUEOUS SOLUTION ION ENRICHMENT. Richard J. Stec and S. R. Koirtyohann, University of Missouri, and Howard E. Taylor, U.S. Geological Survey.

3:10 **BREAK**

3:40 13. APPLICATIONS OF CONTINUOUS FLOW-HYDRIDE GENERATION WITH A SEQUENTIAL ICP SPECTROMETER. M. W. Tikkanen, Applied Research Laboratories.

4:00 14. ANALYZING HAZARDOUS WASTE USING EPA PROCEDURES ON A NEW ICP. C. Anderau, D. A. Yates, Perkin-Elmer Corporation.

4:20 15. THE ANALYSIS OF DRINKING AND WASTE WATER UTILIZING A LOW POWER, LOW FLOW ICP/AES SYSTEM. William J. Kinsey, Labtest Equipment Company.

4:40 16. COMPARISON OF LOW AND ATMOSPHERIC PRESSURE ELEMENT SPECIFIC GC DETECTION USING FLOWING AFTERGLOW EXCITATION. J. T. Clay, T. M. Niemczyk, *Department of Chemistry, University of New Mexico.*

5:00 17. CHARACTERIZATION OF GLASSES AND CERAMICS BY ATOMIC SPECTROSCOPY FOR COMMUNICATIONS APPLICATIONS. Thomas Y. Kometani, AT&T Bell Laboratories.

SYMPOSIUM ON CHEMILUMINESCENCE

Organized by John Birks

Wednesday Morning, August 5 - Gold Room

John Birks, Presiding

9:00 **INVITED SPEAKER**

18. CHEMILUMINESCENCE DETECTION IN FLOWING STREAMS - IMMOBILIZED AND SOLID-STATE REAGENTS. Timothy A. Nieman, University of Illinois.

9:45 **INVITED SPEAKER**

19. PEROXYOXALATE CHEMILUMINESCENCE: DEVELOPMENT OF A HIGHLY SENSITIVE DETECTION METHOD FOR CHEMICAL ASSAYS. Richard S. Givens, Richard L. Schowen, Mirko Orlovic, John Stobaugh, Lanny Venham, and Arun Thakur, University of Kansas.

10:30 **BREAK**

10:45 **INVITED SPEAKER**

20. MICELLE ENHANCED AQUEOUS PEROXYOXALATE CHEMILUMINESCENCE. M. L. Grayeski, N. Dan, and M. L. Lau, Seton Hall University.

11:30 21. PHOTOCHEMICAL AMPLIFIER FOR HPLC BASED ON SINGLET OXYGEN SENSITIZATION. Curtis L. Shellum and John W. Birks, University of Colorado.

Wednesday Afternoon, August 5 - Gold Room

John Birks, Presiding

2:00 22. RECENT ADVANCES IN REDOX CHEMILUMINESCENCE. R. S. Hutte, Sievers Research, Inc., J. W. Birks, and R. E. Sievers, University of Colorado.

2:30 23. TOWARDS AN UNDERSTANDING OF REDOX CHEMILUMINESCENCE DETECTION. Stephen A. Montzka, Robert M. Barkley, and Robert E. Sievers, University of Colorado.

3:00 24. CHEMILUMINESCENCE DETECTION OF SULFUR COMPOUNDS IN GC AND HPLC. Marnie K. Carroll and John W. Birks, University of Colorado, and H. A. Stuber, Sievers Research, Inc.

3:30 **BREAK**

3:45 25. THE CHEMICAL GENERATION OF THE NEW METASTABLE STATES OF PN AND AsN. Thomas L. Henshaw, Michael A. MacDonald, Donald H. Stedman, and R. D. Coombe, University of Denver.

4:15 26. INTERACTION OF TRIFLUOROHALOMETHANES WITH ACTIVE NITROGEN. Andrew P. Ongstad, Shelle J. David, and Robert D. Coombe, University of Denver.

SYMPOSIUM ON CHROMATOGRAPHY

Organized by Kenneth C. Brooks

Tuesday Morning, August 4 - Colorado Room

WALTON SYMPOSIUM: SESSION I

J. L. Otto, Presiding

8:15 Opening Remarks - K. Brooks

8:20 27. ION EXCHANGE IN A SAND AND GRAVEL AQUIFER. E. M. Thurman and M. Ceazan, U.S. Geological Survey.

8:45 28. THE CONCENTRATION AND ISOLATION OF HYDROPHILIC ORGANIC ACIDS FROM WATER ON XAD-4. G. R. Aiken and D. M. McKnight, U.S. Geological Survey.

9:10 29. HIGH-PERFORMANCE ION-EXCHANGE CHROMATOGRAPHY OF PEPTIDES AND OLIGONUCLEOTIDES ON NON-POROUS, ION EXCHANGERS. Yoshio Kato, Takashi Kitamura, Akane Mitsui and Tsutomu Hashimoto, Toyo Soda Mfg. Co, Ltd., Japan.

9:35 30. DETERMINATION OF 7α-HYDROXYRIBOFLAVIN AND CORTISOL IN HUMAN URINE USING COUPLED COLUMNS OF HYDROPHILIC GEL AND ALKYLATED SILICA WITH PROPIONATE BUFFER AS THE MOBILE PHASE. Tokuichiro Seki, Nobuyuki Ashida, Osaka University and Yuzo Yanagihara, Kohji Noguchi, Asahi Chemical Industry Co. Ltd, Japan.

10:00 **BREAK**

10:30 31. GC/MS STUDIES OF ORGANIC COMPOUNDS IN THE TROPOSPHERE. R. M. Barkley and R. E. Sievers, University of Colorado at Boulder.

10:55 32. SELECTIVITY RELATED TO THE PRESENCE OR ABSENCE OF END-CAPPING OF ALKYL-BONDED SILICA GELS IN REVERSED-PHASE MODE LIQUID CHROMATOGRAPHY. Cai Hong, Shenyang College of Pharmacy, P. R. China, and Junko Yamaguchi and Toshihiko Hanai, Gasukuro Kogyo Inc., Japan.

11:20 33. CELLULOSE DIACETATE FIBERS AS THE STATIONARY PHASE IN MICROCOLUMN LIQUID CHROMATOGRAPHY. Yoshiaki Kiso, Toshiyuki Nagoshi and Kiyokatsu Jinno, Toyohashi University of Technology, Japan.

Tuesday Afternoon, August 4 - Colorado Room

WALTON SYMPOSIUM: SESSION II

H. S. Sherry, Presiding

1:30 34. INDIRECT PHOTOMETRIC DETECTION IN MICRO HPLC. Daido Ishii and Toyohide Takeuchi, Nagoya University, Japan.

1:55 35. CHROMATOGRAPHY INTERFACES FOR SUPERSONIC JET SPECTROSCOPY. Murray V. Johnston, University of Colorado at Boulder.

2:20 36. WHOLE COLUMN DETECTION CHROMATOGRAPHY. John W. Birks and Kathy R. Rowlen, University of Colorado at Boulder.

2:45 **BREAK**

3:15 37. CAPILLARY ION EXCHANGE CHROMATOGRAPHY WITH CONDUCTIVITY AND ULTRAVIOLET ABSORPTION DETECTION. H. Hatano and H. Wada, Kyoto University, Japan.

3:40 38. A NEW DETECTOR FOR LIQUID CHROMATOGRAPHY BASED ON CHEMILUMINESCENCE. H. A. Stuber, Sievers Research Inc. and R. E. Sievers and J. J. DeAngelis, University of Colorado at Boulder.

3:55 39. ANTICHROMATOGRAPHY - SEPARATIONS VIA FACILITATED TRANSPORT. C. A. Koval, University of Colorado at Boulder.

4:20 Presentation to Prof. Harold F. Walton - K. Brooks

Wednesday Morning, August 5 - Colorado Room

CHROMATOGRAPHY

WALTON SYMPOSIUM: SESSION III

K. Brooks, Presiding

8:10 40. EFFECT OF COLUMN DIMENSIONS ON HPLC SEPARATIONS USING CONSTANT VOLUME COLUMNS. Haleem J. Issaq, Lawrence Marzo, and Robert E. Gourley, Program Resources Inc., NCI/FCRF.

8:35 41. CHROMATOGRAPHIC ADVENTURES IN BREWING. David M. Ordemann, Adolph Coors Co.

9:00 42. A BONDED CAPILLARY COLUMN FOR ANALYSES OF ACIDIC SAMPLES. L. M. Sidisky, L. Nolan, R. E. Shirey, P. L. Stormer and M. J. Keeler, SUPELCO, Inc.

9:25 43. CHARACTERIZATION OF VOLATILES IN POLYMERS BY HEADSPACE GAS CHROMATOGRAPHY. S. V. Dubiel, Allied Corporation, Bendix Kansas City Division.

9:50 BREAK

10:20 44. EVALUATION OF A SPECTROPHOTOMETRIC TECHNIQUE FOR DETECTING THE TOTAL RETENTION OF MINOR COMPONENTS DURING AN HPLC SEPARATION. Steven K. MacLeod and Phil B. Bowman, The Upjohn Company.

10:45 45. LASER INDUCED PHOTOACOUSTIC SPECTROSCOPY AS APPLIED TO WHOLE COLUMN DETECTION CHROMATOGRAPHY. John W. Birks and Kathy L. Rowlen, James Avery and Ken Duell, University of Colorado at Boulder.

11:10 46. DEVELOPMENT OF AN IMPROVED ABSORBANCE DETECTOR FOR HPLC. Timothy A. Nevius, The Anspec Company, Inc.

11:35 47. CHARACTERIZATION OF THE FLAME PHOTOMETRIC DETECTOR USING A STATISTICALLY DESIGNED EXPERIMENTAL APPROACH. R. H. Kolloff, K. Klein, R. D. DeVeaux and P. A. Larson, Hewlett Packard.

Wednesday Afternoon, August 5 - Convention Lobby

CHROMATOGRAPHY POSTERS.

Authors will be present from 1:30 - 2:30.

48. COLUMN SWITCHING TECHNIQUE FOR RAPID SEPARATION OF FREE AMINO ACIDS BY REVERSED-PHASE ION PAIR LIQUID CHROMATOGRAPHY. Mitsuko Hirukawa and Toshihiko Hanai, Gasukuro Kogyo Inc., Japan.

49. HPLC SEPARATION WITH UV DETECTION OF TRACE AMOUNTS OF 4-METHOXYPHENOL AND ETHYLENE GLYCOL DIMETHACRYLATE IN 2-HYDROXYETHYL METHACRYLATE. Jeffrey A. Hurlbut and Jack D. Cummins, Metropolitan State College.

50. HPLC SEPARATION WITH UV DETECTION OF 2-HYDROXYETHYL METHACRYLATE FROM SOFT CONTACT LENSES. Jeffrey A. Hurlbut and Jack D. Cummins, Metropolitan State College.

51. EVALUATION OF CARRIER GAS PURIFIERS FOR THEIR ABILITY TO REMOVE OXYGEN AND MOISTURE. L. M. Sidisky, R. J. Bartram, W. J. Pinnick, and R. E. Shirey, SUPELCO, Inc.

SYMPOSIUM ON COMPUTER APPLICATIONS

Organized by John A. Lanning

Monday Morning, August 3 - Cedar Room

J. A. Lanning, Presiding

9:00 Opening Remarks - John A. Lanning

9:05 52. FACTOR ANALYSES OF SIMULATED EQUILIBRIA. Joseph M. Conny and Robert R. Meglen, Center for Environmental Sciences, University of Colorado at Denver.

9:30 53. CHEMOMETRIC RESULTS OF A COLORADO LAKES ACIDIFICATION STATUS STUDY. Lynne A. Taylor and Robert R. Meglen, Center for Environmental Sciences, University of Colorado at Denver.

9:55 54. DIMENSIONALITY OF ANALYTICAL DATA AND CONFIDENCE IN QUANTITATION. Avraham Lorber and Bruce Kowalski, Center for Process Analytical Chemistry and Laboratory of Chemometrics, Department of Chemistry, University of Washington.

10:30 BREAK

10:50 55. TREE-STRUCTURED CLASSIFICATION AND ANALYSIS OF PAH AIR SAMPLES USING THE PROGRAM CART. Robert W. Gunderson, Tove Jacobsen, Knut Kolset and Nils Vogt, Utah State University.

11:15 56. SO THE ANALYSES ARE DONE, NOW WHAT? R. Roger Johnson, Solutech Corporation.

11:45 LUNCH

Monday Afternoon, August 3 - Cedar Room

J. A. Lanning, Presiding

1:30 57. A HYBRID EXPERT/DATABASE SYSTEM FOR SELECTING METHODS OF SURFACE ANALYSIS. Frank A. Settle, Jr., Department of Chemistry, Virginia Military Institute and M. A. Pleva, Washington and Lee University.

2:05 58. INEXPENSIVE SOFTWARE FOR GEOLOGISTS AND OTHER SCIENTISTS. Dave Rich, Geotech Computer Systems.

2:30 59. LABORATORY ROBOTICS - THE MISSING LINK IN TOTAL LABORATORY AUTOMATION. Art Ambrose, Perkin-Elmer Corporation.

2:55 BREAK

3:15 60. QUALITY CONTROL FUNCTIONS IN LIMS. Art Ambrose, Perkin-Elmer Corporation.

3:40 61. AUTOMATED MAINTENANCE AND REPORTING OF ANALYTICAL QUALITY ASSURANCE ON A PERSONAL COMPUTER. Richard D. Beaty and Leigh A. Richardson, Telecation Associates.

POSTER

Author will be present 2:00 - 3:00 Monday afternoon.

62. ESR DATA ACQUISITION AND MANIPULATION ON THE IBM PC. Phillip D. Morse, II, University of Illinois, College of Medicine and Illinois ESR Research Center.

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

Organized by Marvin J. Fishman

Monday Morning, August 3 - Denver Room

M. J. Fishman, Presiding

8:25 Introductory Remarks

8:30 63. SELECTED PESTICIDES IN EXTRACTS OF CORE MATERIALS AND IN GROUND WATER FROM KANSAS. Tom R. Steinheimer, U.S. Geological Survey.

8:55 64. GROUND- AND SURFACEWATER MIGRATION OF CORN PRODUCTION PESTICIDES. Terry D. Spittler, Cornell University, Ralph O. Mumma and Jon K. Hall, Pennsylvania State University, William F. Ritter, University of Delaware, and Russell B. Brinsfield, University of Maryland.

9:20 65. A CRITICAL EVALUATION OF THE NEW ION TRAP REVISION 3.00 WITH AUTOMATIC GAIN CONTROL. Theodore J. Galen, John F. Boyd, and Randy A. Peters, Krug International, and Duane L. Pierson, Biomedical Laboratories Branch, NASA/Johnson Space Center.

9:45 BREAK

10:15 66. SCREEN ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN WATER, SOIL, OR SOLID WASTE BY CAPILLARY GAS CHROMATOGRAPHY FLAME IONIZATION DETECTION. David A. Taylor, Enseco Incorporated, Rocky Mountain Analytical Laboratory.

10:40 KEYNOTE SPEAKER

67. REVIEW OF ANALYTICAL METHODS FOR THE DETERMINATION OF CHEMICALS REQUIRING MEASUREMENT

UNDER ENVIRONMENTAL REGULATIONS. J. Lichtenberg, U.S. Environmental Protection Agency.

Monday Afternoon, August 3 - Denver Room

P. F. Rogerson, Presiding

1:30 68. POLLUTANTS IN DRILLING MUD PITS - COMPARISON OF TOTAL ANALYSES WITH TOXICITY CHARACTERISTIC LEACHING PROCEDURE AND LYSIMETER LEACHING RESULTS. Michael P. Phillips, Kevin H. Schilling, and Anthony W. Toth, Enseco Incorporated, Rocky Mountain Analytical Laboratory.

1:55 69. COMPARISON OF LIQUID-CHROMATOGRAPHIC ANALYSES OF CARBAMATE PESTICIDE RESIDUES: 1) POST-COLUMN DERIVATIZATION AND FLUORESCENCE DETECTION OF DIRECT-AQUEOUS INJECTIONS AND 2) MULTI-WAVELENGTH ABSORBANCE DETECTION OF SAMPLE EXTRACT INJECTIONS. Sharon M. Johnson, Stephen L. Werner, and Larry D. Becker, U.S. Geological Survey.

2:20 70. A LOOK AT MERCURY LOSS FROM SOLUTIONS FROM VARIOUS TYPES OF CONTAINERS. James L. Robinson, U.S. Environmental Protection Agency.

2:45 BREAK

3:15 71. DETERMINATION OF CYANIDE AT PARTS PER BILLION LEVELS. Jeffrey J. Rosentreter and R. K. Skogerboe, Colorado State University.

3:40 72. DETERMINATION OF TRACE NICKEL AND COBALT IN NATURAL WATERS BY ADSORPTIVE DIFFERENTIAL PULSE STRIPPING VOLTAMMETRY. Robert S. Tieman and Vinay Kumar, Northern Kentucky University.

4:05 73. ANALYSIS OF LOW LEVEL NUTRIENTS IN THE UG/L RANGE USING A HIGH SPEED RANDOM ACCESS CONTINUOUS-FLOW ANALYZER. Anthony Buccafuri, Aldo Conetta, and Donald A. Burns, Bran+Luebbe, Technicon Industrial Systems.

4:25 74. AN EVALUATION AND COMPARISON OF ION CHROMATOGRAPHY, SEGMENTED FLOW ANALYSIS AND FLOW INJECTION ANALYSIS FOR THE DETERMINATION OF NITRATE IN NATURAL SURFACE WATERS. Eileen M. Burke, F. Xavier Suarez, and Daniel C. Hillman, Lockheed-EMSCO, and Edward M. Heithmar, U.S. Environmental Protection Agency.

Tuesday Morning, August 4 - Denver Room

M. J. Fishman, Presiding

8:30 75. EXAMINATION OF TRACE ELEMENTS IN NATURAL SURFACE WATERS SUBJECT TO ACIDIC DEPOSITION. J. M. Henshaw, Lockheed-EMSCO, and E. M. Heithmar and T. A. Hinners, U.S. Environmental Protection Agency.

8:55 76. THE ANALYSIS OF PARTICULATE COLLECTED ON MEMBRANE FILTERS IN A DICHOTOMOUS SAMPLER.

Dewayne L. Ehman, J. Scott Mgebroff, Vincent C. Anselmo, and J. Maxine Jenks, Texas Air Control Board.

9:20 77. MEASUREMENT OF STONE SURFACE WETNESS WITH THREE ELECTRONIC MOISTURE SENSORS. Randolph B. See, Michael M. Reddy, and Richard G. Martin, U.S. Geological Survey.

9:45 **BREAK**

10:15 78. COMPARISON OF COLLECTION EFFICIENCIES AND CHEMICAL CONCENTRATIONS FROM COLOCATED PRECIPITATION SAMPLERS. LeRoy J. Schroder, U.S. Geological Survey, and Richard C. Graham, John K. Robertson, and John Obal, U.S. Military Academy.

10:40 **KEYNOTE SPEAKER**

79. ACID RAIN ANALYSIS: WHAT'S IN STORE FOR THE FUTURE? Mark E. Peden, Illinois State Water Survey.

Tuesday Afternoon, August 4 - Denver Room

Sharon Johnson, Presiding

2:00 80. KINETICS OF ION REMOVAL FROM DECIDUOUS AND CONIFEROUS CANOPIES BY ACID RAIN. Larry Puckett, U.S. Geological Survey.

2:25 81. DETERMINATION OF ALUMINUM IN NATURAL WATER BY DIRECT-CURRENT PLASMA, OPTICAL-EMISSION SPECTROSCOPY. Edward J. Zayhowski, Merle W. Shockey, Allen J. Heakin, and Mark R. Hill, U.S. Geological Survey.

2:50 82. THE DETERMINATION OF WATER SOLUBLE BORON AT NINE IRRIGATION STUDY SITES IN THE WESTERN UNITED STATES. S. A. Wilson, K. C. Stewart, and R. C. Severson, U.S. Geological Survey.

3:15 **BREAK**

3:45 83. NEW ELECTROANAL TECHNIQUES FOR LOW LEVEL CHLORINE SPECIES. Calvin O. Huber, University of Wisconsin-Milwaukee.

4:10 84. FLUOROMETERIC DETERMINATION OF SELENIUM. Alan L. Dunhill, Donna M. McKinney, and Sharri L. Alexander, Colorado Department of Health.

4:35 85. PULSE POLAROGRAPHIC DETERMINATION OF NATURALLY OCCURRING CR (VI) IN SOILS AND WATERS. George R. Meadows, Larry L. Jackson, and Larry P. Gough, U.S. Geological Survey.

Wednesday Morning, August 5 - Denver Room

L. J. Schroder, Presiding

8:30 86. ANALYTICAL CHEMISTRY OF TRACE METALS: SOME REFLECTIONS AND CHALLENGES. Rm. Panayappan and John C. Cooper, Naval Research Laboratory.

8:55 87. MERCURY-203 LABELING STUDY OF GEOLOGICAL SAMPLE PREPARATION AND DETECTION PROCEDURES FOR DETERMINATION OF TRACE CONCENTRATIONS OF MERCURY BY COLD VAPOR ATOMIC ABSORPTION. A. J. Montoya and D. Knab, Los Alamos National Laboratory.

9:20 88. NONVOLATILE ORGANIC ACIDS IN GROUNDWATER CONTAMINATED WITH CRUDE OIL. George R. Aiken, Kevin A. Thorn, and Myron H. Brooks, U.S. Geological Survey.

9:45 **BREAK**

10:15 89. THE DISTRIBUTION OF OXIDIZED AND REDUCED ARSENIC IN THE SEDIMENT AND INTERSTITIAL WATER OF THE CHEYENNE RIVER ARM OF LAKE OAHE, SOUTH DAKOTA. Walter H. Ficklin and Jerry M. Motooka, U.S. Geological Survey.

10:40 90. TOTAL AND WATER SOLUBLE ARSENIC AND SELENIUM ASSOCIATED WITH DRAINAGE SEDIMENTS COLLECTED FROM NINE IRRIGATION SITES IN THE WESTERN UNITED STATES. S. A. Wilson, D. B. Hatfield, and R. C. Severson, U.S. Geological Survey.

11:15 91. INTERACTIONS BETWEEN OZONE AND ATMOSPHERIC SOOT: TODAY AND FOLLOWING NUCLEAR WAR. Sherry L. Stephens and John W. Birks, Department of Chemistry and Biochemistry, and Cooperative Institute for Research in Environmental Sciences, University of Colorado, and Jack G. Calvert, National Center for Atmospheric Research.

Wednesday, Afternoon, August 5 - Denver Room

M. J. Fishman, Presiding

2:00 92. SURFACE AREA AS A FACTOR FOR NORMALIZING "TOTAL RECOVERABLE" CONCENTRATIONS OF INORGANIC CONSTITUENTS IN DILUTE MINERAL ACID EXTRACTS OF AQUATIC SEDIMENTS. V. J. Janzer and P. N. Johler, U.S. Geological Survey.

2:25 93. HALIDE DETERMINATION IN USED OILS AND NON-AROMATIC ORGANICS FOR RECYCLE OR DISPOSAL BY BOMB COMBUSTION AND ION CHROMATOGRAPHY. H. P. Patterson and M. C. Williams, Los Alamos National Laboratory.

2:50 94. ELECTROCHEMISTRY AND Eh OF MULTIVALENT ELEMENTS IN NATURAL WATERS. J. Houston Kempton and Donald D. Runnells, Department of Geological Sciences, University of Colorado.

3:15 **BREAK**

3:45 95. RECENT DEVELOPMENTS IN ULTRAVIOLET LIGHT DOSIMETRY. Donald H. Stedman, David K. Krehbiel, Doris Kimbrough, and Donald L. McElwee, Department of Chemistry, University of Denver.

4:10 96. PRESSURE DIGESTION OF SEWAGE SLUDGE. Mary C. Williams, Ellen A. Stallings, Trudy M. Foreman, and Ernest S. Gladney. Los Alamos National Laboratory.

10th INTERNATIONAL SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

Organized by Gareth R. Eaton and Sandra S. Eaton

Monday Morning, August 3 - Silver Room

Session I - TRANSITION METAL IONS

G. R. Eaton, Presiding

8:30		Opening Remarks, G. R. Eaton
8:40		PLENARY LECTURE
	97.	ANALYSIS OF TRANSITION METAL ION EPR SPECTRA. J. R. Pilbrow, Monash University, Australia.
9:20	98.	THE SPIN HAMILTONIAN CONCEPT AND NOTATIONS USED IN TRANSITION-METAL ION EPR - A NEED FOR A UNIFIED NOMENCLATURE. C. Rudowicz and R. Bramley, Australian National University.
9:50		BREAK
10:20	99.	ENDOR DETERMINED SOLVATION STRUCTURE OF VO^{2+} IN FROZEN SOLUTIONS. D. Mustafi and M. W. Makinen, University of Chicago.
10:40	100.	EPR ORDER PARAMETERS OF METALLOPHTHALOCYANINE THIN FILMS. M. D. Pace, W. R. Barger, and A. W. Snow, Naval Research Laboratory.
11:00	101.	EPR STUDIES OF SOLID-STATE INTERCALATION REACTIONS IN LAYERED SEMICONDUCTING CHALCOGENIDES. A. H. Francis, E. Lifshitz, and D. A. Cleary, University of Michigan.
11:20	102.	COMPARATIVE Mn (II) EPR STUDIES OF FERROELASTICITY IN DICALCIUM METAL PROPIONATES OF $Ca_2M(C_2H_5COO)_6$; M = Ba, Sr, Pb. S. K. Misra and S. Jerzak, Concordia University.
11:40	103.	ELECTRON PARAMAGNETIC RESONANCE OF ACETAMIDINIUM Cu(II) IN SPIN-1/2 TETRAHEDRAL COORDINATED ANTIFERROMAGNET. J. E. Drumheller and K. L. Wan, Montana State University.
12:00		LUNCH

Monday Afternoon, August 3 - Silver Room

Session II - BIOLOGICAL APPLICATIONS

N. D. Chasteen, Presiding

1:30		PLENARY LECTURE
	104.	METALLOPROTEIN EPR TRUTH DIAGRAMS WITH THE PERSPECTIVE OF TWO DECADES. W. E. Blumberg, AT&T Bell Laboratories.

2:10 105. THE POTENTIAL USE OF ELECTRON SPIN RESONANCE SPECTROSCOPY FOR THE DETECTION OF GENE SEQUENCES. A. M. Bobst, University of Cincinnati.

2:30 106. ELECTRON SPIN ECHO STUDIES OF PHOTOSYNTHETIC OXYGEN EVOLUTION. R. D. Britt, K. Sauer, and M. P. Klein, Lawrence Berkeley Laboratory.

2:55 BREAK

3:25 107. SYNTHESIS OF A NEW SPIN-LABELED DERIVATIVE OF CoA AND IT'S INTERACTION WITH 3-HYDROXYACYL-CoA DEHYDROGENASE. D. Hartmann and W. E. Trommer, Kaiserslautern, West Germany.

3:45 108. KINETICS OF REDUCTION AND REOXIDATION OF NITROXIDES IN LIVING CELLS. K. Chen, P. D. Morse, II, and H. M. Swartz, University of Illinois.

4:05 109. PHOTOREDUCTION OF SPIN LABELS BY EXCITED FLAVIN. K. M. Andrews, D. R. Chrisope, and P. D. Morse, II, University of Illinois.

4:25 110. X-BAND EPR SPECTRA AND SIMULATIONS OF S=2 STATES IN MYOGLOBIN AND IN A MODEL HEME COMPLEX. M. P. Hendrich, G. C. Wagner, and P. G. Debrunner, University of Illinois.

4:45 111. STRUCTURE-FUNCTION RELATIONSHIPS PROBED THROUGH EPR STUDIES OF CHEMICALLY MODIFIED CYTOCHROME C. L. G. Miller, B. L. Ramakrishna, and J. R. Cronin, Arizona State University.

Tuesday Morning, August 4 - Silver Room

Session III - EPR OF NMR CONTRAST AGENTS

H. M. Swartz, Presiding

8:30 Introductory Comments, H. M. Swartz

8:40 112. OVERVIEW AND RATIONALE FOR CLINICAL CONTRAST AGENTS IN MRI. J. S. Cohen, National Cancer Institute, National Institutes of Health.

9:20 113. PHYSICAL CHARACTERIZATION OF PARAMAGNETIC CONTRAST AGENTS. R. B. Clarkson, H. Bennett, and H. M. Swartz, University of Illinois.

10:00 BREAK

10:30 114. LOW FREQUENCY ESR SPECTROMETRY: APPLICATION IN BIOLOGICAL SYSTEMS. H. J. Halpern, D. P. Spencer, G. M. Rosen, L. A. Brunsting, A. S. Wechsler, and M. K. Bowman, University of Chicago, Duke University, and Argonne National Laboratory.

11:10 115. MEASURING OXYGEN AND REDOX METABOLISM BY METABOLICALLY RESPONSIVE NMR CONTRAST AGENTS. H. M. Swartz, University of Illinois.

11:55 **LUNCH**

Tuesday Afternoon, August 4 - Silver Room

Session IV - ORGANIC RADICALS

R. W. Fessenden, Presiding

1:30 116. RECOGNITION OF CHIRALITY BY ENDOR. H. B. Stegmann, H. Wendel, H. Dao-Ba, P. Schuler, and K. Scheffler, University of Tubingen.

2:00 117. SEMIEMPIRICAL MO CALCULATION OF EPR SPLITTING CONSTANTS: TWISTING IN ALKENE CATION RADICALS. S. F. Nelsen and T. Clark, University of Wisconsin and University of Erlangen-Nuernberg.

2:30 **BREAK**

Session V - POSTERS - Convention Lobby

S. S. Eaton, Presiding (joint with NMR Symposium)

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

A 118. HIGH PRESSURE ESR STUDY ON THE MICROVISCOSITY IN THE SURFACTANT MICELLES AND THE LIPID MEMBRANES. H. Yoshioka, Shizuoka College of Pharmacy, Japan.

B 119. RED CELL DEFORMABILITY STUDIED BY EPR. T. Ito and H. Kon, National Institutes of Health.

A 120. THE TRANSITION METAL MEDIATED FORMATION OF HYDROXYL FREE RADICALS DURING THE REDUCTION OF MOLECULAR OXYGEN BY FERREDOXIN-FERREDOXIN:NADP$^+$ OXIDOREDUCTASE. K. M. Morehouse and R. P. Mason, National Institute of Environmental Health Sciences.

B 121. FREE RADICAL METABOLITE OF URIC ACID. K. R. Maples and R. P. Mason, National Institute of Environmental Health Sciences.

A 122. FORMATION OF FREE RADICAL PRODUCTS FROM HYDRALAZINE BY MITOCHONDRIA AND RED BLOOD CELLS. P. K. Wong, J. L. Poyer, C. DuBose, and R. A. Floyd, Oklahoma Medical Research Foundation.

B 123. ESR STUDY OF DELIVERY OF MANGANESE TO LIVER BY LIPOSOMES. M. R. Niesman, G. Bacic, R. Magin, and H. M. Swartz, University of Illinois.

A 124. ESR STUDIES OF COPPER COMPLEXES WITH EHRLICH ASCITES TUMOR CELLS. W. E. Antholine, D. H. Petering, A. Peszhtek, and L. Pickart, Medical College of Wisconsin, University of Wisconsin-Milwaukee, and Ball State University.

B 125. SUPERHYPERFINE COUPLINGS FROM LOW FREQUENCY ESR SPECTRA OF THE TYPE I SITE IN LACCASE. P. M. Hanna, D. R. McMillin, M. Pasenkiewicz-Gierula, and W. E. Antholine, Purdue University and Medical College of Wisconsin.

A 126. PULSE FIELD-SWEEP EPR ON COPPER PROTEINS. C. Fan, C. P. Scholes, and H. Taylor, State University of New York at Albany.

B 127. SPECTROSCOPIC STUDIES ON AURACYANIN - A SMALL BLUE COPPER PROTEIN FROM *CHLOROFLEXUS AURANTIACUS*. J. T. Trost, B. L. Ramakrishna, J. M. Freeman, R. E. Blankenship, Arizona State University.

A 128. BINDING OF SPIN-LABELED ATP AND AMP-PCP TO THE SR ATPASE. C. Coan, C. Garcia, and S. Verjovski-Almeida, University of the Pacific and Federal University of Rio de Janeiro.

B 129. EPR CHARACTERIZATION AND ENDOR STUDIES OF *UBIQUINOL:CYTOCHROME* c_2 OXIDOREDUCTASE ISOLATED FROM RHODOBACTER SPHAEROIDES. K. M. Andrews, A. R. Crofts, and R. B. Gennis, University of Illinois.

A 130. GENERATION OF RADICAL SPECIES FROM GOOD BUFFERS. N. D. Chasteen, J. K. Grady, and D. C. Harris, University of New Hampshire and Naval Weapons Center, China Lake.

B 131. SPIN LABELING EPR IN STUDIES OF MOLECULAR INTERACTIONS IN BIOMEMBRANES. G. Benga, Medical and Pharmaceutical Institute Cluj-Napoca, Roumania.

A 132. ASYST/ASSEMBLY LANGUAGE PROGRAM FOR AN IBM-PC AND A TRANSIAC TRANSIENT RECORDER INTERFACED TO A VARIAN EPR SPECTROMETER: TIME AND FIELD CONTROL. E. Bradford and L. D. Kispert, University of Alabama.

B 133. DUAL CHANNEL COMPUTER INTERFACE OF ESR SPECTROMETER. M. T. Jones, T. Maruo, M. Singh, and J. H. Roble, University of Missouri-St. Louis.

A 134. NMR AND EPR SPECTRA OF SPIN-LABELED NICKEL(II) XANTHATES. S. K. Sheppard, K. M. More, G. R. Eaton, and S. S. Eaton, University of Denver and University of Colorado at Denver.

B 135. THE GRADIENT DEPENDENCE OF RAPID-SCAN NMR SPECTRAL LINESHAPES. H. A. Buckmaster and T. Duczmal, University of Calgary.

A 136. THE SHAPE OF RAPID-SCAN NMR SPECTRAL LINES FOR A SIMPLE PHANTOM. H. A. Buckmaster and T. Duczmal, University of Calgary.

B 137. THE INFLUENCE OF NON-LINEAR FREQUENCY SWEEP ON THE SHAPE OF RAPID-SCAN NMR SPECTRAL LINES. H. A. Buckmaster and T. Duczmal, University of Calgary.

Wednesday Morning, August 5 - Silver Room

Session VI - EPR IMAGING

G. R. Eaton, Presiding

8:30 Opening Remarks, G. R. Eaton

8:45 138. HIGH RESOLUTION ESR IMAGING IN SOLIDS. G. G. Maresch, A. Grupp, and M. Mehring, University of Stuttgart, West Germany.

9:10 139. RAPID DETERMINATION OF TRANSLATIONAL DIFFUSION COEFFICIENTS BY ESR IMAGING. D. A. Cleary, Y.-K. Shin, D. J. Schneider, and J. H. Freed, Cornell University.

9:35 140. CONTINUOUS WAVE EPR-TOMOGRAPHY. U. Ewert, T. Herrling, W. Schneider, Academy of Sciences of GDR, East Germany.

10:10 BREAK

10:40 141. TWO-DIMENSIONAL ENDOR IMAGING. E. G. Janzen, Y. Kotake, and U. M. Oehler, University of Guelph.

11:00 142. IMAGING ELECTROMAGNETIC FIELDS USING THE MAGNETIC RESONANCE ABSORPTION SPECTRUM OF A PARAMAGNETIC GAS. S. A. Marshall, B. H. Suits and M. T. Umlor, Michigan Technological University.

11:20 143. ESR IMAGING OF OXYGEN DEPENDENT PROCESSES IN VIABLE BIOLOGICAL SYSTEMS. G. Bacic, F. Demsar, T. Walczak, J. Dobrucki, and H. M. Swartz, University of Illinois.

11:40 144. ESR IMAGING OF LIVE AND NONVIABLE CELLS IN A MODEL OF TUMOR TISSUE. J. W. Doliwa-Dobrucki, G. Bacic, F. Demsar, and H. M. Swartz, University of Illinois.

12:00 LUNCH

Wednesday Afternoon, August 5 - Silver Room

Session VII, IN-VIVO ESR

H. M. Swartz, Presiding

1:30 145. IN VIVO ESR SPECTROSCOPY AT LOW FREQUENCIES. M. J. Nilges, T. Walczak, and F. Demsar, University of Illinois.

2:00 146. ESR IN-VIVO. L. J. Berliner, Ohio State University.

2:30 BREAK

Session VIII Posters - Convention Lobby

S. S. Eaton, Presiding

Authors present 3:00-4:00 for papers labeled C
Authors present 4:00-5:00 for papers labeled D

C 147. DEVELOPMENT OF ULTRA HIGH RESOLUTION EPR IMAGING. K. Ohno, Hokkaido University, Japan.

D 148. INSTRUMENTATION AND SOFTWARE FOR CW EPR-IMAGING. T. Herrling, U. Ewert, and W. Schneider, Academy of Sciences of GDR, East Germany.

C 149. SPECTRAL-SPATIAL 2-D EPR IMAGING WITH AN ITERATIVE ALGORITHM. M. M. Maltempo, S. S. Eaton, and G. R. Eaton, University of Colorado-Denver and University of Denver.

D 150. SEED GERMINATION: EPR IMAGING STUDY. T. Walczak, F. Demsar, H. Gabrys, and H. M. Swartz, University of Illinois.

C 151. SPIN DIFFUSION AND MAGNETIC BEHAVIOUR OF THE PSEUDO 2-d SYSTEMS NaBp.2Tg and RbBp.2Ttg. M. C. M. Gribnau, C. P. Keijzers, and E. de Boer, University of Nijmegen, the Netherlands.

D 152. EPR STUDIES OF ANISOTROPIES AND DEFECTS IN LINEAR CHAIN $A_2Cu_2X_6$ SALTS. B. Patyal and R. D. Willett, Washington State University.

C 153. SINGLE CRYSTAL ESR STUDIES OF $(n\text{-}BuN_4{}^+Ni(o\text{-}BENZENEDISELENOLATE)_2{}^-$ AND RELATED TRANSITION METAL COMPLEXES. M. T. Jones, J. H. Roble, M. Singh, and T. Maruo, University of Missouri-St. Louis.

D 154. MEASUREMENT OF QUADRUPOLE COUPLINGS IN COPPER COMPLEXES WITH L-BAND PARALLEL POLARIZATION EPR. K. S. Rothenberger, M. J. Nilges, T. E. Altman, K. Glab, R. L. Belford, W. Froncisz, and J. S. Hyde, University of Illinois and Medical College of Wisconsin.

C 155. THE ESR SPECTRA OF THE Mn(II) IONS DOPED INTO TWO CRYSTALLINE FORMS OF DITHIOCYANATOBIS(2,2'-bi-2-THIAZOLINE)IRON(II). A. Ozarowski and B. R. McGarvey, University of Windsor.

D 156. ON THE SYMMETRY ADAPTED EFFECTIVE OPERATORS. R. Chatterjee, University of Calgary.

C 157. FINE STRUCTURE TERMS IN SUPERPOSITION MODEL ANALYSIS OF CHARGE COMPENSATED HIGH SPIN EPR CENTRES. C. Rudowicz, Australian National University.

D 158. APPLICATIONS OF SYMBOLIC PROGRAMMING IN TRANSITION-METAL ION EPR THEORY. C. Rudowicz and R. Bramley, Australian National University.

C 159. MODEL CALCULATIONS FOR THE DISTANCE DEPENDENCE OF FERROMAGNETIC EXCHANGE. R. E. Coffman, University of Iowa.

D 160. AUTOSIMULATE: A COMPUTING PROGRAM FOR DIRECT IDENTIFICATION OF ALL POSSIBLE ESR SIMULATIONS DUE TO A GIVEN MOLECULAR STRUCTURE. D. R. Duling, A. Motten, and R. P. Mason, National Institute of Environmental Health Sciences.

C 161. CHEMOMETRICAL ANALYSIS OF ESR SPECTRA: RESOLUTION ENHANCEMENT BY DECONVOLUTION AND NOVEL ANALYSIS OF HYPERFINE STRUCTURE. H. Hatano, K. Nozaki, A. Naito, and S. Okazaki, Kyoto University.

D 162. MAGRES: AN EXACT SIMULATION PROGRAM FOR EPR, ENDOR, AND ESEEM. M. C. M. Gribnau, E. J. Reijerse, and C. P. Keijzers, University of Nijmegen.

C 163. AUTOMATED LEAST-SQUARES FITTING OF SLOW MOTIONAL ESR SPECTRA. R. H. Crepeau, S. Rananavare, and J. H. Freed, Cornell University.

D 164. ^{13}C HYPERFINE CONSTANTS IN SOME SIMPLE RADICALS. R. W. Fessenden, H. J. McManus, and D. M. Chipman, University of Notre Dame.

C 165. EPR AND ENDOR STUDIES OF PERYLENE RADICALS ADSORBED ON ALUMINA AND SILICA-ALUMINA POWDERS. K. S. Rothenberger, H. C. Crookham, P. A. Snetsinger, R. B. Clarkson, and R. L. Belford, University of Illinois.

D 166. SELECTIVE GENERATION OF ORIENTED DEFECTS IN GLASSES. J. H. Stathis, IBM T. J. Watson Research Center.

C 167. EPR STUDIES OF C-13 LABELED AND MONOMETHYLATED 6-OXY-BENZO(a)PYRENE AND 6-TRIFLUOROACETOXY-BENZO(a)PYRENE RADICALS, X. Chen and P. D. Sullivan, Ohio University.

D 168. SINGLE CRYSTAL ESR AND ENDOR STUDIES OF AN AZOALLYL RADICAL. A. Berthier-Celalyan, M. Geoffroy, and M. V. Reddy, University of Geneva.

C 169. CHEMICAL REACTION STUDIES OF AROMATICS, ALKENES, AND ALKYNES ON HY, H-MORDENITE AND H-ZSM-5 ZEOLITIC SURFACES. S. Shih, University of Colorado Health Science Center.

D 170. VARIATION OF ALKYLMETHYLVIOLOGEN RADICAL CATION-WATER INTERACTIONS IN MICELLES AND VESICLES FROM ESEM SPECTROSCOPY: EFFECT OF ALKYL CHAIN LENGTH. M. J. Colaneri, L. Kevan, D. H. P. Thompson, and J. K. Hurst, University of Houston and Oregon Graduate Center.

C 171. ELECTRON SPIN ECHO ENVELOPE MODULATION STUDIES OF NATURAL ABUNDANCE LOW-GAMMA NUCLEI. P. A. Snetsinger, J. B. Cornelius, R. B. Clarkson, and R. L. Belford, University of Illinois.

Thursday Morning, August 6 - Silver Room

Session IX

J. R. Pilbrow, Presiding

8:30 **PLENARY LECTURE**

172. CONFIGURATION OF THE NEXT GENERATION OF EPR SPECTROMETERS. J. S. Hyde, Medical College of Wisconsin.

9:20 173. 2D - ESR CORRELATION SPECTROSCOPY. J. Gorchester and J. H. Freed, Cornell University.

9:50 **BREAK**

DOI: https://doi.org/10.56902/RMCMR.1987.29.1

10:10 174. APPLICATION OF ABSORPTION MODE RAPID PASSAGE TECHNIQUES TO SOLIDS. W. E. Carlos, Naval Research Laboratory.

10:40 175. ^{14}N ESEEM IN DISORDERED SOLIDS: MULTI-FREQUENCY AND ORIENTATION SELECTION TECHNIQUES FOR ELUCIDATING HYPERFINE AND QUADRUPOLE COUPLING TENSORS. D. J. Singel and H. L. Flanagan, Harvard University.

11:10 176. ESR AT 1 MILLIMETER. B. Lynch and J. H. Freed, Cornell University.

11:40 177. MECHANISTIC AND KINETIC STUDIES OF TRIPLET STATE QUINONE QUENCHING IN ALCOHOLS BY FTESR. R. J. Massoth and M. K. Bowman, Argonne National Laboratory.

Thursday Afternoon

Bruker EPR User's Meeting for present and prospective users of IBM and Bruker spectrometers. Those who wish to attend should contact Dr. Art Heiss at Bruker, 203-775-6252 or 617-667-9580 or at the Bruker booth during the symposium.

SYMPOSIUM ON INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Organized by Howard E. Taylor

Tuesday Morning, August 4 - Cedar Room

Howard E. Taylor, Presiding

9:00 178. THE DETERMINATION OF OSMIUM AND RHENIUM IN MOLYBDENITE BY ISOTOPE DILUTION ICP/MS. F. E. Lichte and J. W. Morgan, U.S. Geological Survey.

9:25 179. THE DETERMINATION OF ARSENIC AND SELENIUM BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY IN ENVIRONMENTAL SAMPLES. Ewa Pruszkowski and Richard Ediger, Perkin-Elmer Corp.

9:50 180. ANALYSIS OF ENVIRONMENTAL REFERENCE MATERIALS USING ICPMS. D. J. Northington and B. M. Hovanec, WCAS.

10:15 **BREAK**

10:30 181. FLOW INJECTION ON-LINE ISOTOPE DILUTION ANALYSIS WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Xiaoru Wang, Miklos Viczian, Alexandra Lasztity, and Ramon M. Barnes, University of Massachusetts.

10:55 182. EVALUATION OF THE INTERFACE IN A UNIQUE ICP-MS INSTRUMENT. R. Duane Satzger and F. L. Fricke, Food and Drug Administration, and J. A. Caruso, University of Cincinnati.

11:20 183. SPECIATION OF MERCURY COMPOUNDS BY LIQUID CHROMATOGRAPHY WITH INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRIC DETECTION. Diane S. Bushee, John R. Moody, and Paul J. Paulsen, National Bureau of Standards.

11:45 **LUNCH**

Tuesday Afternoon, August 4 - Cedar Room

Howard E. Taylor, Presiding

1:00 184. DETERMINATION OF TRACE ELEMENTS IN NATURAL SURFACE WATERS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY. J. M. Henshaw, Lockheed-EMSCO, E. M. Heithmar and T. A. Hinners, U.S. Environmental Protection Agency.

1:25 185. APPROACHES TO THE ANALYSES OF HIGH DISSOLVED SOLIDS SOLUTIONS BY ICP-MS. Robert C. Hutton, Christopher T. Tye, Andrew N. Eaton and Robert Brown, VG Elemental.

1:50 186. BLOOD ANALYSIS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Thomas A. Hinners, Edward M. Heithmar, U.S. Environmental Protection Agency, and John M. Henshaw, Lockheed Engineering and Management Services Company, Inc.

2:15 **BREAK**

2:30 187. THE QUANTITATIVE DETERMINATION OF TRACE ELEMENTS IN SEMICONDUCTOR MATERIALS BY GLOW DISCHARGE MASS SPECTROMETRY. P. M. Charalambous, K. Robinson, and R. Brown, VG Elemental.

2:55 188. TRACE METAL DATA BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER FOR DRINKING WATERS AND REFERENCE MATERIALS THAT IS EQUIVALENT OR SUPERIOR TO ETVAA TECHNIQUES. Richard Robinson, Daryl Knab and Michael G. Bell, Los Alamos National Laboratory.

SYMPOSIUM ON INFRARED SPECTROSCOPY

Organized by Dr. Marvin C. Goldberg

Wednesday Morning, August 5 - Cedar Room

M. C. Goldberg, Presiding

8:55 Introductory Remarks - M. C. Goldberg

9:00 189. THE EFFECT OF METAL SUBSTRATES (Al, Cu, Ag, and Au) ON THE PHOTODEGRADATION OF POLYMERS. W. F. Welch, A. R. Chughtai, and D. M. Smith, University of Denver.

9:30 190. A FLOW CHART FOR THE IDENTIFICATION OF POLYMER MATERIALS BASED UPON CONDENSED PYROLYZATE IR SPECTRA. Michael C. Oborny, Sandia National Laboratories.

10:00 **BREAK**

10:30 191. NEAR-IR REFLECTANCE: A RISING STAR IN ANALYTICAL SPECTROSCOPY. Donald A. Burns, Bran+Luebbe, Technicon Industrial Systems.

11:00 192. APPLICATIONS OF NEAR INFRARED (NIR) ANALYSIS TO THE PHARMACEUTICAL INDUSTRY. F. A. DeThomas, Pacific Scientific Instrument Division.

11:30 193. THE EFFECTS OF SPECTRAL ENHANCEMENT ON NEAR INFRARED (NIR) QUANTITATIVE AND QUALITATIVE ANALYSES. Patrick J. Cooper, Pacific Scientific Instrument Division.

SYMPOSIUM ON ION CHROMATOGRAPHY

Organized by F. W. Williams

Monday Morning, August 3 - Gold Room

F. W. Williams, Presiding

8:15 *Introductory Remarks - F. W. Williams*

8:25 **INVITED SPEAKER**

194. THE "REAL WORLD" OF ION ANALYSIS. Virgil T. Turkelson, Michigan Applied Science & Technology Laboratories, Dow Chemical Co.

9:00 195. CATIONIC INDIRECT CHROMATOGRAPHY USING Ce^{+3} WITH PHOTOMETRIC OR FLUOROMETRIC DETECTION. Neil D. Danielson and Jeffrey H. Sherman, Miami University.

9:25 196. APPLICATIONS OF VACANCY DETECTION TO ION CHROMATOGRAPHY. Bernard G. Sheldon and James R. Benson, Interaction Chemicals, Inc.

9:50 BREAK

10:30 197. APPLICATIONS OF GRADIENT ELUTION IN ION CHROMATOGRAPHY. R. Rocklin, C. Pohl, D. Campbell, and R. Joyce, Dionex Corporation.

10:55 198. TWELVE YEARS OF ION CHROMATOGRAPHY - PAST, PRESENT, FUTURE. A. W. Fitchett, Dionex Corporation.

Monday Afternoon, August 3 - Gold Room

Sonia Atwood, Presiding

1:30 199. AUTOMATION IN ION CHROMATOGRAPHY. Timothy Ward, Alan Henshall, Rosanne Slingsby, John Stillian, Dionex Corporation.

1:55 200. ACCURACY AND PRECISION FOR THE HPLC ANALYSIS OF A PESTICIDE COMPARING AUTOMATED TO MANUAL SAMPLE INJECTION. B. J. Wildman and A. D. Scarchilli, Millipore Corporation, Waters Chromatography Division.

2:20 BREAK

2:55 201. GRADIENT SINGLE COLUMN ION CHROMATOGRAPHY UTILIZING ISOCONDUCTIVE ELUENTS. W. R. Jones, A. L. Heckenberg and P. Jandik, Millipore Corporation, Waters Chromatography Division.

3:20 202. ON THE AUTOMATION OF A DIONEX MODEL 10 ION CHROMATOGRAPH. Vincent C. Anselmo, Ph.D., William C. White, and James Harper, Texas Air Control Board.

3:45 203. A SYSTEMATIC APPROACH TO TROUBLESHOOTING THE ION CHROMATOGRAPH. Maureen Meador, Dionex Corporation.

4:10 204. ION CHROMATOGRAPHIC HPIC SEPARATION AND ANALYSIS OF RADIOSTRONTIUM IN IONIC MIXTURES. Phillip A. Drake, John D. Lamb, Francis R. Nordmeyer, M. Paul Elder, and Adam T. Woolley, Brigham Young University, Department of Chemistry.

Tuesday Morning, August 4 - Gold Room

Renee Hoatson, Presiding

8:30 Introductory Remarks

8:35 205. TRACE RESIDUAL SULFITE ANALYSIS IN DRUG ITEMS. David A. Fay, Norman C. Jamieson, Harold W. Thieman, and Steven R. Villasenor, Mallinckrodt, Inc.

9:00 206. APPLICATIONS OF VARIOUS ION CHROMATOGRAPHIC DETECTORS TO THE ANALYSIS OF ADDITIVES IN PLATING SOLUTIONS. A. L. Heckenberg, W. R. Jones, and P. Jandik, Millipore Corp., Waters Chromatography Division.

9:25 207. QUANTITATIVE ANALYSIS OF TRACE ANIONS IN FOOD PRODUCTS. Lee N. Polite and H. M. McNair, Chemistry Department, Virginia Tech.

9:50 **BREAK**

10:30 208. DETERMINATION OF CYANIDE IN METAL CYANIDE PLATING BATHS AND WASTEWATER. Michael J. Doyle, Roy D. Rocklin, Dionex Corporation.

10:55 209. THE EVOLUTION OF THE CONDUCTIVITY DETECTOR FOR USE IN THE LIQUID CHROMATOGRAPHY OF IONS. Vincent C. Anselmo, Ph.D., Texas Air Control Board.

Tuesday Afternoon, August 4 - Gold Room

Ray Merrill, Presiding

1:30 210. FAST RUN ANALYSIS IN ION CHROMATOGRAPHY. D. Campbell, R. Rocklin, and J. Stillian, Dionex Corporation.

1:55 211. RELATIVE SENSITIVITY OF AMPEROMETRIC DETECTION OF ANIONS USING SEVERAL DIFFERENT WORKING ELECTRODES MATERIALS. J. Jandik and P. J. Jandik, Millipore Corporation, Waters Chromatography Division.

2:20 **BREAK**

3:00 212. A STATISTICAL COMPARISON OF DATA OBTAINED FOR THE ANALYSIS OF NITRATE IN DRINKING WATER. B. J. Wildman, A. D. Scarchilli, and A. L. Jagoe, Millipore Corporation, Waters Chromatography Division.

3:25 213. USING ION CHROMATOGRAPHY TO ANALYZE IONIC CONSTITUENTS IN AN ELECTROLESS NICKEL PLATING BATH. Ken Rice and Steve Stone, *Dionex Corporation.*

3:50 214. ANALYSIS OF NICOTINE BY CATION MPIC. John D. Lamb, Delbert J. Eatough, Lee D. Hansen, Laura J. Lewis, and Brenda Sedar, Department of Chemistry, Brigham Young University.

SYMPOSIUM ON MASS SPECTROMETRY

Organized by P. V. Fennessey

Wednesday Afternoon, August 5 - Cedar Room

P. V. Fennessey, *Presiding*

1:30 **PLENARY LECTURE**

215. TIME ARRAY DETECTION: RENAISSANCE OF TIME OF FLIGHT MASS SPECTROMETRY FOR GC-MS. J. T. Watson, Department of Biochemistry, Michigan State University.

2:30 216. A STUDY OF NUCLEOTIDE-MITOMYCIN COMPLEXES BY EI AND FAB MASS SPECTROMETRY IN BOTH POSITIVE AND NEGATIVE ION MODES. Thomas D. McClure, Bhashyam Iyengar, William A. Remers, and Karl H. Schram, Department of Pharmaceutical Sciences, College of Pharmacy, University of Arizona.

2:50 217. ROLE OF PROSTAGLANDIN SYSTEM IN THE ANTIHYPERTENSIVE EFFECTS OF SEVERAL COMMONLY USED DRUGS IN HUMANS. M. L. Beckmann-Thomas, J. Gerber, M. Loverdi, R. Byyny, R. C. Murphy, and A. Nies, Department of Medicine, Division of Clinical Pharmacology and Department of Pharmacology, University of Colorado Health Sciences Center.

3:10 218. PILOT EVALUATION OF FAB MASS SPECTROMETRY TO DETERMINE ZINC ABSORPTION IN THE PREMATURE INFANT. P. Peirce, K. Micheal Hambidge, Paul V. Fennessey, Leland V. Miller, and Christopher Goss, Departments of Pediatrics and Pharmacology, University of Colorado Health Sciences Center.

3:30 219. ASSAY OF CHOLESTEROL 7-α,HYDROXYLASE BY ISOTOPE DILUTION-MASS SPECTROSCOPY. Donald L. Zogg, Antal Nemeth, Gregory T. Everson, University of Colorado Health Sciences Center.

3:50 220. THE DEVELOPMENT AND VALIDATION OF METHODS FOR AMINO ACID DISPOSAL RATE IN THE FETAL SHEEP. G. L. Loy, P. V. Fennessey, W. W. Hay, and A. N. Quick, Jr., Departments of Pediatrics and Pharmacology, University of Colorado Health Sciences Center.

4:10 221. ANALYSIS OF FAST ACTING ANESTHETIC INDUCTION AGENTS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY. K. Kestin, D. B. Christie, M. Goldstein, and P. V. Fennessey, Departments of Pediatrics and Pharmacology, University of Colorado Health Sciences Center.

POSTER

Author will be present 2:00 - 3:00 Monday afternoon.

222. DAUGHTER ION SPECTRA OF SELECTED CHLORINATED COMPOUNDS. C. E. Rostad, W. E. Pereira, U.S. Geological Survey.

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

Organized by James Haw

Monday Morning, August 3 - Century Room

Morning Session - NMR of Surfaces -

James Haw, Presiding

8:25 Opening Remarks, Welcome to the NMR Symposium - James F. Haw, Department of Chemistry, Texas A & M University.

8:30 223. HETERONUCLEAR CHEMICAL-SHIFT CORRELATIONS OF SILANOL GROUPS STUDIED BY TWO-DIMENSIONAL CROSS-POLARIZATION/MAGIC-ANGLE-SPINNING NMR. Alexander J. Vega, E. I. duPont deNemours and Company.

9:00 224. CHARACTERIZATION OF HETEROGENEOUS CATALYSTS WITH PROTON, CARBON AND XENON NMR SPECTROSCOPIES. Cecil Dybowski, Charles Tirendi, Daniel Barabino, Navin Bansal, and Lori Hasselbring, Department of Chemistry, University of Delaware.

9:30 225. A STUDY BY SOLID STATE NMR OF ^{133}Cs and ^{1}H OF A HYDRATED AND A DEHYDRATED MORDENITE. Po-Jen Chu and B. C. Gerstein, Department of Chemistry, Iowa State University, John Nunan and Kamil Klier, Lehigh University.

10:00 BREAK

10:30 226. N-15 NMR OF SURFACE ADSORBED SPECIES. Paul Ellis and Paul Majors, Department of Chemistry, University of South Carolina.

11:00 227. MULTINUCLEAR NMR STUDIES OF SILYLATED SURFACES. Gregory R. Quinting, Robert C. Zeigler, Charles E. Bronnimann, and Gary E. Maciel, Department of Chemistry, Colorado State University.

11:30 228. USING ^{23}Na NMR TO EXAMINE CATION SITE OCCUPANCY IN ION-EXCHANGED ZEOLITES. Larry B. Welsh and Susan L. Lambert, Allied-Signal.

DOI: https://doi.org/10.56902/RMCMR.1987.29.1

Monday Afternoon, August 3 - Century Room

James Haw, Presiding

2:00 **PLENARY LECTURE**

229. SPIN-LATTICE AND SPIN-SPIN RELAXATION BELOW 1K. P. Kuhns, O. Gonen, P. C. Hammel, and J. S. Waugh, Department of Chemistry, Massachusetts Institute of Technology.

3:00 **BREAK**

NMR OF Non-Diamagnetic Solids -

3:30 230. VARIABLE-TEMPERATURE CP/MAS NMR STUDIES OF ANTIFERROMAGNETIC TRANSITION METAL COMPLEXES. Gordon C. Campbell and James F. Haw, Department of Chemistry, Texas A & M University.

4:00 231. RECENT DEVELOPMENTS IN SOLID-STATE NMR COMBINED WITH DYNAMIC NUCLEAR POLARIZATION. Robert A. Wind, Herman Lock, and Gary E. Maciel, Department of Chemistry, Colorado State University.

4:30 232. NUCLEAR MAGNETIC RESONANCE IN Al-Mn PERIODIC AND QUASIPERIODIC CRYSTALS. Mark Rubinstein and G. H. Stauss, Naval Research Laboratory and L. H. Bennett, National Bureau of Standards.

Tuesday Morning, August 4 - Century Room

High Resolution NMR of Abundant Spins in Solids -
Organized by R. A. Wind and B. L. Hawkins
R. A. Wind, Presiding

8:30 233. HETEROGENEOUS CORRELATION SPECTROSCOPY IN ROTATING SOLIDS. R. G. Griffiin, National Magnet Laboratory, Massachusetts Institute of Technology.

9:00 234. LINE-NARROWING IN 2-D SPACE: LET THE MOLECULES DO IT. H. A. Resing, R. S. Sronko and T. Tsang, Naval Research Laboratory.

9:30 235. ^{1}H CRAMPS STUDIES OF SURFACES AND MODIFIED SURFACES. C. E. Bronnimann, B. L. Hawkins, G. E. Maciel, and R. Zeigler, Department of Chemistry, Colorado State University.

10:00 **BREAK**

10:30 236. SOLID STATE NMR USING HIGH-SPEED MAS. S. F. Dec, Robert A. Wind, and Gary E. Maciel, Department of Chemistry, Colorado State University.

11:00 237. ^{1}H MAGIC ANGLE SPINNING STUDY OF METAL-EXCHANGED ZEOLITE Y. R. Shoemaker and T. Apple, Department of Chemistry, University of Nebraska.

11:30 238. METHODS FOR DETERMINING MIXING IN POLYMER BLENDS BY SOLID STATE NMR. David VanderHart, National Bureau of Standards.

Tuesday Afternoon, August 4 - Century Room

High Resolution NMR of Abundant Spins in Solids (Cont.)

R. A. Wind, Presiding

2:00 239. APPLICATIONS OF DEUTERIUM NMR TO SURFACE CHEMISTRY. Paul D. Ellis, Paul D. Majors, and Tom E. Raidy, Department of Chemistry, University of South Carolina.

2:30 240. NUCLEAR SPIN DYNAMICS OF HYDROGEN IN $H_xZr_yCl_z$ PHASES. Po-Jen Chu, B. C. Gerstein, Robin Ziebarth, and J. D. Corbett, Department of Chemistry, Iowa State University.

3:00 POSTER SESSION - JOINT WITH EPR SYMPOSIUM

Wednesday Morning, August 5 - Century Room

Morning Session - Probes and Polymers

Herb Retcofsky, Presiding

8:30 241. LOW TEMPERATURE SOLIDS. David Doty, Doty Scientific.

9:00 242. SOLID STATE PROJECTION RECONSTRUCTION IMAGING PROBE. John Listerud and Gary Drobny, Department of Chemistry, University of Washington.

9:30 BREAK

10:00 243. SOLID STATE NMR STUDIES OF MOTION IN POLYMERS. E. O. Stejskal, Department of Chemistry, North Carolina State University.

10:30 244. VARIABLE TEMPERATURE NMR STUDIES OF PHOSPHAZENE INORGANIC POLYMERS. Richard C. Crosby and James F. Haw, Department of Chemistry, Texas A & M University.

11:00 245. CP/MAS NMR OF CURED RESINS. David Duff, I.-S. Chuang, and G. E. Maciel, Department of Chemistry, Colorado State University.

Wednesday Afternoon, August 5 - Century Room

Herb Retcofsky, Presiding

General Papers

1:30 246. HIGH FIELD NMR STUDY OF THE MOLECULAR STRUCTURE AND SOLUTION DYNAMICS OF Na_2PHO_3. Ilene C. Locker and Thomas C. Farrar, Department of Chemistry, University of Wisconsin.

2:00 247. CHEMICAL SHIFT TRENDS IN SOLID SILATRANES. Joseph H. Iwamiya and Gary E. Maciel, Department of Chemistry, Colorado State University.

2:30 248. OXYGEN-17 MAGNETIC RESONANCE IMAGING IN MATERIALS AND BIOLOGICAL RESEARCH. G. D. Mateescu, G. M. Yvars and Terri Dular, Department of Chemistry, Case Western Reserve University.

3:00 249. NMR STUDY OF CHARGE TRANSFER AND STRUCTURE OF TERNARY AMMONIA-ALKALI INTERCALATION COMPOUNDS. T. Tsang[a,b], R. M. Fronko[a], H. A. Resing[a], S. A. Solin[c], and X. W. Qian[c], [a]Naval Research Laboratory, [b]Howard University, [c]Michigan State University.

SYMPOSIUM ON SUPERCRITICAL FLUID CHROMATOGRAPHY

Organized by B. Wenclawiak

Monday Morning, August 3 - Colorado Room

B. Wenclawiak, Presiding

8:30 **PLENARY LECTURE**

250. SUPERCRITICAL FLUID CHROMATOGRAPHY: RETENTION, RESOLUTION, AND GRADIENT METHODS. E. Klesper, RWTH Aachen, West Germany.

9:15 251. A COMPARISON OF PACKED AND CAPILLARY COLUMNS FOR PRACTICAL SFC SEPARATIONS. P. J. Barthel, H. E. Schwartz, S. E. Moring and H. H. Lauer, Brownlee Labs.

9:35 252. MULTIDIMENSIONAL SUPERCRITICAL FLUID CHROMATOGRAPHY/CAPILLARY GAS CHROMATOGRAPHY. Joseph M. Levy, John P. Guzowski, Wayne E. Huhak, Standard Oil Research and Development.

9:55 253. ANALYTICAL EXTRACTION OF ORGANICS FROM SOLID SAMPLES USING SUPERCRITICAL FLUIDS. S. B. Hawthorne, D. J. Miller, and M. S. Krieger, University of North Dakota, Energy Research Center.

BREAK

10:45 254. TRACE ANALYSIS WITH SUPER CRITICAL FLUID CHROMATOGRAPHY. H. M. McNair, J. O. Frazier, Virginia Polytechnic Institute and State University.

11:05 255. DRUG ANALYSIS BY CAPILLARY SUPERCRITICAL FLUID CHROMATOGRAPHY. Marion R. Andersen, B. E. Richter, D. E. Knowles, D. W. Later, and E. R. Campbell, Lee Scientific.

11:25 256. SEPARATION OF DIFFERENT OLIGOMERS BY SUPERCIRITCAL FLUID CHROMATOGRAPHY USING GRADIENT ELUTION. Franz P. Schmitz and Bernd Gemmel, RWTH Aachen, F.R.G.

11:45 257. TEMPERATURE EFFECTS IN SUPERCRITICAL FLUID CHROMATOGRAPHY. Bernd W. Wenclawiak, University of Toledo.

LUNCH

Monday Afternoon, August 3 - Colorado Room

F. P. Schmitz, Presiding

1:30 PLENARY LECTURE

258. SUPERCRITICAL FLUID CHROMATOGRAPHY: A TECHNOLOGY UPDATE. C. M. White, D. R. Gere, and F. Pacholec, Suprex Corporation.

2:15 259. INDUSTRIAL APPLICATIONS OF SUPERCRITICAL FLUID CHROMATOGRAPHY: POLYMER ANALYSIS. David E. Knowles, Erin R. Campbell, Marion R. Andersen, Bruce E. Richter and Douglas W. Later, Lee Scientific.

2:35 260. METHODS FOR COMPARING ELUENT PROPERTIES IN SUPERCRITICAL FLUID CHROMATOGRAPHY. Franz P. Schmitz, RWTH Aachen, F. R. G.

BREAK

3:15 261. INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRIC DETECTION IN SUPERCRITICAL FLUID CHROMATOGRAPHY. Kiyokatsu Jinno, Chuzo Fujimoto and Hiroyuki Yoshida, Toyohashi University of Technology, JAPAN.

3:35 262. SUPERCRITICAL FLUID CHROMATOGRAPHY WITH REDOX CHEMILUMINESCENCE DETECTION. William T. Foreman, Robert E. Sievers, and Bernd Wenclawiak, University of Colorado.

3:55 263. ELECTRON-IMPACT SPECTRA OF COMPOUNDS UTILIZING SFC/MS. B. W. Wenclawiak, University of Toledo, and J. Ashraf, Nermag Div. of Delsi Instruments.

4:15 264. SFC/MS SEPARATION AND IDENTIFICATION OF ALKANE, ALCOHOL, ACID, ESTER, AND GLYCERIDE COMPONENTS OF WAXES. S. B. Hawthorne and D. J. Miller, University of North Dakota, Energy Research Center.

4:35 265. INTERFACING TECHNIQUES FOR SFC/MS. James B. Buchner and Ross C. Willoughby, Extrel Corp.

POSTERS - Convention Lobby

Authors will be present 1:30 - 2:30 Wednesday afternoon.

266. A STUDY OF RETENTION CHARACTERISTICS BY FUNCTIONAL GROUP ANALYSIS USING SUPERCRITICAL FLUID CHROMATOGRAPHY. J. R. Wheeler and M. E. McNally, E. I. duPont deNemours & Co.

267. PARAMETERS INFLUENCING THE SEPARATION OF Pd-&-DIKETONATES IN PACKED COLUMN SFC. B. W. Wenclawiak, The University of Toledo, and K. R. Jahn, Westfalische Wilhelms Universitat, Munster, W. Germany.

268. PACKED CAPILLARY COLUMN IN SUPERCRITICAL FLUID CHROMATOGRAPHY. Yukio Hirata and Yoshiyuki Yukawa, Toyohashi University of Technology, JAPAN.

SYMPOSIUM ON QUALITY ASSURANCE

Organized by Victor J. Janzer

Tuesday Morning, August 4 - Spruce Room

V. J. Janzer, Presiding

8:30 Introduction

8:35 **KEYNOTE SPEAKER**

269. THE QUEST FOR QUALITY ASSURANCE. John K. Taylor, Quality Assurance Consultant, Gaithersburg, Maryland.

9:30 270. QUALITY CONTROL OF WATER ANALYSES IN A LABORATORY INFORMATION MANAGEMENT SYSTEM. Berwyn E. Jones and C. Ann Watterson, U.S. Geological Survey.

10:00 BREAK

10:30 271. AN EVALUATION OF THE REPRESENTATIVENESS OF PRECIPITATION VOLUMES MEASURED IN THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK MONITORING PROGRAM. David S. Bigelow, Natural Resource Ecology Laboratory, Colorado State University.

11:00 272. QUALITY ASSURANCE PROCEDURES NECESSARY FOR LITIGATION RELATED DATA. Kenneth E. Dahlin, Environmental Science and Engineering, Inc.

Tuesday Afternoon, August 4 - Spruce Room

D. E. Erdmann, Presiding

1:30 273. QUALITY ASSURANCE FOR FEED ANALYSIS. S. M. Shakeel Akhtar, Feed Testing Laboratory, University of Saskatchewan.

2:00 274. THREE PROTOTYPE "IN-HOUSE" AQUATIC SEDIMENT REFERENCE SAMPLES FOR THE DETERMINATION OF "TOTAL RECOVERABLE" INORGANIC CONSTITUENTS. Paul N. Johler and Victor J. Janzer, U.S. Geological Survey.

2:30 275. CREDIBILITY, PRACTICALITY AND REALITY AS FACETS OF QUALITY ASSURANCE. Sylvan Eisenberg, Anresco, Inc.

3:00 BREAK

3:30 276. INTERLABORATORY VARIABILITY AND ACCURACY IN TRACE ELEMENT ANALYSES. John Lengyel, Jr., Conoco Inc.

4:00 277. PRIMARY STANDARDS: THE BASIS FOR ACCURACY IN THE KJELDAHL NITROGEN METHOD. Clifford C. Hach, Scott V. Brayton, and Yu-Sen Chen, Hach Company.

Wednesday Morning, August 5 - Spruce Room

V. J. Janzer, Presiding

8:30 Introduction

8:35 **KEYNOTE SPEAKER**

278. QUALITY ASSURANCE IN A REGULATORY AGENCY. John A. Winter, U. S. Environmental Protection Agency.

9:30 279. QUALITY-ASSURANCE PRACTICES IN WATER-QUALITY LABORATORIES OF PUBLICLY FUNDED AGENCIES AND INSTITUTIONS IN COLORADO AND OHIO, 1984. Donna Myers, Carolyn J. Oblinger Childress, and Janet Hren, U.S. Geological Survey, Columbus, Ohio; and Thomas H. Chaney and J. Michael Norris, U.S. Geological Survey, Denver, Colorado.

10:00 **BREAK**

10:30 280. QUALITY ASSURANCE MONITORING FOR X-RAY FLUORESCENCE ANALYSIS OF TRACE ELEMENTS IN SOLUTIONS. Carl M. Meltzer and Joseph d. Balser, BEEM Laboratory.

11:00 281. A QUALITY ASSURANCE PROGRAM FOR THE ANALYSIS OF VOLATILE ORGANIC CHEMICALS. Annemary T. Liu, Raymond H. Taylor, Kent Adney, Gary Falling, and Veronica Simion, California Water Service Company.

11:30 282. ORTHO-PHOSPHOROUS REAGENT CONTAMINATION FROM SILICA BREAKTHROUGH IN DEIONIZED WATER SYSTEM. Eric R. Hamilton, William G. Leseman, Jamie J. Shakar, City of Tallahassee, Water Quality Laboratory.

Wednesday Afternoon, August 5 - Spruce Room

B. E. Jones, Presiding

1:30 283. DEVELOPING A COMPREHENSIVE LABORATORY QA PROGRAM TO MEET REGULATORY AGENCY REQUIREMENTS. Richard G. Mealy, Toni L. Stovall, and Kathleen A. Carlberg, Enseco - Rocky Mountain Analytical Laboratory.

2:00 284. QUALITY ASSURANCE FOR CONTRACTUAL ANALYTICAL SERVICES. B. Jones and D. Walker, U.S. Geological Survey.

2:30 285. STATISTICS AND REALITY. Robert A. Crovelli, U.S. Geological Survey.

GENERAL POSTERS

Organized by Carlos E. Arozarena

Monday Afternoon, August 3 - Convention Lobby

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

C. Arozarena, Presiding

286. THE GEOCHEMICAL APPLICATION OF THE SOLID-SAMPLE ICP-OES METHOD FOR HEAVY-MINERAL CONCENTRATES IN THE PICACHO PEAK AND INDIAN PASS WILDERNESS STUDY AREAS, CALIFORNIA. Betty M. Adrian and D. E. Detra, U.S. Geological Survey.

287. SOME (HYDROXYPHENYL)-2-BROMOETHANONE AS ELECTRO-ACTIVE LABELS FOR CARBOXYLIC ACIDS IN LIQUID CHROMATOGRAPHIC DETECTION. Robert K. Munns, Jeffery A. Hurlbut, Jose E. Roybal, and Wilbert Shimoda, Food and Drug Administration.

288. HPLC DETERMINATION OF TETRACYCLINE RESIDUES IN ANIMAL FEEDS. Elizabeth E. Martinez and Wilbert Shimoda, Food and Drug Administration.

289. HIGH PRESSURE LIQUID CHROMATOGRAPHIC DETERMINATION AND CAPILLARY GC/MS CONFIRMATION, USING MULTIPLE ION DETECTION OF DIMETRIDAZOLE (DMZ) AND IPRONIDAZOLE(IPR) IN SWINE FEEDS. Jose E. Roybal and William Morris, Food and Drug Administration.

290. DETERIORATION OF COQUINA BY ACID RAIN AT CASTILLO DE SAN MARCOS NATIONAL MONUMENT. Joni A. Simms, USG Corporation, and David G. Rands, Southern Illinois University at Edwardsville.

291. IMPLEMENTATION OF A LABORATORY INFORMATION SYSTEM ON A UNIX DRIVEN FT-IR. Joseph J. Rafalko, Hoechst Celanese Research Company.

292. SURFACE ACOUSTIC WAVE VAPOR DETECTION OF ORGANOPHOSPHORUS COMPOUNDS. Raymond E. Miller, U.S. Army Chemical Research and John A. Parsons, Geo-Centers, Inc.

293. SPECTROPHOTOMETRIC STUDIES OF THE IRON(III) - THIOCYANATE COMPLEXATION REACTION IN MIXED SOLVENTS. Robert E. Neas and Zaiton Abdul-Majid, Western Illinois University.

294. THERMODYNAMICS OF PROTON TRANSFER EQUILIBRIA OF TRIFLUOROACETYLPINACOLONE IN AQUEOUS DIOXANE MEDIA. Jagdish P. Shukla and Radhey S. Sharma, Bhabha Atomic Research Centre, Bombay, India.

295. TECHNOLOGY FOR THE MEASUREMENT OF TRACE METALS IN ATMOSPHERIC PRECIPITATION USING ICP-MS. J. R. Garbarino and H. E. Taylor, U.S. Geological Survey.

296. PHOTOLYSIS OF AMINO ACIDS SORBED ONTO IRON-OXYHYDROXIDE(GOETHITE). Marvin C. Goldberg, and Kirkwood M. Cunningham, U.S. Geological Survey.

297. THREE DIMENSIONAL CHROMATOGRAMS OF A LASER FLUORESCENCE SPECTROPHOTOMETRIC DETECTOR IN HPLC. Yuko Arai and Toshihiko Hanai, Gasukuro Kogyo Inc., Japan.

298. ANISOTROPY IN THE PROTON NMR PARAMAGNETIC SHIFT OF CYCLOOCTATETRAENE AND CYCLOPENTADIENE ANIONS COORDINATED TO U(IV). Bruce R. McGarvey and Steven T. Nagy, University of Windsor.

299. DETERMINATION OF LOW AMOUNTS OF CARBOXYLATE IN POLYACRYLAMIDE USING FT-IR. James E. Tackett, Marathon Oil Company.

300. ACETYLCHOLINE RECEPTOR--AGONIST BINDING: RESULTS FROM PROTON NMR T_1 MEASUREMENTS AND 2D-NOE'S. Ronald W. Behling, Tetsuo Yamane, Gil Navon, Michael J. Sammon, and Lynn W. Jelinski, AT&T Bell Laboratories, Murray Hill, New Jersey 07974

301. SOLUTION OF THE ^{14}N-^{15}N SPECTRAL OVERLAP PROBLEM USING PULSE EPR. Jun-Jie Yin, Jim. B. Feix, and James S. Hyde, National Biomedical ESR Center, Department of Radiology, Medical College of Wisconsin.

302. RECENT EPR STUDIES OF INDIAN COALS. S. K. De, Dr. S. K. Srivastava, Central Fuel Research Institute, Dist. Dhanbad (Bihar) India.

303. A 9 GHZ LOOP-GAP ENDOR SPECTROMETER. R. A. Isaacson and G. Feher, University of California.

304. AN ESR STUDY OF THE CONFORMATION OF THE TRANSIENT GERMANIUM-CENTRED TRIS- (2-PHENYL-2-METHYLPROPYL) GERMYL RADICAL. Manfred Lehnig, Wilhelm P. Neumann, and Elisabeth Wallis, Universitat Dortmund.

1 LASER-ASSISTED IONIZATION OF ATOMS IN FLAMES AND PLASMAS, S.R. Crouch, Department of Chemistry, Michigan State University, East Lansing, MI 48823

Laser-assisted ionization methods are among the most sensitive trace analytical techniques. Originally, a single pulsed laser, tuned to a resonance transition, enhanced the rate of collisional ionization of analyte atoms. The ions were then detected by means of a pair of biased electrodes. Since then, major improvements have occurred in laser ionization techniques. Experimental developments include the use of multiple laser or multiple photon processes, which make feasible new and more efficient ionization schemes, the application of new electrode materials and shapes and the design of new fast amplifiers. Improvements in pulsed lasers have enabled higher energy transitions to be employed and multiplied the number of practical ionization schemes. Current studies are aimed at optimizing signal-to-noise ratios and minimizing background ionization signals. Several theoretical developments have revealed the experimental factors upon which ionization methods depend and allowed the prediction of the time behavior of ionization signals. Such developments have led to applications of laser ionization methods for flame diagnostic studies and for flame temperature determinations. In addition, a new spectrometric technique, termed "fluorescence dip spectrometry", monitors the resonance fluorescence from a laser-excited level while a second laser is spectrally tuned to provide enhanced ionization. The decrease in the intensity of resonance fluorescence is a measure of the depletion of the population of the first excited level because of ionization. This new, indirect ionization technique should find many applications in diagnostic and analytical studies.

2 A COMPARISON OF ATOMIC ABSORPTION AND PLASMA EMISSION TECHNIQUES FOR THE DETERMINATION OF WATER AND WASTE. Bettina D. Oelke, Mike W. Routh. Applied Research Laboratories, Inc., 3080 Enterprise Avenue, Brea, California 92621

The determination of trace metals in water and waste discharge is common in many industries. When monitoring waste discharge, the analytical laboratory must often adhere to EPA requirements or in-house QC procedures. The most common methodology employed for these analyses are flame and furnace Atomic Absorption and Direct Current *Plasma (DCP) and Inductively Coupled Plasma (ICP) Emission techniques. Certain* techniques have advantages, such as the graphite furnace for ultra-trace determinations. In most cases, the waste water samples are equally well-suited for DCP or ICP. The objective of this paper is to demonstrate the individual benifits of atomic absorption and Plasma Emission techniques in the analysis of water to guide laboratory personnel who are confronted with choosing the proper methodology. Atomic Absorption and Plasma Emission instrumentation will be utilized and proper EPA procedures will be followed. Results will include detection limits, precision values, qualitative and quantitative analyses, linear dynamic ranges, and element ranges. For example GFAA gives superior detection limits for about 35 elements but other factors such as sample preparation must be weighted against the higher cost of plasma emission. The conclusion will provide many features of the methods to give adequate technical information and performance specifications to assure the usefulness of the techniques.

3

BACKGROUND CORRECTION IN GRAPHITE FURNACE AAS.

D.E. Shrader, L.M. Beach, T.M. Rettberg. Varian Instrument Group, 205 W. Touhy Ave., Park Ridge, IL 60068

Though graphite furnace AAS techniques are characterized by excellent analytical sensitivity and are the method of choice for the determination of trace elements in various environmental, industrial, and biological samples, significant levels of background (non-atomic) absorption can be produced as complex matrix constituents are volatilized with analyte during the atomize/read stage. In order to correct for this non-atomic absorption, "simultaneous" background correctors have been developed for GFAAS instruments.

Two types of background correctors available are deuterium and Zeeman. Each has its inherent advantages/disadvantages. Because absorption signals in GFAAS evolve and decay very rapidly (transient peaks), three factors affect the correction accuracy of either type: (1) number of measurements per second, (2) time interval between measurement of total and background absorbance, and (3) means of computing background magnitude.

A discussion of the design and operation of deuterium and Zeeman background correctors will be presented along with means of computing background magnitude. A study was performed comparing performance of the two types of correctors in various sample matrices. Examples of results will be shown. The relative merits of each background corrector will be discussed and guidelines for type selection and use presented.

4

THE CHARRING EFFICIENCY OF BIOLOGICAL MATRICES IN THE GRAPHITE FURNACE.

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

The thermal pretreatment steps in graphite furnace AAS analysis have been much less studied than the atomization stage itself. This is unfortunate because the non-volatile products of the charring clearly become the starting materials for the ensuing atomization. A particular difficulty in the charring of biological materials has been the buildup of carbonaceous residue in the furnace. While several refinements such as surfactant addition and oxygen use have helped, the problem still persists for samples which cannot be diluted due to low analyte levels. This accumulation of residue in the furnace is not a simple function of total organic mass. The nature of the organic material as well as the type and level of inorganic salts is important also. Results will be presented for a number of artificial biological matrices--polymers such as cellulose, starch, and protein and monomeric units such as sugars and amino acids. The effect of various salts upon the degradation of the organic matter will be discussed. The amount of residue remaining upon the L'vov platform or other surface after charring can be measured with a microbalance. In addition, the monitoring of the molecular background signal during both charring and atomization can be used to evaluate the effectiveness of the charring conditions. Effects of temperature and gas composition will be related to measured efficiencies.

5

GETTING THE MOST OUT OF YOUR GRAPHITE FURNACE.

G.R. Carnrick, W. Slavin. Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859-0906.

Compared with flame and plasma techniques, graphite furnaces have the following advantages: 1) Most samples may be determined without a predilution. 2) Samples as small as 1 µL may be determined. 3) Solid samples may be determined. 4) Absolute detection limits are much lower for most elements. However, a major drawback of the furnace is its slow analytical cycle time.

We will discuss how furnace cycle time can be reduced by eliminating all matrix modification and by dramatically changing the furnace program to eliminate all pretreatment steps and shortening drying time. The result is much faster throughput at the expense of higher background absorbances, thus Zeeman background correction is required.

We will also discuss some of our recent work with Ba. We have found that though Ba may be determined in the graphite furnace, it is not as convenient as most other determinations. Careful furnace alignment and selection of analytical parameters is required.

6

GRAPHITE FURNACE DETERMINATION OF MOLYBDENUM BY PALLADIUM-HYDROXYLAMINE HYDROCHLORIDE MATRIX MODIFICATION.

Ernest W. Loya. U.S. Bureau of Reclamation, 2800 Cottage Way, MP-780, Sacramento, California 95825.

By using a reduced palladium matrix modifier for the analysis of molybdenum in high-salinity natural waters, the U.S. Bureau of Reclamation's Mid-Pacific Regional Laboratory has significantly improved results obtained from graphite furnace atomic absorption spectroscopy. The comparison of data acquired with and without the addition of the matrix modifier shows dramatic precision, accuracy, and sensitivity differences. Before the addition of the modifier, the data indicated a duplicate sample outlier rate of 19 percent, a spiked sample outlier rate of 33 percent, and a characteristic mass sensitivity of 11.2 picograms/0.0044 absorbance•seconds. However, addition of the modifier reduced outlier rates to 6 percent, 3 percent, and sensitivity to 7.2 picograms/0.0044 absorbance•seconds, respectively. Corroborative accuracy verifications against reference standards of known concentration, provided by the U.S. Geological Survey and National Bureau of Standards, resulted in consistent agreement. Preliminary studies applying the modifier to graphite furnace determinations for barium, cadmium, and lead have provided equally impressive results.

7

ANALYSIS BY ICP-AES AND AAS OF RESISTANT GEOLOGICAL MATERIALS WITH A SODIUM PEROXIDE SINTER DIGESTION.

Paul H. Briggs, James G. Crock, and E.E. Foord.
U.S. Geological Survey, M.S. 928, Box 25046, D.F.C., Denver, Colorado 80225 .

Some common resistant rock forming minerals are not readily dissolved using a multi-acid decomposition, even under increased pressure. These minerals include beryl, chromite, ilminite, monazite, sphene, topaz, tourmaline, and zircon. These minerals will commonly contain a large portion of the rock's trace elemental content. To completely dissolve these resistant rock forming minerals , a rapid and simple sodium peroxide sinter digestion in a zirconium or vitreous carbon crucible at 420 degrees centigrade has been developed. The procedure uses from 50 to 100 mg of sample and up to 500 mg of sodium peroxide flux. The resulting solution is then analyzed for major, minor, and trace elements (except sodium), by ICP-AES and AAS. Reference standard values are used to verify the accuracy and utility of the method.

8

TRANSFER AND MANIPULATION OF ATOMIC ABSORPTION DATA USING REPORT MANAGER AND LOTUS 123.

F. Delles, J. Douglass, R. Matters, S. Skujins. Varian Instrument Group, 205 W. Touhy Avenue, Suite 204, Park Ridge, IL 60068.

The ready availability of personal computers in the analytical laboratory has stimulated their use for the collection and manipulation of analytical data.

This paper describes the transfer of analytical data from a Varian SpectrAA series atomic absorption spectrophotometer to an IBM PC/AT or XT. It illustrates how the *data may be transferred, incorporated into commercially available* software such as Lotus 1-2-3, and manipulated for specific types of reports simply and automatically using Lotus Macros.

Macros are programs which when executed, usually by a single key stroke, automatically simulate the pressing of a long sequence of key strokes. Several examples, including trend analysis and compositional analysis with tabular and graphical reports, will be presented.

9 NEW DIRECTIONS AND NEW SOURCES IN PLASMA FUNDAMENTAL STUDIES, M.W. Blades, L.L. Burton, and D. Liang, Dept. of Chemistry, 2036 Main Mall, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

Characterization of the inductively coupled plasma from a fundamental standpoint has been one of the long term objectives of this research group. Over the past few years comprehensive measurements of electron number density, "temperature", spectral line emission, and excited state level populations have been made. The results of these measurements indicate that the plasma is best described by a partial local thermodynamic equilibrium (p-LTE) model, the most important "excitation mechanisms" being electron collisions and radiative de-excitation. This fundamental description provides some predictive capability and this has led to the development of a potential application of fundamental studies. This has involved the development of spectral simulation software which can be used as a guide for analytical line selection and for the estimation of realistic detection limits for complex multi-element matrices.

More recently we have begun to explore "rate model" approaches to the study of excitation mechanisms, in particular, the influence of atomic parameters on level populations. These rate model calculations are being tested with experimental measurements over a wide range of operating conditions. We are also assessing the effects of solvent loading on the excitation characteristics of the ICP. Finally we have begun to study excitation mechanisms in low power, capacitively coupled plasma discharges.

10 THE ROLE OF ELECTRONS IN ATOMIC AND IONIC EXCITATION LOW IN THE INDUCTIVELY COUPLED PLASMA (ICP). Laurie J. Prell and S. Roy Koirtyohann. Chemistry Department, University of Missouri-Columbia, Columbia, MO 65211.

Inter-element enhancements of emission intensities are the rule rather than the exception in the initial radiation zone of the ICP. Effects are most pronounced with easily ionized matrix elements. Enhancement factors for specific transitions correlate with known cross sections for excitation by electrons. When the Abel inversion is used to obtain enhancement factors for specific plasma locations, and when Abel inverted absorption data are used to correct for changes in ground state populations, the correlations improve with increasing plasma radius. At a radius of 0.9 mm, the largest value for which reliable absorption data are obtained with the system, most atomic transitions lie on a straight line when the log of $\Delta I/I$ is plotted vs. the log of the excitation cross section. The ionic transitions examined also fall along a straight line but the enhancement factors are roughly 2.5 times as large as for atomic transitions with similar cross sections. An ambipolar diffusion model can be used to explain most of the observations.

11 "PRECONCENTRATION, MATRIX NORMALIZATION, AND SIGNAL ENHANCEMENT FOR ATOMIC SPECTROMETRY VIA ON-LINE DONNAN DIALYSIS". John A. Koropchak, Ewa Dabek-Zlotorzynska, Department of Chemistry & Biochemistry, Southern Illinois University, Carbondale, Illinois 62901.

Donnan dialysis is a phenomenon which results from an ionic strength gradient across an ion exchange membrane. For a cation exchange membrane, this gradient results in the transfer of cations from a sample solution into small volume, high ionic strength receiver solution. The receiver becomes enriched in the cation and anions from the sample are rejected (J. A. Cox and J. E. D. Nunzio, Anal. Chem. 49, 1272 (1977)). The process can employ tubular ion-exchange membranes, allowing continuous preconcentration and matrix normalization (J. A. Cox and Z. Twardowski, Anal. Chem. 52, 1503 (1980)). In this presentation we will discuss the application of these tubular membranes to sample introduction for atomic spectrometry. For flame atomic absorption the effects of tubing length, solution temperature, receiver flowrate and composition will be discussed. Under compromise conditions, enrichment factors above twenty can be achieved. In addition, anion interferences are eliminated and by careful selection of receiver electrolyte components ionization interferences are minimized. For ICP-AES, solution flowrate requirements are more favorable to the kinetics of donnan dialysis and higher signal enhancements can be observed. In addition, ionization interferences occurring in the initial radiation zone can be minimized by proper receiver selection. Parametric factors for this experiment will be discussed. In addition, specific advantage of matrix normalization for ICP-MS will be included.

12

REVERSE OSMOSIS PRECONCENTRATOR FOR AQUEOUS SOLUTION ION ENRICHMENT

Richard J. Stec & S.R. Koirtyohann, University of Missouri, Columbia, MO 65211
and Howard E. Taylor, U.S. Geological Survey, Denver, CO 80225.

A preconcentration system has been developed to enrich trace level ions in aqueous solutions prior to spectroscopic analysis. Using the principle of reverse osmosis, the *concentration effect is achieved simply by removing water from the sample, a process* analagous to evaporation or distillation. Water is pumped through a tubular membrane at a pressure of 475-525 psi. The membrane is a synthetic composite with a polyether sulfone support and a urea skin. The skin lies on the inside of the tube which has an inner diameter of approximently 400 µm. Water permeates through the membrane while the analyte is retained inside the fiber. The rate of water removal from the sample is directly proportional to the surface area of membrane in the system and is a linear function of pressure above 200 psi. Water permeation rates of 20 µL/min/cm^2 have been observed at room temperature. One hundred fold ion enrichments with near quantitative recovery have been obtained in as little as 15 minutes. This presentation will discuss the design and operation of the preconcentrating system as well as enrichment data for both anions and cations.

13

APPLICATIONS OF CONTINUOUS FLOW - HYDRIDE GENERATION WITH A SEQUENTIAL ICP SPECTROMETER.

M.W. Tikkanen, Applied Research Laboratories, 9545 Wentworth, Sunland, CA 91040

Hydride generation (reduction) is a mature sample presentation technique used in the determination of a number of specific elements (As, Se, Sb, Te, Pb, Sn, Ge, Bi, and Hg). It has been interfaced to various spectroscopic techniques to produce analytical systems of exceptional sensitivity. When coupled to the ICP, sub part-per-billion detection limits have been realized.

Development of a continuous flow hydride generation system has made it possible to conveniently use the hydride generation sample introduction with the sequential ICP spectrometer. Benchmark performance results of continuous flow hydride generator coupled to a low-flow, low power sequential ICP spectrometer show good short term precision and long term reproducibility. Further, detection limits and background equivalent concentrations indicate a 100-1000 fold gain in sensitivity when compared to conventional pneumatic nebulization with an ICP spectrometer.

Of significant impact on the health and environment are As, Se, Hg, Pb and Sb. Waters, wastewaters, botanical, and biological samples must be analyzed for ultratrace levels of these potentially hazardous elements. Using the continuous flow hydride generator/sequential ICP spectrometer, these elements have been determined in standard reference materials. Results indicate that matrix effects must be considered. And, for maximum efficiency, chemistries must be optimized to promote simultaneous hydride generation from these multielement samples. Finally, the analytical schemes developed must include sample preparation techniques that produce sample dissolution without loss of any of the analytes. An outline of the chemistries and preparative techniques necessary for multielement hydride generation will be given. Analytical results for several of these sample types will be shown.

14

ANALYZING HAZARDOUS WASTE USING EPA PROCEDURES ON A NEW ICP

C. Anderau, D. A. Yates, Perkin-Elmer Corporation, Main Avenue, Norwalk, Connecticut 06859-0906

Since the enactment of the Superfund and Contract Laboratory Programs, the number of laboratories analyzing hazardous wastes has increased significantly. The EPA procedures for analyzing these types of samples are very specific and involved. Since these procedures must be followed precisely, simplification of the analysis must start with the instrumentation used. The hazardous waste samples analyzed in this program include a wide variety of matrices and analyte concentrations. Many techniques are used to analyze these samples, ICP-AES being one of the primary tools. Although ICP-AES normally does not require involved methods development, it often does require operator adjustments to optimize the plasma for individual matrices. This study documents the performance of a new type of novel, 40 MHz, free-running RF generator. With this system, there is no need to adjust the power to the plasma for varying sample types, reducing the amount of time and effort needed to optimize instrumental performance. Hazardous waste samples have been analyzed using this instrument, and the figures of merit obtained will be discussed.

15 THE ANALYSIS OF DRINKING AND WASTE WATER UTILIZING A LOW POWER, LOW FLOW ICP/AES SYSTEM. William J. Kinsey. Labtest Equipment Company, 9155 Deering Ave Chatsworth, CA 91311.

Due to the increasing awareness of toxic pollutants and the environment the analysis of waste water and drinking water is continuing to attract attention. The analytical laboratory must adhere to stringent EPA methodology and utilize competent instrumentation to complete the task.
Three of the most important instrument features are: 1. Detectability/Precision; 2. Throughput; 3. Cost of operation.
Recent advances in Nebulization has proven to be of great importance for ICP/AES. Specifically, ultrasonic nebulization has improved detectability and thus has enhanced the analysis of drinking water. The necessary throughput of the analysis is completed via a polychromator supplying simultaneous determinations for most elements.
The third factor deals with the economics of the analysis. Cost savings here will help analytical laboratories serve the community in a cost effective manner. Due to the expense of operating analytical equipment instrument manufacturers are continuously striving to decrease this cost. The low power/low flow ICP system addresses this problem and allows laboratory personnel to substantially improve cost/analysis without compromising performance. Performance characteristics of a 40.68 MHz/ low power/low flow ICP simultaneous and sequential spectrometer system will be described. Strict attention will be paid to the application of drinking and waste water analysis. Data gathered utilizing ultrasonic nebulization will be presented and compared to more traditional sample introduction.

16 COMPARISON OF LOW AND ATMOSPHERIC PRESSURE ELEMENT SPECIFIC GC DETECTION USING FLOWING AFTERGLOW EXCITATION. J. T. Clay, T. M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131

Active nitrogen is a mixture of ground and excited state nitrogen atoms and molecules. When mixed with gaseous species, such as the effluent from a gas chromatograph, the active nitrogen initiates luminescence processes characteristic of the gaseous analyte. The radiation produced can be used as the basis of an element specific chromatographic detector. For example, carbon can be detected on the basis of CN radical emission or metals can be detected on the basis of atomic emission. Due to the fact that the emission monitored is correlated to specific elements within the analyte compounds coming off the column, the active nitrogen must participate in the atomization process. Thus, the chemical reactivity of the active nitrogen is a key parameter in the optimization of the detection technique. The chemical and physical characteristics of an active nitrogen plasma vary greatly depending upon the operating conditions of the system. The system pressure is one of the key parameters in the operation of an active nitrogen system. Pressures can range anywhere from one torr to one atmosphere. Some of the effects and the trade-offs that are made in going from low pressure to atmospheric pressure operation will be discussed.

17 CHARACTERIZATION OF GLASSES AND CERAMICS BY ATOMIC SPECTROSCOPY FOR COMMUNICATIONS APPLICATIONS. Thomas Y. Kometani, AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

Quantitative applications of atomic absorption and atomic emission techniques for the determination of ultratrace to major concentrations of elements in telecommunications related materials will be discussed. Successful analyses by flame and graphite furnace AAS and sequential inductively coupled plasma spectroscopy, ICP, are dependent on reliable sample preparation methods, including high temperature fusion and acid digestion in a microwave oven. Possible interferences are discussed and methods developed to compensate for errors are described. In cases where it is difficult or impossible to weigh the sample, complete analysis of all constituents, except oxygen, are performed by ICP on bulk glasses and glass films in order to establish a sample weight for calculating elemental compositions.

18

CHEMILUMINESCENCE DETECTION IN FLOWING STREAMS - IMMOBILIZED AND SOLID-STATE REAGENTS. Timothy A. Nieman, Department of Chemistry, University of Illinois, 1209 W. California St., Urbana, Illinois 61801

Luminol chemiluminescence is of interest because of low detection limits available and because the system is easily adapted to determine catalysts, hydrogen peroxide, luminol, or other analytes that are tagged with or convertible to one of these species. On inconvenience is the necessity to mix together the several solutions containing the individual reaction components. We have investigated ways in which the reaction components can be incorporated as solid-state reactors. One approach uses luminol covalently bound to the surface of small silanized silica particles. These particles are then packed into flow-through reactor/detector cells and incorporated into flow injection systems. Practical aspects (material preparation, detection limits, working range, precision, material lifetime) and fundamental characterization will be presented. In a second approach, a positively biased electrode (rather than a dissolved catalyst) can be used to initiate luminol chemiluminescence. Practical advantiges include the physical localization of emission and the ability to turn the reaction "on" and "off" via control of electrode potential. We have investigated the impact of electrode material, electrode potential, and solution composition. This approach has been applied both to the determination of peroxide and the determination of luminol. Applications for both of these approaches have combined chemiluminescence with enzyme reactions and with liquid chromatography.

19

PEROXYOXALATE CHEMILUMINESCENCE: DEVELOPMENT OF A HIGHLY SENSITIVE DETECTION METHOD FOR CHEMICAL ASSAYS. Richard S. Givens, Richard L. Schowen, Mirko Orlović, John Stobaugh, Lanny Venham, and Arun Thakur, Center for Bioanalytical Research and Department of Chemistry, The University of Kansas, Lawrence, Kansas 66045-0046.

The chemiluminescent emission generated from the reaction of a diaryl oxatate, hydrogen peroxide, a fluorescent acceptor is now being widely investigated for HPLC detectors, for trace assays, etc. We have investigated the time course of the fluorescence emission for a member of oxalate ester/hydrogen peroxide reactions and have been able to successfully model the kinetic pattern under a variety of reaction conditions, e.g. solvent variations, catalytic effects, etc. To achieve maximum luminescence from such a system during the brief period that a sample transits the detection apparatus in HPLC requires optimization of the chemical reactivity and energy transfer steps leading to the excited fluorescent state of the analyte. We have developed new oxalates, new fluorescent and chemiluminescent tags and improved reaction conditions for this chemiluminescent-based analytical methodology.

20

MICELLE ENHANCED AQUEOUS PEROXYOXALATE CHEMILUMINESCENCE, M.L. Grayeski, N. Dan, and M.L.Lau, Chemistry Department, Seton Hall University, South Orange, N.J. 07079.

Micellar solutions have been used to affect photophysical and chemical phenomena by altering the microenvironment of the species involved. Solubilities, rates of reactions, reaction yields and fluorescence efficiencies can be changed by association of an appropriate species with a micelle. These effects have been demonstrated for certain chemiluminescent reactions and can be used to alleviate some of the problems such as solvent limitations or inefficient production of light sometimes associated with the analytical applications of chemiluminescence. This paper reports the effect of micelles on the aqueous peroxyoxalate chemiluminescent reaction of 4-4'-[oxalayl bis [(trifluoromethylsulfonyl)imino] ethylene] bis (4 methylmorpholinium trifluoromethanesulfonate) with hydrogen peroxide in the presence of a fluorophor. The surfactants examined include cationic, anionic, neutral, and zwitterionic types. The effect of the various types of surfactants on chemiluminescence intensity and the analytical implications will be discussed.

21

PHOTOCHEMICAL AMPLIFIER FOR HPLC BASED ON SINGLET OXYGEN SENSITIZATION.

Curtis L. Shellum and John W. Birks. Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO 80309.

A post-column photochemical reaction scheme designed to enhance the detectability of UV-absorbing compounds has been coupled to high performance liquid chromatography (HPLC). Specifically, the method detects members of the large class of organic compounds termed "singlet oxygen sensitizers." These compounds transfer excitation energy to ground state oxygen, forming the excited singlet species, $O_2(^1\Delta_g)$. Singlet oxygen in turn reacts with a substituted furan such as 2,5-dimethylfuran (DMF) or 2,5-diphenylfuran (DPF), and UV absorption or fluorescence is used to detect either the loss of reactant (DMF or DPF) or appearance of a product. The reaction sequence is photocatalytic in nature, resulting in a large chemical amplification of the signal. Detection limits are improved by one to two orders of magnitude for a wide variety of UV-absorbing compounds. This paper will discuss the theory and characterization of the detection system as well as its application to several classes of compounds, including polycyclic aromatic hydrocarbons, substituted anthracenes, anthraquinones, and polychlorinated biphenyls (PCBs).

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RECENT ADVANCES IN REDOX CHEMILUMINESCENCE

R. S. Hutte Sievers Research, Inc., 2905 Center Green Court, Boulder, CO 80301, J. W. Birks and R. E. Sievers, CIRES and Department of Chemistry and Biochemistry, University of Colorado, Campus Box 215, Boulder, CO 80309.

Post-column reactions of analytes with oxides of nitrogen (NO_2 or HNO_3) form the basis of sensitive and selective detectors for chromatography. In the Redox Chemiluminescence Detector (RCD^{TM}) for gas chromatography, reducing agents react with NO_2 in metal catalyzed reactions to form NO, which is detected by a chemiluminescent reaction with ozone.

Gold and palladium have been previously employed as catalysts for the RCD. Recent research has been conducted using other metals and different catalyst supports with the goal of developing catalysts with different selectivities. Of specific interest are catalysts that will permit the selective detection of cycloalkanes in the presence of higher levels on non-cyclic hydrocarbons. The results of these experiments and selected applications will be presented.

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TOWARDS AN UNDERSTANDING OF REDOX CHEMILUMINESCENCE DETECTION.

Stephen A. Montzka, Robert M. Barkley and Robert E. Sievers, Cooperative Institute for Research in Environmental Sciences and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215.

The detection of compounds by chemiluminescence can offer high sensitivity and selectivity in a chromatographic system. One detector which uses these advantages is the redox chemiluminescence detector. In this detector, only compounds that react rapidly with NO_2 or HNO_3 over a heated noble metal catalyst to produce nitric oxide are detected. Reactive compounds such as alcohols, alkenes, aldehydes and ketones are sensitively detected, while water, alkanes, halogenated hydrocarbons and other less easily oxidizable compounds are not sensed. Recent studies in our laboratory have focussed on understanding the chemistry that occurs on catalyst surfaces to produce NO. It has been determined that at least two different reaction mechanisms can result in the production of NO. The reaction that predominates, however, occurs between the organic compound and NO_2 bound to the metal surface. Additional results will be discussed with an emphasis on developing a simple mechanistic picture of the catalytic process.

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CHEMILUMINESCENCE DETECTION OF SULFUR COMPOUNDS IN GC AND HPLC. Marnie K. Carroll and John W. Birks. Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO 80309. Harold A. Stuber, Sievers Research, Inc., 2905 Center Green Ct., Boulder, CO 80301.

Reduced sulfur compounds may be detected with high sensitivity and selectivity in both GC and microbore HPLC by means of fluorine-induced chemiluminescence. Effluent from the GC or vaporized effluent from the LC is mixed with F_2 produced on-line from a non-toxic source gas and the chemiluminescence from several emitting species, especially vibrationally excited $HF(v \leq 6)$ and electronically excited thioformaldehyde, is detected. Detection limits are in the low pg to low ng range for a variety of thiols, sulfides and disulfides, and the working curves are linear over at least three orders of magnitude. *Notable among the compounds that do not respond are* SO_2, CS_2, *COS, and* H_2S. *Selectivity of the* detector for reduced organosulfur compounds over hydrocarbons and alcohols is as much as seven orders of magnitude, making the detector applicable to both liquid chromatography and supercritical fluid chromatography. Applications involving pesticide analysis, consumer products and biological metabolites will be discussed.

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THE CHEMICAL GENERATION OF THE NEW METASTABLE STATES OF PN AND AsN. Thomas L. Henshaw, Michael A. MacDonald, Donald H. Stedman and R.D. Coombe. Department of Chemistry, University of Denver, Denver, CO. 80203.

The kinetics and spectroscopy of the chemiluminescent reaction between $P(^4S_u)$ and $As(^4S_u)$ atoms with $N_3(^2\Pi_g)$ radicals were studied with a discharge-flow apparatus. The PN chemiluminescence exhibited a previously unobserved band system which was identified as $PN(a'^3\Sigma^+)$. From the spectrum of the new system, the molecular constants of the excited state were calculated to be $T_{el} = 25863 \pm 16$ cm^{-1}, $\omega'_e = 957 \pm 8$ cm^{-1} and $\omega'_e x'_e = 18 \pm 2$ cm^{-1}. The new band system of PN appears to significantly Franck-Condon shifted with 0,3 being the most intense. The removal of P atoms by the P + N_3 reaction yields a rate constant value of $4.7 \pm 0.4 \times 10^{-11}$ cm^3 s^{-1}. A new AsN chemiluminescent band system was also observed with the molecular constants determined to be $T_e = 21666 \pm 5$ cm^{-1} and $\omega'_e = 730 \pm 2$ cm^{-1} from its spectrum. The new AsN spectrum is significantly Franck-Condon shifted with 0,4 being the most intense band.

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INTERACTION OF TRIFLUOROHALOMETHANES WITH ACTIVE NITROGEN. Andrew P. Ongstad, Shelle J. David, and Robert D. Coombe. University of Denver, Chemistry Department, University Park, Denver, CO 80208.

Recently, it has been shown that excited triplet N_2 metastables can be produced chemically by the reaction of $N(^4S)$ atoms with N_3 radicals. As part of an effort to couple this chemical system to the IF molecule (a well-known laser candidate), a number of observations of the interaction of CF_3I (used to produce IF by reaction with fluorine atoms) with "active nitrogen" (used as a source of N atoms) were made. The rather unexpected results obtained led us to observe interactions between active nitrogen and the analogous species CF_3Br and CF_3Cl. Further, measurements of rate constants for the quenching of $N_2A^3\Sigma_u^+)$ by collisions with CF_3I, CF_3Br, and CF_3Cl were made. These data and observations are reported, and possible mechanisms for production of the excited species observed are discussed.

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ION EXCHANGE IN A SAND AND GRAVEL AQUIFER. E. M. Thurman and M. Ceazan, U.S. Geological Survey, Water Resources Division, Box 25046, MS 418, Denver Federal Center, Denver, Colorado 80225.

We have measured the transport of both ammonium and potassium in ground water both by a divergent tracer test and by a study of aquifer contamination by sewage. The field site is located in a sand and gravel aquifer on Cape Cod, Massachusetts, which has been contaminated by sewage for 50 years. In the divergent tracer test, we injected ammonium and potassium chloride which were retained on the aquifer solids displacing calcium, magnesium, and sodium from the aquifer exchange sites. In the contaminated aquifer we mapped out the distribution patterns of ammonium and potassium and found a retardation factor of 2.5, which corroborates our ion-exchange hypothesis. Furthermore, displaced magnesium, calcium, sodium, and strontium were found down gradient as the displaced ions. Because ammonium is an important contaminant commonly found in polluted ground waters, the process of ion exchange is important in predicting ammonium transport, as well as the distribution of major cations in ground water.

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The Concentration and Isolation of Hydrophilic Organic Acids from Water on XAD-4 Resin. G.R.Aiken and D.M.McKnight. U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002.

Organic acids were isolated from three surface waters and a groundwater from an aquifer contaminated with crude oil using a two column array consisting of XAD-8 and XAD-4 resin. XAD-8 is an acrylic ester resin with a surface area of 140 m^2/g and an average pore diameter of 250 angstroms. XAD-8 was used in this scheme to isolate the more hydrophobic organic acids present in these samples such as humic substances. XAD-4 is a styrene divinyl benzene resin with greater surface area (750m^2/g) and smaller pore diameter (90 angstroms) than XAD-8. In general, XAD-4 has a greater capacity for lower molecular weight solutes than XAD-8, and was used to isolate the more hydrophilic acids in the samples. In the samples studied, 30-50% of the dissolved organic carbon was isolated on XAD-8, while 10-15% was isolated on XAD-4. ^{13}C-NMR data indicate that the fraction of the organic acids retained on the XAD-4 resin is less aromatic than the aquatic fulvic acid isolated on the XAD-8 resin. In other respects, the spectra show that these samples are very similar to aquatic fulvic acid. Of particular environmental significance is the amount of carboxylic acid functional group content in the hydrophilic acid fraction. These hydrophilic acids may play a significant role in the environment, however, this fraction of the dissolved organic carbon is often ignored in the study of environmental chemistry.

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HIGH-PERFORMANCE ION-EXCHANGE CHROMATOGRAPHY OF PEPTIDES AND OLIGONUCLEOTIDES ON NON-POROUS ION EXCHANGERS

Yoshio Kato, Takashi Kitamura, Akane Mitsui and Tsutomu Hashimoto
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Porous packing materials have been employed with great success for a long time in liquid chromatography. On the other hand, non-porous packings have been examined recently and it has been found that they are very useful in particular for the separation of proteins. We have examined application of ion-exchange chromatography on non-porous ion exchangers to the separation of peptides and oligonucleotides. Peptides and oligonucleotides with wide range of molecular weights were separated under various conditions on non-porous spherical hydrophilic resin based anion and cation exchangers of 2.5 μm mean particle diameter (TSKgel DEAE-NPR and SP-NPR). Peptides with molecular weights higher than 1,300 and oligonucleotides larger than tetramer could be separated very rapidly, in less than 10 minutes, with high resolution and recover. Accordingly, non-porous packings should be useful for rapid analyses and micropreparative separations of these saples.

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DETERMINATION OF 7α-HYDROXYRIBOFLAVIN AND CORTISOL IN HUMAN URINE USING COUPLED COLUMNS OF HYDROPHILIC GEL AND ALKYLATED SILICA WITH PROPIONATE BUFFER AS THE MOBILE PHASE.

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We have recently reported that riboflavin and its derivatives could be separated on a column of hydrophilic gel (Asahipak GS-320H, a cross-linked vinyl alcohol copolymer) using a propionate buffer of pH 4.4 (1.0 mol/kg H_2O) sa a mobile phase. Since we inferred that propionate buffer behaved like a mixture of a buffer and an organic modifier such as a mixture of formate buffer and methanol, we tried elution of riboflavin and its derivatives from a column of alkylated silica (LiChrosorb RP-Select B) with a propionate buffer of pH 4.8 (0.5 mol/kg H_2O) at 40°C. 7α-Hydroxyriboflavin, FMN, FAD and riboflavin were eluted in the order described. Cortisol could be eluted from LiChrosorb RP-Select B with a propionate buffer of pH 3.5 (2.0 mol/kg H_2O). In order to determine 7α-hydroxyriboflavin and cortisol in human urine, we have first fractionated urine samples on Asahipak GS-320H using propionate buffer of pH 5.4 (0.5 mol/kg H_2O) or pH 3.5 (2.0 mol/kg H_2O). The former buffer was used for the separation of 7α-hydroxyriboflavin and the latter for cortisol. The peak of 7α-hydroxyriboflavin or cortisol was transferred to LiChrosorb RP-Select B by the use of a four-way valve and eluted with propionate buffer of pH 4.8 or 3.5. Detection limit of 7α-hydroxyriboflavin (fluorescence at 520 nm) and cortisol (absorption at 254 nm) was 10 pmol/ml and 50 pmol/ml respectively.

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GC/MS STUDIES OF ORGANIC COMPOUNDS IN THE TROPOSPHERE.

Robert M. Barkley and Robert E. Sievers, CIRES and Department of Chemistry and Biochemistry, Campus Box 215, Boulder, CO 80309-0215.

Combined gas chromatography/mass spectrometry has been used in several different studies to assist in the identification of organic compounds that are present in the troposphere. The samples analyzed range from automobile exhaust gases that require no pre-concentration to clean-air vapor phase and particulate phase organics that are detectable only after sample integration times of minutes to hours. Sampling methods employed in these studies include concentration on porous polymer sorbents, solvent extractions of snow and rain, and low-volume collection of particulates. In all cases, GC/MS was used to characterize the samples. The compounds identified are from both natural and anthropogenic sources and represent many different classes of organics, including polynuclear aromatic hydrocarbons, terpenes, aldehydes, carboxylic acids, ketones, lactones, and phenols. The data have been related to the removal of organic compounds by precipitation and to the synchronous changes that occur in oxygen-containing organics in atmospheric particulate matter.

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SELECTIVITY RELATED TO THE PRESENCE OR ABSENCE OF END-CAPPING OF ALKYL-BONDED SILICA GELS IN REVERSED-PHASE MODE LIQUID CHROMATOGRAPHY, Cai Hong*, Junko Yamaguchi and Toshihiko Hanai, Gasukuro Kogyo Inc. 237-4 Sayamagahara, Iruma 358 Japan and * Dep. Anal. Chem., Shenyang College of Pharmacy, Shenyang, P.R. China

A variety of octadecyl-bonded silica gels are commercially available, and each packing has different capacity and selectivity in reversed-phase mode liquid chromatography. The end-cap effect, in particular, was studied from the retention and peak shape of pyridine, and capacity was studied from the difference of capacity ratios of hydrophobic compounds. Four types of octadecyl-bonded silica gels were synthesized from one batch of silica gel, and their selectivity was examined from the comparison of energy and enthalpy effects for polyaromatic hydrocarbons, alkanes, alkylbenzenes, halogenated benzenes and alkylalcohols. In accordance with the energy effect, which is related to the delocalization energy of polyaromatic hydrocarbons, alkanes and alkylbenzenes were more retained on end-capped octadecyl bonded silica gels, and alkylalcohols were more retained on non-end-capped octadecyl bonded silica gels. The chromatographic behavior of these compounds was similar on end-capped but different carbon loaded ODS silica gels.

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CELLULOSE DIACETATE FIBERS AS THE STATIONARY PHASE IN MICROCOLUMN LIQUID CHROMATOGRAPHY. Yoshiaki Kiso, Sanitary Engineering Laboratory, Toshiyuki Nagoshi and Kiyokatsu Jinno, Trace Characterization Laboratory, Toyohashi University of Technology, Toyohashi 440, JAPAN

For separation of structural, chiral and isotopic isomers, several packing materials have been developed and cellulose tri- and diacetates are one of the packings used in chiral separations. However, they have also other functions for LC separations such as very unique characteristics for recognition of structural isomeric compounds. For the isomeric compounds' separations, analysis of aromatic compounds are one of the most important and urgent problems to be solved in environmental and biological chemistry because of their carcinogenicity or mutagenicity. Therefore, stationary phases which can separate those compounds selectively or specifically are required in the practical analytical point. In this presentation, we would like to report the unique characteristics of cellulose diacetate for the selective separation of alkylbenzenes and polycyclic aromatic hydrocarbons, where micro-capillary column packed with cellulose fibers as the stationary phase is used.

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INDIRECT PHOTOMETRIC DETECTION IN MICRO HPLC. Daido Ishii and Toyohide Takeuchi. Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464 Japan

Indirect photometric detection allows sensitive detection of non-UV-absorbing species by adding an UV-absorbing compound in the mobile phase when the analytes displace, transfer or interact with the visualization agent. This technique is frequently utilized in ion-pair or ion-exchange chromatography. The dynamic reserve(defined as the ratio of the background to its noise level), concentration of the visualization agent and the displacement ratio all play important roles in indirect photometry. Applicability of indirect photometry in micro HPLC has been examined in this paper. In ion-exchange chromatography, the limit of the detection is proportional to the concentration of the visualization agent in the mobile phase if the retention time of the analyte can be kept constant. Therefore, it is important to find out a visualization agent with high absorptivity and a column with a very low ion-exchange capacity. On the other hand, the concentration of the visualization agent does not affect the retention time of the non--electrolytes(analytes) very much. The detection limit of non-electrolytes was at the subnanogram level. The analytes eluting close to the system peak give larger siganls, which means that the detectability of the analytes of interest can be improved by selecting the visualization agent.

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CHROMATOGRAPHIC INTERFACES FOR SUPERSONIC JET SPECTROSCOPY. Murray V. Johnston, Department of Chemistry and Biochemistry, Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309-0215.

In this talk, a review will be given of our recent work to develop interfaces between capillary chromatography and supersonic jet spectroscopy. In a gas phase supersonic jet expansion, the analyte is cooled to a low temperature (ca. 10 K) to obtain a dramatic increase in the selectivity of molecular absorption and emission spectroscopy. Recent advances have allowed low picogram detection limits to be achieved with excellent selectivity in capillary gas chromatography. Applications to supercritical fluid and liquid jet expansions have been demonstrated as well. Current research involves coupling supersonic jet spectroscopy to Fourier transform spectroscopy in the ultraviolet-visible region. In this way, complete jet spectra can be obtained on the chromatographic timescale. Applications of this method to chemical analysis will be discussed.

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WHOLE COLUMN DETECTION CHROMATOGRAPHY. John W. Birks and Kathy R. Rowlen. Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO 80309.

In "whole column detection" chromatography, components of a complex mixture are detected simultaneously at multiple detection zones along the entire length of the analytical column. It is anticipated that the added dimension of column position will result in numerous advantages such as 1) increased peak capacity in position-time space, 2) rapid generation of k' data by use of programmed elution, 3) real time control and optimization of the separation process, 4) exact timing information for post-column switching and detector optimization, 5) knowledge of where the last peak is, 6) continuous tracking of the elution order of peaks, 7) the possibility of stopped flow quantification, and 8) continuous monitoring of the integrity of the column packing. Several of these advantages have been demonstrated in theory by means of computer modeling of chromatographic process utilizing whole column detection (*Anal. Chem.* 1986, *58*, 900-903).

In order to implement whole column detection, we are investigating the applications of UV absorption, photoacoustic spectroscopy, fluorescence, and electrochemical detection. These approaches to on-column detection will be described and results given where available.

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CAPILLARY ION-EXCHANGE CHROMATOGRAPHY WITH CONDUCTIVITY AND ULTRA-VIOLET ABSORPTION DETECTION. H. Hatano, H. Wada. Department of Chemistry, Faculty of Science, Kyoto University, Oiwake-cho Kitashirakawa, Sakyo-Ku Kyoto 606 Japan

Microbore capillary ion-exchange chromatography (MCIC) on a fused-silica capillary column packed with ion-exchanger beads has been developed for separation of minute amounts of organic and inorganic ions and for detection by conductivity and ultraviolet (UV)-absorption detectors. Strong anion-exchange resin latex and bonded anion-exchange resin, YEW AX-1, and MCI CQA CQK, were papcked into fused silica capillary tubes. Ion chromatograph, YEW 100 IC Analyzer was used throughout these experiments with major modifications for miniaturized capillary chromatographic instrumentation. Eluents, a mixure solution of sodium bicarbonate and sodium carbonate, and of potassium hydroxide and several organic modifiers in stead of a potassium biphthalate solution for improving sensitivity and detectability were used for separating of strong and weak anions. Separation of silicate, IO_3^-, F^-, arsenite, BrO_3^-, Cl^-, HS^-,CN^-, NO_2^-, CNO^-, ClO_3^-, Br^-, NO_3^-, BF_4^-, I^-, SCN^-, ClO_4^-, weak acid mono- and di-carboxylic and ketoacids anions was performed with nanomole quantities. Several applications of the MCIC analysis were carried out to water sample of river and lake, and fruit juice samples. About 20 compounds of nucleic acid bases, nucleosides and nucleotides were separated and detected with the MCIC, at a detection range about 20 to 200 ppb.

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A NEW DETECTOR FOR LIQUID CHROMATOGRAPHY BASED ON CHEMILUMINESCENCE, H. A. Stuber, Sievers Research, Inc., 2905 Center Green Court, Boulder, CO 80301, R. E. Sievers and J. J. DeAngelis, CIRES and Department of Chemistry and Biochemistry, University of Colorado, Campus Box 215, Boulder, CO 80309.

A new detector for liquid chromatography (LC) is based on the post-column oxidation of analytes with dilute nitric acid to form nitric oxide (NO). The NO is separated from the liquid stream in a simple device and detected by its chemiluminescence with ozone. The reactions of analytes with nitric acid (typically 0.1 normal) have been conducted in uncoated fused silica capillary GC columns at temperatures of 150-300 °C and pressures sufficient to maintain the liquid phase. Any organic or inorganic analyte which can be oxidized under these conditions can be detected in theory. Glucose has been detected at the 1-10 nanogram level, and alcohols, acids and other compound types respond. We are investigating the detection limits achievable, compatibility with solvents and buffers, and promising applications. Sensitive detection of analytes having no chromphores (such as carbohydrates and many monofunctional compounds) is theoretically possible with this approach.

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ANTICHROMATOGRAPHY - MEMBRANE SEPARATIONS VIA FACILITATED TRANSPORT. C.A. Koval Department of Chemistry and Biochemistry, Campus Box 215, University of Colorado Boulder, CO 80309

Chromatographic separations result from differential affinities of analytes for the stationary phase which retards movement with respect to the mobile phase. While chromatographic separations are selective and efficient, separation takes a long time and the amount of material that can be separated is limited. Therefore, chromatography is far more applicable to analytical separations than to industrial separations.

Facilitated transport is a process in which the flux of a particular species (permeate) across a membrane is enhanced over its diffusional flux. This enhancement is the result of a reversible complexation reaction between the permeate and a mobile carrier within the membrane and can be as great as a factor of 100. If the reaction between the permeate and carrier occurs for only one component of a mixture, facilitated transport can result in a selective and rapid separation for large amounts of material.

In this presentation, a brief conceptual and mathematical description of facilitated transport will be followed by several examples and the author's views on important areas for ongoing research.

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EFFECT OF COLUMN DIMENSIONS ON HPLC SEPARATIONS USING CONSTANT VOLUME COLUMNS.

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Todays analytical HPLC columns have different dimensions ranging from approximately 1 to 4.6 mm in diameter and 30 to 300 mm in length. So, it becomes difficult to decide which column to use in order to achieve optimum resolution of a mixture. This work studies the effect of column dimensions on resolution, peak shape, detection, and column capacity. Three columns having the same volume were selected for this study, 153 x 4 mm, 116 x 4.6 mm, and 50 x 7 mm. Results will be presented and recommendations will be made.

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ABSTRACT NOT AVAILABLE

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A BONDED CAPILLARY COLUMN FOR ANALYSES OF ACIDIC SAMPLES

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Carboxylic acids, in their free form, have been difficult to analyze quantitatively by capillary gas chromatography. The high polarity of the carboxylic acid group and the molecules' tendency to form hydrogen bonds have caused peak tailing and irreversible absorption. This, in turn, causes poor peak resolution and quantitation. Many types of columns have been evaluated for analyses of free carboxylic acids. None of these columns, however, have taken advantage of the technology and improvements available in the form of bonded phase capillary columns. In response to this problem, a new bonded phase capillary column has been developed to perform quantitative analyses of the free carboxylic acids. To demonstrate the value of this new column, chromatograms and reproducibility data will be presented for analyses of volatile free fatty acids, glycols/diols, cresylic acids, acrylic acids, and other acidic compounds.

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CHARACTERIZATION OF VOLATILES IN POLYMERS BY HEADSPACE GAS CHROMATOGRAPHY.

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Physical and chemical properties including materials compatability are significantly influenced by the presence and outgassing of volatile components in polymeric materials. These components can include monomers, solvents, blowing agents, catalysts, moisture, plasticizers, impurities, antioxidants, ultraviolet absorbers and degradation products. They affect strength, dimensional stablity, chemical and environmental resistance, and processing characteristics. Electrical and structural failure resulting from corrosion, crazing and depolymerization have been typical compatibility problems associated with volatile components from materials in past polymer systems. Recent publications have shown headspace gas chromatography to be a valuable tool for monitoring the volatile components evolved from plastics at ambient or elevated temperatures. Analytical methods have been established to provide a new capability for material characterization, certification and to enhance the overall quality assurance program for plastic production parts. Instrumentation and analytical techniques including examples of analyses performed will be discussed.

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EVALUATION OF A SPECTROPHOTOMETRIC TECHNIQUE FOR DETECTING THE TOTAL RETENTION OF MINOR COMPONENTS DURING AN HPLC SEPARATION.

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A common area of uncertainty in establishing a Reference Standard by HPLC is the possible retention of a component on the analytical column. This occurrence could result in an over-estimate of the purity. Rossi, et.al. (Anal. Chem., 58, 1410 (1986)) described a procedure, using a photodiode array detector and a data storage system, for detecting the total retention of sample components on the column. Their intent was to detect and extract the spectra of retained components. Their model system used large fractions of components having grossly different spectra. In an attempt to find the applicability of this approach to Reference Standard characterization, their technique was applied to a real-world, model system using a late eluting compound as the totally retained component. Pump and detector noise prohibited detecting even five percent of the retained dimer. An understanding of the limitations of the previous approach has led to the development of an off-line system to estimate the spectral contribution of species retained on the HPLC column. Using a simple dual beam UV-Visible spectrophotometer, detection of retained components amounting to one percent or less is possible. Noise due to pumping and long term spectrophotometer drift is eliminated while maintaining the characterization capabilities of the original technique. A detailed discussion of the applicability, benefits and limitations of this technique will be presented.

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LASER INDUCED PHOTOACOUSTIC SPECTROSCOPY AS APPLIED TO WHOLE COLUMN DETECTION CHROMATOGRAPHY.

John W. Birks and Kathy L. Rowlen. Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO 80309. James Avery and Ken Duell. Department of Computer Science and Electrical Engineering and CIRES.

Laser induced photoacoustic spectroscopy is used to detect analytes along the length of a quartz HPLC column. A tunable, pulsed dye laser is used as the excitation source. The column is mounted on a translation stage and scanning achieved by moving the column past the fixed laser beam. A piezoelectric transducer, attached to the quartz, is employed as the detector. Delay tme analysis indicates that a sizable portion of the photoacoustic wave is transferred directly to the quartz in the form of a Rayleigh wave. A frequency spectrum of the raw photoacoustic wave is obtained by Fast Fourier Transformation of the averaged signal. The frequency maximum is found to be independent of excitation position. The amplitude of the frequency maximum, however, is found to have a slight dependence on column position due to acoustic attenuation and resonance effects for this particular geometry. A chracteristic reponse pattern of the column is currently being developed for use in normalizing the frequency spectrum. It is anticipated that the amplitude maximum in the normalized frequency spectrum will be directly proportional to analyte concentration.

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DEVELOPMENT OF AN IMPROVED ABSORBANCE DETECTOR FOR HPLC

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Measurement of ultraviolet absorbance is the single most important detection technique in LC practice. In principle, a conventional absorbance measurement should have a shot noise limit of less than one microabsorbance. In practice, the latest commercial detectors achieve short term noise of 50 microabsorbance (one sec. time constant) and long term drift of 100 microabsorbance. A major source of the excess noise is the presence of random thermal lenses formed by energy deposition in the flowing sample.

A detector which is based on a retroreflective array (RRA) in the phase conjugate configuration is being developed. The detector is expected to find its greatest use in chromatographic systems where the working volume must be less than one microliter. Previous applications of the RRA demonstrated signal-to-noise ratio improvements of a factor of 4-6, suggesting that this detector could supersede conventional absorbance detectors where quiet, stable operation is needed. The retroreflective array will provide substantial optical compensation for refractive index gradients, over-illumination of the cell, and imperfectly aligned optical components.

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CHARACTERIZATION OF THE FLAME PHOTOMETRIC DETECTOR USING A STATISTICALLY DESIGNED EXPERIMENTAL APPROACH

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As part of the characterization of the Flame Photometric Detector, the response of the detector was studied as a function of the flow rates of the gases, the concentration of sulfur containing compounds, and the detector temperature. The quenching observed when carbon is present was studied using factorial experimental design. The results of the quenching experiment will be discussed in terms of their implication on the mechanism. Other supporting data also suggests that there are two regions - one of higher sensitivity and one of greater selectivity. A model for the response will be presented.

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COLUMN SWITCHING TECHNIQUE FOR RAPID SEPARATION OF FREE AMINO ACIDS BY REVERSED-PHASE ION PAIR LIQUID CHROMATOGRAPHY, Mitsuko Hirukawa and Toshihiko Hanai, Gasukuro Kogyo Inc., 237-4 Sayamagahara, Iruma 358 Japan

A rapid and simple separation technique is required in the analysis of amino acids. Amino acids are classified into three groups, and very delicate eluents are required for amino acid analyzer using ion-exchange resin. Polar compounds have been separated by reversed-phase mode ion pair liquid chromatography instead of ion-exchange liquid chromatography, however, the separation of free amino acids by ion-pair liquid chromatography required a long analysis time, and the separating power of reversed-phase columns was not fully exploited. Column switching techniques have been used for sample cleaning and for selective separation. A column switching technique using different alkyl-bonded silica gels was therefore applied to ion-pair liquid chromatography for developing a rapid separation of free amino acids. Some ghost peaks led to misidentification, but such problems were resolved by monitoring three dimensional chromatograms of effluent. This flexible separation system for free amino acids was demonstrated in food analysis.

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HPLC SEPARATION WITH UV DETECTION OF TRACE AMOUNTS OF 4-METHOXYPHENOL AND ETHYLENE GLYCOL DIMETHACRYLATE IN 2-HYDROXYETHYL METHACRYLATE. Jeffrey A. Hurlbut and Jack D. Cummins, Chemistry Department, Metropolitan State College, 1006 11th Street, Denver, Colorado 80204

Soft contact lenses consist of polar plastics made by free radical polymerization of 2-hydroxyethyl methacrylate (HEMA, CAS 868-77-9); and trace impurities in the HEMA liquid influence the physical properties of the finished lenses. Three of the common impurities in HEMA are methacrylic acid (MA; CAS 79-41-4), 4-methoxyphenol (MOP; CAS 150-76-5; an inhibitor), and ethylene glycol dimethacrylate (EGDMA; CAS 97-90-5). These impurities can be separated from HEMA by HPLC using a RP-C18, 5 micron, 25 cm Beckman column with a mobile phase of 50% methanol:50% water (10% methanol). The MA, HEMA and the EGDMA absorb at 230 nm, and the MOP has a wavelength maximum at 292 nm. The retention times range between 4 and 23 minutes. Calibration curves for MOP and EGDMA are linear between 5 - 200 and 50 - 500 ug/ml respectively. Typical concentrations for MOP and EGDMA in HEMA samples tested are 10 - 300 and 500 - 7000 ug/ml respectively. The HPLC results compare favorably with a colorimetric MOP determination and with a gas chromatographic EGDMA determination.

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HPLC SEPARATION WITH UV DETECTION OF 2-HYDROXYETHYL METHACRYLATE FROM SOFT CONTACT LENSES. Jeffrey A. Hurlbut and Jack D. Cummins, Chemistry Department, Metropolitan State College, 1006 11th Street, Denver, Colorado 80204.

Soft contact lenses are generally made from 2-hydroxyethyl methacrylate (HEMA; 2-methyl-2-propenoic acid, 2'-hydroxyethyl ester; CAS 868-77-9) by a free radical polymerization. The resulting polymer is carefully ground and then hydrated to give the finished lense. Preliminary results indicate that up to 2% of the HEMA remains unreacted, and can be leached out of the finished lense. The HEMA is extracted from the lense with either water or methanol, diluted to volume, injected into the HPLC, and detected at 230 nm. The mobile phase is 50% methanol: 50% water (10% methanol) at a flow of 1.0 ml/min; the column is a 5 micron RP-C18, 25 cm, Beckman column. The calibration curve is linear between 0.50 and 250 ug/ml with 20 ul injections, and the detection limit is 0.6 ng at 230 nm. Factors such as extraction solvents, extraction times, and extraction temperatures are discussed; mass spectrometry, infrared, and nuclear magnetic resonance data for HEMA are presented; and a comparison of this HPLC method with a gas chromatographic method is also presented.

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EVALUATION OF CARRIER GAS PURIFIERS FOR THEIR ABILITY TO REMOVE OXYGEN AND MOISTURE L.M. Sidisky, R.J. Bartram, W.J. Pinnick, and R.E. Shirey
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A careful evaluation of carrier gas purifiers has shown that many of these devices do not provide the protection that is claimed. In fact, many of the purifiers are admitting high quantities of moisture and some oxygen into the carrier gases. High purity gas was introduced into each of seventeen gas purifying devices. Oxygen and moisture levels were monitored in the effluent from each device. Increased contaminant levels were attributed to the purifier. Those devices that caused the highest levels of contamination were further tested to identify the specific sources of the contamination. Results will be presented in detail.

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FACTOR ANALYSES OF SIMULATED EQUILIBRIA. Joseph M. Conny and Robert R. Meglen. Center for Environmental Sciences, University of Colorado at Denver, 1100 14th Street, Denver, CO 80202.

Factor analyses involving principal component extraction followed by Varimax rotation were performed on simulated complex equilibria. Using a modification of the program COMPLEX, equilibrium data vectors were generated as a function of the total concentration of selected reactants. Factor analyses were performed using the multivariate statistical package ARTHUR. Results show that abstract factors are chemically interpretable as associations of chemical species or "sub-equilibria", and these associations change with pH. The effects of a slack variable and error perturbation on the factor analyses were also investigated to simulate the effect of measurement error. In addition to single equilibria, factor analyses were performed on data matrices containing multiple equilibria. The equilibria contained the same chemical species but differed in the concentrations of the reactants. Results showed that each equilibrium can be identified as a factor. Simulated complex equilibria appear to be suitable as test data for studying the strengths and weaknesses of factor analytical techniques.

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CHEMOMETRIC RESULTS OF A COLORADO LAKES ACIDIFICATION STATUS STUDY.

Lynne A. Taylor and Robert R. Meglen, Center for Environmental Sciences, University of Colorado at Denver, Denver, Colorado 80202.

Various chemometric techniques have been applied to a study of the acidification status of Colorado lakes. The study intends to 1) define the baseline chemical characteristics for Colorado's lakes 2) produce more reliable, sensitive, and varied measurements of lake acidification 3) identify the major influences on lake chemistry and 4) develop a classification model for monitoring and predictive purposes. This continuing study currently involves 250 different lakes sampled during the years 1984 to 1986, from all areas of Colorado. The lake waters were analyzed for 30 different chemical variables including major anions and cations, trace cations, and electrochemical measurements. Additional data on the surrounding bedrock geology, soil, vegetation, morphology, and usage characteristics have also been gathered and incorporated into the study. The data have been interpreted by the use of three different pattern recognition techniques. Cluster analysis and factor analysis have been used as exploratory techniques, and classification analysis used in developing a model. These techniques have also been applied to other lake studies from different areas of the country to compare and then combine the Colorado data with other lake studies. This paper presents the results of the cluster and factor analysis, and the classification model developed for the Colorado lakes.

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DIMENSIONALITY OF ANALYTICAL DATA AND CONFIDENCE IN QUANTITATION.

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The avaliability of analytical instruments that are capable of producing high dimensional data arise the question: are there any advantages for having such data? The types of data are arranged according to the information each sample produces. Zeroth order: scalar (single measurement); First order: vector (spectrum, chromatogram); Second order: matrix (LC/UV, MS/MS, 2-D NMR); Third order: triade (MS/MS/LC). It will be shown that first and second order data are special cases of third order. Third order data is very flexible and does not require any information on the analytes present in the sample. Only a comparison to a single reference value of the determined analyte is required. Therefore, even data from a non-repetative instrument is still useful. Second order data also does not require knowledge of all component present in the sample but requires the calibration data matrix of the determined analyte. Therfore, repeatability is the crucial factor in obtaining good results. First order requires the knowledge all analytes present in the sample, and a large bias results when an analyte that does not occur in the calibration samples appears in the unknown sample. Zeroth order data requires a fully selective response and interferences can not be corrected nor detected.

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TREE-STRUCTURED CLASSIFICATION AND ANALYSIS OF PAH AIR SAMPLES USING THE PROGRAM CART,

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The program CART implements algorithms for constructing classification and regression trees based upon a methodology described by Breiman, Friedman, Olshen, and Stone in their recent book, "Classification and Regression Trees" (Wadsorth, 1984). While the methodology offers a number of important and useful features, it has yet to be used to any great extent in chemical data analysis. Among these features are the simple and easy to use form of the resulting tree-structured algorithms; a ranking of the measurement variables relative to their importance in building the algorithms; the ability of the methodology to simultaneously handle measurement variables of both ordered and categorical types; the effective use of cross-validation to provide estimates for classification and prediction accuracies; and its ability to handle data sets with missing measurements or differing numbers of sample measurements. For this paper we shall concentrate upon the classification aspects of CART. The program is applied to a set of data generated by the Norwegian Air Research Laboratory at Lillestrom, Norway, and which consists of 24-hour polycyclic aromatic hydrocarbon (PAH) air samples collected at four different sites in southeastern Norway. CART is used to explain the chemical structure of the sample data and to generate a simple tree-structured classification algorithm which could be used to identify the extent automobile traffic is a contributing source to the PAH of atmosphere samples in that part of Norway. Research sponsored by Royal Norwegian Council for Scientific and Industrial Research.

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SO THE ANALYSES ARE DONE, NOW WHAT? R. Roger Johnson, Solutech Corporation, 12600 W. Colfax Avenue, Suite C420, Lakewood, CO 80215

This talk is directed toward the environmental manager who receives analytical data from the laboratory. It is also directed toward the chemist who is interested in what happens after the results have been submitted as well as anyone curious as to how the personal computer has been applied to handle environmental information.

Managing and reporting information on personal computers can ease the drudgery of reporting data to environmental agencies. It can also speed the process and enable trend evaluations not feasible when manual analysis is the alternative. The speaker will briefly review EPA guidelines for reporting ground water monitoring data then describe an applications software package used by companies to help manage the reporting of data to the APA and state agencies.

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A HYBRID EXPERT/DATABASE SYSTEM FOR SELECTING METHODS OF SURFACE ANALYSIS. Frank A. Settle, Jr., Department of Chemistry, Virginia Military Institute, Lexington, VA 24450 and Michael A. Pleva, Department of Chemistry, Washington & Lee University, Lexington, VA 24450.

The development of a hybrid information system to assist persons unfamiliar with methods of surface analysis will be presented. The system utilizes commercially available software running on an IBM-XT. Several expert system tools including EXSYS, KDS, Insight 2+, Rulemaster, PC-Easy and PC-Plus were considered for developing the expert system component. The criteria for choosing the shell used in the current system will be discussed. The database component selected was dBASE III PLUS. The system user describes his or her analytical problem by responding to questions posed by the expert system. After receiving this information, the expert system produces a prioritized list of methods suitable for the analysis described by the user and a list of codewords to be used by the data base. The user then has the option of using the data base component of the system to receive more detailed information from the dBASE III PLUS on the methods selected by the expert system. The structure and operation of both the expert system and the database will be described.

This work is funded by NSF grant #CHE-8517147.

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INEXPENSIVE SOFTWARE FOR GEOLOGISTS AND OTHER SCIENTISTS. Dave Rich, Geotech Computer Systems, 10875 E. Orchard Pl., Englewood, CO 80111

A wide variety of software has become available for technical applications. This talk covers public domain and user-supported software for geologists and other scientists. Topics covered include data bases, mapping, statistical analysis, and graphics. General purpose programs with technical application will also be discussed. Most examples will be programs that run on IBM PC or compatibles.

The emphasis is on programs which are easy to use and provide reliable results at minimal or no cost. Many of the programs to be presented provide capabilities comparable to commercial programs.

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LABORATORY ROBOTICS - THE MISSING LINK IN TOTAL LABORATORY AUTOMATION.

Art Ambrose, Perkin-Elmer Corporation, 4036 Youngfield, Wheatridge, CO 80033

Most samples take several distinct steps as they pass through the laboratory: identification, preparation, analysis, and data reduction. In the past 40 years significant progress has been made in automating the measurement step, making it faster and of better quality. Also, the data reduction step has been automated with the introduction of LIMS systems. Now, tedious and time consuming sample preparation steps are frequently the bottleneck of sample flow.

Recently a laboratory robotics system has been introduced which fills in this missing link of laboratory automation. A flexible and accurate arm performs the necessary sample manipulations. A high level, fourth generation laboratory robotics language makes it easy to program the application and incorporate extensive verification. A powerful RS-232 communication facility allows the system to intelligently communicate with any device, including the analytical instrument and a LIMS system, thus yielding a completely automated laboratory from sample receipt to the final report.

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QUALITY CONTROL FUNCTIONS IN LIMS,

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Theoretically, LIMS systems have tracked sample status and the associated analytical data. Real time systems allow users anywhere on the system to instantly call up any information about a sample as soon as it is entered. Powerful tabular and graphical reporting modules provide instant and meaningful interpretation of results. Recently, the addition of powerful new QC functions allows LIMS to track the quality of laboratrory data as well. Work lists automatically encorporate predefined QC parameters such as standards, spikes, blanks, duplicates, etc. when they are generated. The printed work list is reproduced on a CRT screen for spreadsheet style results entry. Powerful calculations automatically generate calibration curves and calculate sample concentrations, as well as determine sample accuracy and precision. Sample results can be compared to multiple specification ranges. Special reports can then be produced to give an instant indication of the quality of the laboratory procedures.

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AUTOMATED MAINTENANCE AND REPORTING OF ANALYTICAL QUALITY ASSURANCE ON A PERSONAL COMPUTER,

Richard D. Beaty and Leigh A. Richardson, Telecation Associates, P.O. Box 1118, Conifer, Colorado 80433

In order to support the validity of analytical results, a certain amount of overhead work is required for quality control. This overhead involves not only additional analyses of spiked samples, duplicates, and quality control samples, but also requires additional bookkeeping to track, document, and report quality assurance data. SMARTLOG (R) and SMARTLAB (R) are two laboratory data management programs, developed by TELECATION ASSOCIATES for personal computers, which vary in the amount of laboratory information maintained in the data files. Both programs store analytical results for all analyzed samples, including all quality control work. After analysis, data may be reviewed and evaluated on the computer screen. Quality control data are identified and processed according to the type of QC calculation to be performed, including calculation of spike recovery, determination of agreement between sample replicates, and analysis of quality control standards to verify the accuracy of the analysis. The programs support all of these techniques, generating both tabular and graphical output of results. For laboratories involved in the Contract Laboratory Program, SMARTLOG and SMARTLAB offer automatic generation of the CLP QC forms. This includes the reporting of sample data with all the required flags, according to CLP specifications. Report formats may be customized for individual purposes or to allow for changes which may occur in the CLP protocols.

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ESR DATA ACQUISITION AND MANIPULATION ON THE IBM PC

Philip D. Morse, II University of Illinois College of Medicine and Illinois ESR Research Center, 506 S. Mathews, Urbana, IL 61801

We have developed software which will allow data acquisition from both Varian and IBM/Bruker ESR spectrometers. The software runs on an IBM PC and currently uses analog/digital boards manufactured by Metrabyte and IBM. Other A/D boards could be used with minimal changes. The program permits collection of data from the spectrometers either during a sweep of the magnetic field, or, for observation of transient phenomena, independently of the magnetic field sweep. Data are collected as rapidly as 50 µsec/point (although faster speeds are possible). During collection in field sweep mode, the A/D converter averages data at each recorder position (magnetic field) for a time determined by the sweep speed of the spectrometer. Data scale directly to height independently of the length of time of the scan. Marker data from a field frequency lock and gauss meters can also be collected independently. Data are plotted to the computer screen after every scan.

The program uses menus to select data collection, plotting, data manipulation, and disk access. The menus are displayed on the first five lines of the screen and the rest of the screen is devoted concurrent display of data. The displayed data can be expanded and shifted by using the cursor arrow keys. Access to the display manipulation routines is from any menu. Data can be plotted to the spectrometer plotter, the computer monitor, or a digital plotter such as the Houston HI-PLOT. Data are stored on disk as ASCII-readable files and can be retrieved by FORTRAN, BASIC, FORTH, and PASCAL programs. Some simple manipulation of the data is permitted as well. This includes double integration, baseline correction, scaling, "glitch" correction, spectral subtraction, and smoothing. The current version of the program is written in 8086 assembly and compiled BASIC. Program listings, operational software, and hardware suggestions are available from the author at the University of Illinois ESR Research Center. Supported by NIH RR 01811.

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SELECTED PESTICIDES IN EXTRACTS OF CORE MATERIALS AND IN GROUND WATER FROM KANSAS.

Thomas R. Steinheimer, U.S. Geological Survey, MS 407, Box 25046, Federal Center, Denver, CO 80225

Soil cores from test plots on agronomy farms owned and operated by Kansas State University have been analyzed for residues of pesticides. Cores extended through the root zone of each tilled plot from land surface to a depth of about 1.5 m. At one site, two herbicides, alachlor and atrazine, were identified in a ground-water sample. Results of studies on the recovery of pesticides from fortified soil cores and from ground water are presented along with various options for extraction of core materials. The nine pesticides examined--atrazine, cyanazine, alachlor, metolachlor, metribuzin, trifluralin, terbufos, triadimefon, and triadimenol--are representative of the second- and third-generation chemicals commonly used in agriculture today.

Electron-impact mass spectra recorded on a triple-stage-quadrupole instrument are compared with mass spectra recorded on an ion-trap detector. A single nine-component mixture of standard-reference-grade pesticides dissolved in benzene were run on each instrument configured as a GC/MS with the injector operated in the splitless mode. Mass-spectral comparisons focus on the quality of the spectra as compared to those in the *EPA/NBS Library of Toxic Chemicals*, sensitivity of the instruments, and measured differences in ion abundances.

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GROUND- AND SURFACEWATER MIGRATION OF CORN PRODUCTION PESTICIDES.

T.D. Spittler, R.O. Mumma[1], J.K. Hall[2], W.F. Ritter[3] and Russell B. Brinsfield[4].

The movement of applied pesticides through soil and into groundwater or as surface runoff, is being studied in a series of paired watersheds--one of each set producing corn by conventional techniques, *the others under conservation or "No-Till"* methods. Four soil types are under investigation in NY, PA, DE and MD. Water samples are obtained via measured surface runoff through calibrated flumes, wells, suction lysimeters and pan lysimeters. Soil samples are derived from waterborne silt and horizon cores. After solid phase extraction/concentration/elution of water samples on C_{18} reverse-phase cartridges, atrazine, simazine, propazine, cyanazine, metolachlor and alalchlor are determined by capillary GLC at a sensitivity of 1 ppb, or less. Soils are extracted with 90% methanol and analyzed in a similar manner (sensitivity 10 ppb). Cartridges are subsequently eluted with MeOH for determination of carbofuran and 3-hydroxy carbofuran by HPLC (sensitivity 2 ppb). Water samples are also solid-phase extracted on amino ion exchange columns, and, following elution, dicamba and its metabolite (3,6 dichlorosalicyclic acid) are determined by ion-pair HPLC. Preliminary data showing the differential downward movement of pesticides as a function of both tillage practices and soil type are presented, as are comparative runoff measurements for the pairs of watersheds.

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A CRITICAL EVALUATION OF THE NEW ION TRAP REVISION 3.00 WITH AUTOMATIC GAIN CONTROL.

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Positive results have been obtained in the preliminary investigations of the Ion Trap Detector System (ITDS) revision 3.00 software which includes an automatic gain control (AGC). Cryoconcentrated gas phase samples and split injections of liquid phase standards prepared in isopentane were used to evaluate the "working" limit of detection and the overall performance of the ITDS system. The limits of detection have been improved by the new software revision to below 10 pg (on column) for most compounds investigated. The "working" linear dynamic range of the system has been improved to include on column amounts from 10 pg to 10 ug. However, mass spectra acquired for on column amounts above 100 ng of many compounds still contain mass fragments with m/z rations greater than those found in quadrupole-generated spectra for identical compounds. These high-mass fragments reduced the reliability of spectral matches between sample spectra and library spectra from the prepackaged National Bureau of Standards library.

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SCREEN ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN WATER, SOIL, OR SOLID WASTE BY CAPILLARY GAS CHROMATOGRAPHY FLAME IONIZATION DETECTION.

David A. Taylor. Enseco Incorporated, Rocky Mountain Analytical Laboratory, 4955 Yarrow Street, Arvada, CO 80002.

The volatile organic compounds are extracted into dodecane or methanol depending on the sample matrix. Bromofluorobenzene is added to the extracts as a retention time reference standard. The extracts are analyzed by gas chromatography, flame ionization detection using a wide-bore capillary column. The dilution for further analysis by gas chromatography mass spectrometry or gas chromatography Hall detector is determined by external standard quantitation.

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REVIEW OF ANALYTICAL METHODS FOR THE DETERMINATION OF CHEMICALS REQUIRING MEASUREMENT UNDER ENVIRONMENTAL REGULATIONS.

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A number of environmental regulations including: the Safe Drinking Water Act; the Clean Water Act; the Resources Conservation and Recovery Act; the Comprehensive Response, Compensation, and Liability Act; and the Toxic Substances Control Act, require the monitoring and measurement of a large number of chemicals in a variety of environmental matrices. This paper reviews the development and present status of the analytical methods that have been promulgated by the U. S. Environmental Protection Agency to meet the requirements of these regulations. Emphasis will be placed on the hazardous and toxic organic chemicals since they constitute the area of greatest interest and concern to the environment and present the most difficult analytical problems in terms of matrix effects and interferences.

The regulations have resulted in a number of analytical methods for the same or similar chemicals. These methods will be compared and efforts to reduce the total number of methods will be discussed. New method approaches with potential future regulatory application will also be considered. Analytical quality control practices required for regulatory application of the methods will be presented.

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POLLUTANTS IN DRILLING MUD PITS - COMPARISON OF TOTAL ANALYSES WITH TOXICITY CHARACTERISTIC LEACHING PROCEDURE AND LYSIMETER LEACHING RESULTS.

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The environmental impact from surface runoff and leachate from drilling mud pits is currently being investigated by the American Petroleum Institute (API) and the Environmental Protection Agency (EPA). The basic components of water-base drilling fluids include fresh or saline water, clays (bentonite) to increase viscosity and create a gel, barium sulfate (barite) to serve as a weighting agent, chromium lignosulfonates to control viscosity, and lime/caustic soda to increase pH. Normally, the waste drilling fluids and the associated drill cuttings are disposed of in an on-site pit. Soluble constituents present in the disposed mud as additives, constituents of the drill cuttings, unauthorized materials placed in the pits, or other trace contaminants may have the potential to leach into the groundwater near the site or move into the surrounding environment as surface runoff. The transport and fate of these constituents involves processes such as absorption, microbial degradation, ion exchange, chemical precipitation, particulate transport, and others. The purpose of this study was to attempt to simulate the conditions found in mud pits in the field using both the Toxicity Characteristic Leaching Procedure (TCLP) and also using lysimeter (column) leaching techniques. The results of these leaching tests will be compared to the results of total analyses of the drilling mud wastes in order to determine the mobility of various inorganic, metal, and organic species in the environment.

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COMPARISON OF LIQUID-CHROMATOGRAPHIC ANALYSES OF CARBAMATE PESTICIDE RESIDUES: (1) POST-COLUMN DERIVATIZATION AND FLUORESCENCE DETECTION OF DIRECT-AQUEOUS INJECTIONS AND 2) MULTI-WAVELENGTH ABSORBANCE DETECTION OF SAMPLE EXTRACT INJECTIONS.

Sharon M. Johnson, Stephen L. Werner, and Larry D. Becker. U.S. Geological Survey, Branch of Analytical Services, 5293 Ward Road, Arvada, CO 80002.

Six carbamate pesticides (aldicarb, carbaryl, carbofuran, methomyl, oxamyl, and propham) and four degradation products (aldicarb sulfone, aldicarb sulfoxide, 3-hydroxycarbofuran, and 1-naphthol) were examined using both solvent extraction and a direct-aqueous injection method. This comparison study involved two separate determinations on each sample, but used the same liquid-chromatographic system. Samples, both direct-aqueous and extract injections, were separated on a C_{18} column and absorbance was measured at four wavelengths. The effluent was then derivatized and the fluorescence of the resulting products measured, all in a continuous flow-stream system. Direct-aqueous injections alternated with injections of the corresponding extract, enabling direct comparison of results. The major problem involved in the post-column derivatization and fluorescence detection method is that only N-methyl compounds will form this fluorescent derivative, and neither propham nor 1-naphthol have N-methyl groups. 1-Naphthol does exhibit natural fluorescence, and by choosing an absorbance wavelength near the propham maximum, acceptable detection limits can be achieved. Results indicate that better efficiency is achieved by the direct-aqueous injection method, both in terms of time per sample and in total recovery of residues from spiked solutions. The detection limit varies for each compound, but the limits are all less than 0.1 microgram per liter.

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A LOOK AT MERCURY LOSS FROM SOLUTIONS FROM VARIOUS TYPES OF CONTAINERS.

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Aqueous mercury samples and standards are routinely preserved using nitric acid. It is known that some mercury is lost with time even if preserved with nitric acid. This study looks at mercury loss from solutions using the variables of time, container type, initial mercury concentration, and preservative type. Also proposed is the mechanism by which mercury ion stays in solution and nitric acid, as a preservative, is evaluated using this mechanism. A possibility for using other preservatives is studied in the light of this mechanism. Experimental work confirming theoretical ideas is done and the use of containers and preservaties is evaluated. Nitric acid is found to be an inadequate preservative for mercury solutions under some conditions and a more universal preservative is suggested.

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DETERMINATION OF CYANIDE AT PARTS PER BILLION LEVELS; Jeffrey J. Rosentreter, R. K. Skogerboe, Department of Chemistry, Colorado State University, Ft. Collins, Colorado 80523.

The measurement of cyanide at the low parts per billion levels characteristic of regulatory requirements has remained a pressing problem. In the present research, selective reaction chemistry has been used to develop an indirect measurement of cyanide. Cyanide containing samples are reacted with silver metal to form the soluble dicyano-silver complex and the silver concentration is determined by atomic absorption. It has been shown that cyanide can be determined at the one ppb level using flame methods and at lower levels using non flame methods. It has also been demonstrated that reaction kinetics can be used to differentiate between free cyanide, weak acid dissociable cyanides, and total cyanide. Data will be presented to illustrate the features of the method.

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DETERMINATION OF TRACE NICKEL AND COBALT IN NATURAL WATERS BY ADSORPTIVE DIFFERENTIAL PULSE STRIPPING VOLTAMMETRY; Robert S. Tieman and Vinay Kumar, Physical Sciences Dept., Northern Kentucky University, Highland Heights, KY 41076.

Adsorptive differential pulse stripping voltammetry (ADPSV) at a static mercury drop electrode was used for the trace determination of nickel and cobalt in natural waters (river, lake, ocean etc.). The measurements were carried out in the presence of ammonia buffer (pH 9.3) and dimethylglyoxime. The electrochemical reduction of Ni(II) and Co(II) and the consequent occurrence of voltammetric peaks is due to the formation of their dimethylglyoximates. After optimization of the instrumental parameters, the linear ranges and the detection limits were established. The results from the calibration plot and standard addition methods have been compared. The concentration of nickel was found to be in the 5 - 20 ppb range with a relative standard deviation of 12%. The preliminary results for the cobalt determination indicate its concentration to be 1 - 5 ppb.

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ANALYSIS OF LOW LEVEL NUTRIENTS IN THE UG/L RANGE USING A HIGH SPEED RANDOM ACCESS CONTINUOUS-FLOW ANALYZER, Anthony Buccafuri, Aldo Conetta, Donald A. Burns, Bran+Luebbe, Technicon Industrial Systems, 511 Benedict Avenue, Tarrytown, N.Y. 10591, (914) 631-8000, Telex No. 131-418

It is well documented that segmented continuous-flow analysis is ideally suited for the automation of chemical analyses in a wide variety of samples. Most recently a new generation, fully integrated wet chemical analytical system has been introduced. It employs state-of-the-art hydraulics, electronics, and software for data reduction. All operating functions are computer controlled. The system has the required sensitivity and stability that is ideal for low-level nutrient analyses in pristine, estuarine, and seawater samples, where the nutrient concentrations typically fall in the range from 1 to 100 ug/L. Because of the high sample workload and associated ease with which these sample types can be contaminated, the nutrient determinations are best done by automation using well established colorimetric procedures. In the analytical scheme, for all low-level measurements, samples are minimally diluted with reagents specified for the particular test and, yet, the stoichiometry is maintained for completeness of reaction. In addition, high optical amplification is required to achieve a minimum detection limit of approximately 1 ug/L. Use of a 50 mm pathlength flowcell provides the optical expansion required. The hydraulics have also been optimized, whereby "bubble-through-the-flowcell" is used, thus ensuring analytical sample rates of 100 - 120/hour. Experimental details will be provided for the low-level analyses of ammonia, o-phosphate, nitrate - nitrite, nitrite and silica.

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AN EVALUATION AND COMPARISON OF ION CHROMATOGRAPHY, SEGMENTED FLOW ANALYSIS AND FLOW INJECTION ANALYSIS FOR THE DETERMINATION OF NITRATE IN NATURAL SURFACE WATERS. Eileen M. Burke, F. Xavier Suarez, and Daniel C. Hillman. Lockheed-EMSCO, 1050 E. Flamingo, Las Vegas, Nevada 89109.
Edward M. Heithmar. U.S. Environmental Protection Agency, EMSL-Las Vegas, P.O. Box 15027, Las Vegas, Nevada 89114.

A study to evaluate the comparability of IC, SFA, and FIA for the determination of nitrate in natural surface waters has been completed. Assessment of method performance was based on the precision, accuracy, and detection limit obtained from analyses of synthetic and natural samples by each technique. Under optimum conditions, the long-term (one week) precision (as RSD) and accuracy (as % bias) for each method are typically 5% and -9% for IC, 5% and 0.6% for SFA, and 4% and 3% for FIA, respectively. The short-term (1 day) precision (as RSD) and accuracy (as % bias) are similar with typical values of 4% and 9% for IC, 4% and 4% for SFA, and 3% and 6% for FIA. The detection limits for each method are 0.004 mg/L for IC, 0.001 mg/L for SFA, and 0.002 mg/L for FIA. Similar results were obtained for each method when natural samples were analyzed. IC analysis time is 5.5 min/sample, however chloride and sulfate can be analyzed simultaneously with nitrate. SFA and FIA can analyze 30 to 60 samples/hr, but only nitrate can be determined.

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EXAMINATION OF TRACE ELEMENTS IN NATURAL SURFACE WATERS SUBJECT TO ACIDIC DEPOSITION. J. M. Henshaw, Lockheed-EMSCO, 1050 E. Flamingo # 120, Las Vegas, NV 89109 and E. M. Heithmar, T. A. Hinners, U.S. Environmental Protection Agency, P.O. Box 15027, Las Vegas, NV 89114.

Despite increasing awareness of the need to determine the chemical status of natural waters, the examination of trace elements in these waters has been limited by the analytical semsitivity or sample throughput of existing techniques. The ability of inductively coupled plasma - mass spectrometry to scan the entire mass range with ng/L sensitivity has facilitated the study of trace elements in natural waters. More than 250 lake samples from the EPA's Eastern Lakes Survey were analyzed by ICP-MS to examine the distribution of trace elements. Correlations of trace element concentrations with pH and other water quality parameters were examined, as were the relationships between trace elements and watershed characteristics. Possible relationships between elements will also be discussed.

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THE ANALYSIS OF PARTICULATE COLLECTED ON MEMBRANE FILTERS IN A DICHOTOMOUS SAMPLER. Dewayne L. Ehman, Ph.D., J. Scott Mgebroff, Vincent C. Anselmo, Ph.D., and J. Maxine Jenks, Ph.D. Texas Air Control Board, 6330 Highway 290 East, Austin, Texas 78723.

The Texas Air Control Board (TACB) is part of the PM-10 network and this includes the deployment of dichotomous samplers which collect particulate in two aerodynamic ranges: 0 to 0.2 micrometers, and 2 to 10 micrometers. The TACB has the capacity of analyzing the particulate on the filters by X-ray fluorescence spectroscopy as well as measuring the total particulate mass on the filter. As a part of the continuing process of evaluating our analytical methods, we evaluated the distribution of particulate on selected filters and we extracted others and analyzed the extractates by independent methods and compared these results with the XRF analytical results. Our results show that the distribution of particulate is a function of the design of the samples. The analytical results will show that the polypropylene ring on the filter contributes to the background if an entire filter is extracted and that the results by XRF can be influenced by the fact that the beam of X-rays does not "see" the entire filter. Also, the results of the analysis of selected filters by scanning electron microscopy will be discussed.

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MEASUREMENT OF STONE SURFACE WETNESS WITH THREE ELECTRONIC MOISTURE SENSORS, Randolph B. See, Michael M. Reddy and Richard G. Martin, U.S. Geological Survey, Box 25046, MS 407, Denver Federal Center, Denver, CO 80225, and Martin Enterprises, 3150 Xenon Street, Lakewood, CO 80215.

A relative-humidity probe, a calcium sulfate coated circuit grid, and a limestone-block resistor were tested for determination of surface wetness at stone surfaces exposed to conditions that produce moisture deposition. The sensors were tested under controlled laboratory conditions of constant relative humidity and temperature. Laboratory tests indicated that relative humidity did not cause snesors to become saturated. However, relative humidity levels did control the rate at which sensors dried after being saturated with distilled water. The sensors were also tested for 8 weeks under field conditions in Newcomb, New York. Onsite testing of the relative-humidity probe and calcium sulfate coated circuit grid indicated that these sensors responded to a duirnal wetting and drying cycle; the limestone-block sensor responded only to precipitation. Each sensor provided a unique estimate of surface wetness; further study will be required to determine the most appropriate sensor to use for estimating actual wetness of stone surfaces.

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COMPARISON OF COLLECTION EFFICIENCIES AND CHEMICAL CONCENTRATIONS FROM COLOCATED PRECIPITATION SAMPLERS. LeRoy J. Schroder, U.S. Geological Survey, Denver, Colorado, Richard C. Graham, John K. Robertson, and John Obal, U.S. Military Academy, West Point, New York.

Nine precipitation samplers were compared at the National Trends Network site located at the U.S. Military Academy at West Point, New York. Six of the precipitation samplers were Aerochem Metrics model 301, and three samplers were Geotech model 650. The precipitation sensors were set at different electrical resistances to test this effect on collection efficiency. All nine samplers were operated for weekly sampling periods; the precipitation sample was removed each Tuesday. The mass of precipitation in the sampler bucket was compared to a precipitation gage that was assumed to be 100% efficient. Weekly collection efficiencies ranged from 15 to greater than 100%. The model 301 samplers usually had a greater collection efficiency than the model 650 samplers. Weekly collection efficiency was least when the collected sample weight was 200g or less. However, the sampler collection efficiency is minimal for storms with light or misty rain. Eleven analytes were determined for samples with a volume of at least 40 mL. If the volume was less than 40 mL, determination of pH and specific conductance was performed onsite, and the remaining sample was discarded. A non-parametric test was used to determine if analyte concentrations were significantly different among the samplers. Results of this test indicates that statistically significant differences exist for analyte concentrations among the samplers.

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ACID RAIN ANALYSIS: WHAT'S IN STORE FOR THE FUTURE?

Mark E. Peden. Illinois State Water Survey, 2204 Griffith Drive, Champaign, Illinois 61820.

"As a rule, rain is not acid far from towns. If it is acid, artificial circumstances must be suspected." This succinct summary of the acid rain phenomenon was written by Robert Angus Smith in a book published in 1872 in England. Entitled Air and Rain: The Beginnings of a Chemical Climatology, this early monograph linked emissions from coal combustion in urban areas to a general decline in air quality and the creation of acid rain. Smith's book also described differences in air and rain quality that existed between urban and rural environments and presented the first documented procedures for the collection and analysis of precipitation. Since Smith's pioneering work in the nineteenth century, chemical measurements of rainwater have been made in most other European countries, Canada, Japan, the United States, and virtually every industrialized nation in the world. The analysis techniques that have been employed during the past century have evolved to the point where instrument sensitivities are no longer the limiting factor in accurately measuring the trace levels of compounds contained in precipitation. Sample collection and handling protocols have, therefore, become increasingly important as the interest in precipitation chemistry extends to measurement of trace metals and organic priority pollutants. A review of the techniques and difficulties associated with sampling and processing samples for these low level constituents will be presented along with a retrospective assessment of analytical methodology development.

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KINETICS OF ION REMOVAL FROM DECIDUOUS AND CONIFEROUS CANOPIES BY ACID RAIN.

Larry J. Puckett. U.S. Geological Survey, 432 National Center, Reston, VA 22092.

Rainfall collected under forest canopies is generally found to have higher concentrations of most dissolved constitutents as a result of washoff of dry-deposited particulates and leaching from canopy surfaces. For this investigation rainfall and deciduous and coniferous throughfall samples were collected sequentially in approximately 2.5 mm increments at the Mill Run watershed in northwestern Virginia. All samples were analyzed for H^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, and SiO_2. Concentrations and net fluxes of dissolved constitutents decreased as the event proceeded. Those ions which originate primarily as dry deposition (Ca^{2+}, H^+, NO_3^-, SO_4^{2-}) exhibited large and rapid decreases in both concentration and net deposition during the first 5.0 - 7.0 mm of rain, after which a more gradual negative trend became established. Ions leached from inside vegetative components of the canopy (K^+, Mg^{2+}, Na^+, Cl^-) decreased in concentration and net deposition at a fairly shallow and constant rate. The exception to these trends was H^+ which exhibited negative net deposition under the deciduous canopy as the result of buffering and ion exchange reactions. For both canopy types Ca^{2+} and SO_4^{2-} removal rates were similar indicating dissolution of $CaSO_4$ particulates, or rapid exchange of H^+ for Ca^{2+}. Given that SiO_2 concentrations were at or near the detection unit, dissolution of dry-deposited alumino-silicate minerals did not appear to be a major source of cations.

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DETERMINATION OF ALUMINUM IN NATURAL WATER BY DIRECT-CURRENT PLASMA OPTICAL-EMISSION SPECTROSCOPY

Edward J. Zayhowski, Merle W. Shockey, Allen J. Heakin, Mark R. Hill, U.S. Geological Survey, Mail Stop 407 Box 25046, Denver Federal Center Denver, Colorado 80225

In 1986, the U.S. Geological Survey's national water quality laboratory in Denver, Colorado analyzed about 8,000 natural-water samples for aluminum by direct-current plasma optical-emission spectroscopy (DCPOES). Filtered and digested natural-water samples were analyzed for dissolved and total-recoverable aluminum by the DCPOES technique. The 308.215-nm wavelength, where a detection limit of 10 µg/L is obtainable, was chosen over the 396.152-nm wavelength even though far superior detection limit and sensitivity are obtainable at the 396.152-nm wavelength. Despite the superior detection limit and sensitivity at the 396.152-nm wavelength, stray light from strong emission of calcium at 393.366-nm and 396.847-nm results in positive interference that needs to be eliminated by a lengthy, two-point background-correction technique. Although the detection limit at the 308.215-nm wavelength is less superior than the detection limit at the 396.152-nm wavelength, precision and accuracy is comparable, and the rate of analysis is increased substantially. Lithium chloride is added to samples and standards to help control enhancement from alkali and alkaline earth metals. Glycerin also is added to samples and standards as a viscosity modifier to normalize transport efficiency. Comparison of precision, accuracy, and detection limits with the alternative techniques of inductively coupled argon-plasma optical-emission spectroscopy, graphite-furnace atomic-absorption spectroscopy, and flame atomic-absorption spectroscopy with chelation extraction, will be presented.

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THE DETERMINATION OF WATER SOLUBLE BORON AT NINE IRRIGATION STUDY SITES IN THE WESTERN UNITED STATES. Stephen A. Wilson Kathleen C. Stewart, Ron C. Severson. U.S. Geological Survey P.O. Box 25046 MS 928 Denver Co. 80225

The irrigation of arid and semi-arid lands in the western United States has prompted concern over the transport of selected trace elements during the movement of irrigation waters through the soil and into return flow systems. An element of particular interest is boron due to its adverse impact on citrus and other plants. One measure of potential boron effects is the "available boron" determined using a hot water extraction of soils and bottom sediments. Extractable boron concentrations in bottom sediments from the nine sites ranged from less than 0.4 to 130 mg/Kg in the solid samples. Upon closer examination of the data it was determined that the available boron varied, depending upon the soil to water ratio used. Increasing the extracting ratio from 1/2 (soil/water) to 1/100 resulted in a 33% increase in the amount of boron removed from the sample. The mechanism governing this process will be discussed, especially as it relates to the transport of boron and other oxyanions in bottom sediments.

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NEW ELECTROANAL TECHNIQUES FOR LOW LEVEL CHLORINE SPECIES. Calvin O. Huber, Department of Chemistry and Center for Great Lakes Studies, University of Wisconsin-Milwaukee, P.O. Box 413, Milwaukee, WI 53201

Environment considerations are causing decreased levels of chlorine and chloramines in discharges to surface waters from disinfection or biofouling operations. These new requirements often strain the capabilities of even the best of the prescribed standard methods. Further, the number of determinations needed and the nature of the samples are such that field personnel, not necessarily experienced laboratory analysts, must often perform the determinations. Often distinguishing free hypochlorous acid/hypochlorite from combined chloramines is needed. Several new instruments for low level chlorine have been developed here in response to the requirements outlined above. The new instruments are aimed at selectivity, low levels (< 0.1 mg/L Cl), speed, and operator convenience. They involve new electrode materials, on stream reaction flow injection analysis, coulometry and new electrode reactions. Results for novice operators are compared to those for experienced analysts. Applications to water chlorination and other research studies have been made.

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FLUOROMETERIC DETERMINATION OF SELENIUM, Alan L. Dunhill, Donna M. McKinney, and Sharri L. Alexander. Colorado Department of Health, 4210 E. 11th Avenue, Denver, Colorado 80220.

Colorado waters contain both selenium and sulfate. Sulfate is known to interfere with selenium when analyzing by graphite furnace atomic spectroscopy. Because of this interference the Colorado Department of Health (CDH) Inorganic Laboratory has received permission from the United States Environmental Protection Agency (USEPA) to use this method as an alternate test procedure (ATP). The procedure used is a nitric acid-perchloric acid digestion followed by addition of hydrochloric acid. The selenium is then complexed with EDTA, the pH is adjusted to 4.5, followed by complexing with diaminonaphthalene and extracted with cyclohexane. The fluorescence is read on a Turner Model 111 fluorometer, the curve calculated and the concentration determined. Also included is a short overview in comparative testing needed for USEPA approval as an alternate test procedure.

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PULSE POLAROGRAPHIC DETERMINATION OF NATURALLY OCCURRING CR(VI) IN SOILS AND WATERS. George R. Meadows, Larry L. Jackson, and Larry P. Gough. U.S. Geological Survey, MS928, Box 25046, DFC, Denver, CO 80225.

The traditional method for determination of hexavalent chromium in soils has been a colorimetric test, utilizing a redox reaction between the chromium and the indicator diphenylcarbazide. This method is quick and reliable over a limited concentration range. The lack of stability of the colored compound at higher concentrations of Cr(VI) and the inability of the test to detect concentrations less than 100 ppb, necessitates the development and utilization of new techniques in environmental studies, where concentrations of Cr(VI) less than 50 ppb are important.

This paper will discuss the application of an electrochemical technique, differential pulse polarography (DPP), for the analysis of low concentrations of hexavalent chromium in soils collected from an ultramafic area in northern California. Initial testing of these soils, with the colorimetric method, showed the presence of Cr(VI), but at levels too low for quantitative determination. Using DPP, however, we have determined levels as low as 10 ppb in both phosphate extract solutions of these soils and in surface waters draining the area.

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ANALYTICAL CHEMISTRY OF TRACEMETALS: SOME REFLECTIONS AND CHALLENGES. Rm. Panayappan and John C. Cooper. Naval Research Laboratory, Code 6170, Washington, DC 20375-5000. 202-767-2703.

During the past 15 years trace metal analysis has become a prominent branch of analytical chemistry. A quantitative estimate of trace metals of a particular sample can really solve many industrial chemical problems. This presentation will address three important topics related to the field. First, some historical aspects of different types of analytical techniques will show its emergence from a field characterized by individual instrumental methods to the present day multi-technique field. Second, applications of different analytical methods such as AA, emission spectroscopy, XRFS, ESCA and others to the quantitative determinations in different kinds of samples and relative advantages of each will be discussed. Third, areas that will be important for the future development of science and technology and that offer significant intellectual challenges will be explored.

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MERCURY-203 LABELING STUDY OF GEOLOGICAL SAMPLE PREPARATION AND DETECTION PROCEDURES FOR DETERMINATION OF TRACE CONCENTRATIONS OF MERCURY BY COLD VAPOR ATOMIC ABSORPTION, A. J. Montoya and D. Knab. Los Alamos National Laboratory, P. O. Box 1663 MS K484, Los Alamos, New Mexico 87545

In CVAA determinations of trace concentrations of mercury in geological samples, matrix effects can cause interferences with the extraction, reduction, aeration, and/or detection of mercury. In an effort to develop a procedure to minimize these effects, variations in sample preparation procedures were evaluated by labeling samples with Hg-203 to monitor the relative concentrations of mercury through all stages of the analysis. Gamma count data for Hg-203 labeled soil samples and USGS and NBS standard reference materials indicate that dissolution with HF, HNO_3, and $HCLO_4$ and moderate heat cause no significant loss of mercury. Further, results indicate that treatment of samples with $KMNO_4$ and $K_2S_2O_8$ is still necessary to eliminate nearly all interferences to the detection of mercury by CVAA. The three procedures evaluated yielded the following Hg concentrations for USGS sample GXR no. 3 (Accepted value 360 ppb Hg): Leach only - 201 ppb Hg; Leach with $KMNO_4/K_2S_2O_8$ treatment - 262 ppb Hg; Dissolution with $KMNO_4/K_2S_2O_8$ treatment - 363 ppb Hg. Modification of procedures and techniques to incorporate these findings should lead to improved accuracy and precision in CVAA determinations of trace concentrations of mercury in geological samples.

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NONVOLATILE ORGANIC ACIDS IN GROUNDWATER CONTAMINATED WITH CRUDE OIL.

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Nonvolatile organic acids resulting from the microbiological degradation of crude oil were isolated from a contaminated aquifer in Bemidji, Minnesota. A two column array consisting of XAD-8 resin followed by XAD-4 resin was used to isolate the acids. XAD-8 retained the more hydrophobic organic acids in the sample, such as long chain fatty acids, while the more hydrophilic acids, with a greater concentration of carboxylic acid functional groups, was retained by the XAD-4 resin. Initial studies on the chemical composition of the isolates involved gas chromatography-mass spectrometry (GC-MS) and ^{13}C nuclear magnetic resonance spectroscopy (NMR). Preliminary GC-MS studies indicated that these samples are complex mixtures of organic acids. Positive identification of the individual compounds in these mixtures was hampered by the complexity of the chromatograms. The solution state ^{13}C-NMR spectra suggest that aromatic and isoparaffinic components of the crude oil have been selectively preserved in the form of carboxylic acids.

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THE DISTRIBUTION OF OXIDIZED AND REDUCED ARSENIC IN THE SEDIMENT AND INTERSTITIAL WATER OF THE CHEYENNE RIVER ARM OF LAKE OAHE, SOUTH DAKOTA.

Walter H. Ficklin and Jerry M. Motooka. U.S. Geological Survey, Federal Center, Box 25046, MS 955, Denver, CO 80225

Arsenic-rich mine wastes reside in the flood plains and overbank deposits along the Cheyenne and Belle Fourche (a tributary) Rivers. The Cheyenne River arm of Lake Oahe, S. Dak., receives water and sediment from the Cheyenne River system. Sediment and interstitial water samples were collected from nine gravity cores taken throughout the Cheyenne River arm. We determined Arsenic (III) and Arsenic (V) in the interstitial water, and determined Arsenic (III) and Arsenic (V) from 4N HCl extracts of the sediment. The HCl reagent did not completely extract all the arsenic; the remainder was solubilized by potassium chlorate and hydrochloric acid and called sulfide arsenic. The *occurrence of only Arsenic (V) in the shallow sediment and the low concentration of* arsenic in the interstitial water define an oxidizing zone of approximately 10-12 cm depth in the upper part of sediments of the Cheyenne River arm. The oxidizing zone gradually decreases to 4 cm depth in the lower part of sediments of the reservoir. Beneath the oxidizing zone, a reducing zone, present throughout the system, is defined by Arsenic (III) and sulfide arsenic occurrence in the sediment and by the occurrence of Arsenic (III) in the interstitial water, where Arsenic (III) makes up approximately 78 percent of the total arsenic concentration. The makeup of the arsenic in sediments greater than 40 cm is similar to that in the reduced zones, except that the solid phase arsenic is mostly sulfide-arsenic with lesser amounts of Arsenic (III) and Arsenic (V).

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TOTAL AND WATER SOLUBLE ARSENIC AND SELENIUM ASSOCIATED WITH DRAINAGE SEDIMENTS COLLECTED FROM NINE IRRIGATION SITES IN THE WESTERN UNITED STATES.

Stephen A. Wilson D. Brooke Hatfield, Ron C. Severson. U.S. Geological Survey P.O. Box 25046 MS928 Denver Co. 80225

Concern over the transport of selected elements due to the irrigation of arid and semi-arid lands in the western United States has prompted a series of nine studies into the effect of irrigation on water quality associated with return flow waters. Elements of primary concern are selenium and arsenic, especially their transport and subsequent accumulation in bottom sediments. An examination of sediments from these nine sites demonstrate that the total selenium concentration ranges from 0.1 to 120 ppm in the solid material. Total arsenic concentrations ranged from 0.5 to 15ppm in the solid material. While total concentrations are significant in many areas, a measure of element transport can best be estimated using extractable concentrations of these elements. Initial studies have demonstrated that up to 40% of the selenium and 25% of the arsenic can be remobilized using water extractions. These results will be discussed with regard to the association of selenium and arsenic with particle size and the potential for remobilization, under normal environmental conditions.

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INTERACTIONS BETWEEN OZONE AND ATMOSPHERIC SOOT: TODAY AND FOLLOWING NUCLEAR WAR

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In recent years the environmental consequences of nuclear war have been expanded to include the repercussions of the atmospheric injection of huge quantities of smoke ahnd dust. Solar heating of a large scale soot cloud could cause this soot to rise to stratospheric heights were it could increase local temperatures in the upper troposphere and lower stratosphere as much as 100K. Soot is also a major pollutant of the present day atmosphere; soot in the form of carbon aerosol particles is found in both urban and remote regions of the troposphere were it is often responsible for much of the absorption of solar radiation associated with tropospheric aerosols. Carbon aerosol particles are also found in the lower stratosphere, and are thought to be meteoritic in origin.

To understand the fate of carbon aerosols in the atmosphere and their effects on other atmospheric species, accurate, quanitative models must be developed. However, very little informantion is available for incorporating heterogeneous chemistry into these models. The main efforts of our studies are directed towards characterization of of the reaction rate of ozone with soot surfaces.

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SURFACE AREA AS A FACTOR FOR NORMALIZING "TOTAL RECOVERABLE" CONCENTRATIONS OF INORGANIC CONSTITUENTS IN DILUTE MINERAL ACID EXTRACTS OF AQUATIC SEDIMENTS.

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Numerous minor and trace elements dissolved in surface waters are known to be concentrated or sorbed by aquatic sediments. Some sorption occurs as a result of the interaction of the dissolved species reacting with the mixed iron and manganese oxides and hydrous oxides commonly coating aquatic sediment mineral particles. These coatings essentially integrate the long-term exposure of sediment to dissolved constituent concentrations. Analysis of dilute mineral acid extracts, prepared from representative sediment samples, can thus provide a capability for determining operationally defined "total recoverable" concentrations of inorganic constituents that are useful for evaluating a variety of environmental pollution effects. Intuitively, one would expect higher concentrations of sorbed materials per unit weight in the fine grained particle fraction, i.e., the size having the greater surface area. Because the proportion of grain coating and sorbed constituents "should" vary as a function of particle size, numerous investigators have isolated and analyzed specific size fractions or ranges of sediments. However, disproportionate concentrations of sorbed constituents commonly are found on the large particle size fractions. This occurs when the "large" particles are actually agglomerations of fine grained smaller particles. This paper details the improved results obtained when using BET surface area measurements instead of particle size, to normalize "total recoverable" concentrations of minor and trace elements in dilute mineral acid extracts of aquatic sediment samples. Comparisons are made for 17 constituents determined by inductively coupled argon plasma analyses on replicate samples. Natural sediments in addition to three U.S. Geological Survey prototype aquatic sediment reference samples were used for the comparisons.

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HALIDE DETERMINATION IN USED OILS AND NON-AROMATIC ORGANICS FOR RECYCLE OR DISPOSAL BY BOMB COMBUSTION AND ION CHROMATOGRAPHY,

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The Los Alamos National Laboratory (LANL) is a small to medium size generator of non-PCB and non-radioactive waste oils and organics. Due to recent EPA regulations it has become necessary to dispose of these materials by incineration or recycling. LANL does not have at present the ability to treat or dispose of these materials on-site. Before most recyclers will accept materials, a preliminary analysis is necessary to determine the halide content and heat capacity. Detection limits for bromide, chloride, fluoride and iodide by activation analysis are 0.01, 0.1, 5.0 and 0.01 respectively. A method to determine heat capacity and halides simultaneously has been developed. With this method samples are combusted in a platinum lined Parr oxygen combustion bomb under controlled conditions with a reductant if necessary. The anions are subsequently determined by ion chromatography on a Dionex 4000i with an AS5A column, standard eluant and conductivity meter for F and Cl and an electrochemical detector for Br and I. Procedures for weighing and handling of volatile and toxic materials and the possible formation of toxic materials on combustion will be discussed.

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ELECTROCHEMISTRY AND EH OF MULTIVALENT ELEMENTS IN NATURAL WATERS. J. Houston Kempton and Donald D. Runnells. Department of Geological Sciences, University of Colorado, Boulder, Colorado 80309-0250.

Eh is a master variable that is often used in aqueous geochemistry to predict mineral solubilities and ionic speciation. Eh is typically measured as the relative potential induced on a platinum electrode submersed in aqueous solution. The ability of a given redox couple in solution to poise the potential of a platinum electrode depends on the concentration of the couple, its thermodynamic E^o, and the heterogeneous kinetics of the electron transfer between the couple and the platinum electrode. Heterogeneous kinetics were measured for dissolved Fe, As, H, O, Se, and U species to determine if these elements were likely to poise a platinum electrode in near-neutral solutions. Of the elements tested, Se, U, and As are unlikely to affect the potential of the platinum electrode, O_2 has a moderate influence, and H^+ and Fe^{++} may produce a Nernstian response.

An alternative to a platinum Eh measurement is valence-specific analysis for the redox couples of interest. Polarographic methods are well suited for analysis of Fe(II)/Fe(II), Se(IV) /Se(VI), and As(III) /As(v) at levels and at pH values typically found in natural waters.

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RECENT DEVELOPMENTS IN ULTRAVIOLET LIGHT DOSIMETRY, Donald H. Stedman, David K. Krehbiel, Doris Kimbrough, and Donald L. McElwee. Department of Chemistry, University of Denver, University Park, Denver, CO 80208.

Workplace exposure to ultraviolet radiation has been a long-standing problem, particularly among welders, and other persons directly exposed to actinic arcs. The recent upsurge of interest in outdoor, recreational and fitness oriented activities, together with the advent of cosmetic suntanning salons has greatly increased the potential among the general population for exposure to damaging ultraviolet radiation. In order to monitor the exposure of these people to the radiation, it becomes imperative that techniques be developed that permit simple, reliable measurement of the degree of exposure in the wavelength ranges of primary interest, UVA and UVB. In answer to this need, a new chemical actinometer has been developed that provides reliable, easily analyzed dosimetry for ultraviolet light. Experimental results of wavelength-specific studies show excellent linearity over a wide range of exposures. The dosimeter system provides, in a low-cost badge, a means of monitoring UV dosages for phototherapy patients, clients and employees of suntanning establishments, and other workers subject to such exposure. The use of the badge format permits such measurement with the minimal inconvenience and the least possible danger to the person.

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PRESSURE DIGESTION OF SEWAGE SLUDGE, Mary C. Williams, Ellen A. Stallings, Trudy M. Foreman, and Ernest S. Gladney. Los Alamos National Laboratory, P. O. Box 1663 MS E518, Los Alamos, NM 87545

The pressure cooker digestion of sewage sludge was compared to convential digestion procedures. Various acid combinations were evaluated to determine the highest recovery. Non-destructive neutron activation analyses, which are free of digestion problems, were used to access the reliability of the wet digestion results. The agreement between the neutron activation and pressure digestion results allowed better mean and confidence limits than the Environmental Protection Agency published data for their Municipal Digested Sludge (WP 976). This has enabled us to have tighter quality control than was previously possible. The pressure cooker recovery was as good or better than more time-consuming and hazardous wet digestion procedures. We used only HNO_3 and HF to reduce ICP-MS background interferences.

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ANALYSIS OF TRANSITION METAL ION EPR SPECTRA. JohnR.Pilbrow, Physics Department,Monash University,Clayton,Victoia,Australia 3168.

Electron paramagnetic resonance (EPR) stands apart from other forms of *spectroscopy in that spectra are obtained as a function of magnetic* field rather than frequency (or wavelength). This has theoretical consequences which had been overlooked up to the time Abragam and Bleaney published their book "Electron Paramagnetic Resonance of Transition Ions" in 1970. As Coffman showed in 1975 it is straightforward to describe both field-swept and frequency-swept EPR with a single master equation. The author and his associates have shown that this theoretical framework is conceptually simple and thoroughly consistent with quantum mechanical transition probability theory . It leads to an expectation of asymmetric lines, an insight into certain kinds of linewidth anisotropy and the ready incorporation of realistic line broadening mechanisms into powder simulation programs. The lecture will focus on a number of highlights in transition ion EPR over the past decade or including the Aasa-Vanngard 1/g factor , modern ligand field theories, statistical models of line broadening, use of low microwave frequencies,selected examples from a range of applications from crystals to glasses , metal-metal and metal-radical coupling. In conclusion, recent work in the author's laboratory will be presented on some new symmetry relationships for S=3/2 crystal EPR, lineshapes for non-Kramers doublets and a critique of powder simulation methods.

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THE SPIN HAMILTONIAN CONCEPT AND NOTATIONS USED IN TRANSITION-METAL ION EPR - A NEED FOR A UNIFIED NOMENCLATURE. Czeslav Rudowicz and Richard Bramley. Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601, Australia

The aim of this crictical review is twofold [C. Rudowicz, Magn. Res. Review - in press]. First it is to outline the theoretical foundations of the concept of spin Hamiltonian (SH) used in EPR studies of transition-metal and lanthanide ions with orbitally nondegenerate ground states. A concise overview of the "derivational" and "constructional" approach to SH is presented. A recent controversial question [C. Rudowicz and R. Bramley, J. Phys. C - in press] of the odd-order terms in SH for S-state ions is discussed. Misconceptions concerning the relationship between the zero-field splitting Hamiltonian and the crystal field Hamiltonian are clarified. Second it is to present the various notations used for the operators, forms of spin Hamiltonian, and parameters in a systematic way. The Stevens operator notation is chosen as a reference notation for conversion relations between the ZFS parameters. Conventional forms of ZFS Hamiltonian are revieved for those higher symmetries which involve no 'imaginary' ZFS terms and for orthorhombic symmetry. Several pitfalls in notations and a number of errors of varying degrees of importance existing in the EPR literature are pointed out. Forms of the electronic Zeeman Hamiltonian are also discussed. The paper is aimed at bringing about an internationally accepted standardization of notation and units and clarification of nomenclature used in the EPR and related areas. Virtues of such standardization for the EPR community as a whole are discussed.

99 ENDOR DETERMINED SOLVATION STRUCTURE OF VO^{2+} IN FROZEN SOLUTIONS.

D. Mustafi and M. W. Makinen, Dept. of Biochem. & Mol. Biol., Univ. of Chicago, Chicago, IL

The solvation structure of the vanadyl ion (VO^{2+}) in methanol and in aqueous-methanol mixtures is investigated by application of ^1H and ^{13}C electron nuclear double resonance (ENDOR) spectroscopy. The ligand origins of the proton ENDOR resonances have been assigned with use of selectively deuterated materials. The principal hyperfine coupling (hfc) components of both ^1H and ^{13}C in solvent molecules coordinated to the VO^{2+} ion have been determined by analysis of the H_0 dependence of the ENDOR spectra. The hfc components of ^1H and ^{13}C of both metal-bound water and methanol exhibit axial symmetry. Under the point-dipole approximation the anisotropic hfc components yield estimates of the separation between the paramagnetic center and the ^1H and ^{13}C nuclei of axially and equatorially bound solvent molecules for a tetragonally symmetric complex. Axially coordinated H_2O molecules exhibit metal-proton distances of 2.92 and 3.47 Å respectively, corresponding to an inner sphere coordination site on one side of the equatorial plane and to a site with hydrogen-bonding to the V=O group on the other side. Equatorially coordinated H_2O molecules exhibit metal-proton distances of 2.60 and 4.80 Å, corresponding to an inner sphere coordinate site and a hydrogen-bonded outer sphere coordination site. These results are in excellent agreement with X-ray crystallographic data. In pure methanol there are similarly equatorially and axially bound methanol molecules, and the coordination structure estimated on the basis of the metal-proton distances is confirmed with ENDOR of ^{13}C-enriched methanol. The coordination geometries of the two types of VO^{2+} complexes are deduced from ENDOR estimates of metal-nuclear distances using computer based molecular graphics. These procedures are extended to assign coordination geometries of VO^{2+} complexes of nucleotides and transferrin. (Supported by NIH GM 21900).

100 EPR ORDER PARAMETERS OF METALLOPHTHALOCYANINE THIN FILMS.

M. D. Pace, W. R. Barger, and A. W. Snow, Naval Research Laboratory, Code 6120, Washington, D.C., 20375-5000

EPR spectroscopy is a powerful tool for the morphological characterization of metallophthalocyanine thin films. An order parameter, S, can be assigned to a film based upon the mean value of the angle between the monolayer plane and the phthalocyanine ring. The order parameter, expressed $S=(3<\cos^2\theta>-1)/2$, is widely used to characterize mobile spin labels in solution. As shown by recent EPR studies, thin films of ligand substituted copper phthalocyanine have order parameters ranging from 0.98 to -0.45 depending upon the peripheral substituent groups. This indicates that molecular ordering of a monolayer may be controlled during preparation and monitored by EPR. Studies of metallophthalocyanine thin films using Cu^{2+}, and VO^{2+} ions as the metal substituents will be discussed.

101 EPR STUDIES OF SOLID-STATE INTERCALATION REACTIONS IN LAYERED SEMICONDUCTING CHALCOGENIDES.

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The transition-metal (M) chalcogenophosphates ($M_2P_2S_6$) crystallize in a layered structure of the $CdCl_2$ type in which adjacent planes of sulfur atoms are only weakly bound by van der Waals interactions and, therefore, can accommodate guest species (I) between the layers to form intercalation compounds, $M_2P_2S_6(I)x$. In many cases, the physical properties of the host (conductivity, magnetic behavior, etc.) may be dramatically altered by intercalation. Although the mechanism of the solid-state intercalation reaction remains unclear and the structure of the products are frequently poorly understood, a considerable amount of study indicates that the process involves either ion exchange or charge donation to the host lattice. EPR spectroscopy is a very useful technique with which to study these novel materials. We will report preliminary results from EPR studies of the intercalation of $M_2P_2S_6$ (M=Fe, Cd, Mn, Zn) with pyridine, and several Metallocenes. The EPR measurements have revealed unusual, first-order, phase transitions in these materials, provided insight into the mechanism of the intercalation reaction and yielded details of the structure and dynamical behavior of the intercalated species. Work is presently in progress to detect and characterize free electrons donated from the intercalated species to the host lattice.

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COMPARATIVE Mn^{2+} EPR STUDIES OF FERROELASTICITY IN DICALCIUM METAL PROPIONATES OF $Ca_2M(C_2H_5COO)_6$; M = Ba, Sr, Pb.

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Hypothetical cubic-tetragonal phase transitions of dicalcium strontium propionate (DSP), dicalcium lead propionate (DLP) and dicalcium barium propionate (DBP) have been studied by EPR of Mn^{2+}. A big change in the overall splitting of spectra with temperature in the ferroelastic phase is observed, and is ascribed to thermal expansion and spontaneous strain. It is found that in the cubic phase of DBP the oxygen octahedra surrounding the Cu^{2+} ion (replaced by Mn^{2+}) are trigonally distorted along [111] directions, while in the tetragonal phase of DSP (and probably in DLP also) the octahedra are distorted along the tetragonal axes, indicating the correlation between the orientation of the B_2^m tensor and the spontaneous deformation of DSP and DLP crystals. The anistropies of the spectra in the ferroelastically mono-and poly-domain crystals are explained in terms of the orientations of the principal axes of the B_2^m tensor. The existence of microdomains in the cubic phase of DBP crystal has been verified. The observed large differences in the linewidths in all the three crystals suggest static distribution of the crystal field parameters within the crystal due to the disorder of α and β carbons of the propionate molecules. The Mn^{2+} spin Hamiltonian parameters in the three crystals are evaluated.

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ELECTRON PARAMAGNETIC RESONANCE OF ACETAMIDINIUM Cu^{2+} OF SPIN-1/2 TETRAHEDRAL COORDINATED ANTIFERROMAGNET,

John E. Drumheller and K. L. Wan, Department of Physics, Montana State University, Bozeman, MT 59717

EPR measurements at temperature range from 3.75°K to room temperature have been made for single crystal Acetamidinium Tetrachlorocuprate(II) which is spin-1/2 antiferromagnet. The angular dependences of the resonance position show that there are two magnetic sites with z-axis deviated from the crystalline c-axis by about 10° respectively. The g-tensors, i.e., $g_{xx} = 2.061$, $g_{xx} = 2.078$, $g_{zz} = 2.361$, for site 1; $g_{xx} = 2.062$, $g_{yy} = 2.078$, $g_{zz} = 2.346$ for site 2, respectively, are determined from the experiment data. Within the experiment error, the g-tensors are invariant with the temperature. And, by employing the superposition model, the theoretical analysis is done for d-levels and g-tensors with D_{2d} approximation. The more interesting thing is that the temperature dependence of the EPR line width indicates a possibility that there exist two transition temperatures to ordered antiferromagnetic state.

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METALLOPROTEIN EPR TRUTH DIAGRAMS WITH THE PERSPECTIVE OF TWO DECADES.

William E. Blumberg, *AT&T Bell Laboratories, Murray Hill, N.J. 07974.*

In 1969 Jack Peisach and I presented some diagrams which summarized the results of Electron Paramagnetic Resonance experiments on low spin ferric heme compounds. These diagrams presented the EPR parameters in the form of "structural parameters," but these referred to the spin Hamiltonian rather than the molecular structure in the vicinity of the iron atom. Extensive measurements on compounds of hemoglobin were presented on one diagram, and the question was asked "Do all low spin ferric heme compounds have structures analogous to those of hemoglobin?" Diagrams for other heme proteins and model compounds provided "yes" or "no" answers to the questions of structural similarity. Thus these diagrams were quickly nicknamed "Truth Diagrams." Summaries of EPR structural data have later been cast in similar formats using the same philosophy for results of experiments on other types of biological metal binding sites. Notable among these are the Cu(II) EPR experiments on copper proteins and model compounds and the EPR of paramagnetic states of the two-iron ferredoxins. As work has continued on EPR studies of paramagnetic metal sites and their model compounds, both in our own laboratories and in the laboratories of others, over the intervening two decades numerous additions have been made to these diagrams. How have they held up after this time interval? Have they been useful in assigning molecular structure? Have they had predictive value in suggesting other types of experiments relating to molecular structure? Many published experiments can be called upon to provide answers to these questions. The talk will give examples of these and will present extensions of these analytic techniques introduced by other groups in attempts to remove ambiguities in the Truth Diagrams.

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THE POTENTIAL USE OF ELECTRON SPIN RESONANCE SPECTROSCOPY FOR THE DETECTION OF GENE SEQUENCES.

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A series of spin labeled thymidine analogs (T*) were synthesized which are excellent substrates for the template reading enzyme E. coli polymerase I. These analogs are easily incorporated into viral DNA such as double stranded (ds) lambda DNA by nicktranslation. Microgram quantities of nicktranslated DNA containing T* in the nicktranslated regions give after purification by gel chromatography an ESR lineshape which is characteristic for a spin labeled ds DNA as was reported earlier for spin labeled homopolymer double strands such as $(dT, dT^*)_n(dA)_n$ (Biochemistry 24, 5465 (1985)). Melting of the nicktranslated lambda DNA by heat denaturation allows the formation of single stranded (ss) lambda DNA which gives an ESR lineshape characteristic for ss DNA such as $(dT, dT^*)_n$. These ESR active ss lambda DNA probes hybridize to complementary base sequences under annealing conditions, i.e., the spin labeled nucleic acid segment will undergo a conformational change from single to double strands. This hybridization process can be readily detected by determining the h_+/h_0 and/or h_-/h_0 of the ESR spectra of the spin labeled systems. Since the detection of gene sequences is often based on hybridization, ESR spectroscopy is a sensitive tool for detecting such sequences with sequence specifically spin labeled nucleic acids.

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ELECTRON SPIN ECHO STUDIES OF PHOTOSYNTHETIC OXYGEN EVOLUTION.

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Oxygen evolution in higher plants is thought to involve reactions through a cycle of states by which electrons are removed from H_2O and donated to the photo-oxidized $P680^+$ reaction center of Photosystem II (PSII). The most successful interpretation of the data regarding this cycle is Kok's S-state scheme, which posits a series of five ($S_0 - S_4$) states through which electrons are cycled during oxygen evolution (Kok, Forbush, and McGloin, Photochem. Photobiol. 11, 457). Manganese plays a central role in the chemistry of these reactions. There are approximately four Mn atoms for each PSII reaction center. The S_2 state exhibits a complex multiline EPR signal which closely resembles the spectra of synthetic Mn(III)Mn(IV) dimers (Dismukes and Siderer, PNAS 78, 274). We have studied this multiline EPR signal with Electron Spin Echo (ESE) Spectroscopy. Our principal focus has been to use the Nuclear Envelope Modulation (NEM) of two and three pulse electron spin echoes to measure the ENDOR frequencies of paramagnetic nuclei coupled to the electron spin. The multiline signal exhibits deep envelope modulation at the proton Zeeman frequency. The modulation is virtually all shifted to the deuteron Zeeman frequency for PSII particles prepared in D_2O buffer. We see no evidence of protons or deuterons with ENDOR frequencies significantly shifted from their respective Zeeman frequencies. The multiline ESE envelope also exhibits a weak 4.6 MHz component, probably from ^{14}N. We are comparing the multiline results with data from mixed valence Mn models such as the Mn(III) Mn(IV) bipyridyl dimer to help determine the origin of this ^{14}N component. We have also studied the effect of NH_3 binding to the Mn site by examining the altered multiline EPR signal formed in the presence of 100 mM NH_4Cl at pH=7.5 (Beck, de Paula, and Brudvig, JACS 108, 4018). This altered multiline signal exhibits very deep ^{14}N envelope modulation with a principal frequency of 4.6 MHz. We will compare this ^{14}N modulation with data obtained with $^{15}NH_3$. We will also present multiline NEM data for PSII particles prepared with $H_2{}^{17}O$. The temperature dependence of the multiline EPR spin-lattice relaxation will also be discussed, along with implications of this relaxation data for determining the structure of the Mn site.

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SYNTHESIS OF A NEW SPIN-LABELED DERIVATIVE OF CoA AND IT'S INTERACTION WITH 3-HYDROXYACYL-CoA DEHYDROGENASE.

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NAD^+, spin-labeled at N^6 of the adenine ring with 4-(2,2,6,6-tetramethylpiperidin-1-oxyl) (N^6-SL-NAD^+) is an active coenzyme of (L)-3-Hydroxyacyl-CoA dehydrogenase exhibiting 65 % of v_{max} of NAD^+ itself. The crystal structure of the apo-enzyme revealed a "Rossmann-fold" typical for adenine nucleotides. In close contact to this binding site is a cleft in which 3-hydroxyacyl-CoA could be bound (J.J. Birktoft, St. Louis). The orientation of the latter in this cleft, however, is not yet known. In order to gain information on the relative arrangement of the cofactor and the CoA-bonded substrate we have now synthesized a spin-labeled derivative of (L)-3-Hydroxybutyryl-CoA from N^6-SL-AMP and 3-hydroxybutyryl-phosphopantetheine according to the general procedure of Furuzawa. Spin-spin interaction between the two nitroxide radicals should occur in one of the possible orientations of 3-hydroxybutyryl-SL-CoA, only.

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KINETICS OF REDUCTION AND REOXIDATION OF NITROXIDES IN LIVING CELLS.

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The uses of nitroxides in complex biological systems including as biophysical tools to study membrane dynamics and as contrast agents for in vivo NMR has led to a need to understand thoroughly the reduction and reoxidation of nitroxides in living cells, especially that of the lipid soluble nitroxides. The products of the reduction of nitroxides in cells are the corresponding hydroxylamines, which cells can reoxidize back to the nitroxides in the presence of oxygen. For the lipid soluble nitroxides, the rate of reduction and reoxidation is very sensitive to oxygen. The rate constants of enzymatic reduction and reoxidation, chemical reduction, and autooxidation have been measured and indicate that enzymatic mechanisms predominate at 37°C. The observed kinetics of reduction and reoxidation can be described adequately by a simple differential equation. The reduction kinetics of 5-doxyl stearate, whose doxyl moiety is close to the surface of the membrane, is first order, while the rate is zero order for the 10 and 12-doxyl stearates whose doxyl moieties are deep in the membrane. Reduction appears to occur near the surface of membranes with the kinetics of reduction of doxyl moieties controlled by their accessibility to reducing equivalents. Reoxidation has first order kinetics and appears to occur in the membrane.

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PHOTOREDUCTION OF SPIN LABELS BY EXCITED FLAVIN

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The need often arises in biological studies using spin labels to reduce these compounds to ESR-silent species. Reduction of spin labels by excess ascorbate gives variable rates on a timescale of minutes to hours. We will present a simple, rapid, and general procedure for catalytic reduction of spin labels in aqueous solutions and in model membranes by photochemically excited flavin.

The kinetics of spin label reduction are zero-order with respect to flavin and spin labels over the range of 10 µM to 1 mM and varies quantitatively with light intensity. Reduction of spin labels at concentrations of 0.1 mM using 10 µM flavin occurs in 1-2 seconds for piperidine (TEMPONE, TEMPOL, TEMPAMINE, CAT_1), pyrrolidine (PCA), and oxazolidine (5-doxyl stearic acid) spin labels in aqueous or ethanolic solution. When CAT_1 is trapped inside large unilamellar vesicles made with *dipalmitoyl phosphatidylcholine and dipalmitoyl phosphatidylglycerol, flavin added externally cannot* reduce CAT_1. This shows that flavin does not cross the membrane. However, when a permeable spin label is present (^{15}N TEMPONE), that label is rapidly reduced by flavin, crosses the membrane, and reduces endogenous CAT_1. When the light is turned off, the TEMPONE signal recovers if some CAT_1 remains. Doxyl stearic acid labels in large unilamellar vesicles are reduced a factor of 10 more slowly than in ethanolic solution, but this is fast enough to calculate an exchange rate between the inner and outer halves of the lipid bilayer for these spin labels.

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X-BAND EPR SPECTRA AND SIMULATIONS OF S=2 STATES IN MYOGLOBIN AND IN A MODEL HEME COMPLEX.[+]

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EPR spectra of the inactive ferric state of myoglobin (Mb) are well documented. In contrast EPR signals have not been reported for the native ferrous (S=2) complexes of Mb. We observe a broad low-field X-band resonance from deoxy Mb, photolyzed MbCO, and photolyzed MbO_2 at 4K. The spectra are similar to that of other S=2 ferrous complexes of comparable coordination geometry. We have simulated the frozen solution spectra assuming distributions of the zero-field parameters D and E, and utilizing either perturbation methods or a full matrix diagonalization of the spin Hamiltonian. Preliminary analysis of the deoxy Mb and photolyzed MbCO spectra gives a g_z value of $2 < g_z < 2.05$. The spectrum of photolyzed MbO_2 and its temperature dependence are significantly different from that of the deoxy Mb and MbCO complexes. This suggests a dipolar coupling to the O_2. We have also observed a S=2 spectrum from the 2-methylimidazole Fe^{+2} model heme complex[1] and find a g_z value of 2.2. The g_z value implies $D < 0$ in agreement with previous Mössbauer[2] findings.

+ Supported by NIH GM 16406

1. J.P. Collman and C. A. Reed, JACS 95, 2048-9 (1973).
2. Kent et al., BBA 580, 245-58 (1979).

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STRUCTURE-FUNCTION RELATIONSHIPS PROBED THROUGH EPR STUDIES OF CHEMICALLY MODIFIED CYTOCHROME C.

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EPR investigations of lysine and tyrosine modified cytochrome C have revealed the existence of multiple low spin forms and their equilibria at different pH conditions. From the spin Hamiltonian parameters, the relative energies of the Fe d orbitals have been calculated. Following Blumberg-Peisach, we were able to predict the nature of the axial ligands. An attempt is made to bring together the EPR results with paramagnetic NMR shift studies, magnetic susceptibility, optical spectra due to change transfer and redox potentials in an effort to understand the details of the changes that occur with the various chemical modifications.

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OVERVIEW AND RATIONALE FOR CLINICAL CONTRAST AGENTS IN MRI

Jack S. Cohen, Clinical Pharmacology Branch, NCI/NIH, Bethesda MD, 20892

The basis for the use of paramagnetic contrast agents in MRI will be reviewed. Factors affecting choice of an agent include: relaxivity, solubility, stability, *in vivo* distribution, and toxicity. The relaxivity is a measure of the efficiency by which the unpaired electron spin increases the relaxation rate ($1/T_1$) of bulk water. Relaxivity is affected by such criteria as number of unpaired spins (for a metal ion), the electron correlation time, and the number and rate of exchange of water ligand sites. Examples of the use of spin labels, metal ion chelates, metalloporphyrins, attachment to specific antibodies, and ferromagnetic particles, to enhance contrast in clinical MRI studies will be compared.

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PHYSICAL CHARACTERIZATION OF PARAMAGNETIC CONTRAST AGENTS.

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University of Illinois, Urbana, Illinois 61801.

The clinical and research value of in vivo NMR techniques can be extended significantly with the use of paramagnetic contrast agents (CA's) to enhance relaxation differences between tissues. Optimum development of effective CA's with minimal toxicity can be facilitated through a better understanding of the physical factors that influence the relaxivity exhibited by these materials. Both NMR and ESR are effective tools for such characterizations, and are especially informative when used in combination. We will discuss the key physical interactions that are believed to control relaxivity, and analyze the effect of several using Solomon-Bloembergen-Morgan theory to generate computer-simulated NMRD curves. We will discuss our experimental approaches to the independent measurement of these important variables. Results from metal chelates, protein bound metal chelates, and stable free radicals (nitroxides) will be discussed. Work supported by NIH RR01811.

114 LOW FREQUENCY ESR SPECTROMETRY: APPLICATION IN BIOLOGICAL SYSTEMS. H.J. Halpern, D.P. Spencer, G.M. Rosen, L.A. Brunsting, A.S. Wechsler, M.K. Bowman. Radiation Oncology Dept., U. of Chicago, Chicago, IL, Depts. of Pharmacology and Surgery, Duke University, Durham, NC, Argonne Nat'l Lab., Argonne, IL

Electron spin resonance techniques provide a means of obtaining several critical pieces of information pertaining to biological systems in a noninvasive or nondestructive fashion. Electron spin resonance oxymetry can in principle provide information pertaining to the oxygenation status of both cellular systems and tissues *in vivo*. Cellular and tissue metabolism may be monitored using the rates of bioreduction of nitroxide spin label. The pharmacokinetics of nitroxide spin label is of intrinsic interest. Furthermore it is a prerequisite for the direct measurement of hydroxyl and superoxide species *in vivo*. The identification of these species in whole organs or *in vivo* may provide profound insight into the mechanisms of cellular, organ, and malignant tissue injury. In pursuit of this information, we have developed a low-frequency electron spin resonance spectrometer capable of imaging. This spectrometer has been specially designed for *in vivo* measurement; the spectrometer has been electronically stabilized to allow measurements of live animals. We will report data from experiments on oxymetry and on nitroxide pharmacokinetics in live animals and in intact heart preparations. Supported in part by American Cancer Society grants #PDT-262, BC-453, National Institute of Health grant HL-33550, and The Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. D.O.E., under contract W-31-109-ENG-38.

115 MEASURING OXYGEN AND REDOX METABOLISM BY METABOLICALLY RESPONSIVE NMR CONTRAST AGENTS. Harold M. Swartz, College of Medicine at Urbana-Champaign, Illinois ESR Center, 506 S. Mathews Avenue, Urbana, Illinois 61801

Contrast in *in vivo* NMR studies can be altered by the presence of paramagnetic species because the NMR images (or spectroscopic data) are based in part on relaxation of nuclei and paramagnetic species can alter these relaxation rates. If the concentration of the paramagnetic species is affected by oxygen concentration and related redox metabolism, these parameters should then be able to be followed by *in vivo* NMR techniques. We are studying the use of the stable free radical nitroxides for this purpose. Nitroxides have the advantageous chemical properties of being available in a variety of forms enabling one to tailor the physical chemical properties (e.g., stability, solubility, and charge) to fit the experimental needs. They have the advantageous biological properties of being reduced in cells and tissues to the non-paramagnetic hydroxylamines at a rate that is affected especially by the oxygen concentration. The presentation will review the current status of our knowledge of the metabolism and distribution of nitroxides in living cells and tissues, especially in relationship to redox metabolism. We also will review our current data on the effectiveness of nitroxides as relaxers of water and lipid protons under biologically pertinent conditions. Possible extensions to other paramagnetic substances will also be considered.

116 RECOGNITION OF CHIRALITY BY ENDOR. Hartmut B. Stegmann, Helmut Wendel, Hoang Dao-Ba, Paul Schuler, and Klaus Scheffler. Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, West-Germany

The unequivocal detection of enantiomeric compounds and the determination of their concentrations have gained increasing importance in the last few years. Hitherto, polarimetry and NMR spectroscopy as well as chromatographic methods were employed for chiral recognition, whereas the use of ENDOR spectroscopy has so far never been described. The great advantages of this technique are that very little sample material is required and the spectra thus obtained are virtually solvent-independent. Moreover, proton-containing matrices (solvent, chiral auxiliaries or other diamagnetic components) do not interfere with ENDOR investigations through self-absorption, and, other than in MNR spectroscopy, no signal multiplets occur, which sometimes make the analysis of ^{1}H-NMR spectra very difficult. In order to describe whether an EPR or ENDOR spectroscopic recognition of chiral compounds is possible, we synthesized some appropriate phenols. Oxidation of these racemic compounds, bearing a common chiral center in the substituent, in toluene furnished the corresponding phenoxyl radicals. Addition of a chiral auxiliary did not alter the EPR spectrum since the hyperfine structure could not be resolved completely. In the ENDOR spectrum, however, the signals at about 25 MHz split into two lines. These couplings are assigned to the protons on the assymmetric C-atoms. We attribute these splittings to diastereomeric solvates. The machanism of the "chiral splitting" and the results obtained with other chiral radicals will be discussed.

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SEMIEMPIRICAL MO CALCULATION OF EPR SPLITTING CONSTANTS: TWISTING IN ALKENE CATION RADICALS. Stephen F. Nelsen[a], Timothy Clark[b]. a. Department of Chemistry, University of Wisconsin, Madison, WI 53706. b. Institut fuer Organische Chemie der Universitaet Erlangen-Nuernberg, Henestrasse 42, D-8525 Erlangen, Federal Republic of Germany.

Geometry-optimized AM1-UHF calculations on $CH_n(CH_3)_{n-3}$ radicals give <S2> values of 0.761-0.762, but the spin contamination is almost exclusively quartet, because Bischof's spin projection proceedure gives <S2> values under 0.7501. Notably, $(CH_3)_nX$ radicals with $X = C\cdot, N\cdot, N^{+}\cdot, O\cdot, O^{+}\cdot$, and $S^{+}\cdot$, propanal cation, and biacetyl anion give AM1-UHFQ H(1s) spin densities multiplied by 1177 which correlate for both α and β hydrogens with r=0.999 when plotted against experimental splittings (range -23 to +135, average deviation 1.1 Gauss). Application of these calculations to the question of how twisted substituted alkene cation radicals are is discussed. It is important to separate the question of whether the calculated energy minimum is the experimental one from that of how twisting affects the EPR splittings. Comparison of observed splittings with calculated effects of increasing twist indicate that increasing alkyl substitution decreases the amount of twist, in contrast to previous conclusions from MNDO calculations.

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HIGH PRESSURE ESR STUDY ON THE MICROVISCOSITY IN THE SURFACTANT MICELLES AND THE LIPID MEMBRANES. Hisashi Yoshioka, Shizuoka College of Pharmacy, Oshika 2-2-1, Shizuoka-shi 422, Japan.

A high pressure ESR spectrometer was constructed using a helix resonator in place of a conventional cavity. Though the Q value of the resonator was smaller than that of the cavity, it was possible to study the pressure effect on the spectra of a spin probe in the surfactant micelles or in the lipid bilayers under a few thousand atm. The spin probe used was a hydrophobic 16-doxylstearic acid methyl ester. The spectra of the probe in a sodium dodecyl sulfate micelle was not largely altered with pressure. The microviscosity in the micelle calculated from the rotational correlation time using Stokes-Einstein relation showed that it increases about 2.5 times under 3000 atm. In egg phosphatidylcholine bilayer, pressure effect was far larger than in the micelle. The spectrum under 1 atm consists of the ordinary three line hyperfine structure suggesting that the microviscosity in the lipid bilayer is somewhat larger than in the usual solvents. But, it turned into the rigid limit spectrum under 3000 atm. It means that the pressure-induced gelation occurrd in the lipid bilayer, showing that pressure affects seriously on the biological functions. In dilauroylphosphatidylcholine bilayer, spin probe was segregated from the bilayer with the pressure increase. Pressure effect on these systems is compared with temperature effect and is discussed in detail.

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RED CELL DEFORMABILITY STUDIED BY EPR. Toshiharu Ito and Hideo Kon. Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, Maryland 20892.

The ability of a red blood cell to deform easily without fragmentation in response to an applied shear force is a vital function for its survival. Deformability is determined by (1) visco-elastic properties of the membrane assembly, (2) geometry of the cell, and (3) state of the cell contents. EPR can be used to assess the whole cell deformability and orientation in laminar shear flow with some advantage over other methods. When a deformable cell suspension with spin labels (doxyl fatty acid, or phospholipid) in the membrane is forced to flow through a flat channel, the two outer EPR peaks increase and the center peak decreases in intensity as the flow rate is increased, indicating that more labels are oriented with the chain axes in the direction of H_0. This is due to that the cells in flow are deformed to flat boat shapes and orient more or less along the flow direction. Non-deformable cells do not orient and do not cause such a spectral change. Utilizing the phenomenon, the relative cell deformability can be assessed. Advantages of this method are its sensitivity to change of cell deformability, and capability to study cell suspensions at physiologically realistic hematocrit. Investigation of the effect of Cu(II) on the red cell deformability and investigation of the mechanism, and the effect of increased dimeric fraction (in place of tetrameric) of spectrin on deformability of red cell ghosts will be shown as examples.

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THE TRANSITION METAL MEDIATED FORMATION OF HYDROXYL FREE RADICALS DURING THE REDUCTION OF MOLECULAR OXYGEN BY FERREDOXIN-FERREDOXIN:NADP$^+$ OXIDOREDUCTASE.

Kim M. Morehouse and Ronald P. Mason, Laboratory of Molecular Biophysics, National Institute of Environmental Health Sciences, PO Box 12233, Research Triangle Park, NC 27709.

The NADPH-supported enzymatic reduction of molecular oxygen by ferredoxin-ferredoxin:NADP$^+$ oxidoreductase was investigated. The ESR spin trapping technique was employed to identify the free radicals. The spin trap DMPO was used to trap and identify the oxygen-derived free radicals from the characteristic ESR spectra of its oxygen-centered radical adducts. The formation of the hydroxyl radical, during the reduction of oxygen, was shown by competition experiments with ethanol or formate, and the resulting scavenger-derived free radical is trapped. If H_2O_2 is added to the enzymatic reaction a stimulation of the production of the hydroxyl radical is obtained. This stimulation is manifested in both the concentration and the rate of formation of the DMPO/$^{\bullet}$OH adduct. Catalase was shown to inhibit formation of the hydroxyl radical adduct. All three components: ferredoxin, ferredoxin:NADP$^+$ oxidoreductase and NADPH, are required for reduction. The effects of transition metal chelators on the hydroxyl radical adduct suggest that the enzymatic reduction of chelated iron is responsible for the reduction of hydrogen peroxide to the hydroxyl radical via Fenton chemistry.

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FREE RADICAL METABOLITE OF URIC ACID.

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During the last decade much attention has been focussed on determining the mechanism by which antioxidants protect cells from oxygen radicals and other activated oxygen species. In a recent report, uric acid was proposed as an important antioxidant in humans. Although the ability of uric acid to scavenge radicals is believed to play a significant role in its function as an antioxidant, the chemistry of the actual scavenging reaction has received little attention. Our current research was performed to determine whether a free radical metabolite of uric acid could be produced via one-electron redox processes and, if so, to characterize by electron spin resonance the resulting radical species. With the use of the rapid-mixing, continuous-flow technique, we successfully generated and characterized the free radical derived from uric acid oxidation in both enzymatic and nonenzymatic radical-generating systems. The spectral characterization for this radical entailed extensive use of autocorrelation and tune computer programs. In addition, we flowed uric acid which was isotopically labelled with nitrogen-15 at nitrogens 1 and 3 to aid the assignment of hyperfine splitting constants.

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FORMATION OF FREE RADICAL PRODUCTS FROM HYDRALAZINE BY MITOCHONDRIA AND RED BLOOD CELLS.

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Isolated rat liver mitochondria incubated with malate-glutamate in the presence of hydralazine and spin-traps yielded free radical spin adducts. Studies with mitochondrial inhibitors and the use of succinate as substrate showed that free radical formation was dependent upon mitochondrial electron transport in the NADH dehydrogenase region. The spin adducts showed that the free radicals trapped were carbon centered with coupling constants for PBN $A_N = 16.1$ G and $A_H^\beta = 4.6$ G and DMPO $A_N = 15.9$ G and $A_H^\beta = 18.9$ G. Red blood cells treated with hydralazine produced free radicals which could be spin-trapped. MNP trapped a hydrogen free radical whereas DMPO trapped a nitrogen centered free radical and PBN trapped a carbon centered radical as well as the hydrogen free radical. Free radical formation was dependent upon the presence of oxygen indicating the involvement of oxy-hemoglobin. One of the spin trapped free radicals which could be identified was the 3-phthalazyl radical. Bovine hemoglobin plus hydralazine yielded trapped free radicals that were similar to those observed with red blood cells. Carbon monoxide inhibited free radical formation in both the red blood cell and bovine hemoglobin systems. This work was supported in part by NIH Grant No. 2-R01-ES03067-04.

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ESR STUDY OF DELIVERY OF MANGANESE TO LIVER BY LIPOSOMES.

Michael R. Niesman, Goran Bacic, Richard Magin, and Harold M. Swartz, University of Illinois College of Medicine at Urbana-Champaign, 506 S. Mathews, Urbana, IL 61801

Encapsulation of an MRI contrast agent ($MnCl_2$) within liposomes affects both its rate of delivery and the initial site of accumulation within the liver. As a consequence, factors which affect the NMR proton relaxation--such as the state of the ion (bound vs. free) and location within the organ (hepatocytes vs. Kupffer cells)--differ between free and encapsulated forms. We demonstrate the ability of ESR to study these effects and to aid in the understanding of proton NMR relaxation studies. An ESR spectrum of liposomes containing $MnCl_2$ showed a six line spectrum characteristic of free Mn^{2+} superimposed on a very broad line characteristic of bound Mn^{2+}. Mice were injected with free and encapsulated Mn to determine the rate of clearance from the blood and in the case of encapsulated Mn, to determine how much Mn was released and bound after heating. Also free and bound Mn were measured in excised liver slices, with free Mn representing liposomes in the livers that were still intact. The results of the ESR and NMR experiments indicate that: 1) Mn encapsulated in intact liposomes lodged in the Kupffer cells is ineffective at increasing relaxation in the liver; and 2) that Mn when released from the liposomes and bound to sites in the tissue is very effective at reducing T_1 and T_2 in blood and liver.

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ESR STUDIES OF COPPER COMPLEXES WITH EHRLICH ASCITES TUMOR CELLS.

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Room temperature ESR spectra have been obtained for cupric complexes of phenylhydantoin, $Cu(Niv)_2(py)_2$; diisopropylsalicylate, $Cu(Dips)_2$; and glycyl-L-histidyl-L-lysine, CuGHL, in the presence of cells. These data are compared to previous data for cupric bleomycin, CuBlm; monothiosemicarbazones, CuL^+; bisthiosemicarbazones, CuKTS and $CuKTSM_2$; salicylaldehyde-benzoylhydrazones, CuSBH; and pyridine-2-carboxyaldehyde-2'-pyridylhydrazones; CuPCPH, in the presence of cells. Under our conditions (1 mM cupric complex plus 10^8 cells/ml), little interaction between CuGHL or CuBlm and cells is observed. $CuKTSM_2$ partitions favorably into the membrane, is immobile, and is innert. Either adducts or new complexes are formed after addition of $Cu(Dips)_2$, $Cu(Niv)_2(py)_2$, or CuL^+ to cells because the ESR parameters in the presence of cells differ from the ESR parameters in the absence of cells. The ESR signals from CuKTS, CuL^+, CuSBH, CuPCPH, $Cu(Dips)_2$ and to a lesser extent $Cu(Niv)_2(py)_2$ decrease due to reduction by cellular reducing agents, presumably primarily GSH. Residual signals from CuL^+, CuSBH, and to a lesser extent $Cu(Dips)_2$, have components which are attributed to complexes in slow motion. The ESR signals after addition of CuGHL, $Cu(Dips)_2$, and $Cu(Niv)_2(py)_2$, are primarily attributed to complexes in fast motion. Thus, it seems reasonable to expect diverse activities after addition of these copper complexes to cells.

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SUPERHYPERFINE COUPLINGS FROM LOW FREQUENCY ESR SPECTRA OF THE TYPE I SITE IN LACCASE. P. M. Hanna[a], D. R. McMillin[a], M. Pasenkiewicz-Gierula[b], and W. E. Antholine[b], [a]Dept. of Chemistry, Purdue University, West LaFayette, IN 47907 and [b]National Biomedical ESR Center, Medical College of Wisconsin, Milwaukee, WI 53226.

Seven years ago Froncisz and Hyde (J. Chem. Phys. 73, 1 (1980)) calculated a minimum line width at about 2 GHz for the turning point of the $M_I = -1/2$ copper nuclear quantum number. Subsequently, investigators have used the improved resolution of the nitrogen hyperfine structure in the $M_I = -1/2$ line at this low frequency to determine the number of nitrogen donor atoms bound to cupric ion in Type II square planar copper complexes.

This is the first report, to our knowledge, that demonstrates improved resolution of the superhyperfine structure in both the $g_\parallel$ and $g_\perp$ regions of the ESR spectrum of a Type I cupric complex. At least six lines and possibly seven lines are resolved in the $M_I = -1/2$ line in the $g_\parallel$ region and at least nine lines are obtained in the $g_\perp$ region. A computer simulation, which includes an anisotropic tensor for the g-value and separate anisotropic tensors for each nitrogen and/or proton coupling, fits the experimental spectrum. Superhyperfine couplings of 8 to 10 Gauss are used to simulate this S-band data, while a 13 Gauss coupling (Roberts *et al.*, JACS, 106, 5324 (1984)) or even an 18 G coupling (Desideri *et al.*, BBA, 831, 8 (1985)) from ENDOR data has been reported. Configurations for simulation are comprised of either three approximately equivalent nitrogen donor atoms or two nitrogens and two protons with approximately equivalent couplings.

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PULSE FIELD-SWEEP EPR ON COPPER PROTEINS. Chaoliang Fan, Charles P. Scholes, and Harold Taylor. Department of Physics, State University of New York at Albany, Albany, NY 12222.

Pulse Field-Sweep EPR (PFSEPR) is a low power, technically straightforward pulse method developed to resolve underlying hyperfine coupling from inhomogeneously broadened EPR lines. Saturating, hole-burning microwave pulses are followed by a magnetic field sweep to monitor the spread of saturation away from the original hole. The splittings of the satellite holes are related to the underlying hyperfine couplings [Falkowski et al., J. Magnetic Resonance 68 (1986) 453-468]. We report the use of PFSEPR in resolving large copper hyperfine couplings from the blue protein stellacyanin and from Cu_A in cytochrome *c* oxidase. These couplings are unresolved by standard X-band EPR, and their broad, high frequency signals are inherently difficult to resolve by ENDOR. The details of hyperfine and quadrupole couplings, energy levels, and state mixing which account for PFSEPR transitions in these copper systems will be presented. (This work was supported by NIH grant GM 35103.)

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SPECTROSCOPIC STUDIES ON AURACYANIN, A SMALL BLUE COPPER PROTEIN FROM *Chloroflexus aurantiacus*. Jeffrey T. Trost, B. L. Ramakrishna, John M. Freeman, and Robert E. Blankenship. Department of Chemistry, Arizona State University, Tempe, AZ 85287.

A small blue copper protein was isolated from the thermophilic green photosynthetic bacterium *Chloroflexus aurantiacus*. The protein shows absorption maxima at 280, 455, and 598 nm with a shoulder at 715 nm. Atomic absorption analysis yields a molar extinction coefficient, $E_{598}=2900\ M^{-1}cm^{-1}$. Redox titrations of auracyanin gave a midpoint potential of +240 mV (vs NHE) with a n=1 curve. ESR spectra were taken at X (77K and 4.2K) and Q (77K) bands. The spin Hamiltonian parameters obtained by computer simulation are, gx=2.018 with Ax=0.0062 cm^{-1}, gy=2.065 with Ay=0.0012 cm^{-1} and gz=2.218 with Az=0.0047 cm^{-1}. These parameters are very similar to those of stellacyanin and indicate a rhombic distortion at the copper site. The function of auracyanin is not yet clear.

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BINDING OF SPIN-LABELED ATP AND AMP-PCP TO THE SR ATPASE. Carol Coan, Celia Garcia,* and Sergio Verjovski-Almeida*, Department of Physiology, University of the Pacific 2155 Webster St., San Francisco, CA 94115 and Department of Biochemistry, Institute of Biomedical Sciences, Federal University of Rio de Janeiro, 21910 Rio de Janeiro, Brasil*

A spin-labeled ATP derivative with a nitroxide moiety on the 3' position of the ribose [3'(3-carboxyl-2,2,5,5-tetramethyl-pyroline-1-oxyl) ATP, or 3'SL-ATP] was used to study the substrate binding sites on the ATPase of sarcoplasmic reticulum. The 3'SL-AMP-PCP derivative was also synthesized as the derivative cannot be hydrolized by the enzyme. The highly anisotropic spectrum of the bound SL-ATP, or SL-AMP-PCP, could be obtained by spectral substraction. Double integrations then provided an estimation of the binding stoichiometry. The decrease in line height of the isotropic signal of the free SL-ATP, which followed the binding of the label to the enzyme, provided an alternate means of determining the stoichiometry. It has been known for some time that millimolar additions of ATP increase the rate of enzyme hydrolysis. It has not been established whether this is due to a separate, regulatory ATP site, or a thermodynamic effect induced by a second mole of ATP binding to the catalytic site at an intermediate step in the enzyme cycle. We were able to obtain binding stoichiometries through the millimolar range and saw no evidence of a second site.

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EPR CHARACTERIZATION AND ENDOR STUDIES OF UBIQUINOL:CYTOCHROME C_2 OXIDOREDUCTASE ISOLATED FROM RHODOBACTER SPHAEROIDES

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A highly active large-scale preparation of ubiquinol:cytochrome c_2 oxidoreductase (*bc_1* complex) has been obtained for biochemical and spectroscopic studies. The complex was extracted from chromatophores with dodecyl maltoside, in the presence of glycerol, and was purified by ion-exchange and gel filtration chromatography. It catalyzes the reduction of horse heart cytochrome c with a turnover in excess of 300 mol s^{-1} (mol c_1)$^{-1}$. Full spectrum redox titrations, in the presence and absence of antimycin, show two thermodynamically distinct *b* cytochromes and cytochrome c_1, with spectra and midpoint potentials similar to those in chromatophores. Redox titrations monitoring low-temperature EPR spectra at g=1.90 and g=2.00 show the presence of the Rieske iron-sulfur center and the antimycin-sensitive semiquinone, respectively. We are currently investigating the chemical structure of the semiquinone binding sites by ENDOR spectroscopy. This work was supported by NIH grants PHS 5 RO1 GM 26305 and GM 35438. We gratefully acknowledge support by the University of Illinois ESR Research Center (NIH RR 01811).

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GENERATION OF RADICAL SPECIES FROM GOOD BUFFERS. N. Dennis Chasteen*, John K. Grady*, and Daniel C. Harris**. *Department of Chemistry, University of New Hampshire, Durham NH 03824; **Chemistry Division, Research Department, Naval Weapons Center, China Lake, CA 93555.

Oxidation of Fe(II) in Good buffer solutions by molecular oxygen to produce O_2^- causes the formation of buffer radicals. Radicals with half lives of approximately 10 min are produced with HEPES [4-(2-hydroxyethyl)-1-piperazineethane sulfonic acid] and other piperazine ring based buffers such as EPPS and PIPES. The HEPES radical displays an EPR spectrum consisting of at least 30 lines with an a_H splitting of 2.42 G. The HEPES radical can also be produced directly by the addition of KO_2 to the buffer or by electrolysis at a potential of 1.25V. Alkyl radicals are also observed during Fe(II) oxidation when DMPO [5,5-dimethyl-1-pyrroline-N-oxide] is employed as a spin trapping reagent in the presence of HEPES, piperazine, dimethylpiperazine, or MES [4-morpholineethane sulfonic acid], suggesting that the radical is centered on an alpha amino carbon of the ring in all cases. Such radicals probably are formed from hydrogen extraction reactions during decomposition of the more stable amine cation radical. These results indicate that Good buffers readily participate in radical reactions and should be employed with caution in studies of radical production in biological systems.

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SPIN LABELING EPR IN STUDIES OF MOLECULAR INTERACTIONS IN BIOMEMBRANES. Gheorghe Benga, Department of Cell Biology, Faculty of Medicine, Medical and Pharmaceutical Institute Cluj-Napoca, Roumania.

Spin labeling EPR and a variety of probes have been used in studies of protein-lipid and lipid-lipid interactions and drug effects. It was shown that the use of fatty acid spin labels may not give an accurate picture of protein-lipid interactions in model biomembrane systems. This is because the protein itself can bind fatty acids. The combination of spectra due to the label bound to the protein and free in the lipid phase may give an overall impression of immobilization, but this need not be due to the interaction between protein and phospholipids. On the contrary, the use of spin labeled phospholipids provide a more accurate representation of intrinsic protein-lipid interactions, as shown in studies of the cytochrome oxidase-lipid complex. Spin labeled fatty acids were used to probe the fluidity of membrane in human liver mitochondria compared to rat liver mitochondria. A greater mobility of spin label motion was noticed in the human case. There were pecularities of lipid composition in human liver membranes, and therefore the higher fluidity of human membranes was explained by a lesser immobilization of lipids in human compared with rat membranes.

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ASYST/ASSEMBLY LANGUAGE PROGRAM FOR AN IBM-PC AND A TRANSIAC TRANSIENT RECORDER INTERFACED TO A VARIAN EPR SPECTROMETER: TIME AND FIELD CONTROL. Eric Bradford and Lowell D. Kispert, Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487.

An IBM personal computer with 640 kbytes of memory has been interfaced to a Varian E12 EPR spectrometer via a DT2801 Data Translation card. Through the DT2801, the IBM-PC generates a 0-10 V D/A ramp to control the magnetic field via a magnetic field scan card from the Denver Research Institute. At each of 200 magnetic field values, a 512 point transient decay is recorded by a Transiac recorder (DSP Technologies). The Transiac recorder has a sampling rate which can be varied from 10 ns to 1 µs with the option of collecting pre-trigger data. The transient decay signals can be stored in the Transient recorder and averaged with subsequent signals to improve S/N. Stored data can be transferred to the IBM-PC through the one remaining DMA channel (provided the DMA channel on the DT2801 is disabled) with a Transiac DMA card. The control language for this system has been written with the ASYST (Macmillan Software) package. Supplied with the Transiac recorder are assembly drivers to permit control of data collection with a higher level language. Because these drivers were not equipped for communication with ASYST, they were modified to work with the described system. After the software program and assembly drivers are loaded into the ASYST environment, 100 kbytes of memory are available for data collection. This limitation allows the collection of a 200 x 512 data matrix. Typically, a two minute magnetic field scan is used when the transient spectra are generated by a laser with a 40 Hz repetition rate averaging over four transient signals or 4 minutes when 16 transients are averaged. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research of the U. S. Department of Energy under Grant no. DE-FG05-86ER13465.

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DUAL CHANNEL COMPUTER INTERFACE OF ESR SPECTROMETER. M. Thomas Jones, Toshio Maruo, Megh Singh, and James H. Roble. University of Missouri-St. Louis, Department of Chemistry, St. Louis, MO 63121.

A Varian E-12 ESR spectrometer was interfaced with a microcomputer (IBM PC-XT). The spectra were analyzed at the microcomputer level or were sent to minicomputer (micro-VAX) for faster analysis. Dual cavity techniques using suitable references for both organic and inorganic samples are described. Dual channel A/D conversion of dual cavity signals are employeed to calibrate the field differences in the reference and sample cavities and to standardize the field by the hf-splitting of the reference sample. The baseline correction and the limits of cut-off field in Lorentzian shaped spectra are discussed in terms of errors in the magnetic susceptibility measurements. The effects of smoothing techniques and the use of second-derivative for the determination of g-values are described. Three-dimensional spectral representations of variable temperature and single crystal studies are illustrated. Finally, the advantages and disadvantages of the automated, menu-driven, programs are discussed.

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NMR AND EPR SPECTRA OF SPIN-LABELED NICKEL(II) XANTHATES. Scott K. Sheppard, Kundalika M. More, Gareth R. Eaton, and Sandra S. Eaton, Departments of Chemistry, University of Denver, Denver, CO 80208, and University of Colorado at Denver, Denver, CO 80202.

^1H and ^{13}C NMR spectra were obtained for bis(alkylxanthate)Ni(II)bipyridyl complexes. The extent of electron spin delocalization into the alkyl chain was compared with the magnitude of electron-electron spin-spin interaction in analogous spin-labeled nickel(II) xanthate complexes. The ^1H NMR spectrum of a spin-labeled Ni(II) xanthate indicated that the Ni(II) provided an efficient relaxation mechanism for protons that were interacting with the nitroxyl unpaired electron. The resolution of NMR spectra of 0.1 M solutions of the spin-labeled Ni(II) complex was comparable to that of 1.0 M solutions of nitroxyl radicals. The contributions to the isotropic shifts of protons in the nitroxyl ring from the Ni(II) and nitroxyl unpaired electrons were additive.

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THE GRADIENT DEPENDENCE OF RAPID-SCAN NMR SPECTRAL LINESHAPES. H.A. Buckmaster and T. Duczmal, Department of Physics, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

Recently it has been shown that the shape of an observed "wiggles" signal is a very sensitive indicator for B-field inhomogenities. This paper establishes the functional relationships between the quantitative parameters describing the "wiggles" signal and the modulus of the B-gradient. The effect of various instrumentation parameters on the B-gradient calibration curves has been investigated. This was achieved by numerical simulations of the "wiggles" signal using approximations to the Fourier and convolution theorems. It is shown that some of these parameters produce linear perturbations and that superposition of various instrumental effects have non-linear influence on the calibration curves.

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THE SHAPE OF RAPID-SCAN NMR SPECTRAL LINES FOR A SIMPLE PHANTOM. H.A. Buckmaster and T. Duczmal, Department of Physics, The University of Calgary, Calgary, Alberta, Canada T2N 1N4.

Recently, it has been shown that the sensitivity achievable using rapid-scan NMR spectroscopy is comparable with that for pulse FT-NMR. This paper reports the results of a modelling study of inhomogeneous samples in a B-gradient using rapid-scan NMR spectroscopy. A simple phantom consisting of two cylindrical slices of active nuclei was simulated and its rapid-scan NMR spectra was computed. The computational modelling is based on the Fourier and convolution theorems. The main objective of this paper was to investigate the potential of using rapid-scan NMR spectroscopy as an imaging technique. The influence of the sweep rate on high fidelity spin-density function reproduction, "wiggles" signal and the deconvolution algorithm for the absorption mode is discussed.

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THE INFLUENCE OF A NON-LINEAR FREQUENCY SWEEP ON THE SHAPE OF RAPID-SCAN NMR SPECTRAL LINES. H.A. Buckmaster and T. Duczmal, Department of Physics, The University of Calgary, Calgary, Alberta, Canada T2N 1N4.

This paper reports the results of an investigation of modelled "wiggles" signal obtained using Rapid-Scan NMR spectroscopy when the sweep is non-linear. For a linear sweep excitation, its frequency domain spectrum is represented by an oscillating function with constant amplitude. The resultant "wiggles" signal has an exponential decay shape which depends on the T_2 relaxation time of the spin system and the sweep rate. The frequency domain spectrum of an exponential frequency sweep is represented by an oscillating function whose amplitude satisfies a Lorentzian function. Computational modelling of "wiggles" signal based on the Fourier and convolution theorems is used to obtain the relation between the exponential sweep function parameters and the relaxation time T_2.

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HIGH RESOLUTION ESR IMAGING IN SOLIDS. G.G. Maresch, A. Grupp and M.Mehring, 2.Physik.Inst., Universität Stuttgart, Pfaffenwaldring 57, D-7000 Stuttgart 80/Germany

We report on technique and application of pulsed field gradients for ESR imaging in an X-band slotted tube resonator (STR). To achieve fast switching times and large gradients a small saddle coil was mounted inside the resonator. Using stripline technique and minimizing eddy currents results in a switching time of 100 ns for pulsed field gradients of 1T/m. We demonstrate high resolution ESR imaging in solids with a spatial resolution of 10 µm by applying a stepped gradient technique.
A standard method with fixed gradients was used to reconstruct an image of two crystalline samples from 180 ESR spectra at different orientations of the magnetic field gradient.

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RAPID DETERMINATION OF TRANSLATIONAL DIFFUSION COEFFICIENTS USING ESR IMAGING D.A. Cleary, Y-K. Shin, D.J. Schneider and J.H. Freed, Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853

ESR imaging has been used to rapidly determine translational diffusion coefficients. Translational diffusion coefficients on the order of $D=10^{-8}$ cm^{2} sec^{-1} have been determined in 1-2 hours. One dimensional concentration profiles in space were Fast Fourier Transformed, and the decay of the Fourier components in time was analyzed to determine D. The rapidity of the method is based upon the high resolution permitting D to be accurately measured after a total diffusion distance of only ca. 100 microns. The method of analysis and several systems that have been studied will be discussed. The lateral translational diffusion coefficient of 12-PCSL in the lipid bilayer POPC has been determined over a range of temperatures from 20° - 60°C. The diffusion coefficient varied from 7.0×10^{-8} to 14.0×10^{-8}cm^{2} sec $^{-1}$. The parallel and perpendicular translational diffusion coefficients of TEMPONE and P-Probe in the smectic A liquid crystal S2 have also been studied over a range of temperature. The application of this technique to studying critical fluids will also be discussed.

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CONTINUOUS WAVE EPR-TOMOGRAPHY. Uwe Ewert, Thomas Herrling, Wilfried Schneider. Academy of Sciences of GDR, Centre of Scientific Instruments, Rudower Chaussee 6, GDR-1199 Berlin.

Up to now the development of continuous wave EPR-tomography seems to be more successfull compared with the pulse techniques due to the higher sensitivity. The universal application is limited by the splitting of EPR-spectra, superposition and dependence of spectrum shape on spatial distribution. The spectrally resolved investigations are based on modulated gradient [1] and graduated gradient [2] technique. The graduated variation of stationary gradient [2] and the acquisition of broadened spectrum for every gradient level is used in connection with projection reconstruction algorithm to separate spectral and spatial information. In opposite to modulated gradient distortions appear from long range neighbour elements. The projection at spatial axis yields the spatial distribution independent of concentration variations of the spectrum. We discuss the possibility of acquisition time reduction in connection with rapid scan and a resolution enhancement by a second phase sensitive detection.

[1] T. Herrling, N. Klimes, W. Karthe, U. Ewert, B. Ebert, J. Magn. Reson. 49 (1982) 203, U. Ewert, T. Herrling, J. Magn. Reson. 61 (1985) 11.
[2] U. Ewert, T. Herrling, Chem. Phys. Lett. 129 (1986) 516

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TWO-DIMENSIONAL ENDOR IMAGING.

Edward G. Janzen, Yashige Kotake, and Uwe M. Oehler. Guelph Waterloo Centre for Graduate Work in Chemistry. Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G2W1.

ENDOR images were obtained by mapping the intensity of N-14 ENDOR lines of nitroxide spin probes (Fremy's salt and di-t-butylnitroxide) in two-dimensional aqueous systems. ENDOR induced ESR was recorded with the applied field gradient within the xy plane. Thus obtained projections were reconstructed to a 2D image by using an iterative reconstruction technique. The following characteristics of ENDOR imaging are shown by using both phantom and actual biological samples: 1. The dependence of ENDOR intensity on viscosity can be used to image viscosity distribution. 2. The oxygen concentration can be mapped by using the sensitivity of ENDOR intensity on the concentration of oxygen. 3. The solvent effect on the hfs can be utilized to image the different portions of the solution by choosing the appropriate ENDOR frequency. 4. Images of different nuclei such as nitrogen and proton can be obtained. 5. More than two probes can be used at the same time and individual images can be obtained.

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Imaging Electromagnetic Fields Using the Magnetic Resonance Absorption Spectrum of a Paramagnetic Gas.*

S. A Marshall, B. H. Suits, and M. T. Umlor, Department of Physics, Michigan Technological University Houghton, Michigan 49931

The magnetic component of an electromagnetic field confined to a cavity resonator operating in the 3.2 centimeter wavelength region has been mapped using the noninvasive technique of electron paramagnetic resonance (EPR) imaging. The active agent used for this purpose was molecular oxygen. One dimensional images were obtained of the fields of two distinct cylindrical cavity resonators. Images were found to correspond to predictions from waveguide theory.

*This work supported by the U.S. Office of Naval Research.

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ESR IMAGING OF OXYGEN DEPENDENT PROCESSES IN VIABLE BIOLOGICAL SYSTEMS.

G. Bacic, F. Demsar, T. Walczak, J. Dobrucki, H. Swartz, University of Illinois College of Medicine at Urbana-Champaign, Illinois ESR Center, 506 S. Mathews Avenue, Urbana, Illinois 61801

The purpose of these studies is to demonstrate the ability of ESR to indicate the spatial distribution in biological materials of nitroxide spin labels that can reflect metabolic events. The method uses two sets of computer controlled gradient coils and the filtered back-projection technique to make a 2D 256x256 grid image reconstruction. Using different nitroxides we demonstrate the feasibility of measuring oxygen concentrations and distributions. Oxygen dependent images were obtained utilizing several different approaches to obtain contrast and improve resolution: 1) oxygen induced line broadening; 2) oxygen induced changes in microwave power saturation; and 3) oxygen dependent metabolism of nitroxides by viable mammalian cells. Development of a fast scan ESR imaging enabled the study of fast processes such as oxygen diffusion and spatially resolved metabolic reduction of nitroxides. The different solubility of nitroxides in aqueous and lipid-rich areas in tissues as well as differences in oxygen solubility served as basis for contrast enhancement in ESR imaging of these samples. The use of a perdeuterated ^{15}N substituted nitroxide led to resolution of the order of cellular dimensions and is illustrated by ESR images of multicellular spheroids which show viable and necrotic areas within spheroids.

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ESR IMAGING OF LIVE AND NONVIABLE CELLS IN A MODEL OF TUMOR TISSUE. Jerzy W. Doliwa-Dobrucki, Goran Bačić, Franci Demsar, and Harold M. Swartz. ESR Center, University of Illinois, 506 South Mathews Avenue, 190 Medical Sciences Bldg., Urbana, Illinois 61801.

Recent improvements in ESR imaging equipment in our laboratory now make it possible to extend this method to investigating biological objects at the microscopic level. A technique of contrasting and two-dimensional imaging of live and nonviable mammalian cells in multicellular spheroids is reported here. Spheroids are three-dimensional cell aggregates grown under laboratory conditions and are known as a model system for investigating tumors. The imaging set-up in our laboratory consists of computer-controlled coils for 2D imaging and a Zenith Z-100 dedicated computer interfaced with a X-band Varian E-12 spectrometer. Nineteen projections over 180 degrees are collected. The acquisition time is 20 seconds per projection and the field gradient is 60 G/cm. Data files are processed on the IBM-PC-AT computer. A suitable uncharged nitroxide and nontoxic broadening agent are added to the culture medium with a spheroid of a diameter 1200 μm. The nitroxide freely enters all cells in the spheroid. The broadening agent remains extracellular for live cells but enters cells whose membranes have been damaged and therefore broadens away the signal from these cells. The resulting ESR image is a 2D map of live and dead cells inside the spheroid. This is a unique, noninvasive method of investigating the effects of antitumor drugs and ionizing radiation on viability of cancer cells without removing them from the spheroid.

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IN VIVO ESR SPECTROSCOPY AT LOW FREQUENCIES

Mark J. Nilges, Tadeusz Walczak, and Franci Demsar; College of Medicine at Urbana-Champaign, Illinois ESR Center, Urbana, Illinois 61801

Due to the lower dielectric loss at lower frequencies, ESR at L-band (1-2 GHz) allows one to probe about 1 cm into tissue. Construction and design of a state-of-the-art L-band spectrometer for in vivo ESR spectroscopy is detailed. Several types of probes have been designed which consist of a lumped capacitance and inductance (variation of loop-gap resonators) and have resonant frequencies of 1.1 to 1.3 GHz. The probes have been designed with either imaging or topical ESR in mind. Resonators with good Q and a large and uniform B_1 but small electric field in the sample region have been designed for samples up to 5/8" thick. Resonators which can be used to probe into the surface of a thick sample have also been designed, but the size and uniformity of B_1 must suffer somewhat. Results are presented for tissues containing either nitroxides or melanin.

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ESR IN-VIVO, Lawrence J. Berliner, The Ohio State University, Department of Chemistry, 120 W. 18th Avenue, The Ohio State University, Columbus, OH 43210

The promise of new methods of non-invasive detection of tissues, organs and physiological metabolites has come with the advent of magnetic resonance imaging (MRI) and in-vivo magnetic resonance spectroscopy. Most recently electron spin resonance (ESR) has been developed for in-vivo systems. While free radical processes in mechanisms of carcinogenesis and aging have been studied intensively in the past principally by in-vitro methods, we are now utilizing ESR spectroscopy for non-invasive detection of living animals. Due to the intense interest in nitroxides as potential NMR contrast agents (and built-in ESR imaging agents) we are currently studying the pharmacokinetics of nitroxides directly in-vivo, as a probe of redox metabolism in various tissues. The results are also promising in assessing the feasibility for ESR imaging measurements at the tissue site of interest.

147 DEVELOPMENT OF ULTRA HIGH RESOLUTION EPR IMAGING. Keiichi Ohno. Faculty of Eng., Hokkaido University, Sapporo, 060, Japan

The resolution of EPR imaging depends upon magnetic field gradients, linewidths, concentrations of paramagnetic species and signal-to-noise ratios. To obtain ultra high resolution and sufficient signal using an ordinary EPR cavity one needs so high concentration of the species in a small sample volume that dipole-dipole or exchange interactions may occur. If submicron dimension samples with less spins concentration can be used by means of a novel miniature detector with high sensitivity, all factors except for the linewidths are improved to a great extend. This small scale is also advantageous for obtaining a large magnetic field gradient due to setting an anti-Helmholtz coils very closely each other. Experimental results will be presented.

148 INSTRUMENTATION AND SOFTWARE FOR CW EPR-IMAGING. Thomas Herrling, Uwe Ewert, Wilfried Schneider. Academy of Sciences of GDR, Centre of Scientific Instruments, Rudower Chaussee 6, GDR-1199 Berlin.

Now EPR-imaging needs routine instrumentation and software for laboratory computers.We discuss the tomography accessory (ZZG1) for EPR-spectrometers. It is designed for sample size of 5 x 5 x 5 mm. The resolution is 20 µm for a line width of 0.1 mT. The standard mode is based on the modulated gradient technique. Spectrally resolved investigations are realised for 1D spatial analysis by direct measurement. For graduated gradient technique [1] and spatial 2D measurement the ZZG1 is used in connection with a personal computer. We discuss software and instrumentation for application on polymeres, catalysts and semiconductors.

[1] U. Ewert, T. Herrling, Chem. Phys. Lett. 129 (1986) 516.

149 SPECTRAL-SPATIAL 2-D EPR IMAGING WITH AN ITERATIVE ALGORITHM. Martin M. Maltempo, Department of Physics, University of Colorado-Denver, Denver, CO 80202, Sandra S. Eaton, Department of Chemistry, University of Colorado-Denver, Denver, CO 80202, and Gareth R. Eaton, Department of Chemistry, University of Denver, Denver, CO 80208.

Spectral-spatial EPR imaging gives the EPR spectrum as a function of position in the sample. Spectra are obtained at a series of static magnetic field gradients that correspond to projections in a spectral-spatial plane. For a given maximum magnetic field gradient, the spatial resolution of the image can be improved by collection of data for less than a full 180° angular range. We have used the projection slice algorithm iteratively to estimate the "missing" information. Images have been obtained that show variations in nitroxyl lineshape due to collisional broadening and changes in motional averaging of the hyperfine interaction at different locations in the sample.

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SEED GERMINATION: EPR IMAGING STUDY, T.Walczak,F.Demsar,H.Gabrys and H.M.Swartz, University of Illinois, College of Medicine at Urbana-Champaign, ESR research center, Urbana, Illinois 61801

EPR Imaging at X-band allows us to measure biological samples with high water content, in appropriate configurations, with dimensions of up to a few millimeters. Most plant seeds are within the optimal dimensional range for X-band two dimensional EPRI. Using perdeuterated ^{15}N nitroxides as an imaging substance sufficient sensitivity was obtained to achieve resolution of tens of micrometers. With an addition of nontoxic broadening agent $K_3Fe(CN)_6$, which remains extracellular only for live cells, we were able to observe contrast in seeds between the embryo and regions containing storage food. We then could follow changes that occurred during time course of germination. We performed our experiments on lettuce seeds and we obtained a series of 2D-EPR images over the first 50 hours of germination. The time for collection of data for one image using 19 projections was 6 minutes. Our results demonstrate the feasibility of kinetic studies of the first steps of seed germination by 2D-EPRI.

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SPIN DIFFUSION AND MAGNETIC BEHAVIOUR OF THE PSEUDO 2-d SYSTEMS NaBp.2Tg AND RbBp.2Ttg. M.C.M. Gribnau, C.P. Keijzers and E. de Boer. Department of Molecular Spectroscopy, Research Institute of Materials, University of Nijmegen, Toernooiveld, 6525 ED NIJMEGEN, The Netherlands

The crystal structures of NaBp.2Tg and RbBp.2Ttg (Bp = Biphenyl = $C_{12}H_{10}^-$; Tg = triglyme = $CH_3O(CH_2CH_2O)_3CH_3$; Ttg = tetraglyme = $CH_3O(CH_2CH_2O)_4CH_3$) show the presence of layers of biphenyl anions separated by layers of alkali-glyme complexes. This structure suggests two-dimensional magnetic character. Above 20 K the anisotropy in the linewidth of the exchange-narrowed EPR line and the deviations from the lorentzian lineshape show the importance of spin diffusion in both compounds. The effects of spin diffusion are typical for pseudo 2-d systems. The arrangement of biphenyl anions in the layers is different in the two compounds. In NaBp.2Tg each biphenyl is approximately hexagonally surrounded. EPR and magnetization measurements show the presence of various intralayer exchange interactions. Above 80 K the average of these interactions, which is positive, is observed. At lower temperatures the antiferromagnetic interactions determine the magnetic behaviour. Moreover, at 1.5 K a crossover takes place from a 2-d to a 3-d magnetic structure and an antiferromagnetically ordered state evolves. In RbBp.2Ttg one of the neighbours is clearly nearer than the others. This is reflected in the susceptibility which may be described by the singlet-triplet model with $J = -13$ K. Upon cooling no EPR signals of isolated triplets are observed. Instead, at 1.2 K fine structure due to a doublet state arises. This is attributed to the presence of neutral biphenyl molecules in the crystals.

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EPR STUDIES OF ANISOTROPIES AND DEFECTS IN LINEAR CHAIN $A_2Cu_2X_6$ SALTS. Baldev Patyal and Roger D. Willett, Department of Chemistry, Washington State University, Pullman, Washington 99164-4630.

EPR measurements have been made on a series of $A_2Cu_2X_6$ salts containing pseudo-planar $Cu_2X_6^{2-}$ ions. These dimers stack to form chains. Magnetic interactions occur between copper ions within the dimers and weaker coupling occurs between dimers. The EPR spectra generally consist of two overlapping lines: (1) a very broad line, due to the exchange coupled chains; (2) a narrower line due to impurities, presumably lattice defects. The broad lines generally show a g-tensor anisotropy consistent with a distorted elongated octahedral coordination geometry and their linewidths yield the spin anisotropies of the magnetic interactions. The g values of the defects correspond to a reversed anisotropy ($g_{\parallel} < g_{\perp}$) consistent with a distorted trigonal bypyramidal geometry. Single crystal studies allow the deduction of their geometry and orientation in the lattice.

153 SINGLE CRYSTAL ESR STUDIES OF (n-BuN$_4^+$Ni(o-BENZENEDISELENOLATE)$_2^-$ AND RELATED TRANSITION METAL COMPLEXES.

M. Thomas Jones, James H. Roble, Megh Singh and Toshio Maruo. University of Missouri-St. Louis, Department of Chemistry, St. Louis, MO 63121.

Previously reported temperature dependent studies of the ESR spectral envelope of polycrystalline samples of n-tetrabutylammonium salts of Nickel(o-benzenediselenolate(bds))$_2^-$ and o-benzenedithiolate(bdt) reveal that the g-tensors for the bds and bdt salts are axial and psuedo axial, respectively. There was concern that the g-tensor for the bds salt might actually be psuedo axial also because of the poorer resolution possible as a result of the increased spectral linewidth in the selenium salt due to the enhanced spin-lattice relaxation rate caused by the heavier atom. In addition, an abrupt change in $g_{\parallel}$ was observed at *ca* 150 K for the Ni(bds)$_2$ salt which based on other physical studies has been identified as due to a crystalline phase change. The results of single crystal ESR experiments upon Ni(bds)$_2$ and Ni(bdt)$_2$ are described which demonstrate that the g-tensor for the Ni(bds)$_2$ salt is psuedo axial and the phase transition is very sharp(i.e., less than 1 degree). The single crystal ESR Ni(bdt)$_2$ results are in complete agreement with the polycrystalline data. Based on the known crystal structures of the two Ni salts, the molecular based g-tensors are reported. As time permits, single crystal ESR studies on related complexes such as Ni doped in Cu(bdt)$_2$ and bds will be presented.

154 MEASUREMENT OF QUADRUPOLE COUPLINGS IN COPPER COMPLEXES WITH L-BAND, PARALLEL POLARIZATION EPR.

Kurt S. Rothenberger, Mark J. Nilges, T. E. Altman, K. Glab, R. Linn Belford, W. Froncisz, and James S. Hyde. Department of Chemistry and Illinois ESR Research Center, University of Illinois, Urbana, IL 61801 & National Biomedical ESR Center and Department of Radiology, The Medical College of Wisconsin, Milwaukee, WI 53226.

An L-band (1-2 GHz) electron paramagnetic resonance (EPR) spectrometer with collinear static and oscillating magnetic fields was used to obtain central metal quadrupole coupling information from copper(II) complexes in disordered states through direct measurement of secondary ($\Delta m_S = \pm 1$, $\Delta m_I = \mp 1$) transitions. Reliable copper quadrupole coupling information had previously been available only from single crystal studies, or from a complicated analysis of lineshapes and intensities at several frequencies. Good signal/noise is obtained from a locally constructed L-band bridge with a GaAs FET amplifier, computer time averaging capability and a loop gap resonator that accommodates 4mm sample tubes. A test case, ^{63}Cu/Pd(acac)$_2$ powder, yielded a quadrupole coupling constant consistent with that previously reported from single crystal and other work. The technique has also been successfully applied to other compounds containing oxygen, sulfur, and nitrogen ligands in doped powder and frozen solution forms. [Work supported by NIH (RR01811 and RR01008).]

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THE ESR SPECTRA OF THE Mn(II) IONS DOPED INTO TWO CRYSTALLINE FORMS OF DITHIOCYANATOBIS(2,2'-BI-2-THIAZOLINE)IRON(II). Andrzej Ozarowski, Bruce R. McGarvey, Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada.

The title compound when recrystallized from ethanol at elevated temperature forms triclinic crystals (1) which undergo a sharp 'spin crossover' transition with pronounced hysteresis (T↓=171K, T↑=181K). The triclinic crystals (2) obtained by recrystallization at the room temperature do not exhibit 'crossover' transitions over the temperature range 77-300K. The X-ray structures determined in this work revealed, that both crystal lattices are built up of cis-configurated molecules being very similar in both cases. The large crystals of both forms, doped with the analogous manganese complex were investigated by ESR. The Zero-Field-Splitting parameters were calculated by fitting of the spectra. The D parameters found for (1) and (2) are similar (0.0342 cm^{-1} and 0.0309 cm^{-1}, respectively), while the E parameters differ considerably (0.0091 cm^{-1} and 0.0029 cm^{-1}, respectively). This difference is not directly supported by the molecular structures. The D and E parameters are strongly temperature dependent in the diamagnetic phase of (1) but less so in the paramagnetic phase of (1) and in (2). A very slow rate of the high spin-low spin conversion was observed for single crystals of (1), while the rate was fast for powder samples. The transition from low to high spin state resulted in pulverizing each crystal examined. The difference in the behavior of both crystalline forms with respect to the 'crossover' phenomenon will be explained in terms of the intermolecular interactions.

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ON THE SYMMETRY ADAPTED EFFECTIVE OPERATORS, R. Chatterjee, Physics Department, University of Calgary, Calgary, Alberta, Canada T2N 1N4

The common usage of the "Effective Operators" in the interpretation of EPR and ENDOR spectra, will be examined under the invariant requirement of the parity (P) and the time reversal (T) operations. Although the point group symmetry has been applied in the past for the classification of these operators, the other two symmetry operations (PT) have not been simultaneously taken into consideration. In this paper, it will be shown that when these two operations are applied along with the point group symmetry for the classification of the effective operators, then certain new terms appear whose importance will be discussed.

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FINE STRUCTURE TERMS IN SUPERPOSITION MODEL ANALYSIS OF CHARGE COMPENSATED HIGH SPIN EPR CENTRES. Czesław Rudowicz. Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601, Australia

The approach based on superposition of two uniaxial zero-field splitting (ZFS) terms originally proposed by Takeuchi et al. [J. Phys. Soc. Japan 51, 3166 (1982)] for the vacancy associated Cr^{3+} impurity centres in A_2MF_4 is reanalysed in terms of effective ZFS contributions. It is shown that the authors' approach is a particular case of a more general model suitable for any charge compensated EPR centre, while the original approach seems valid only for spin S=1 or 3/2 centres. In our approach an effective spin Hamiltonian is obtained by superposition of ZFS terms for an undistorted site, for a vacancy or charge-compensating ion contribution and for the remaining nearest neighbour ligands. Takeuchi et al. have derived expressions relating the observed D and E with the uniaxial D_1 and D_2 for the Cr^{3+} centre associated with a nearest (i) K^+-vacancy along the <111> axis and (ii) M^{2+}-vacancy along the [010] direction. Their conventional technique cannot be applied for the higher-order ZFS terms. The extension of the model to the fourth- and sixth-order ZFS terms, which is the aim of this paper, enables testing the 'effective contributions' model for centres with higher spin, e.g. S = 5/2 or S = 7/2. Expressions relating the orthorhombic or lower symmetry parameters B_k^q, k=2,4 and 6, with the pertinent uniaxial parameters are derived by computer using ALTRAN and the transformation matrices for the extended Stevens operators [C. Rudowicz, J. Phys. C18, 1415 (1985)]. As an example, applications to paramagnetic centers in A_2MF_4 compounds and in alkali halide - type ones are considered.

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APPLICATIONS OF SYMBOLIC PROGRAMMING IN TRANSITION-METAL ION EPR THEORY. Czeslav Rudowicz and Richard Bramley. Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601, Australia

The paper reviews recent research based on the application of the symbolic programming language ALTRAN to theoretical problems in EPR of transition-metal ions. After a brief outline of ALTRAN's capabilities several practical problems are discussed. The first problem concerns the transformation properties of the extended (O_k^q) as well as the normalized Stevens operators and their significance in the spin Hamiltonian (SH) formalism. Transformation matrices with k=1 to 6 for a general rotation (Φ,Θ) of the frame of coordinates derived by computer using ALTRAN [C. Rudowicz, J. Phys. C18, 1415 (1985)] are discussed. Secondly, the relations between SH parameters B_k^q, k=2, 4 and 6, and the components of the g-tensor expressed in several axis systems [C. Rudowicz, J. Mag. Res. 63, 95 (1985)] particularly useful in EPR studies are considered. The third problem concerns the standardization of conventions for orthorhombic SH for spin $S \leq 7/2$ d^n and f^n ions. Relations allowing for extension of the standardization to SH for high spin EPR centres are discussed. Several EPR studies of $3d^n$ and $4f^n$ ions in crystals are reconsidered [C. Rudowicz and R. Bramley, J. Chem. Phys. 83, 5192 (1985)]. The theoretical and practical significance of this work with regard to low symmetry effects in EPR studies are elucidated. Applications of the above results in crystal field theory and other recent works in this area are briefly discussed. Further applications of ALTRAN, e.g. in the microscopic SH theory for d^4 and d^6 ions at sites of symmetries requiring the 'imaginary' zero-field splitting terms as well as the perturbation calculations of SH energies, are outlined.

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MODEL CALCULATIONS FOR THE DISTANCE DEPENDENCE OF FERROMAGNETIC SUPEREXCHANGE. R. E. Coffman, Chemistry Department, University of Iowa, Iowa City, IA. 52242.

A model is presented for the distance dependence of ferromagnetic superexchange. The two center exchange integral between molecular orbitals is expanded in a linear combination of atomic orbitals. Nearest neighbor two-center coulombic, hybrid and exchange integrals are kept in the resulting expansion. The ferromagnetic contribution to $J_o S_1 \cdot S_2$ may then be analyzed in terms of the AO substructures which contribute to the total ferromagnetic contribution to the superexchange coefficient 'J_o'. Such substructures are identical to the usual idea of the 'path' of the exchange interaction.

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AUTOSIMULATE: A COMPUTING PROGRAM FOR DIRECT IDENTIFICATION OF ALL OF POSSIBLE ESR SIMULATIONS DUE TO A GIVEN MOLECULAR STRUCTURE. David R. Duling, Ann Motten, and Ronald P. Mason. National Institute of Environmental Health Sciences, Laboratory of Molecular Biophysics, PO Box 12233, Research Triangle Park, NC 27709

A direct method of computing all possible ESR simulations for a given structure and assessing their quality of fit is presented. All unique combinations of nuclear spins and hyperfine splitting constants are generated by a group selection with replacement process and coupled with pre-simulation filters for spectral length, smallest splitting inclusion, and finite spin density. Simulations are then compared to the experimental spectrum by calculation of a correlation coefficient. Some knowledge of the molecular structure and possible splitting constants is required beforehand. By calculating the entire field of relevant simulations, the solution set contains all parameter combinations which produce satisfactory spectra. Considered as examples are the Nitrofurantoin and Nifuroxime spectra. In addition, the procedure is easy to program and operates in a time frame often suitable for faster processing desktop computers.

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CHEMOMETRICAL ANALYSIS OF ESR SPECTRA: RESOLUTION ENHANCEMENT BY DECONVOLUTION AND NOVEL ANALYSIS OF HYPERFINE STRUCTURE

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Kyoto 606 Japan

Resolution enhancement of e.s.r spectra by Fourier-transforms in the computation of deconvoluted and first- and third-oder derivative e.s.r. spectra is performed. E.s.r. measurements were carried out by a JES-PE spectrometer (JEOL Co., Tokyo) with a PAR 124 Rock-in, or an AM 430 OP amplifier. Neumerical treatments were by a PU-ADX A/D converter (Japan Protec Co., Tokyo) and a NEC PC-9801 VM-2 computer (Nippon Electric Co., Tokyo) with MS-FORTRAN-77 languages. An e.s.r. spectrum of 2,2,6,6-tetramethyl-piperadine-1-oxyl (TEMPO) in benzene or 9,10-dimethylanthracene (DMA) in acetonitrile radicals was deconvoluted by a Fourier-transform and deconvolution technique, and the resolution within about 0.2 gauss line width, of the resulted spectrum was enhanced and the signal-noise ratio (S/N) was decreased. Mixing of first- and third-order derivative spectra showed resolution enhancement and narrowing of the line-widths. An e.s.r. spectrum of a perylene cation radical was observed in acetonitrile. A new analytical technique was applied for higher resolution and compared with those of cepstral analysis of hyperfine structure in the e.s.r. spectra of perylene cation radicals. Deconvolution and new analytical techniques with neumerical treatments are discussed comparing with cepstral analysis of e.s.r. spectra.

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MAGRES: AN EXACT SIMULATION PROGRAM FOR EPR, ENDOR AND ESEEM.

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A major step in the analysis of single crystal spectra from EPR and EPR-related techniques is to obtain the interaction tensors from the experimental data. For that reason we developed the program package MAGRES (MAGnetic RESonance) which is able to calculate EPR, ENDOR (without relaxation) and ESEEM spectra for, in principle, any spin system in single crystals as well as in powders. The spin-Hamiltonian may be constructed from one or more electron and/or nuclear Zeeman interactions, exchange and hyperfine interactions as well as zero-field splittings and nuclear quadrupole interactions. All integer and half-integer spins are allowed. No restrictions are placed upon the different tensors: they may contain isotropic, symmetric and antisymmetric elements. The program uses exact diagonalization, hence no assumptions have to be made about the relative magnitude of the interactions nor about the directions of the tensors. Spectra may be calculated both in the field and in the frequency domain. Comparison of the calculated *frequencies* with the experimental data of single crystal spectra allows for the optimization of the interaction tensors. The computed tensors may be checked by comparison of the experimental and calculated *intensities* of single crystals and powders. Simulation of the ESEEM spectra are possible both for the 2- and the 3-pulse sequence and the effect of the dead-time can be included.

163 AUTOMATED LEAST-SQUARES FITTING OF SLOW MOTIONAL ESR SPECTRA

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The theory of slow-motional ESR spectra is well established and has been used to analyze experimental spectra primarily by interactive simulation and comparison. These methods are subjective, very tedious to carry out, and require extensive operator intervention. We have implemented an automated nonlinear least-squares approach to both the rigid limit and slow motional data analysis. A Levenberg-Marquardt-type algorithm is employed to optimize the agreement between experiment and simulation and to provide estimation of uncertainties in the parameters. One may first obtain the principal values of the magnetic tensors from a rigid limit spectrum by the least-squares analysis. Then the slow motional spectra are used to optimize for the parallel and perpendicular components of the diffusion tensor and its orientation, as well as the coefficients in any ordering potential that is present. The repeated calculations of spectra required are computationally very demanding even for the very powerful Lanczos algorithm. Thus they were carried out on the Cornell National Supercomputer Facility achieving a reduction in time by a factor of about ten over previously available computers. Application of these techniques to nitroxide labeled polymers and spin probes in liquid crystals will be presented.

164 ^{13}C HYPERFINE CONSTANTS IN SOME SIMPLE RADICALS.

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The ^{13}C hyperfine constants in some simple radicals have been measured using enriched starting materials and the values so determined are compared with those calculated by *ab initio* methods. The radicals were produced by *in situ* radiolysis of aqueous solutions with a 2.8 MeV electron beam and include the fundamentally important allyl radical $(H_2C\overset{\cdots}{-}CH\overset{\cdots}{-}CH_2)$ produced from propene, and the species H_2CN, $(HO)HCN$, $(-O)HCN$, and $CONH_2$ all derived from CN^- or HCN. The allyl radical is the simplest conjugated π radical and provides a test of theory for an odd-alternant radical with negative spin density at the center carbon. The ^{13}C interaction at this position is expected to be large and negative because the contributions from both local and adjacent spin density add. The measured splittings are 21.93 at the 1 position and 17.21 G at the 2 position. The calculated values are 21.8 and (-)23.7 G, respectively, in reasonable agreement with experiment. A discussion of these values in terms of the Karplus-Fraenkel equation will be given. The radicals H_2CN and $(HO)HCN$ are of interest because of their relationship to normal and OH substituted cyclohexadienyl radical. The calculated ^{13}C hyperfine constants of (-)26.9 and (-)28.1 are in agreement with the experimental values of 28.8 and 21.2 G, respectively. The calculated value for the σ radical $CONH_2$, 184.6 G, agrees well with the value of 158.4 G found experimentally.

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EPR AND ENDOR STUDIES OF PERYLENE RADICALS ADSORBED ON ALUMINA AND SILICA-ALUMINA POWDERS.

Kurt S. Rothenberger, Harry C. Crookham, Penny A. Snetsinger, Robert B. Clarkson, and R. Linn Belford. Department of Chemistry and Illinois ESR Research Center, University of Illinois, Urbana, IL 61801.

Electron Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance (ENDOR) spectra were obtained from the radicals formed on activated alumina and silica-alumina powders exposed to solutions of perylene in benzene. Multi frequency EPR studies at L-, X-, and Q-bands indicate nearly isotropic electron Zeeman interactions (g), but perylene ring-proton hyperfine coupling (A) information was obscured by insufficient spectral resolution. These hyperfine couplings, which were fully resolved by the ENDOR technique, are highly anisotropic. The absolute values of the principal elements of the hyperfine coupling matrices, obtained from ENDOR simulations based on the approach of Dalton and Kwiram, agree well with values calculated for the cation. Chemical manipulation of the system, including isotopic labeling of the solvent and perylene molecules, has provided information about the molecular environment of the surface radical through analysis of matrix ENDOR features. ENDOR signals attributed to protons, deuterium and aluminum-27 near the radical have been detected. From our results, we infer that a single radical species, the cation, is formed but that its environment is different on the two surfaces. [Work supported by NIH (RR01811), US DOE (PETC; DEFG-22-84PC70782), and Illinois Coal Development Board/CRSC.]

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SELECTIVE GENERATION OF ORIENTED DEFECTS IN GLASSES.

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Defects in glasses, whether present in the as-prepared material or introduced by irradiation, are usually oriented completely randomly. The EPR spectrum therefore consists of a powder pattern, corresponding to an angular average over all orientations. We discuss here a novel approach in which paramagnetic centers are created directly in an aligned state in a glass, by using polarized light to generate the centers. Analytic expressions are derived for the EPR spectra of centers produced by polarized excitation, and are compared to experimental results obtained in amorphous silicon dioxide. Analysis of the EPR anisotropy provides information concerning the generation mechanism of the paramagnetic center and about the degree of lattice relaxation following the formation of the center.

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EPR STUDIES OF C-13 LABELED AND MONOMETHYLATED 6-OXY-BENZO(a)PYRENE AND 6-TRIFLUOROACETOXY BENZO(a)PYRENE RADICALS,

Xinhua Chen and Paul D. Sullivan, Department of Chemistry, Ohio University, Athens, Ohio 45701.

The EPR spectrum of 6-oxy-benzo(a)pyrene (6-oxy-BaP) radical in CH_2Cl_2 has been reanalyzed in light of data obtained from ^{13}C singly labeled 6-oxy-BaP radicals, in terms of 11 proton splittings: 0.105, 0.270, 1.102, 1.135, 1.275, 1.415, 1.660, 4.460, 4.720, 4.803, 5.603 (±0.005). Assignments of these splittings have been made mainly on the basis of relative magnitudes of the methyl splittings of monomethyl 6-oxy-BaP radicals, and with the aid of HMO calculations. In addition, assignments of the proton splittings extracted from an ENDOR spectrum of 6-trifluoroacetoxy-BaP (6-TFA-BaP) cation radical have been made by analogy with the methyl splittings of monomethyl 6-TFA-BaP cation radicals. Comparison of the experimental proton and ^{13}C splittings of both the BaP and 6-TFA-BaP cation radicals showed that the electronic effects of the TFA substitution are too small to account for the changes in biological activities of the substituted BaP molecules. The assignments of proton splittings for both 6-oxy-BaP and 6-TFA-BaP radicals are supported by the consistency of the ^{13}C splittings obtained under the same conditions from the twelve singly labeled ^{13}C- 6-oxy-BaP and ^{13}C- 6-TFA-BaP radicals.

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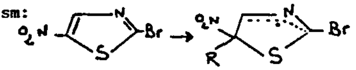
SINGLE CRYSTAL ESR AND ENDOR STUDIES OF AN AZOALLYL RADICAL.

Alice Berthier-Celalyan, Michel Geoffroy and Malledi V. Reddy. Department of Physical Chemistry, 30 Quai Ernest Ansermet, University of Geneva, Geneva, Switzerland.

A single crystal of 2-bromo,5-nitrothiazol has been X-irradiated at room temperature and studied by ESR. The angular variation of the ESR spectra is very complex and indicates that forbidden lines are preponderant for almost all the orientations of the magnetic field. The ENDOR study of the irradiated crystal clearly shows the presence of a single proton and the corresponding coupling tensor has been determined. The ESR spectra can be analyzed when the magnetic field is aligned along the crystallographic axes. The analysis needs to calculate the positions and intensities of the $\Delta M_I=0,\pm 1,\pm 2$ transitions resulting from magnetic and quadrupolar interactions with $^{79/81}Br$. It is then possible to estimate an additional hyperfine coupling with ^{14}N. After determination of these six tensors ($\tilde{g}$, $^{79/81}Br\text{-}\tilde{T}$, $^{79/81}Br\text{-}\tilde{P}$, $^{1}H\text{-}\tilde{T}$) we have calculated the various spin densities and shown that they are consistent with the following mechanism:



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Chemical Reaction Studies of Aromatics, Alkenes and Alkynes On HY, H-Mordenite and H-ZSM-5 zeolitic surfaces.

S. Shih, Department of Radiology, CUHSC. Denver, Colorado 80262

Zeolites are important catalytic materials both for chemical reactions and molecular Separations in various industries. The use of electron spin resonance spectroscopy to study the nature of the reactive intermediates on activated zeolites has been carried on in different research laboratories for some years. However, because of the large line widths in powder samples and translation diffusions of the reactive species, the chemical pathways of the intermediates will be highly depended on the pore structures of the zeolites. We have made a systematical studies of unsaturated hydrocarbons in various pore size zeolites. Symmetry principles between ionic radicals, computer simulation programs and thermodynamics are used to establish the various intramolecular and intermolecular processes inside the zeolitic pores.

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VARIATION OF ALKYLMETHYLVIOLOGEN RADICAL CATION-WATER INTERACTIONS IN MICELLES AND VESICLES FROM ESEM SPECTROSCOPY: EFFECT OF ALKYL CHAIN LENGTH.

Michael J. Colaneri and Larry Kevan. University of Houston, Department of Chemistry, Houston, TX 77004. David H.P. Thompson and James K. Hurst. Department of Chemical and Biological Sciences, Oregon Graduate Center, Beaverton, Oregon 97006.

The variation in alkylmethylviologen radical cation-water interactions with the alkyl chain length in frozen sodium dodecylsulfate (SDS) micelles and dihexadecylphosphate (DHP) vesicles were investigated by electron spin echo modulation spectroscopy. In the DHP vesicle system the measured deuterium modulation depth associated with deuterated water indicated a significant decrease in the magnitude of these interactions with an increase in the alkyl chain length of the viologen. However, a comparable trend was absent in the SDS micelle system. In addition the strength of the dimethylviologen radical cation-water interactions in SDS micelles was much weaker than those measured for any of the viologen radicals in the vesicle system. These observations were found to be in qualitative agreement with currently proposed models of the binding characteristics of alkylmethylviologens to DHP vesicles and SDS micelles, and may also reflect structural differences between these two types of assemblies. Supported by Department of Energy Contract No. DE-AS05-80ER10745.

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ELECTRON SPIN ECHO ENVELOPE MODULATION STUDIES OF NATURAL ABUNDANCE LOW-GAMMA NUCLEI. Penny A. Snetsinger, Jeffrey B. Cornelius, Robert B. Clarkson, and R. Linn Belford. Department of Chemistry and Illinois ESR Research Center, University of Illinois, Urbana, IL 61801.

Electron spin echo envelope modulation (ESEEM) has been used to study matrix interactions from natural abundance low-gamma nuclei in two different systems: an Illinois #6 whole coal and perylene radical adsorbed on alumina powder. We have attributed the modulation to carbon-13 nuclei in the coal sample and aluminum-27 nuclei in the perylene radical system. The modulations were simulated and values were obtained for a_{iso}, the hyperfine coupling, r, the interaction distance, and n, the number of nuclei. These values are quite different than those obtained from the simulation of the proton matrix peaks in the same spectra and, consequently, give additional information about the environment of the radical. The magnetic field dependence of the depth of the low frequency modulation has also been studied. [Work supported by NIH (RR01811), US DOE (PETC; DEFG-22-84PC70782), and Illinois Coal Development Board/CRSC.]

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CONFIGURATION OF THE NEXT GENERATION OF EPR SPECTROMETERS. James S. Hyde, National Biomedical ESR Center, Dept. of Radiology, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, WI 53226.

Using loop-gap resonators, demodulation of phase noise from the microwave source is reduced. Because of the low Q of these resonators, automatic frequency control (AFC) requirements are changed, and it becomes possible additionally to use phase-lock techniques that reduce the phase noise itself. This reduction of both phase noise and phase-noise demodulation permits the use of FET microwave signal amplifiers under conditions where the limiting noise source is the amplifier noise figure and not the microwave source. "I" and "Q" signals can be formed using a balanced quadrature mixer, where I and Q are in-quadrature signals with arbitrary mixtures of absorption and dispersion. A computer unambiguously can create pure dispersion, pure absorption and power spectrum displays, and can also generate AFC information that is independent of the phase of the microwave reference signal at the quadrature mixer. Thus the combination of loop-gap resonator, phase-locked source, FET amplifier, and real-time computer eliminates the need for control of relative phases in the reference and signal arms of the microwave bridge. It is this phase problem that has necessitated the use in the past of rotary-vane attenuators, high quality circulators, and other expensive microwave components. With the phase problem solved, microstrip bridges become feasible, thereby decreasing the cost and permitting convenient development of more complex microwave bridges. Overall, the signal-to-noise ratio can be substantially improved.

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2D - ESR CORRELATION SPECTROSCOPY Jeff Gorcester and Jack H. Freed, Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853

Two dimensional spectroscopies based on the Fourier Transform technique may now be applied to the ESR of (fast motional) nitroxides. Correlation spectroscopy (COSY) gives a vivid picture of the couplings between hyperfine lines which are introduced either by the coherent microwave field or by dynamical processes which induce nuclear spin flips. The COSY spectrum may be regarded as a correlation diagram of the spin system, with auto and cross correlations appearing as diagonal and off-diagonal peaks, respectively. The off-diagonal peaks one obtains with a sequence of three 90 degree pulses represent couplings between the longitudinal components of magnetization in the absence of the radiation field. Thus we have a two-dimensional form of ELDOR spectroscopy where one obtains all of the ELDOR information in a single spectrum. Such a spectrum typically requires ten minutes of data acquisition time on our current FT spectrometer. A review of our recent efforts with these methods will be given with emphasis on instrumentation and applications. A discussion of the application and extension of these techniques to slow-motional studies will be presented.

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APPLICATION OF ABSORPTION MODE RAPID PASSAGE TECHNIQUES TO SOLIDS

William E. Carlos, Naval Research Laboratory, Washington, DC 20375

Rapid passage techniques have long been employed in electron spin resonance (ESR) studies of defects in solids. Most of these use the dispersion mode, i.e. the microwave component in phase with the source. Slow passage experiments are generally performed by detecting the signal in quadrature with the source. The major advantage of the dispersion mode is that the signals are invariably larger than absorption mode signals under rapid passage conditions. The major disadvantages are the increased klystron noise and the decrease in resolution due to the broader lineshapes obtained by detecting this mode. In this paper it is demonstrated that, in many cases, the absorption mode offers a superior alternative (to the dispersion mode) by detection of signals in quadrature with the magnetic field modulation, either at the first or second harmonic of the modulation frequency. Two detailed examples, the E' center in a-SiO_2 and donors in Si are then presented to illustrate the effects of these methods on the observed signals. Less detailed examples are then discussed which illustrate the ability of these techniques to resolve relatively weak signals and to differentiate between overlapping resonances. General conclusions regarding the applicability of these techniques will be discussed.

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^{14}N ESEEM IN DISORDERED SOLIDS: MULTI-FREQUENCY AND ORIENTATION SELECTION TECHNIQUES FOR ELUCIDATING HYPERFINE AND QUADRUPOLE COUPLING TENSORS.

David J. Singel, and Heather L. Flanagan. Department of Chemistry, Harvard University,
12 Oxford Street, Cambridge, Massachusetts 02138.

Determination of electron-nuclear hyperfine and quadrupole coupling tensors of nitrogen-14 nuclei in disordered solids provides a means to elucidate aspects of electronic structure and molecular geometry in such materials. We have implemented extensions to the technique of ESEEM (electron spin-echo envelope modulation) specifically targeted toward this objective. In multi-frequency ESEEM, we exploit the sensitive dependence of the modulation patterns on external field strength to manage their features; the variation in ^{14}N ESEEM patterns with field strength (hence electron spin excitation frequency) has been used to test and to refine quantitative analysis of the modulation patterns in terms of hyperfine and quadrupole principal values, and can also be exploited for selective enhancement or suppression of the contribution of specific nuclei to ESEEM patterns. Orientation selection experiments have proven useful in establishing the directions of principal axes of the tensors within a common axis system - e.g. the principal axes of the g-matrix of a paramagnetic ion. The utility and feasibility of these methods is discussed with reference to specific experimental examples, involving free-radical and metal-ion electron spin systems, as well as to a broad survey of theoretical simulations of modulation patterns.

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ESR at 1 MILLIMETER

Bryan Lynch and Jack H. Freed, Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853

ESR spectra have for the first time, been observed at 90 kG and 250 GHz for nitroxide spins around room temperature. Millimeter wave ESR is important for the study of structure and slow motions in solids and fluids and allows for the application of existing FIR laser and pulsed laser techniques.

Our spectrometer consists of a superconducting magnet having a sweep coil which can be swept ± 500 G while the 90 kG coil is persistent. The millimeter wave source consists of a gunn oscillator whose output frequency is phase locked at 83.3 GHz. This is then tripled to yield an extremely stable 250 GHz source with 5mw power. Gaussian optics are used to propagate the beam, via a series of low-loss feedhorns and lenses, to a semi-confocal Fabry-Perot cavity with attached field-modulation coils. A high sensitivity Schottky diode is used for FIR detection followed by lock-in detection at the field-modulation frequency.

High field ESR spectra of nitroxide spin probes in fluids and solids will be presented and discussed.

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MECHANISTIC AND KINETIC STUDIES OF TRIPLET STATE QUINONE QUENCHING IN ALCOHOLS BY FTESR. Richard J. Massoth and Michael K. Bowman. Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

Fourier Transform Electron Spin Resonance (FTESR) is a powerful method for the study of photochemical reactions involving free radicals. One measures a high resolution ESR spectrum at a single point in time by converting the total sample magnetization into an observable signal. This is in contrast to direct detection ESR methods where one tries to measure the magnetization at a single ESR frequency as a function of time without perturbing the magnetization. FTESR provides both high sensitivity and high resolution for the identification of radical products and measurement of reaction kinetics.

We have studied the quenching of the triplet excited state of quinones by electron and hydrogen atom donors in alcohol solutions with FTESR. For quenching by triethylamine, electron transfer and hydrogen atom abstraction occur in parallel in methanol and isopropanol. Kinetic measurements were made of the competition between triplet spin lattice relaxation and reactive quenching. The triplet spin lattice relaxation of 1-10nsec provides a useful "clock" for the measurement of reaction rates of 10^7-10^9 s^{-1} while competition with triplet intersystem crossing to the ground state allows measurement of rate constants from 10^5-10^7 s^{-1}.

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy under contract W-31-109-ENG-38.

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THE DETERMINATION OF OSMIUM AND RHENIUM IN MOLYBDENITE BY ISOTOPE DILUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY, F.E. Lichte and J.W. Morgan*, U.S. Geological Survey, Box 25046, M/S 928, Denver Federal Center, Denver, Colorado 80225.

The age of molybdenite can be determined from the ^{187}Re/^{187}Os ratio. ^{187}Re and ^{187}Os were determined by isotope dilution using inductively coupled plasma mass spectrometry (ICP-MS). Calibration of the method using isotope dilution assures the accuracy of the elemental determination.

For this method, MoS_2 samples were spiked using ^{190}Os as ammonium hexachlorosmate and ^{187}Re dissolved in 0.1M HNO_3, and were dissolved using a NaOH-Na_2O_2 fusion. Re was separated from the matrix using an ion exchange procedure, and Os distilled and collected in HBr. The solutions were taken to dryness and the salts were dissolved in 3M HCl.

The ICP-MS was optimized for sensitivity for these elements by adjusting the plasma power, gas flow rates, and ion lens settings for maximum response. Stock solutions of naturally occurring osmium and rhenium were used to calibrate the instrument for mass dependent biases. Samples >4 mL were introduced to the plasma using a Babington type nebulizer, and smaller samples were introduced with a glass frit nebulizer. A measurement precision of >1 percent was attained with the procedure.

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THE DETERMINATION OF ARSENIC AND SELENIUM BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY IN ENVIRONMENTAL SAMPLES. Ewa Pruszkowski and Richard Ediger. Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0906.

The technique of ICP-MS has a promising future for the determination of many elements in environmental samples. This paper evaluates the performance of two of the more important elements, arsenic and selenium, giving particular attention to the compensation of potential interferences in samples of an environmental nature. Samples containing high chloride concentrations exhibit a spectral interference from ArCl on the monoisotopic arsenic isotope at mass 75. Several means of compensation of this interference are evaluated, and the accuracy, precision, and detection limits obtained with each correction procedure are measured. Selenium is one of the less sensitive elements determined by ICP-MS. This is the result of the spectral overlap of the ArAr polyatomic ion at the most abundant selenium isotope, necessitating the use of a less sensitive isotope. Figures of merit for the determination of selenium are presented, comparing ICP-MS methodology with that of alternate analytical techniques.

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ANALYSIS OF ENVIRONMENTAL REFERENCE MATERIALS USING ICPMS, D.J. Northington and B. Michael Hovanec, WCAS, 9840 Alburtis Avenue, Santa Fe Springs, CA 90670.

The results from analysis of reference materials from NBS, EPA, NIOSH, and USGS will be discussed. Advantages and disadvantages compared to AA and ICPOES will be reviewed. Problems due to solvent ions and disolved solids have been found to be minimal with latest instrument designs. Results compare very favorably with other techniques.

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FLOW INJECTION ON-LINE ISOTOPE DILUTION ANALYSIS WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Xiaoru Wang, Miklos Viczian, Alexandra Lasztity, and Ramon M. Barnes, University of Massachusetts, Department of Chemistry, GRC Towers, Amherst, MA 01003-0035.

A procedure has been developed to implement isotope dilution analysis by inductively coupled plasma mass spectrometry (ICP-MS) automatically on-line with flow injection techniques. Based upon commercially available flow injection equipment (Fiatron SHS-200 and SHS-300) interfaced with a Sciex Elan ICP-MS, lead concentrations in biological and environmental samples were determined. The isotope spike solution was cycled continuously through the flow injection sampling valve, and various sample and spike injection times along with other experimental parameters were evaluated. A description of the apparatus, the procedure, and results for experimental parameter evaluation as well as standard reference materials will be presented.

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EVALUATION OF THE INTERFACE IN A UNIQUE ICP-MS INSTRUMENT. R. Duane Satzger and F. L. Fricke, Food and Drug Administration, 1141 Central Parkway, Cincinnati, Ohio 45202 and J. A. Caruso, University of Cincinnati, Cincinnati, Ohio.

ICP-MS is a potentially powerful technique which provides solution detection limits superior to those obtainable by its ICP-emission counterpart with the advantage of isotopic information. With the development of this analytical tool, it has become evident that the interface between the plasma and the mass filter, specifically sampler/skimmer and ion optics, plays a major role in the quality of the data obtained when a sample matrix which is more sophisticated than a multi-element standard in 2% HNO$_3$ is introduced. The interface affects the background count rate, the structure of the background and the stability or precision of ion counting measurements. Presently, the aerosol gas flow rate and the mass of interest have major effects on the background count level. Measures taken to reduce this 'continuum' type of background in this 'homemade' instrument will be discussed. The structured background composed of gas and solvent peaks and how it is effected by the skimmer design will be evaluated by comparison of a laboratory built skimmer with one commercially available. Finally, the effect of lens stack design on stability will be discussed as observed experimentally with the introduction of samples to this instrument. Initial observations suggest that field charge effects in the lens stack are responsible for a degradation in both sensitivity and precision of the response.

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SPECIATION OF MERCURY COMPOUNDS BY LIQUID CHROMATOGRAPHY WITH INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRIC DETECTION.

Diane S. Bushee, John R. Moody, and Paul J. Paulsen. National Bureau of Standards, Physics Building, Room A21, Gaithersburg, MD 20899

A liquid chromatograph (LC) has been interfaced to an inductively coupled plasma-mass spectrometer (ICP/MS) for the separation and detection of mercury species. The ICP/MS acts as a sensitive and element selective detector for the mercury species without post-column derivatization as is necessary in LC-ICP. In the first application methylmercury chloride, ethylmercury chloride and inorganic mercury are fully retained and separated within twenty minutes by reversed phase chromatography. Detection limits range from 7 to 16 ppb mercury and the technique is linear to the low part-per-million region. The method has been evaluated using a single blind spiked water study and has been applied to NBS RM-50, Albacore tuna. A second separation of mercury containing drugs has been accomplished using similar chromatographic conditions. Mersalyl, thimerosal and inorganic mercury are separated within 15 minutes with detection limits in the low parts-per-billion range. A number of commercial samples have been analyzed by LC-ICP/MS and the results compared favorably to direct ICP/MS.

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DETERMINATION OF TRACE ELEMENTS IN NATURAL SURFACE WATERS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY.

J. M. Henshaw, Lockheed-EMSCO, 1050 E. Flamingo Suite 120, Las Vegas, NV 89109 and E. M. Heithmar, T. A. Hinners, U.S. Environmental Protection Agency, P.O. Box 15027, Las Vegas, NV, 89114.

The feasibility of using ICP-MS for the determination of trace elements in surface waters was examined. Analyses were conducted on more than 250 lake samples from the Eastern U.S., along with associated quality assurance samples. Samples were filtered, acidified with nitric acid, and spiked with internal standards. Intensity data were collected from wide mass-range scans. The data were transferred to a personal computer, and concentrations were determined from calibration standard data for 19 trace elements. Concentrations for other elements were calculated from element mass and ionization potential dependent response factors. The QA program included independent calibration-verification standards (NBS 1643b), interference check solutions, continuing calibration blank solutions, field duplicate and blank solutions, and spiked samples. Short term (within day), medium term (day-to-day) and long term (weekly) stabilities were examined for the entire study. Formulas were derived to reduce calibration drift effects, and several internal standards were evaluated. Precision and accuracy, as determined by percent recovery, were determined. Oxide formation, presence of doubly charged ions, and interference by matrix components (Na, Mg, Fe, Si, Ca, sulfate) were also examined.

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APPROACHES TO THE ANALYSES OF HIGH DISSOLVED SOLIDS SOLUTIONS BY ICP-MS

Robert C Hutton, Christopher T Tye, Andrew N Eaton, Robert Brown
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Early work in ICP-MS was often restricted to analysing solutions of low dissolved solids content (typically 0.1% w/v). This restriction was mainly due to problems associated with sampler orifice blockage. However, current ICP-MS instruments now operate with sampler orifice sizes in excess of 1.0mm which reduces orifice associated problems. However, prolonged exposure to high dissolved solids can still cause problems.

The quadrupole, unlike a sequential optical spectrometer can acquire data at a very fast rate. This alone allows a great deal of flexibility in sample types. High dissolved solids can be analysed with reduced integration times with little or no degradation in performance. In this paper, a discussion of these problems will be presented and a variety of solutions evaluated.

186 BLOOD ANALYSIS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Thomas A. Hinners, Edward M. Heithmar, U.S. Environmental Protection Agency, P.O. Box 15027, Las Vegas, Nevada 89114, and John H. Henshaw, Lockheed Engineering and Management Services Company, Inc., P.O. Box 15027, Las Vegas, Nevada 89114.

Acid digests of six whole blood samples were analyzed using the semiquantitative program on an ICP-MS instrument. Spectral scans involved one 0.5-second measurement at each mass for the range 6-238 amu, but excluded mass locations for the major elements Ca, Cl, Fe, K, Mg, N, Na, P, and S (as well as intense background regions) to protect the detector when analyzing digests that are 10-fold dilutions of whole blood. At a 10-fold dilution, blood digests are expected to contain dissolved solids near 850 ug/l. The semiquantitative program identified 29 trace elements among the blood digests at signal levels exceeding three times the noise level above the digestion blank values. Interferences are indicated by the atypically high values obtained for some of the elements (Cr, Mn, Ni, Se and Zn). In addition, $ArCl^+$ ions are probably included in the ^{75}As signal, ClO^+ ions in the ^{51}V signal, Ca^+ and SO^+ ions in the apparent ^{48}Ti signal. Examination of alternative isotopes, isotope patterns and interference corrections are needed to fully evaluate the application of ICP-MS for the multielemental analysis of blood samples. This evaluation is being conducted in consultation with the Exposure Evaluation Division in the Office of Toxic Substances.

187 THE QUANTITATIVE DETERMINATION OF TRACE ELEMENTS IN SEMICONDUCTOR MATERIALS BY GLOW DISCHARGE MASS SPECTROMETRY P M Charalambous, K Robinson, R Brown, VG Elemental, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX, UK

The direct analysis of trace impurities in semiconductor materials has proved troublesome for many analytical techniques. A wide range of elemental sensitivity factors and/or spectral interferences often limit the required detection capability. A glow discharge mass spectrometer utilising a high resolution mass analyser has been used to monitor trace elements at ppb levels directly in the solid in a wide range of materials. The technique overcomes the problems of doubly charged species and molecular overlap normally associated with MS determinations (eg SIMS and SSMS). Examples will be shown of the direct determination of ppb levels of transition elements in traditionally difficult matrices, eg Fe, Ni, Cu in cadmium telluride, Fe and Ni in semiconductor grade silicon. The development of a cryocooled cell will be described enabling the direct determination of ppb impurities in low melting point materials such as gallium and indium. Precision, accuracy and limits of detection achieved will be discussed.

188 TRACE METAL DATA BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER FOR DRINKING WATERS AND REFERENCE MATERIALS THAT IS EQUIVALENT OR SUPERIOR TO ETVAA TECHNIQUES, Richard Robinson, Daryl Knab, and Michael G. Bell. Los Alamos National Laboratory, P. O. Box 1663 MS K484, Los Alamos, New Mexico 87545

The Inductively Coupled Plasma-Mass Spectrometer, because of its sensitivity and multielement capabilities, is an important instrumental technique. Excellent average recoveries (100% +/-10%) can be obtained for Ag, As, Ba, Cd and Pb with only one internal standard with the addition of a chiller to the scott spray chamber. The chiller has reduced the water load and molecular interferences previously encountered so that the choice for the internal standard is no longer critical. The average recoveries obtained now are better but poor precision is still a problem with the relative standard deviations of 10 to 20%.

The ICP-MS data, as low as 1 ug/l, is equivalent if not better than the ETVAA data for reference materials and drinking waters.

189 ABSTRACT NOT AVAILABLE

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A FLOW CHART FOR THE IDENTIFICATION OF POLYMER MATERIALS BASED UPON CONDENSED PYROLYZATE IR SPECTRA*. Michael C. Oborny. Sandia National Laboratories, Division 1823, Albuquerque, NM 87185.

The combination of pyrolysis and infrared spectroscopy provides a method by which polymers can be readily identified from the infrared spectra of their condensed pyrolysis products. Since the preparation of polymer samples for normal transmission or ATR infrared spectroscopy can sometimes be difficult or impossible, pyrolysis can offer a rapid alternative technique for sample preparation. Pyrolysis-IR analyses have been used to construct a polymer reference collection of condensed pyrolyzate spectra. Using this collection, a flow chart has been developed which allows the systematic identification of polymeric materials based upon the presence or absence of specific absorption bands in the condensed pyrolyzate spectra. *This work performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract number DE-AC04-76DP00789.

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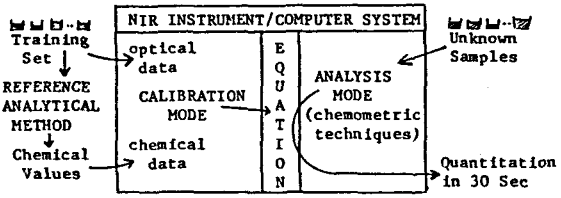
NEAR-IR REFLECTANCE: A RISING STAR IN ANALYTICAL SPECTROSCOPY. Donald A Burns, Bran+Luebbe, Technicon Industrial Systems, 511 Benedict Ave, Tarrytown NY 10591.

Two decades ago Near Infrared (NIR) measured moisture in meat, and ten years ago it was giving fast answers to agricultural chemists who were analyzing wheat for protein. Today it's doing all this and much more in such diverse fields as these: pharmaceutical, dairy, tobacco, textiles, polymers, foods & beverages, forage, and petrochemicals. Names include NIRS (Near-IR Spectroscopy) and NIRA (Near Infrared Reflectance Analysis), and it is now in the exponential growth phase. In the 7000+ instruments now in use, powerful computers with sophisticated algorithms employ popular chemometric techniques to extract information from the optical and chemical data. Equations created from a "training set" (solids or liquids) are used for both qualitative (discriminant) and quantitative analysis, providing fast answers, for multiple constituents, often with little or no sample preparation. The examples cited will include spectra, calibration procedures and statistics, and comparisons with alternative methods. Newcomers to the field may learn how to become heros within their companies.



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APPLICATIONS OF NEAR INFRARED (NIR) ANALYSIS TO THE PHARMACEUTICAL INDUSTRY

F.A.DeThomas, Pacific Scientific Instrument Division, 2431 Linden Lane, Silver Spring MD 20910

As the world-wide demand for pharmaceutical products increases with vigor, so does the development and demand for NIR methods of analysis for these products. Near infrared offers fast and precise qualitative and quantitative measurements of liquids, solids and slurries in transmission and reflection modes. Qualitative pharmaceutical applications are based upon a spectral matching algorithm that identifies samples through than algorithm sensitive to NIR absorption patterns and qualifies samples using some pre-established acceptable variation of the algorithm when applied to a set NIR reference spectra. Quantitative NIR measurements are based upon calibrations using analytically selected wavelength exhibiting correlation between absorbance data and concentration data from a set of known samples. Applications to coatings, active ingredients, raw materials and tablets will provide insight into the abilities of NIR.

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THE EFFECTS OF SPECTRAL ENHANCEMENT ON NEAR INFRARED (NIR) QUANTITATIVE AND QUALITATIVE ANALYSES.

Dr. Patrick J. Cooper, Pacific Scientific Instrument Division, 2431 Linden Lane, Silver Spring MD 20910

As the use of NIR quantitative and qualitative techniques becomes increasingly popular, interest in improving the results obtained using these techniques becomes increasingly intense. Generally, there are two modes by which NIR methods, or any other analytical methods for that matter, may be improved. The first involves improvement in the performance of the instrument used. Obviously, one would always prefer to use the best possible instrumentation. The second mode involves improvement in the mathematical or statistical methods used to extract information from the raw data measured by the instrument. Since an analyst is sometimes constrained to using the instrumentation at hand, this mode can, in such cases, be very desirable. This paper investigates the effects of spectral resolution enhancement on NIR calibrations and spectral library searches.

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THE "REAL WORLD" OF ION ANALYSIS.

Virgil T. Turkelson, Michigan Applied Science and Technology Laboratories, The Dow Chemical Company, 1602 Building, Midland, MI 48674.

Ion chromatography (IC) is now recognized as a "workhorse" technology for the analysis of numerous anions and cations in a wide variety of sample matrices. During the past decade, a broad range of separation and detection schemes have been developed making today's IC technology more versatile and effective for day-to-day analytical problem-solving. While this expanded flexibility is a major advantage for the IC user, it can also complicate the selection of the most suitable approach for a given application. In addition, "dilute and shoot" sample preparation has become so synonymous with IC usage that the utility of the technique for "real world" sample analyses is at times not fully pursued for a particular application. Consequently, the intention of this paper is to provide some insight into practical strategies for problem-solving with today's IC technology. The impact of various time-tested approaches will be demonstrated via a review of selected applications of the IC technology in our laboratory.

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CATIONIC INDIRECT CHROMATOGRAPHY USING Ce^{+3} WITH PHOTOMETRIC OR FLUOROMETRIC DETECTION. Neil D. Danielson and Jeffrey H. Sherman, Department of Chemistry, Miami University, Oxford, Ohio 45056.

Copper(II) and cerium(III) were compared as mobile phase counterions with a strong cation exchange column for indirect photometric chromatography. At 254 nm, the molar absorptivity of Ce(III) was about 20 times greater than Cu(II). Because of the higher charge and greater size of Ce(III), low mobile phase concentrations on the order of 0.10 mM could be used. Therefore, detection limits on the order of 100 times less (3.5 pmole Na^+) could be attained using Ce(III) as compared to Cu(II). The isocratic separation of a mixture of alkali and alkaline earth metals could be accomplished in 20 minutes. The determination of Na^+, K^+, Ca^{+2}, and Mg^{+2} in a variety of milk samples has been carried out. The separation of Na^+, NH_4^+, and K^+ using 0.01 mM Ce(III) using indirect fluorometric detection gave detection limits similar to UV detection. The determination of these three monovalent ions in urine was straightforward with fluorometric detection. In contrast, using indirect UV detection, interference from the sample matrix due in part to caffeine was a problem. The separation of cationic surfactants is currently under investigation.

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APPLICATIONS OF VACANCY DETECTION TO ION CHROMATOGRAPHY. Bernard G. Sheldon and James R. Benson. Interaction Chemicals, Inc., 1615 Plymouth Street, Mountain View, CA 94043.

Ion-exchange chromatography has become a widely used method in analytical chemistry. Conductivity has traditionally been the detection technique of choice, both for single-column and post-column suppression types. Use of vacancy techniques allows analyses to be performed using ordinary HPLC instrumentation with increased sensitivity over conductivity detection. For instance, the detection limit for sodium determination by direct injection (no sample pre-concentration) is as low as 5 ppb using the ION-210 column and a cerium (III) eluent. Examples of both cation and anion separations will be shown which demonstrate the simplicity and utility of single-column ion exchange separations coupled with vacancy detection.

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APPLICATIONS OF GRADIENT ELUTION IN ION CHROMATOGRAPHY.
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Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3603,
(408) 737-0700

Gradient elution has recently been introduced as a new technique in Ion Chromatography. By varying the eluant concentration, it is possible in one run to separate weakly retained ions such as fluoride and acetate, as well as elute strongly retained ions such as citrate. In this presentation, applications using gradient elution will be compared to isocratic elution. Emphasis will be on environmental, food, and agricultural applications.

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TWELVE YEARS OF ION CHROMATOGRAPHY - PAST, PRESENT, FUTURE. A. W. Fitchett, Dionex Corporation,
1228 Titan Way, Sunnyvale, CA 94088-3603, (408) 737-0700

As Harry Truman once said, "there is nothing as new as the history you don't know". The past twelve years in Ion Chromatography have shown tremendous advances in all types of analyses from anions to transition metals, from packed-bed suppressors to MicroMembrane suppressors, from single column IC to indirect photometric methods, and from isocratic to gradient elution. The types of compounds determined by Ion Chromatography are growing. New column packing technologies and advances in detection methodology are making IC faster and more sensitive than ever before. This paper will take a nostalgic look at Ion Chromatography - where we have been, where we are now, and where we are going.

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AUTOMATION IN ION CHROMATOGRAPHY. Timothy Ward, Alan Henshall,
Rosanne Slingsby, John Stillian, Dionex Corporation, 1228
Titan Way, Sunnyvale, CA 94088-3603, (408) 737-0700

A number of analytical procedures may be integrated into an automated system for routine and repetitive analysis. This can be especially advantageous when the analyst is faced with a large number of samples requiring a large amount of manpower and thus expense. Automated systems offer minimal sample preparation since most clean-up procedures may now be performed on line. This includes filtering, dilution, and preconcentration as well as sample matrix clean-up. A totally automated Ion Chromatography system will be described which allows complete automation of analysis from pretreatment and injection through data acquisition and hard copy reporting of chromatograms. The use of automation in conjunction with rapid (2.5 minutes) run times and recycling regeneration systems will be discussed as well. A number of these applications will be presented and discussed.

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ACCURACY AND PRECISION FOR THE HPLC ANALYSIS OF A PESTICIDE COMPARING AUTOMATED TO MANUAL SAMPLE INJECTION, B. J. Wildman and A. D. Scarchilli,
Millipore Corporation, Waters Chromatography Division, 34 Maple Street,
Milford, MA 01757.

With the increasing useage of robotic sample processing units and well established existence of automated and manual high performance liquid chromatography (HPLC) injectors, this study was conducted in order to assess the performance of a robotic system. The basic system used for all three injection systems consisted of the following; a Waters™ Model 590 pump, an octadecylsilane column, and a Model 440 series fixed wavelength ultraviolet/visible (UV/VIS) detector. The manual system utilized a Rheodyne™ Model 7010 fixed loop injector. The automatic injection system featured a Waters ™ WISP Model 712B, which allows variable injection volume. The robotic sample processing unit, a Waters™ MilliLab, also employed a fixed volume loop injector. A series of injections of a pesticide over a range of concentrations was performed using all three systems. The linearity of each of the standard curves obtained are described. The accuracy and precision of each injector system shall be discussed and compared.

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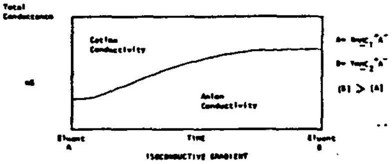
GRADIENT SINGLE COLUMN ION CHROMATOGRAPHY UTILIZING ISOCONDUCTIVE ELUENTS.
W.R. Jones, A.L. Heckenberg, P. Jandik. Waters Chromatography Division of
Millipore Corporation, 34 Maple Street, Milford, Massachusetts 01757

Gradients using ion exchange and conductivity detection usually require baseline subtraction routines to level out upward baseline drift generated from increasing eluent strength.

Isoconductive gradients can be achieved with proper choice of eluents. One approach for such a gradient using anion exchange is to vary the associated cation from one with a high ionic equivalent conductance to a cation with a low ionic equivalent conductance, thereby, allowing the anionic portion of the eluent to increase without changing the background conductance (Figure A).

Applications will be shown for various industries using a single pump with quarternary gradient capability.

FIGURE A



ISOCONDUCTIVE GRADIENT

202 ON THE AUTOMATION OF A DIONEX MODEL 10 ION CHROMATOGRAPH. Vincent C. Anselmo, Ph.D. William C. White, and James Harper. Texas Air Control Board, 6330 Highway 290 East, Austin, Texas 78723.

We have two Dionex (TM) System 10 ion chromatographs that were not being used efficiently and a decision was made to automate one of them using equipment on hand and a software package we had purchased for another use. The sampling system is a "liquid handler" available from Gilson, and a complimentary interface between the liquid handler and the microcomputer. A 64K Apple II+ (TM) serves as the heart of the system with CHROMATOCHART (TM), a product of Interactive Microware, Inc., as the software package that is programmed to drive the entire system. The Apple II+ (TM) requires a super serial card, a printer card, as well as the card for the software system. The modifications to the ion chromatograph will be discussed as well as the dynamics of the interfacing system. Applications to the analysis for cations will be presented.

203 A SYSTEMATIC APPROACH TO TROUBLESHOOTING THE ION CHROMATOGRAPH. Maureen Meador, Dionex Corporation, 1228 Titan Way, Sunnyvale, California 94086

This talk is designed to provide some helpful hints to troubleshooting the Ion Chromatograph. It will emphasize some useful techniques which can be applied if problems should occur when using the Ion Chromatograph. The emphasis of the discussion will be on troubleshooting an instrument as an interelated modular system. As such, a useful approach will be emphasized with the intention being to demystify the process of troubleshooting, thereby giving the user some easily applied tools to minimize the time involved in remedying possible problems which may arise.

204 ION CHROMATOGRAPHIC HPIC SEPARATION AND ANALYSIS OF RADIOSTRONTIUM IN IONIC MIXTURES. Phillip A. Drake, John D. Lamb, Francis R. Nordmeyer, M. Paul Elder, and Adam T. Woolley. Department of Chemistry, Brigham Young University, Provo, UT 84602.

An automated ion chromatographic method for the separation of ^{90}Sr in nuclear reactor and nuclear waste simulated solutions has been developed. Improvements in time required for separation and % recovery from solution were noted in the HPIC method compared to conventional precipitation and solvent extraction procedures. 85%+ recoveries were achieved with an automated system from high volume solutions containing transition elements, trivalent cations, alkali metals and other alkaline earths. Acid suppression procedures for the separation of radiostrontium from acidic samples were also investigated.

205 TRACE RESIDUAL SULFITE ANALYSIS IN DRUG ITEMS. David A. Fay, Norman C. Jamieson, Harold W. Thieman and Steven R. Villasenor, Mallinckrodt, Inc., 3600 N. Second Street, St. Louis, MO 63147.

The FDA has established a 10 ppm limit for sulfite in food and has recommended that drug manufacturers monitor their products at the same sulfite level. A literature survey reveals a number of approaches to sulfite analysis, however inherent limitations make direct adaptation to many products impractical. The Monier-Williams (M-W) method is the accepted standard by which other sulfite determinations are gauged. Disadvantages to the M-W procedure include: sample size, accuracy and precision at low levels and several critical procedural parameters. Other approaches suffer similar complications. Sulfite ion undergoes a variety of chemical reactions and is especially susceptible to oxidation. The reaction of sulfite with alcohols has been demonstrated to inhibit oxidation via the formation of a stable adduct. Our method traps the sulfite with formaldehyde to yield a formaldehye-bisulfite addition product. Quantitation of the resultant adduct is then achieved by ion chromatography (IC). The detection limit for the new method is less than 2 ppm. The accuracy of the new method, based on recovery of spiked samples, is better than 90%. The accuracy was also probed by comparison of sulfite results obtained by IC and an independent means of analysis, polarography. Parallel determinations agreed within 3 mg/Kg. Precision was within 10% relative standard deviation.

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APPLICATIONS OF VARIOUS ION CHROMATOGRAPHIC DETECTORS TO THE ANALYSIS OF ADDITIVES IN PLATING SOLUTIONS, A. L. Heckenberg, W. R. Jones and P. Jandik.

Because of the broad variety in the chemical and physical properties of the plating additives, more than one detection technique is frequently required for a comprehensive analytical assay of additives in plating bath samples. Examples of applications of conductivity, refractive index and amperometric detection will be discussed in this report. Also presented are numerous examples of separations followed by single wavelength or scanning UV detection. Based on our results, refractive index with UV can be described as the most universal combination of detection techniques for the analysis of plating additives.

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QUANTITATIVE ANALYSIS OF TRACE ANIONS IN FOOD PRODUCTS. Lee N. Polite and H. M. McNair. Chemistry Department, Virginia Tech, Blacksburg, VA 24061

A quantitative study has been done to determine the linear working range and minimum detectable quantities of F^- and Cl^- in standards as well as in food products. These determinations were done simultaneously using High Performance Ion Chromatography with chemical suppression. Quantities as low as sub ppb have been measured. Typical chromatograms and linearity curves will be shown.

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DETERMINATION OF CYANIDE IN METAL CYANIDE PLATING BATHS AND WASTEWATER. Michael J. Doyle, Roy D. Rocklin, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3603, (408) 737-0700

Considerable interest has been observed in the development of analytical methods which reduce the time required to determine weakly bound cyanide in metal cyanide matrices. A method is presented which combines ligand exchange techniques with ion exclusion liquid chromatography and electrochemical detection. The method, including sample preparation, requires less than 15 minutes and gives essentially complete recoveries of those "cyanides amenable to chlorination" with low ppb detection limits. The chromatography and detection methods used separate cyanide from interfering sulfide and thiocyanate as well as allow analysis of chlorinated wastewater samples containing percent levels of chloride.

209

THE EVOLUTION OF THE CONDUCTIVITY DETECTOR FOR USE IN THE LIQUID CHROMATOGRAPHY OF IONS. Vincent C. Anselmo, Ph.D. Texas Air Control Board, 6330 Highway 290 East, Austin, Texas 78723.

A conductivity detector designed for liquid chromatography of ions was first described in literature by Duhne and de Ita in 1962. The detector system designed by the authors included measuring the conductance of the eluant and the effluent streams and electronically measuring the difference between the two and relating this difference to concentration of the ions. Since then other experimenters have used similar dual-conductivity detectors to separate groups of anions, eg. the anions of the phosphorus oxyacids, as well as other ionic species. Gradient elution was introduced shortly thereafter for analytical systems that included both a conductivity detector and radiochemical detector. The introduction of a single conductivity cell and the use of the term "ion chromatography" was a later development.

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FAST RUN ANALYSIS IN ION CHROMATOGRAPHY. D. Campbell, R. Rocklin, J. Stillian, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3603, (408) 737-0700

Continued development of polymer based resins for high performance Ion Chromatography (HPIC) has lead to major improvements in the speed and selectivity of ion exchange columns. The original columns, developed over ten years ago, were capable of complete separation of 7 common anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^{2-}) in under 24 minutes. During the past ten years, advances in polymer technology has resulted in the development of ion exchange resins capable of providing separation of the 7 common anions in under 7 minutes. In this paper, I will discuss a new resin which provides baseline resolution for the 7 common anions in two minutes. Advantages are increased sample throughput, higher sensitivity, and reduced method development time. A disadvantage is lower sample loading capacity. A comparison of the anion analysis speed of high performance Ion Chromatography to that of automated wet chemistry (AWC) will also be discussed. Finally, specific examples of the capability of this new fast run column will be shown for environmental and other applications.

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RELATIVE SENSITIVITY OF AMPEROMETRIC DETECTION OF ANIONS USING SEVERAL DIFFERENT WORKING ELECTRODES MATERIALS, J. Jandik, P. J. Jandik, Millipore Corporation, Waters Chromatography Division, 34 Maple Street, Milford, MA 01757.

Several different working electrode materials have been recommended for the amperometric detection of inorganic anions. Certain anionic species such as, for example, the sulfite can be successfully detected on two or more types of working electrodes. Additional variation is introduced by the availability of various separation modes for the inorganic anions in question. With some electrode materials sensitivity of detection is a function of the composition of chromatographic eluents. This report investigates the usefulness of the common electrode materials for amperometric detection of sulfite, cyanide and iodide in the most frequently employed chromatographic mobile phases.

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A STATISTICAL COMPARISON OF DATA OBTAINED FOR THE ANALYSIS OF NITRATE IN DRINKING WATER, B. J. Wildman, A. D. Scarchilli, and A. L. Jagoe, Millipore Corporation, Waters Chromatography Division, 34 Maple Street, Milford, MA 01757.

In the paper a comparison of data obtained from the analysis of nitrate/nitrogen (NO_3-N) in drinking water by two ion chromatographic methods is presented. The two systems utilized different eluents, anion exchange resins and also different detector types, conductivity and ultraviolet/visible (UV/VIS) spectrophotometry. The linearity of the standard curves generated by both methods as well as the accuracy and precision of standard check and Water Supply Quality Control Check Samples (U.S.E.P.A./EMSL Cincinnati, OH) is detailed. Replicate analyses of a water supply sample were performed and six random grab samples from one source were analyzed in quadruplicate by both methods. The results are discussed in terms of the normality of distribution, and analysis of variance (ANOVA) in addition to the accuracy and precision of the data. The statistically significant differences and (method superiority) between the methods are presented.

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USING ION CHROMATOGRAPHY TO ANALYZE IONIC CONSTITUENTS IN AN ELECTROLESS NICKEL PLATING BATH. Ken Rice and Steve Stone, Dionex Corporation, 1228 Titan Way, Sunnyvale, California 94086

Process control in plating baths has become a necessity in the plating industry. In the electroless nickel, borohydride plating baths, monitoring of nickel, ethylenediamine, sulfamate and borate, along with other major analytes, is vital to insure a high quality product. Through the use of ion exchange and flow injection techniques, a rapid and precise measurement was obtained for these analytes. This paper will discuss the techniques and applications of monitoring these analytes as well as the potential capability of using an automated on-line system.

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ANALYSIS OF NICOTINE BY CATION MPIC. John D. Lamb, Delbert J. Eatough, Lee D. Hansen, Laura J. Lewis, and Brenda Sedar. Department of Chemistry, Brigham Young University, Provo, UT 84602.

Nicotine is an important potential tracer of ambient tobacco smoke. Sampling for nicotine by acidic denuder and subsequent extraction into water solution prohibits analysis by gas chromatography. Mobile phase ion chromatography (MPIC) offers an attractive alternative. Nicotine was successfully determined in such water extracts with a Dionex Ion Chromatograph using cation MPIC with 10% acetonitrile/5.0 mM hexanesulfonic acid in water. A UV/Vis detector with wavelength set at 254 nm was optimal. It was found that the retention time was affected little by the concentration of hexanesulfonic acid, whereas acetonitrile concentration had a strong effect. Using benzenesulfonic acid denuders followed by MPIC analysis, it was shown that approximately 90% of the nicotine in environmental tobacco smoke exists in the gas phase, with 10% in the suspended particle phase.

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Time Array Detection: Renaissance of Time-of-Flight Mass Spectrometry for GC-MS. J. Throck Watson, Departments of Biochemistry and Chemistry, Michigan State University, East Lansing, MI, 48824.

Improvements in high resolution gas chromatography have made increasingly stringent performance demands on mass spectrometry. Rapid scan rates generating more than two complete spectra per second with picomol sensitivity are representative of the requirements for state-of-the-art instrumentation for GC-MS. Array detection in mass spectrometry permits the continuous detection of all ion currents at all mass values. The increased signal-to-noise ratio (S/N) available from array detection can be manifested in lower detection limits or in higher rates of spectrum generation at the same detection limit achieved in conventional mass spectrometry with exclusive detectors. At Michigan State University, an integrating transient recorder (ITR) has been designed and constructed which can continuously acquire data at a rate of 200 MHz from a time-of-flight mass spectrometer for periods up to one hour. By integrating time-resolved ion currents from many transient mass spectra, the ITR provides the basis for time array detection. Summation of 10^3 transients generates 10 bar graph spectra per second and substantially improves the S/N ratio over that for the same data acquired by time slice detection, the conventional approach used in TOF mass spectrometry. Preliminary results obtained in time-resolved ion momentum spectroscopy will be presented to establish "benchmarks" for the ITR and to project applications of time array detection to GC-MS.

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A STUDY OF NUCLEOTIDE-MITOMYCIN COMPLEXES BY EI AND FAB MASS SPECTROMETRY IN BOTH POSITIVE AND NEGATIVE ION MODES. Thomas D. McClure, Bhashyam Iyengar, William A. Remers, and Karl H. Schram; Department of Pharmaceutical Sciences, College of Pharmacy, University of Arizona, Tucson, AZ 85721

Mitomycin C is a powerful antineoplastic agent currently in wide use. Mitomycin C is known to bind to DNA, but the mode of action is not well understood. An understanding of the binding mechanism as well as the specificity of this drug is of great concern to medicinal chemists at this time.

Structural information will be presented from several synthetically prepared mitomycin-nucleotide complexes. The information will include data derived from low resolution, high resolution, and MIKES techniques with EI and FAB ionization in positive and negative ion modes. The value of TMS derivatives of these compounds for fragmentation information in FAB will also be demonstrated. This work supported by NIH grant CA42309.

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ROLE OF PROSTAGLANDIN SYSTEM IN THE ANTIHYPERTENSIVE EFFECTS OF SEVERAL COMMONLY USED DRUGS IN HUMANS.

M.L. Beckmann-Thomas, J. Gerber, M. Loverdi, R. Byyny, R.C. Murphy, and A. Nies, Department of Medicine, Division of Clinical Pharmacology and Department of Pharmacology, University of Colorado Health Sciences Center, Denver, CO 80262

The ability of non-steroidal anti-inflamatory drug (NSAID) to inhibit the therapeutic effects of several antihypertensive drugs is associated with an inhibition of vascular prostacyclin (PGI2) synthesis which is enhanced by the antihypertensive drug alone. Ten patients with moderate, essential hypertension were studied in a randomized, double-blinded trial with propranolol (P) alone and in combination with the NSAID, indomethacin (I). Total body PGI2 production was measured by GC/MS monitoring the stable metabolite 2,3-dinor-6-keto-PGF1a-methoxime-PFB-TMS ether. The PGI2 production after I alone decreased significantly ($p<.01$) and did not recover during subsequent added P. Patients that received P alone showed a significant 9$p<0.1$) increase in PGI2 production. Treatment with I plus P fail to show such an increase over baseline PGI2 production. Nonresponders to P regarding MAP, also failed to show an increase in PGI2 production with P alone. These data suggest that the anithypertensive effect of the nonspecific beta adrenergic blocker propranolol is associated with an increase in total body PGI2 production that is inhibited with the NSAID, indomethacin.

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PILOT EVALUATION OF FAB MASS SPECTROMETRY TO DETERMINE ZINC ABSORPTION IN THE PREMATURE INFANT.

P. Peirce, K.M. Hambidge, P.V. Fennessey, L.V. Miller, and C. Goss, Departments of Pediatrics and Pharmacology, University of Colorado Health Sciences Center, Denver, CO 80262

The objective of this study was to apply a newly developed stable isotope technique (1) to the study of Zn absorption in the preterm infant. Fast atom bombardment mass spectrometry was used to analyze 70-Zn/64-Zn ratios in aliquots of extrinsically labeled infant formula and fecal samples. The 4 infants studied were 31 +/- 0.8 weeks gestation at birth with a mean birthweight of 1470 +/- 170g. Infants were studied at 21.7 +/- 9.7 days of postnatal life, when clinically stable. Weight gain averaged 23 +/- 3g/day. An aqueous preparation of 70-Zn was equilibrated with infant formula for 12-14 hours. The formula was fed by gavage in one or two consecutive feedings. The Zn from the isotope preparation did not exceed 30% of the total zinc content of the enriched feeding(s). Isotopic enrichment of feces was detectable for a maximum for 40 hours after administration of the 70-Zn. Apparent absorption of the isotope administered ranged from 0 to 23% with a mean of 10 +/- 9.8%. These low apparent absorption data are compatible with the hypothesis that zinc is absorbed poorly by the gastrointestinal tract of the preterm infant.

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ASSAY OF CHOLESTEROL 7-α,HYDROXYLASE (7-α,OHase) BY ISOTOPE DILUTION-MASS SPECTROSCOPY (ID-MS). Donald L.Zogg, Antal Nemeth, & Gregory T. Everson.
U. of Colorado Health Sciences Center, 4200 E. 9th Ave., Denver, CO 80262

The purpose of this study was to develop an ID-MS assay for 7-α,OHase. This is the rate limiting enzyme in cholesterol catabolism to bile acids. Procedure: $_2$7-α,OH-β,^{2}H-Cholesterol was synthesized by reduction of 7-keto-Cholesterol with LiAl^{2}H$_4$ and used as internal standard. All sterols are derivatized to trimethylsilyl ethers and analyzed by Selective ion monitoring (SIM) GLC-MS. Enrichment of the isotope ratio (M+1)/M for 7-α,OH-Cholesterol (m/e=457/456) by the deuterated standard provides mass quantitation. This technique was then utilized to assay 7-α,OHase activity in hepatic microsomal preparations from control rats and rats with either increased or decreased synthesis of bile acids. Results: Isotope enrichment was linear from about 30-100 molar% of deuterated standard. The lower limit of detection was in the nanogram range. The variability between repeat ID-MS determinations on a single microsomal sample is 1-5% and between duplicate samples ≤10%. Acitivities found in rats: Control- 45.5±1.5, Bile acid fed- 29.0±3.7, Cholestyramine fed- 135±4 (pMole/mg protein/min). Discussion: ID-MS is a sensitive and specific tool for the assay of membrane bound enzymes such as 7-α,OHase. We show here increases in 7-α ,OHase activity in cholestyramine-fed rats and decreases in bile acid-fed rats. These findings parallel reported changes in total synthesis of bile acids.

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THE DEVELOPMENT AND VALIDATION OF METHODS FOR AMINO ACID DISPOSAL RATE IN THE FETAL SHEEP. G.L. Loy, P.V. Fennessey, W.W. Hay, and A.N. Quick, Departments of Pediatrics and Pharmacology, University of Colorado Health Sciences Center, Denver, CO 80262

The essential amino acid leucine is used by the fetus primarily for protein synthesis and oxidation. The disposal rate is the sum of these processes. The rapidly growing fetus may alter the rate of use of amino acid in response to intrauterine stress. Stable isotope methodology can be applied to determine disposal rate not only in animal models of the fetus, but also in the human fetus through their pregnant mothers, and in the human neonate. We measured leucine disposal rate in the chronically catheterized sheep fetus by infusing into the fetus, at a constant rate, both 1-C14 labeled and 1-C13 labeled leucine. At steady state, we determined the plasma enrichment of leucine. In addition we measured by GC/MS the trimethylsilyl quinoxalinol derivative of 1-C13 alpha-ketoisocaproate (KIC), the immediate metabolite of leucine, to compare with leucine enrichment. The disposal rate calculated by either radioactive or stable isotope enrichment method gave the same value. GC/MS assay for leucine and KIC was sensitive to 0.2 APE (sensitivity = +/- 2SD). The final derivatives of leucine and KIC were stable for at least two weeks. Enrichment ratio of KIC to leucine was 78% +/- 3. If disposal rate can be determined by either method, then by this experimental design, measurement of either stable isotope or radioactive isotope enrichment enables calculation of the other.

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ANALYSIS OF FAST ACTING ANESTHETIC INDUCTION AGENTS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY.

K. Kestin, D.B. Christie, M. Goldstein, and P.V. Fennessey, Department of Pediatrics and Pharmacology, University of Colorado Health Sciences Center, Denver, Co 80262

Local and fast acting anesthetic agents are used for a variety of purposes and in many fields of medicine. We wish to report on the methods used to measure two different agents used commonly in medical practices. The first agent bupivacaine (1-N-Butyl-2',6'-dimethyl-2-piperdine carboxanilide) was measured in patients where it was used to block pain during joint surgery (knee) and to relieve pain after major chest surgery. Bupivacaine was quantitatively measured by comparison of its concentration to that of an internal standard mepivacaine. It was found that the use of a 0.5% solution gave blood levels that approached the toxic levels of 2000 ng/ml.

In a second study we determined the difference in the effect of leaving methohexatone (1-methyl-5-allyl-5-(1-methyl-2-Pentynyl) barbituric acid) in place or removal after induction of anesthesia with this agent. In this study we quantitatively measured methohexatone concentration by comparing its peak height (SIM) to that of an internal standard (hexobarbitol). More importantly, the patient who had the drug removed showed more rapid recovery as measured by a return to voluntary breathing, movement and eye opening.

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DAUGHTER ION SPECTRA OF SELECTED CHLORINATED COMPOUNDS.

C. E. Rostad and W. E. Pereira. U.S. Geological Survey, P.O. Box 25046, Mail Stop 407, Denver Federal Center, Denver, Colorado 80225.

Molecular ions of selected chlorinated compounds were generated by positive and negative chemical ionization using methane as reagent gas on a Finnigan TSQ 46B GC/MS/MS.* The chlorinated compounds studied included chlorobenzene; 1,2-, 1,3-, and 1,4-dichlorobenzene; 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzene; 1,2,3,5-, 1,2,4,5-, and 1,2,3,4-tetrachlorobenzene; pentachlorobenzene; hexachlorobenzene; octachlorostyrene; octachloronaphthalene; and hexachlorobutadiene. The resulting molecular ions were then fragmented into daughter ions by collision activated decomposition using argon as collision gas. A variety of conditions for collision energy and collision gas pressure were used. The negative daughter ions appeared to be neutralized in the collision cell, and were not detected. The positive daughter ions at any given collision energy and pressure were produced primarily by loss of one and/or two chlorines. Intensities of the ions varied with the severity of the fragmentation conditions. The effect of various conditions on the resulting daughter ion spectra of these compounds will be described.

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*The use of brand names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

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HETERONUCLEAR CHEMICAL-SHIFT CORRELATIONS OF SILANOL GROUPS STUDIED BY TWO-DIMENSIONAL CROSS-POLARIZATION/MAGIC-ANGLE-SPINNING NMR.

Alexander J. Vega. E. I. du Pont de Nemours and Company, Central Research and Development Department, Experimental Station, E356/B37, Wilmington, Delaware 19898.

A two-dimensional ^{1}H-^{29}Si MAS NMR experiment is proposed as a method to characterize peaks in conventional proton MAS spectra of surface species on silicas and zeolites. Mixing is achieved by cross polarization. The 2D spectra identify the protons that are rigidly bound to silicon atoms in the substrate. The application of heteronuclear or homonuclear decoupling is not necessary, as sample spinning is sufficient to suppress the effects of dipolar interactions in the systems of interest. The criteria for proton line narrowing by MAS and for effective cross polarization will be discussed. The assignment of proton signals is further aided by proton MAS spectra obtained following a spin-lock pulse and by ^{29}Si MAS spectra taken with varying cross-polarization periods. The method will be demonstrated in various anhydrous and hydrated forms of zeolites A and rho.

224 CHARACTERIZATION OF HETEROGENEOUS CATALYSTS WITH PROTON, CARBON AND XENON NMR SPECTROSCOPIES.

Cecil Dybowski, Charles Tirendi, Daniel Barabino, Navin Bansal, and Lori Hasselbring, Center for Catalytic Science and Technology, Departments of Chemistry and Chemical Engineering, University of Delaware, Newark, Delaware 19716.

The investigation of surface species with NMR spectroscopy yields information on the chemical nature and dynamic properties of the intermediates in catalytic systems, as in other chemical systems. We describe several applications of the techniques to catalytic systems which have been on going in our laboratory.

We have investigated the effects of treatment of alumina and alumina-supported platinum catalysts on the NMR spectroscopy of benzene sorbed on these systems. At multilayer sorption, there is seen to exist more than on phase. The results can be interpreted in terms of exchange between several phases. At submonolayer coverages, the structure formed by the benzene interacting with platinum can be determined from the dipole-dipole couplings. A value of 2.1 Angstroms for the distance to nearest platinum atom is determined in this manner.

The nature of sorption of hydrogen, ethylene and propylene by supported palladium and palladium powder is addressed with NMR spectroscopy. We find that the NMR spectroscopy of hydrogen can determine the form of hydride formed at the surface. The sorption of ethylene and the resulting decomposition can investigated with carbon and proton NMR.

We also use xenon probes to investigate the nature of ionic interactions in cation-exchanged zeolites. The carbon NMR analysis of supported orgnaometallics provides structural information on these interesting systems.

225 A STUDY BY SOLID STATE NMR OF ^{133}Cs and ^{1}H of a HYDRATED AND A DEHYDRATED MORDENITE.

Po-Jen Chu, Bernard C. Gerstein, 229 Spedding ISU, Ames, IA 50011, and John Nunan and Kamil Klier, Dpt. Chem. Lehigh Univ., Bethlehem, PA 18015

The dehydration of a Cs exchanged mordenite has been followed by the solid state NMR of 1-H add1133- Cs. In the fully hydrated mordenite, 133-Cs exhibits a single line 64 ppm upfield of saturated aqueous CsCl. The fully anhydrous sample exhibits two major lines with relative intensities of 3:1 with centers of mass -57 ppm and - 190 ppm under MAS. The major intensity if upfield of the line observed in the hydrated sample. The electric field gradient parameters for Cs in the anhydrous sample are e^2qQ = 3.1 MHz, = 0.65, which reduce to 210 KHz and zero, respectively in the hydrated sample. Assignment of the three sites occupied by Cs in the anhydrous sample are: Site II: - 157 ppm; Site IV: - 186 ppm; Site VI: -24 ppm after correction for the second order quadrupolar shift. Static proton spectra decrease in intensity by a factor of 35 from the hydrated to the anhydrous sample. While maintaining a roughly constant linewidth of 6.6 KHz, the shape of the proton line changes with decreased water content.

226 ABSTRACT NOT AVAILABLE

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MULTINUCLEAR NMR STUDIES OF SILYLATED SURFACES. Gregory R. Quinting, Robert C. Zeigler, Charles E. Bronnimann and Gary E. Maciel. Department of Chemistry, Colorado State University, Ft. Collins, CO 80523

The combination of MAS NMR experiments with ^{13}C, ^{29}Si, ^{1}H and, where appropriate ^{31}P or ^{15}N, provides a powerful approach for the characterization of silylated surfaces. ^{1}H experiments that employ CRAMPS (Combined Rotation and Multiple Pulse Spectroscopy) yield valuable information on the nature of surface hydroxyl groups prior to and after silylation, information that is advantageously interpreted in conjunction with the surface-selective ^{29}Si data obtained by cross polarization (CP). A variety of ^{13}C relaxation studies provide insight into the configuration and dynamics of C_{18} groups attached to the silica surface via silylation. The role of "solvent" in this problem is being explored, as is the role of acid-base (e.g., hydrogen bonding) interactions with basic groups in other systems.

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USING ^{23}Na NMR TO EXAMINE CATION SITE OCCUPANCY IN ION-EXCHANGED ZEOLITES. Larry B. Welsh and Susan L. Lambert. Allied-Signal Engineered Materials Research Center, 50 East Algonquin Road, Des Plaines, Illinois 60017-5016.

High resolution magic angle spinning NMR (MAS NMR) has been used extensively in the analysis of zeolites. Such analyses generally involve NMR studies of the zeolite framework nuclei, with relatively few studies being devoted to the information available from the charge compensating cations. In this effort, ^{23}Na MAS NMR studies of zeolitic cations have been made for several series of Y zeolites, cation exchanged with either Ca^{+2} or NH_4^+ ions at levels up to 65% of the exchange sites. The ^{23}Na MAS NMR spectra were obtained at 8.45 and 11.7 Tesla, to minimize the interference of quadrupolar interactions with chemical shift determinations. Each spectrum consists of a series of lines from about -1.0 to -35 ppm, depending on sample treatment. The relative strength of these lines depends on the level of cation exchange and the degree of sample hydration. The intensity of the lines with the least negative chemical shifts decreases as the sodium is progressively removed. This suggests that the various spectral lines can be associated with cation sites in the supercages, sodalite cages and hexagonal cages. In agreement with X-ray diffraction determinations of Na cation site occupancy, different Na distributions are observed in hydrated and dried Y-zeolites.

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SPIN-LATTICE AND SPIN-SPIN RELAXATION BELOW 1K. P. Kuhns, O. Gonen, P. C. Hammel and J. S. Waugh. Massachusetts Institute of Technology, Cambridge, MA. 02139.

Extensive preliminary experiments have been performed to establish conditions for high-sensitivity NMR spectroscopy at very low temperatures. In the process a number of unusual or unexpected effects have been observed, e.g. 1) Bulk T_1 processes many orders of magnitude faster than theory suggests, 2) an apparent T_1 maximum for protons in gypsum at ~60 mK, 3) attainment of internal spin-temperature equilibrium on a time scale much larger than expected, 4) a possible line width transition for protons on SiO_2 between 10 mK and 30 mK.

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VARIABLE-TEMPERATURE CP/MAS NMR STUDIES OF ANTIFERROMAGNETIC TRANSITION METAL COMPLEXES. Gordon C. Campbell and James F. Haw, Department of Chemistry, Texas A & M University, College Station, TX 77843.

Antiferromagnetic transition metal complexes are characterized by diamagnetic ground states and thermally-accessible triplet electronic energy states. Magnetic coupling between the two or more metal atoms present is described by the hamiltonian $H = -2J\, S_1 \cdot S_2$, where 2J is the energy difference between the singlet and triplet states. Our research involves the study of systems having metal atoms which are coupled either directly through metal-metal bonds or indirectly via the orbitals of ligands which bridge them (the superexchange pathway). In either case, CP/MAS NMR provides quantitative electronic and structural information about antiferromagnetic solids — especially when variable-temperature (VT) operation is possible. Not only do resonances from nuclei closer to metal centers become observable as the sample temperature is lowered, but the temperature dependence of the chemical shifts is consistent with the bulk magnetic properties exhibited by these materials and can be used to determine 2J values. Also, the r^{-6} dependence of dipolar relaxation can be used to determine electron-nuclear distance information analogous to that available using x-ray crystallography. Current quantitative efforts will be discussed which are directed towards a wide variety of transition metal systems including copper carboxylate dimers and active site models of ferredoxins.

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RECENT DEVELOPMENTS IN SOLID-STATE NMR COMBINED WITH DYNAMIC NUCLEAR POLARIZATION. Robert A. Wind, Herman Lock and Gary E. Maciel, Dept of Chemistry, Colorado State Univ., Ft Collins, CO 80523.

In solids containing unpaired electrons, nuclear spin polarization can be enhanced via Dynamic Nuclear Polarization (DNP). This can be used, among other things, to increase the signal-to-noise ratio of an NMR signal, to investigate the molecular environment of the unpaired electrons and to discriminate between mobile and fixed electrons. We applied DNP both on rare spin systems such as ^{13}C and ^{29}Si, and on abundant spin systems like protons. In this presentation results of recent DNP investigations on a varyity of solids will be discussed, such as polymer conductors, amorphous silicon and fossil fuels.

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NUCLEAR MAGNETIC RESONANCE IN AL-MN PERIODIC AND QUASIPERIODIC CRYSTALS. Mark Rubinstein and G.H. Stauss, Naval Research Laboratory, Washington D.C. 20375 and L. H. Bennett, National Bureau of Standards, Gaithersburg MD 209

Recently, Shechtman et al. (D. Shechtman, I. Blech, D. Gratias, and J.W. Cahn,Phys Rev. Lett. 53, 1951 (1984) discovered a rapidly quenched Al-Mn alloy whose structure appeared to question the validity of one of the accepted bases of crystallography. Named the icosahedral phase, the material exhibited an electron diffraction pattern with sharp spots, which is indicative of crystallinity, but the pattern had a forbidden five-fold symmetry. Long-range periodic translational order is incompatible with five-fold symmetry. We have observed the ^{27}Al and the ^{55}Mn nuclear magnetic resonance spectra of polycrystalline Al_6Mn, Al_4Mn and $Al_{12}Mn$, as well as that of the quasiperiodic icosahedral (and decagonal) phase of Al-Mn melt-spun samples. After acquiring the NMR spectra of the crystalline compounds, and obtaining their quadrupole coupling and Knight parameters, we conclude that the ^{55}Mn icosahedral -phase spectrum is significantly broader than the analogous crystallinecompounds, and cannot be deconvolved into only two types of sites (as some quasicrystalline models might appear to suggest). We have examined the relationship of the magnetic susceptibility to the intensity of the ^{55}Mn spectrum in these compounds (W.W. Warren, H.S. Chen and G.P. Espinosa, Preprint (1986) and we conclude it is not intrinsic.

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ABSTRACT NOT AVAILABLE

234 ABSTRACT NOT AVAILABLE

235 ABSTRACT NOT AVAILABLE

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SOLID-STATE NMR USING HIGH-SPEED MAS.

Steven F. Dec, Robert A. Wind, and Gary E. Maciel. Department of Chemistry, Colorado State University, Ft. Collins, CO 80523.

Magic-angle spinning (MAS) NMR experiments with sample-spinning speeds up to 23 KHz have been carried out on a variety of solids, especially in applications to ^{1}H, ^{19}F and ^{27}Al measurements. The results of representative applications will be presented. Emphasis will be on the investigation of structure in polymer and surface/catalyst systems. The potential application to heavy-metal nuclides will be considered. Prospects and limitations of the high-speed MAS approach will be discussed.

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^{1}H MAGIC ANGLE SPINNING STUDY OF METAL-EXCHANGED ZEOLITE Y

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Proton NMR has been performed on NaY zeolites prior to and following the exchange of NH_4^+ and heat treatment. Both the resultant HY and NaY zeolites were then exchanged with $Rh(NO_3)_3$ solutions. Rhodium preferentially exchanges with the most acidic protons in HY zeolite as evidenced by the loss of intensity in the most deshielded proton resonance upon exchange. Reduction of the rhodium with hydrogen occurs through heterolytic cleavage of the hydrogen forming protons to charge compensate the zeolite lattice. In HY zeolite these protons are acidic. In the NaY form the chemical shift of the charge compensating protons formed upon reduction of the metal indicates that these protons are less acidic. The implications of these results will be discussed.

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METHODS FOR DETERMINING MIXING IN POLYMER BLENDS BY SOLID STATE NMR.

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The phenomenon of spin diffusion in abundant spin-(1/2) systems has been used for many years to deduce information about minimum domain dimensions (MDD's) in spatially heterogeneous systems where the origins of the heterogeneity include chemical differences or a contrast in the degree of molecular ordering. In phase-separated blends of two homopolymers, proton spin diffusion can be used to determine MDD's. The spin diffusion experiment always entails the production and monitoring of magnetization gradients between the two different regions. The advent of solid-state ^{13}C and ^{1}H high-resolution techniques offers new possibilities both in the production and monitoring of these magnetization gradients; particularly when both polymer components have a high degree of molecular rigidity. The range of MDD's able to be probed with proton spin diffusion is 2-30 nm. In particular, the experimental ambiguities at MDD's smaller than 2 nm will be discussed. In this range, where domains are on the order of a few molecular diameters, it makes more sense to use methods for detecting the presence of one polymer chain near another via direct dipolar interactions. Two such approaches will be compared, both based on the deuteration of one of the polymers.

239 ABSTRACT NOT AVAILABLE

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NUCLEAR SPIN DYNAMICS OF HYDROGEN IN $H_xZr_yCl_z$ PHASES. Po-Jen Chu, B.C. Gerstein, Robin Ziebarth, and J.D. Corbett, Dpt. Chem. ISU, Ames, IA 50011

Transient techniques in NMR have been used to study the identities of hydrogen in $H_xZr_yCl_z$ phases. Hydrogen in HZr_6Cl_{12} has been studied using the temperature dependence of the chemical shift, and homonuclear decoupling at fields of 1.3 and 5.5T. The protons in this phase are shifted 500 ppm upfield of water at 298K and exhibit a temperature dependent chemical shift of the form Shift/ppm = $2.234 \times 10^5/T - 241.04$. The signal from these species disappears under homonuclear decoupling with an MREV-8 cycle time of 36 μ sec. This species is identified as being in a Zr_6Cl_{12} cluster, and moving within the cluster with a correlation time of order of 18 μ sec.

A second proton species is identified as being associated with the phase $ZrClO_xH_{1-x}$. These protons are found to be localized pairs, with an internuclear distance of 2.5 A. Each proton of these pairs is found to exhibit heteronuclear dipolar coupling to one or more chlorine atoms, at a proton-chlorine distance of 2.6 A. Homonuclear decoupling, and sample spinning on, and off the magic angle are used to arrive at these conclusions. Possible locations of these pairs in the $ZrClO_xH_{1-x}$ structure are identified.

241 ABSTRACT NOT AVAILABLE

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SOLID STATE PROJECTION RECONSTRUCTION IMAGING PROBE
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This laboratory has recently completed construction of a solid state imaging probe for use in our Bruker CXP 200 MHz spectrometer. The probe is doubly tuned, with interchangable tuning capacitor on the multinuclear circuit. It includes two orthogonal gradient systems, an opposed Helmholtz coil pair producing a gradient field parallel to the main magnetic field, and a quadrupole coil producing a transverse gradient field. Stepper motor driven goniometer rotates the sample about an axis perpendicular to the gradients. A commercially available 2D NMR software package has been modified to perform the projection reconstruction algorithm on the two dimensional data produced with this probe. The maximum sample diameter is 7 millimeters, and maximum gradient strength is 100 Gauss/centimeter.

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SOLID STATE NMR STUDIES OF MOTION IN POLYMERS. E. O. Stejskal, Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204.

The direct dipolar coupling between a pair of nuclear spins contains information about molecular structure and motion in the solid state. The dipolar interaction is determined primarily by the distance between the coupled spins. Molecular motion (of frequency greater than the interaction itself) reduces the strength of the interaction and provides a measure of the amplitude of the motion. For an isolated ^{13}C-^1H pair, the ^{13}C dipolar powder lineshape is the familiar Pake pattern which, under magic angle spinning, breaks up into spinning sidebands. Dipolar rotational spin-echo (DRSE) NMR generates this C-H sideband pattern in a 2-D NMR experiment and correlates it with the chemical shift of each carbon spin observed. In order to observe isolated C-H sideband patterns in a system with coupled protons, the spin pair must be isolated from the surrounding protons. This is done by applying a multipulse sequence (WAHUHA or semi-windowless MREV-8) to the protons. When combined with $T_1(C)$ and $T_{1\rho}(C)$ experiments, which are sensitive to the frequencies of motions, ^{13}C-DRSE NMR allows a detailed characterization of molecular motion in glassy polymers.

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VARIABLE TEMPERATURE NMR STUDIES OF PHOSPHAZENE INORGANIC POLYMERS

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Variable temperature (VT) multinuclear magic-angle spinning (MAS) NMR is being used to study several important problems in polyphosphazene chemistry. These inorganic polymers, which are composed of alternating phosphorus and nitrogen atoms with two side groups attached to each phosphorus, are important because of their mechanical and thermal properties, solvent resistance, and potential for providing biocompatible materials. We report results which demonstrate that ^{31}P MAS NMR can be used to elucidate the cross-linking mechanisms in the linear chloropolymer (one of the most important problems in polyphosphazene chemistry). We are also using VT ^{31}P MAS NMR in conjunction with VT ^{13}C CP/MAS NMR to probe the molecular dynamics of several poly[bis(alkoxy)phosphazenes]. ^{31}P MAS NMR and ^{13}C CP/MAS NMR are likewise being used to examine the thermal degradation of poly[bis(ethoxy)phosphazene] and poly[bis(methoxy)phosphazene]. The results of these studies are presented. The mechanisms of both the uncatalyzed and BCl_3 catalyzed melt polymerization reactions of the phosphonitrilic chloride trimer are being studied using a multinuclear NMR approach. We report ^{11}B MAS NMR and ^{31}P MAS NMR results which help resolve the question of whether the melt polymerization proceeds through a ring-opening or chloride abstraction mechanism.

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CP/MAS NMR STUDIES OF CURED RESINS.

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High-resolution solid-state NMR experiments with ^{13}C and ^{15}N, employing high-power ^{1}H decoupling with cross polarization (CP) and magic-angle spinning (MAS), provide valuable information on the structures of cured resins and, by inference, on the curing processes. This paper will report results on urea-formaldehyde (UF) resins, phenolic resins and polyurethane resins. For the latter, a paucity of previous solid-state NMR results calls for a substantial effort on model systems, especially for ^{15}N NMR approaches. Extensive NMR data have been obtained on the hydrolytic stability and fate of UF resins. The issue of the optimum magnetic field strength for the study of these types of resins is addressed.

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HIGH FIELD NMR STUDY OF THE MOLECULAR STRUCTURE AND SOLUTION DYNAMICS OF Na_2PHO_3.

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The presence of two relaxation processes, dipolar and chemical shift anisotropy (CSA), in high field NMR experiments has a number of important consequences. In the two spin system $PHO_3^{=}$, the ^{31}P NMR relaxation time at 4.7 tesla and higher can no longer be described by a single relaxation time $T_1 = T_2$. The longitudinal (T_1) relaxation times for each line are different and neither can be described by a single exponential; each of them shows triple exponential recovery. Using a density matrix formalism, we have analyzed the longitudinal relaxation of the two ^{31}P resonance lines. From this analysis we obtain informtion about the P-H bond distance (r_{PH} = 149 pm), the ^{31}P CSA [($\sigma_{\parallel} - \sigma_{\perp}$ = 115 ppm), and the molecular correlation time, τ_c). The sign and magnitude of the spin coupling constant is obtain from the spectrum and the T_2 values of the two lines (J_{PH} = −565 Hz). Such information can be obtained only if a carefully selected set of experiments is executed. The experiments required and the steps in their analysis are described.

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CHEMICAL SHIFT TRENDS IN SOLID SILATRANES. Joseph H. Iwamiya and Gary E. Maciel, Department of Chemistry, Colorado State University, Ft. Collins, CO 80523.

Silatranes, 5-aza-2,8,9-trioxa-1-silabicyclo[3.3.3]-undecanes, constitute an interesting bicyclic system in which transannular N → Si interactions have been studied previously. The ^{13}C, ^{29}Si, ^{17}O and ^{15}N chemical shifts, including the chemical shift anisotropy (CSA) patterns, provide promising NMR parameters for studying subtle structural differences in these systems. This paper presents ^{29}Si, ^{15}N and ^{13}C results on unsubstituted (R = H) and silicon-substituted (R = CH_3, CH_2=CH-, C_6H_5-, C_2H_5O- and $ClCH_2$-) silatranes. Correlations among the chemical shift parameters and structural parameters will be explored in terms of the structural issues of interest.

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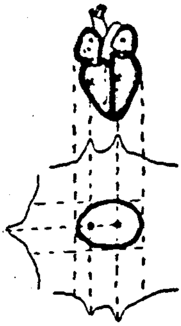
OXYGEN-17 MAGNETIC RESONANCE IMAGING IN MATERIALS AND BIOLOGICAL RESEARCH G.D. Mateescu, G.M. Yvars and Terri Dular, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

We demonstrate that ^{17}O magnetic resonance imaging is feasible. It is particularly useful in combination with proton imaging when water is the principally observed species, because this offers the benefit of two-source information on the same specimen. Hence, improved image interpretation, particularly in terms of subtle lipid(fat)-protein contribution and in terms of H^+ versus H_2O exchange dynamics. Useful imaging of (O-17 enriched) ions and other metabolites becomes possible. Images of water and acids ingress in polymeric materials will be presented. The Figure, a back-projection reconstruction, demonstrates the outstanding potential in obtaining sharp images of blood (or other fluid) filled cavities (cardiac, pulmonary, renal, vascular, etc.) using enriched water (or other compounds, e.g., ^{17}O-enriched glucose). The strong signals protruding from the natural abundance background of the heart belong to ^{17}O enriched water, introduced, via catheters (located at the x signs in the heart sketch) through the openings of the systemic arch (dorsal aorta) and the pulmonary arterial arch, into the corresponding ventricles. We hope to present 3D images of materials and biological samples taken with our new 20 G/cm system. Financial support from NSF and NIH is greatfully acknowledged.



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NMR STUDY OF CHARGE TRANSFER AND STRUCTURE OF TERNARY AMMONIA-ALKALI INTERCALATION COMPOUNDS, T. Tsang[a,b], R. M. Fronko[a], H. A. Resing[a], S. A. Solin[c], and X. W. Qian[c], [a]Naval Research Laboratory, Washington, DC 20375-5000, [b]Howard University, Washington, DC 20059, [c]Michigan State University, East Lansing, MI 48824.

The ternary GIC $C_{24}K(NH_3)_{4.3}$ was formed by the reaction of $C_{24}K$ (derived from HOPG) with NH_3 at room temperature under 9.5 atm. pressure. At various temperatures and orientations, the ^1H NMR spectra consist of three sets of triplet resonance lines due to the ^1H-^1H and ^1H-^{14}N dipolar interactions. The simple spectral features and narrow spectral lines indicate fast diffusion and reorientation of NH_3 molecules in the graphite gallery. The spectral splittings indicate that the C_3-axes of NH_3 molecules are nearly perpendicular to the crystallographic c-axis of the ternary. The indirectly determined ^{14}N quadrupolar coupling constant of 3.7 MHz is intermediate between the gas and solid values of 4.1 and 3.2 MHz. The ^{13}C NMR chemical shift tensor for the ternary has principal values $\delta_\parallel = 58$ and $\delta_\perp = 145$ ppm with respect to tetramethylsilane for B_0 parallel and perpendicular respectively to the c-axis of the GIC. Based on the band structure of pure graphite, we propose the correlation

$$\delta_\parallel - \delta_\perp = -178 + 540\ q^{1/2},$$

where q is the electronic charge per carbon atom. Thus we found q=0.035 for the ternary, which gives a formal charge on the carbon layer of -0.84 per 24 carbon atoms, i.e., per alkali atom. Thus there is allowed a relatively weak partial solvation of the electronic charge from the carbon layers to the intercalated NH_3. The potential energy of the GIC, based on Coulombic and vanderWaals interactions, supports a model in which the electrostatic interaction of the alkali ion with the dipole of the ammonia molecule maintains the C_3 axis of NH_3 parallel to the planes (orienting potential 9 kcal/mol) so that the proton - carbon repulsive potential provides the d-spacing of 6.7A for the GIC. Very similar results have also been observed for $Rb(NH_3)_{4.1}C_{24}$ and $Cs(NH_3)_{3.7}C_{24}$.

250 SUPERCRITICAL FLUID CHROMATOGRAPHY: RETENTION, RESOLUTION, AND GRADIENT METHODS,

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The behavior of the chromatographic parameters, capacity ratio, selectivity, plate number, and resolution, in supercritical fluid chromatographiy is discussed. The dependence of the parameters on temperature, pressure/density, mobile phase composition, and linear velocity is presented by experimental data which have been obtained by series of isothermal-isobaric-isocratic runs. A standard chromatographic system, consisting of a substrate of four aromatic hydrocarbons, separated on unbonded silica as the stationary phase in a small particle packed column, has been used throughout to allow direct comparison. The behavior of this standard system, as well as of other combinations of substrate and stationary phase which have been studied, is dependent on effects of density, partition coefficient, diffusivity, and viscosity. The gradient methods which are possible in SFC are enumerated. Often used at present are pressure gradients and binary composition gradients, while the programming of temperature and linear velocity is lagging behind. Multiple gradients are more difficult to employ, but, from the general behavior of retention and resolution in SFC, appear to be particularly attractive. The most effective use of single and multiple gradient methods depends, however, on the detailed knowledge of the chromatographic parameters for a given system, particularly of capacity ratios and resolution. Separations by temperature, pressure, composition, and multiple gradients are presented, as well as the apparative requirements for utilizing multiple gradients.

251 A COMPARISON OF PACKED AND CAPILLARY COLUMNS FOR PRACTICAL SFC SEPARATIONS.

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Although the first instrument (designed for packed column SFC) was introduced in 1982, work in recent years has focussed mainly on capillary SFC. However, a survey at this years Pittsburgh Conference learns that a surprising number of papers involved packed columns. Recently, a theoretical comparison in terms of speed, efficiency and sample load was made between packed- and capillary columns (1). The model utilized the Golay and Horvath & Lin equations to compare state-of-the-art packed- and capillary columns, respectively. In order to solubilize higher molecular weight solutes and to extend the limits of gas chromatography, densities higher than ca. 0.3 g/ml CO2 have to be applied. In these density regions calculated Van Deemter plots strongly favor the packed column if short analysis times are required. In this paper these predictions will be experimentally verified. The utility of small bore packed columns will be demonstrated for simulated distillation analyses, for which capillary SFC already has proven to be competitive with high temperature GC (2).

(1) H.H. Lauer, H.E. Schwartz and P.J. Barthel, PitCon '87, paper 1049.
(2) H.E. Schwartz, J.W. Higgins and R.G. Brownlee, LC.GC 4(1986)639.

252 MULTIDIMENSIONAL SUPERCRITICAL FLUID CHROMATOGRAPHY/CAPILLARY GAS CHROMATOGRAPHY.

Joseph M. Levy, John P. Guzowski, Wayne E. Huhak. Standard Oil Research and Development, 4440 Warrensville Center Road, Cleveland, Ohio 44128

A new analytical technique which combines packed column supercritical fluid chromatography on-line with high resolution capillary gas chromatography will be described. After separation in a supercritical fluid chromatograph, the supercritical fluid sample effluent is decompressed directly into a capillary inlet of a gas chromatograph for further analysis. This technique also allows for selective or multi-step heartcutting of fractions from the supercritical fluid chromatograph to the gas chromatograph. Heartcut times are based on the ultraviolet absorbance or flame ionization detector responses from the supercritical fluid chromatograph. Results will be shown from studies of heartcut reproducibilities, discrimination ratios, and transfer efficiencies.

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ANALYTICAL EXTRACTION OF ORGANICS FROM SOLID SAMPLES USING SUPERCRITICAL FLUIDS, Steven B. Hawthorne, David J. Miller, and Mark S. Krieger, University of North Dakota Energy Research Center, Campus Box 8213, Grand Forks, North Dakota, 58202

Supercritical fluids are useful for the analytical extraction of organic compounds from a variety of solid samples ranging from the extraction of PAHs and PCBs from environmental solids such as sediment and air-borne particulates to the extraction of flavor compounds from food products. Solvent strengths of supercritical fluids can surpass those of liquids, and can be varied by the choice of the fluid, the extraction pressure, or by the addition of solvent polarity modifiers. Extractions performed with supercritical fluids such as CO_2 and N_2O can be performed at low temperatures (e.g., 40 °C) to protect thermally labile analytes. Quantitative extraction of analytes can often be achieved in 10-30 minutes. Since many supercritical fluids are gases at room temperature, analyte concentration steps are simplified and the direct coupling of the supercritical fluid extraction step with gas chromatography (SFE-GC) is possible. The use of supercritical fluids and the coupled SFE-GC technique for the extraction and quantitation of PAHs from NBS standard reference materials, PCBs from sediment, and flavor compounds from a variety of spices and food products will be presented.

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TRACE ANALYSIS WITH SUPER CRITICAL FLUID CHROMATOGRAPHY. H. M. McNair, J. O. Frazier. Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

The separation mechanism for super critical fluids is primarily a function of mobile phase density. Utilizing a "home built" SFC system, this principle is exploited for trace analysis. Trace analysis is affected by multiple injections of a dilute solution of analyte which is concentrated at the head of the column. This is accomplished by maintaining the density of the mobile phase below the elution density of the solute. After concentration, the solute of interest is chromatographed using a pressure ramp which takes the density of the mobile phase above the elution density. This technique has proven to be applicable to sample concentrations of less than 1 ppm. Besides trace analysis, results of a study involving maximization of column coating techniques for SFC will be covered. The importance of surface deactivation and a comparison of various crosslinking agents will be discussed.

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DRUG ANALYSIS BY CAPILLARY SUPERCRITICAL FLUID CHROMATOGRAPHY, Marion R. Andersen, B.E. Richter, D.E. Knowles, D.W. Later, and E.R. Campbell, Lee Scientific, Inc., 4426 South Century Drive, Salt Lake City, UT 84123 USA

Capillary supercritical fluid chromatography (SFC) is currently realizing explosive growth in interest and application. In particular, capillary SFC is well suited for the analysis of high molecular weight, chemically reactive, polar, and thermally labile compounds. Many classes of drugs possess these chemical properties and, therefore, capillary SFC is a viable alternative for their chromatographic analysis. In this paper, SFC methods developed for the analysis of several classes of drugs will be presented. Methods of analysis for drugs of abuse, such as tetrahydrocannabinol and its polar metabolites, as well as for therapeutic drugs such as antibiotics and prostaglandins will be discussed.

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SEPARATION OF DIFFERENT OLIGOMERS BY SUPERCRITICAL FLUID CHROMATOGRAPHY USING GRADIENT ELUTION.

Franz P. Schmitz and Bernd Gemmel. Lehrstuhl für Makromolekulare Chemie, RWTH Aachen, Worringerweg, D-5100 Aachen, F.R.G.

With supercritical fluid chromatography (SFC), oligomer separations have been achieved over wide molecular weight ranges. In addition to temperature and pressure/density programming, gradients of eluent composition (gradient elution) have been applied. By use of the latter gradient technique, variations of solvent properties are produced by changing the chemical nature of the eluent. For the separation of vinylarene oligomers with gradient elution, combination of an alkane or carbon dioxide as the primary and 1,4-dioxane as the secondary component has been used successfully. It was shown that these separations could be optimized by changing temperature and pressure. Additionally it was found that the application of binary or ternary gradients between temperature, pressure, and eluent composition can lead to further enhancement of the separation quality. With CO_2-acetonitrile, another eluent pair has been studied with respect to its applicability to oligomer separations. When detection is performed by means of UV-absorption, this eluent pair is of special interest for the separation of oligomers not having a chromophore; this is due to the high spectral transparency of both components even at low wavelengths down to 200 nm.

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TEMPERATURE EFFECTS IN SUPERCRITICAL FLUID CHROMATOGRAPHY.

Bernd W. Wenclawiak, University of Toledo, Department of Chemistry, 2801 W. Bancroft St., Toledo, OH 43606.

It is standard practice in supercritical fluid chromatography (SFC) to use pressure gradients to increase the density. The density contributes most to a separation under supercritical conditions. The largest density change can be obtained very close to the critical temperature. Yet in many applications the temperature is kept at a constant value and far above Tc. The temperature contribution to chromatographic performance and the use of temperature for density programming will be reported. For this study a system utilizing capillary columns and flame ionization detector was used. Samples studied were waxes, crude oils and distillates.

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SUPERCRITICAL FLUID CHROMATOGRAPHY: A TECHNOLOGY UPDATE.

C.M. White, D.R. Gere, and F. Pacholec. Suprex Corporation, SFC Research Center, 125 William Pitt Way, Pittsburgh, PA 15238.

Significant advances continue to be made in supercritical fluid chromatography (SFC) both in the instrumentation and applications areas. SFC is rapidly moving beyond the "demonstrate the feasibility" stage of development, where it was sufficient to show pretty chromatograms of samples that were difficult to elute or detect by gas or liquid chromatography. It's now moving on to a "solve the problem" stage, where analysts are asking a lot of questions with regard to sensitivity, reproducibility and selectivity. To address these questions, both packed columns and wider bore capillary columns (200 um) are being extensively investigated. Detector designs and interfaces are being reviewed, with a great deal of work also going into restrictor and injection technology. This paper focusses on these current developments and how they impact the role of SFC in the analytical laboratory.

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INDUSTRIAL APPLICATIONS OF SUPERCRITICAL FLUID CHROMATOGRAPHY: POLYMER ANALYSIS

David E. Knowles, Erin R. Campbell, Marion R. Andersen, Bruce E. Richter and Douglas W. Later, Lee Scientific, Inc., 4426 So. Century Dr., Salt Lake City, UT 84123 USA

Polymers can be difficult to fully characterize by conventional chromatographic methods (i.e. Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), and Size Exclusion Chromatography (SEC)) due to temperature instability, detector incompatibility, nonvolatility, molecular weight considerations or insufficient chromatographic efficiency. Capillary Supercritical Fluid Chromatography (SFC) offers several advantages for polymer analysis. Complex distributions can be resolved, low temperatures can be used and individual oligomres can be detected, allowing differences in molecular weight distributions to be quantitatively and qualitatively to be measured.

Like other chromatographic techniques, varying one or more chromatographic parameters (oven temperature, detector temperature, stationary phase, ramp rates) can be advantageously used to improve resolution. In this presentation, results will be shown for the analysis of oligomeric mixtures that demonstrate how simultaneous density and temperature programming can facilitate improved results. Data will also be presented showing the analysis of various types of polymers by capillary SFC.

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METHODS FOR COMPARING ELUENT PROPERTIES IN SUPERCRITICAL FLUID CHROMATOGRAPHY.

Franz P. Schmitz. Lehrstuhl für Makromolekulare Chemie, RWTH Aachen, Worringerweg, D-5100 Aachen, F.R.G.

Comparison of chromatographic properties of different supercritical eluents has been performed in three ways: by comparing retention and other chromatographic properties at equal density and at equal free volume of the different mobile phases, and by a comparison on the basis of an empirical correlation between resolution and retention . At equal density, the temperature dependence of the capacity ratios of aromatic hydrocarbons determined with different alkane mobile phases is the same, whereas significant deviations are observed when carbon dioxide is used as the mobile phase. Comparison of capacity ratios measured with carbon dioxide and alkane eluents at equal free volume showed a strong similarity of the transport behavior of the chemically different mobile phases when the free volume is low, i.e. at high densities. With increasing free volume the chemical differences of the alkane and carbon dioxide eluents become more apparent in their elution behavior. Additionally, several different mobile phases are compared by plotting resolution versus capacity ratio; thus, information is provided on separation efficiency per unit capacity ratio offered by the different eluents. In this comparison, CHF_3 turned out to be an interesting eluent, combining high resolution with short analysis ~~time~~ for the separation of aromatic compounds.

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INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRIC DETECTION IN SUPERCRITICAL FLUID CHROMATOGRAPHY.

Kiyokatsu Jinno, Chuzo Fujimoto and Hiroyuki Yoshida, School of Materials Science, Toyohashi University of Technology, Toyohashi 440, JAPAN

The coupling techniques of chromatography to inductively coupled plasma atomic emission spectrometry (ICP-AES, ICP) offers new and attractive approaches for elemental analysis in a wide variety of compounds. The utilization of ICP as a detector for supercritical fluid chromatography (SFC) provides a powerful and versatile method for chromatographic separations. In this presentation, the basic approach to combine packed microcolumn SFC with ICP, in which carbon dioxide is used as the mobile phase is described. The effects of SFC separation conditions such as column pressure and temperature, and plasma conditions such as sample Ar-gas and plasma Ar-gas flow rates to the signal intensity of iron-containing organometallic compounds monitored at 259.7 nm iron characteristic emission line are studied in details. The potential of this hyphenated approach in SFC is also discussed.

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SUPERCRITICAL FLUID CHROMATOGRAPHY WITH REDOX CHEMILUMINESCENCE DETECTION.

William T. Foreman, Robert E. Sievers, and Bernd Wenclawiak. Cooperative Institute for Research in Environmental Sciences, and Department of Chemistry and Biochemistry, Campus Box 449, University of Colorado, Boulder, CO 80309.

The gold-catalyzed redox reaction of analytes with NO_2 or HNO_3 forms the basis for the selective and sensitive redox chemiluminescence detector (RCD^{TM}) in GC. In the post-column detection scheme, NO produced from the redox reaction is detected by its chemiluminescent reaction with O_3. Some analytes that are more easily oxidized than others react to form NO at lower catalyst temperatures (T). Thus, the selectivity of the detector can be controlled by varying the catalyst T. In this way it can function either as a general or specific detector by selection of appropriate T and catalyst. Current research efforts are aimed towards extending the utility of the RCD to high molecular weight or thermally labile compounds that can be oxidized. Particularily desirable is the detection of species that contain no chromophores and are difficult to measure at trace levels with other detectors. Systems are being developed to interface the RCD with a HPLC and a SFC. The first example of a prototype SFC-RCD interface was demonstrated with a methanol-2,6-dimethylphenol mixture using a Model 207 RCD. Possible applications of this new separation-dectection scheme to some environmental and biological compounds will be presented.

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ELECTRON-IMPACT SPECTRA OF COMPOUNDS UTILIZING SFC/MS.

B.W. Wenclawiak, University of Toledo, Dept. of Chemistry, 2801 W.Bancroft St. Toledo, OH 43606 and J. Ashraf, Nermag Div. of Delsi Instruments, 10 Kingsbridge Road, Fairfield, N.J. 07006.

Amongst the many detectors commonly used in supercritical fluid chromatography a mass spectrometer provides more important information about the sample. Cluster formation of the carrier fluid CO_2 and chemical ionization conditions limit the obtainable information.

In this study we report some of our preliminary results involving EI SFC/MS.

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SFC/MS SEPARATION AND IDENTIFICATION OF ALKANE, ALCOHOL, ACID, ESTER, AND GLYCERIDE COMPONENTS OF WAXES

Steven B. Hawthorne and David J. Miller, University of North Dakota Energy Research Center, Campus Box 8213, Grand Forks, North Dakota, 58202

Capillary supercritical fluid chromatography (SFC) is a powerful and rapid technique for separating the high molecular weight components of synthetic and natural waxes. High resolution separations of individual wax components can be achieved at relatively low temperatures (100-150 °C), and even polar species such as underivatized carboxylic acids show good chromatographic behavior. SFC/MS analyses of several natural and synthetic waxes have been performed using direct introduction of the capillary SFC column effluent into the ion source of a Hewlett-Packard 5985B GC/MS. Methane chemical ionization mass spectrometry yielded intense pseudomolecular ions and characteristic fragmentation patterns allowing the identification of individual wax components ranging in molecular weight from approximately 300 to 1000 amu. The length of acid and alcohol portions of individual esters was also easy to determine based on the ester's fragmentation pattern. The SFC/MS separation and identification of the individual alkane, alcohol, acid, ester, and glyceride components of several natural and synthetic waxes will be presented.

265 INTERFACING TECHNIQUES FOR SFC/MS. James D. Buchner, Ross C. Willoughby. Extrel Corporation, 240 Alpha Drive, Pittsburgh, Pennsylvania 15238.

We wish to report on recent efforts to interface SFC with Mass Spectrometry (MS). In particular, we will compare and contrast three different interfaces, namely; direct fluid introduction (DFI), atmospheric pressure ionization (API), and momentum separation particle beam (PB) SFC/MS. DFI is perhaps the simplest interface in terms of hardware requiring only a μ size precision aperture for depressurization at or near the MS ion source. Clustering and the density of the emerging jet can be a problem with electron ionization (EI). These problems have been addressed by Voorhees et al. and others to achieve better EI performance. Chemical ionization (CI) performance appears adequate especially when employing CO_2 mobile phase modifiers such as formic acid or methanol. Other general problems with clogging during the analysis of high molecular weight compounds are usually addressed by heating the restrictor aperture. With SFC/API/MS, clogging problems are not as severe due to depressurization occurring to atmospheric pressure. The technique can handle the higher gas flows provided in packed column SFC and yield sensitivities in the ppm/ppb range. However, as a result of the soft ionization process, qualitative information content is often limited to molecular ion and associated neutral loss data. Coupling SFC/API/MS with MS/MS has been done by Henion et al. to gain further structural information and successfully solve many problems. However, these systems are very expensive and complex. ThermaBeam™ is a momentum separator particle beam interface for combined LC/MS as commercialized by Extrel. The interface thermally nebulizes the LC effluent generating submicron particles which pass into the ion source after two stages of momentum separation. A variation of this interface has been evaluated using SFC and offers good EI performance characteristics with minimal clogging problems. In the CI mode of operation, a variety of reagent gases may be used since the mobile phase and modifiers are removed.

266 A STUDY OF RETENTION CHARACTERISTICS BY FUNCTIONAL GROUP ANALYSIS USING SUPERCRITICAL FLUID CHROMATOGRAPHY. J.R. Wheeler and M.E. McNally, E.I. duPont deNemours & Co., Agricultural Products Dept., Experimental Station, 402/3104, Wilmington, DE, 19898.

Factors governing retention characteristics of different compounds in supercritical fluid chromatography (SFC) are complex and not well understood. Solute affinity for the mobile phase versus stationary phase in SFC is dependent on mobile phase density and temperature as well as mobile and stationary phase compositions. It has been proposed in supercritical fluid chromatography that the occupation of the active sites on the stationary phase by the modifiers in the mobile phase is the primary interaction effecting solute retention (Reference 1). However, specific structural features of the solute may be equally as important in influencing chromatographic retention. Studies have revealed the role of free hyroxy functional groups in effecting the retention behavior of polyglycerol esters (Reference 2). Such studies enlighten the understanding of the separation process occuring and enable trends and predictions for separation strategies to be devised. In this study, retention behavior of representative compounds will be presented with respect to functional group specificity.

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267 PARAMETERS INFLUENCING THE SEPARATION OF PD-β-DIKETONATES IN PACKED COLUMN SFC. B.W. Wenclawiak, The University of Toledo, Department of Chemistry, 2801 W. Bancroft St., Toledo, OH 43606 and K.R. Jahn, Anorganisch Chemisches Institut der Westfälischen Wilhelms Universität, Correnstrasse 36; D-4400, Münster, W. Germany.

Three different Pd-β-diketonates of Hacac, Hmhd and Htod have been separated on normal and bonded phase packed columns under identical SFC conditions.

van Deemter plots at subcritical conditions show LC-like behavior. Physical properties and chromatographic behavior in the supercritical state are different as anticipated. At supercritical conditions, however, the influence of a flow profile must be put into consideration.

The influence of modifier content on retention and on the supercritical state and the eluent viscosity has been tested. With methanol as modifier and Pd-β-diketonates, a polar stationary phase is preferable. The dependence of temperature and pressure on polar and bonded phases for Pd-β-diketonates has been studied.

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PACKED CAPILLARY COLUMN IN SUPERCRITICAL FLUID CHROMATOGRAPHY

Yukio Hirata and Yoshiyuki Yukawa, Materials Science, Toyohashi Universty of Technology, Toyohashi 440, JAPAN.

Packed capillary column with 0.25 mm i.d. was employed for supercritical fluid chromatography. Flow rate was typically an order of µl/min as supercritical fluid, or a few ml/min as gas when carbon dioxide was used as mobile phase. The total effuluent was directly introduced into flame ionization detector through restrictor. Also, UV-detection was performed using micro flow-through cell which withstand high pressure. Sample loadability of packed capillary column was significantly greater than that of capillary column with 0.1 mm i.d. Sample injection using sub-µl injector was feasible without flow splitting.

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THE QUEST FOR QUALITY ASSURANCE.

John K. Taylor, Quality Assurance Consultant, 12816 Tern Drive, Gaithersburg, MD 20878.

Data quality is an important issue whenever it is used for decision purposes. Limits of uncertainty must be assigned to every measurement result in order to use it logically. These are best estimated by an on-going quality assurance program, consisting of:

Quality Control—what is done to control the quality of the measurement process, and

Quality Assessment--What is done to evaluate the quality of the data output.

The general principles of quality assurance will be discussed with emphasis on trace analysis and high-accuracy analysis.

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ABSTRACT NOT AVAILABLE

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AN EVALUATION OF THE REPRESENTATIVENESS OF PRECIPITATION VOLUMES MEASURED IN THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK MONITORING PROGRAM.

David S. Bigelow. Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Colorado 80523.

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) monitoring program uses two types of precipitation collectors to estimate the volume of precipitation that is used to calculate wet deposition at and in the various sites, states and regions of the United States and North America where it operates. Each type of collector has limitations that become significant when these devices are used in a standardized manner in the monitoring program.

This paper identifies spatial and temporal bias in precipitation collection efficiency and in rain gage and wet/dry collector volumes. Isopleth maps of the bias are presented and comparisons to the National Weather Service and other U.S. and Canadian deposition networks are made in an attempt to quantify the magnitude of the problem.

272 QUALITY ASSURANCE PROCEDURES NECESSARY FOR LITIGATION RELATED DATA. Kenneth E. Dahlin. Environmental Science and Engineering, Inc., 7332 S. Alton Way, Ste. H-1, Englewood, Colorado 80112

The generation of environmental analytical data to be used in litigation places special requirements on a laboratory generating this data. Not only must the data be of sufficient quality to withstand critical review for technical completeness, but must also meet a host of requirements specified by our legal system. Legal requirements include: Complete and detailed documentation of all sample collection and analysis procedures used; maintenance of sample integrity and accountability throughout the analysis process; continuous critical review of the quality of the analytical data generated by the laboratory; and, scrupulous maintenance of all documentation. ESE has developed procedures that meet these requirements. They include: training of personnel in proper procedures; performance of field and laboratory audits; specification of minimum QC requirements that must be met; use of statistical methods to evaluate analytical results; and, continuous QA review and validation of analysis results. ESE's experience has been that diligent application of these procedures can siginificantly reduce the risk of environmental analysis data being successfully challenged in court.

273 QUALITY ASSURANCE FOR FEED ANALYSIS. S.M. Shakeel Akhtar, Saskatchewan Feed Testing Laboratory, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, S7N 0W0.

Quality assurnace for feed analyses includes three major components. Each of these must be considered in order to ensure the validity of the analytical data and its use in subsequent ration formulation and diagnostic evaluation. The first phase i.e. sampling may incorporate a number of factors that influence the analytical data. Commercially prepared feeds particularly those in the form of pellets or crumbs pose least problems, however, feed mixed by individual producers utilizing grains, forages, and supplements and employing a variety of grinding or mixing implements may be subject to considerable variations. Sampling of fresh plant material for toxicological investigation may require special considerations of the location. The size of the sample submitted for analysis is important. The second phase dealing with the sample preparation prior to the analysis is in most cases easily manageable. Most problems associated with the non uniformity of the samples as received may in large part be compensated by processing a larger portion of the sample. The third phase deals with the analysis of the sample and requires an extensive quality control program including calibration, standardization, monitoring of the repeatability and accuracy of the analysis and participation in quality control check sample program.

274 THREE PROTOTYPE "IN-HOUSE" AQUATIC SEDIMENT REFERENCE SAMPLES FOR THE DETERMINATION OF "TOTAL RECOVERABLE" INORGANIC CONSTITUENTS. Paul N. Johler and Victor J. Janzer, U.S. Geological Survey, 5293 Ward Road, Arvada, CO 80002.

Large numbers of aquatic sediment samples are collected and analyzed each year to provide indications of environmental water quality conditions and changes. Samples commonly are digested with dilute mineral acids and the resulting solutions are then analyzed to determine "total recoverable" concentrations of inorganic constituents of interest. This information is valuable for evaluating environmental pollutants commonly associated with the oxidized surface coatings of aquatic sediments. Many rock, sediment, and soil standards are available for quality assurance purposes, but they are only defined for total decomposition or dissolution methods. The three aquatic sediment reference samples described in this paper however, are believed to be the first intended for the operationally defined "total recoverable" digestions and analysis. The reference samples were prepared from natural sediments collected from the South Platte River in Denver (SED1), the Clark Fork in Montana (SED2), and Barr Lake northeast of Denver (SED3). After the samples were prepared, they were distributed to laboratories participating in the U.S. Geological Survey's Standard Reference Water Sample program. The mineral acid digestion procedures to be used were not specified. Data for 16 to 25 inorganic constituents were reported by 25 laboratories for SED1, by 16 laboratories for SED2, and by 21 laboratories for SED3. Most probable values for most of the analyzed constituents were determined by statistical analysis of the data. "Total recoverable" concentrations of the constituents determined for the three samples ranged from 22.8 mg/g for iron in SED2 to near detection limits for beryllium and cadmium in SED 1 and 3. During the course of the the study, the coefficient of variation improved from a mean of 54.3 percent for constituents determined in SED1 to 28.4 percent in SED3 to 25.0 percent in SED2, the last sample distributed.

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CREDIBILITY, PRACTICALITY AND REALITY AS FACETS OF QUALITY ASSURANCE.

Sylvan Eisenberg Anresco, Inc., 1370 Van Dyke Avenue, San Francisco, CA 94124.

Regulatory authorities in their need for "sharp" analytical data (is the sulfur-dioxide content above or below 10 ppm?) have inspired mandatory reliance on "official" analytical methods such as those defined by the AOAC. Such authorities appear more concerned with giving "credible" testimony in court than with minimizing the need for such testimony by encouraging use of "practical" though not official quality control methodology during production. For example, FDA Regulation 573.920 Selenium permits addition of selenium to animal feeds, but only by means of a premix containing sodium selenite or selenate, and only if each production batch of the premix is analyzed for selenium. This requirement is indeed prudent since each batch of premix may affect 20,000,000 pounds of complete feed. But the AOAC offers four distinct "official" methods, gravimetric, titrametric, fluormetric and AA-Hydride. The latter is the most recent, but requires bomb digestion then ashing with magnesium nitrate. Possibly each method individually will yield credible results, but collectively they may not. If they do not, then one may question which, if any, correspond to reality. None are practical. There must be a way to achieve good, legal, practical implementation of regulations.

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INTERLABORATORY VARIABILITY AND ACCURACY IN TRACE ELEMENT ANALYSES,

John Lengyel, Jr., Conoco Inc., Coal Research Division, 4000 Brownsville Road, Library, Pennsylvania 15129

To assess the reliability of the analysis of trace elements in coal, a blind interlaboratory study of seventeen trace elements in coal was conducted using five different methods of analysis. Four commercial laboratories and our own laboratory analyzed three coal samples three times and an NBS coal standard twice over a period of three years. Each laboratory analyzed for as many of the seventeen trace elements as it was capable of measuring. The techniques used were inductively coupled plasma emission spectroscopy (ICPES), atomic absorption spectroscopy (AAS) which included graphite furnace (GFAA) and hydride evolution (HAA), neutron activation analysis (NAA), proton induced x-ray emission (PIXE) and spark source mass spectrometry (SSMS). Comparison of the interlaboratory results showed a high degree of variability among the participating laboratories. The coefficient of variation ranged from 20 to 120 percent. The intralaboratory repeatability for most trace element analyses was good for all the analytical techniques except spark source mass spectrometry (SSMS). The interlaboratory accuracy results reported for the SRM 1635 standard coal showed a positive bias for most of the elements. The overall average bias was +33%. As used in our laboratory, a combination of the inductively coupled plasma (ICP) and atomic absorption (AAS) techniques provided the sensitivity and ability to analyze 16 of the 17 selected trace elements in coal (F was determined by ion chromatography), and provided the best overall precision and accuracy considering the number of elements analyzed.

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PRIMARY STANDARDS: THE BASIS FOR ACCURACY IN THE KJELDAHL NITROGEN METHOD.

Clifford C. Hach, Scott V. Brayton, and Yu-Sen Chen, Hach Company, 100 Dayton Avenue, Ames, Iowa 50010.

The Kjeldahl nitrogen method consists of two principle steps: 1. sample digestion - Oxidation of organic materials and conversion of nitrogen to ammonium sulfate in sulfuric acid. 2. Conversion of ammonium sulfate to ammonia and subsequent ammonia determination. Various modifications have been made as a result of extensive research on this method with the intention of method improvement. Many operations are involved and numerous sources of error are possible in the over-all analytical procedure, with the error most frequently arising from the digestion step. A reliable method for checking the whole analytical procedure, especially the digestion step, is analyzing primary standard compounds - a variety of compounds with known nitrogen content and varying ease of digestibility. If the exact value of nitrogen is obtained when analyzing the compound with least digestibility the proper performance of the whole analytical systems, with whatever modifications, is established and the accuracy of nitrogen value of a sample, when analyzed under the same conditions, is guaranteed. Several compounds have been evaluated and a set of compounds which meet the strict criteria as primary standards have been developed and prepared. Properties of these compounds and their function as primary standards for the accuracy of the Kjeldahl nitrogen method and quality assurance of analytical data will be presented.

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QUALITY ASSURANCE IN A REGULATORY AGENCY. John A. Winter, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, Cincinnati, Ohio 45268.

The history of quality assurance (QA) in the U.S. Environmental Protection Agency (USEPA) is traced from its establishment as an agency program in 1972, with responsibility for operation assigned to the Office of Research and Development (ORD). Its status was upgraded to mandatory in 1979, by the Administrator, Douglas Costle. The program was further strengthened by the Deputy Administrator, Al Alm, in 1984, when he added the requirement that all environmental data collection activities of USEPA must develop data quality objectives (DQOs). Standardization and application of QA in USEPA is complicated by the wide range of environmental regulations, each with differences in: regulatory timetables, analytes, standards or limits under regulation, and differences in concentrations and sample matrices of interest, which in turn required differences in sample preparation and analytical methodology. QA is further complicated by the wide-difference in capabilities of staff, facilities and instrumentations in the range of public and private laboratories of agencies, industries and dischargers under regulation. QA activities are tailored to the needs of a program such as drinking water, ambient monitoring, or discharge monitoring and yet efforts continue toward standardizations of QA and methodology. Examples are given of QA applied to the various water programs. Conclusions are drawn about current data quality and what changes in QA are expected in the future.

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QUALITY-ASSURANCE PRACTICES IN WATER-QUALITY LABORATORIES OF PUBLICLY FUNDED AGENCIES AND INSTITUTIONS IN COLORADO AND OHIO, 1984. Donna Myers, Carolyn J. Oblinger Childress, and Janet Hren; U.S. Geological Survey, 975 W. Third Avenue, Columbus, Ohio 43212; and Thomas H. Chaney and J. Michael Norris, U.S. Geological Survey, Denver Federal Center, Denver, Colorado 80225.

A multiphase study was conducted by the U.S. Geological Survey in Colorado and Ohio to determine whether water-quality data collected by different organizations for various reasons could be combined and used for regional water-quality assessments. Combining data from diverse sources requires that laboratory (and field) practices used to produce the data be equivalent and meet specific quality-assurance guidelines. Information about laboratory (and field) quality-assurance programs was provided by 12 publicly funded laboratories in Colorado and 17 in Ohio. This information was evaluated against a set of criteria developed from publications of the American Public Health Association, the U.S. Environmental Protection Agency, and the U.S. Geological Survey. Nearly all laboratories reported participation in interlaboratory and intralaboratory testing, adherence to published quality-assurance guidelines, and statistical measures of precision and accuracy. The most commonly referenced test methods are those of the U.S. Environmental Protection Agency. Methods and practices for physical properties, major inorganics, trace metals, nutrients, and organic constituents were examined. In both States, most data generated by water-quality laboratories met a broad set of widely published quality-assurance criteria. Field rather than laboratory criteria limit to a greater degree the amount of data applicable for regional water-quality assessments.

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QUALITY ASSURANCE MONITORING FOR X-RAY FLUORESCENCE ANALYSIS OF TRACE ELEMENTS IN SOLUTIONS. Carl M. Meltzer and Joseph d. Balser, BEEM Laboratory, 1785 Barcelona Street, Livermore, California 94550.

An X-ray Fluorescence Method for analysis of the elements from sodium (Z=11) to Uranium (Z=92) at low levels of concentration (<1 ppm) in solutions has been developed. The basic attributes of this method will be described. Sample Analysis quality control procedures which are appropriate to the method have been developed and will be reported. Features of this analytical method which are relevant to the subject of quality assurance of measurements are the high level of instrument stability, preservation of the samples as analyzed and the inherently smooth variation of instrumental sensitivity for elements across wide ranges in the periodic table.

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A QUALITY ASSURANCE PROGRAM FOR THE ANALYSIS OF VOLATILE ORGANIC CHEMICALS. Annemary T. Liu, Raymond H. Taylor, Kent Adney, Gary Falling and Veronica Simion, *California Water Service Company, 1720 North First Street, San Jose, California 95112.*

Quality results in the quantification of volatile organic chemicals (VOC) are dependent on the quality assurance (Q.A.) programs designed and executed by the analytical laboratory. Q.A. is critical in trace VOC analysis where state-of-the-art measurement technology is used to identify and quantify those chemicals at or near their detection levels. A Q.A. program was designed at California Water Service Company, to encompass all actions taken by the laboratory to achieve accurate and reliable VOC results. Quality control data for 21 purgeable organic chemicals, analyzed by gas chromatography have been compiled over the last three years. The survey objectives were to gather a large database which is representative of VOC occurrance in well water, and to define method acceptability on a routine analysis basis. Overall accuracy parameters range from 85% to 102% recovery for all chemicals measured at high concentrations (≥1 ppb), and 60% to 115% recovery for chemicals measured at lower concentrations. Precision tolerances for all chemicals are less than ±20% relative standard deviation at all concentrations. The precision and accuracy measurements and procedures will be discussed further, as well as standard method detection levels, calibration curves and interlaboratory quality assurance as practiced in the California Water Service laboratory.

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ORTHO-PHOSPHOROUS REAGENT CONTAMINATION FROM SILICA BREAKTHROUGH IN DEIONIZED WATER SYSTEM. *Eric R. Hamilton, William G. Leseman,* Jamie J. Shakar. City of Tallahassee, Water Quality Laboratory 3805 Springhill Road, Tallahassee, FL 32304

An intermittent reagent contamination of the combined reagent for ortho-phosphorous (ortho-p) analysis was found to be caused by a silicomolybdate complex. The heteroblue complex color normally due to the analysis of ortho-p was obtained upon initial preparation of the combined reagent. The blue color intensity was greater than that found from analysis of a 5 ppm ortho-p sample. Contamination checks of glassware, reagents, and techniques showed the cause to be silica contamination in the deionized water (DI) system. The blue complex color was only observed when ammonium molybdate, one of the combined reagents, contained silica. Ammonium molybdate containing 5ppm silica showed increased base lines corresponding to 0.02 ppm ortho-p and a 10% increase in spike recoveries. Conductivity, usually a quick, reliable method to determine DI quality, was not a satisfactory method for measuring uncharged silica compounds. Several methods to determine DI Quality were reviewed.

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DEVELOPING A COMPREHENSIVE LABORATORY QA PROGRAM TO MEET REGULATORY AGENCY REQUIREMENTS. Richard G. Mealy, Toni L. Stovall, and Kathleen A. Carlberg. Enseco - Rocky Mountain Analytical Laboratory, 4955 Yarrow Street, Arvada, Colorado 80002

Commercial environmental testing laboratories are subject to the quality assurance requirements of many governmental agencies. In many instances, the QC requirements are ill-defined or conflicting and the laboratory must continually modify the internally established QA/QC program requirements to comply with client needs. Additionally, the control limit windows for quality control samples, as established in accepted methodologies, are either non-existent, or too wide to be realistically used as laboratory performance indicators. Enseco - Rocky Mountain Analytical Laboratory has developed a Quality Assurance Program to meet the requirements of the various regulatory agencies which emphasizes the use of laboratory control samples (LCS) to monitor laboratory performance. LCS samples are prepared by spiking a designated group of compounds for each method into a standard matrix. The use of a standard matrix for control spikes eliminates the effect of sample matrix interferences on spike recovery, and provides for a much more narrow control limit window. This approach also enables the analyst to make an instantaneous decision regarding the effectiveness of the analytical method and the quality of the data. Laboratory Control Sample results demonstrate more realistic control limit windows for both accuracy and precision.

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QUALITY ASSURANCE FOR CONTRACTED ANALYTICAL SERVICES.

Berwyn E. Jones and Dorothy M. Walker. U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002.

Quality assurance for contracted analytical services begins with incorporation of quality assurance requirements into the contract specifications. Proposals from the bidders are carefully screened for compliance with quality-assurance requirements as well as for evidence that the bidder possesses the resources necessary to perform quality analyses. Analysis of pre-award performance-evaluation samples determines bidders' analytical capabilities. On-site inspection of laboratories prior to award verifies the stated descriptions of facilities, personnel, and equipment, and permits discussion of problems detected in the analysis of performance-evaluation samples. Continuing quality assurance throughout the period of contract utilization documents the precision, accuracy, completeness, and timeliness of analyses. The contract officer monitors performance through the blind insertion of blanks, reference materials, and spikes in sample shipments, and through careful evaluation of data and reports. Finally, communication with contractor and clients is a critical function of the contract officer.

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STATISTICS AND REALITY.

Robert A. Crovelli, U.S. Geological Survey, P.O. Box 25046, MS 971, Denver Federal Center, Denver, Colorado 80225.

This paper is a metaphysical analysis of the nature of the relationship between statistics and reality. Reality is absolute truth that exists independently of ideas concerning it. Statisticians use mathematical procedures to analyze observations of a phenomenal world under certain assumptions. A flow chart is designed to describe the metaphysical relationship between statistics and reality as a system. The physical reality system consists of two main subsystems. The first subsystem is the perceptual process which is diagrammed in detail. A phenomenal world is based on the perceptual process. The second subsystem is the observational process which depends on a phenomenal world.

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THE GEOCHEMICAL APPLICATION OF THE SOLID-SAMPLE ICP-OES METHOD FOR HEAVY-MINERAL CONCENTRATES IN THE PICACHO PEAK AND INDIAN PASS WILDERNESS STUDY AREAS, CALIFORNIA.

Betty M. Adrian and D. E. Detra. U.S. Geological Survey, Denver Federal Center, Box 25046, MS 973, Denver, Colorado 80225.

Commonly heavy-mineral-concentrate samples cannot be analyzed by conventional atomic absorption methods because the samples are too small to provide adequate detection limits. The solid-sample inductively coupled plasma-optical emission spectrographic (ICP-OES) method is a workable method for analyzing heavy-mineral concentrates because it requires only a 60-mg sample for analysis. Lower limits of determination, in parts per million, are As, 1; Au, 0.01; Bi, 0.1; Cd, 0.1; Hg, 1; Pb, 1; Sb, 5; Te, 2; and Tl, 0.5. In our study we analyzed 65 heavy-mineral-concentrate samples from the Picacho Peak and Indian Pass Wilderness Study Areas, Imperial County, California, using the solid-sample ICP-OES method, which gave a wide range of analytical values. An area of moderate to high mineral potential in our study area had been previously located by semiquantitative d.c. arc emission spectrography, atomic absorption, and other instrumental analyses of a variety of sample media, which included rocks, stream sediments, and heavy-mineral concentrates. The previously located areas of moderate to high mineral potential correlate well with the areas located by our supplemental analyses of these 65 concentrates using the solid-sample ICP-OES method. This study demonstrates that the solid-sample ICP-OES method is a valid and useful tool in delineating and mapping areas containing element anomalies.

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SOME (HYDROXYPHENYL)-2-BROMOETHANONE AS ELECTRO-ACTIVE LABELS FOR CARBOXYLIC ACIDS IN LIQUID CHROMATOGRAPHIC DETECTION.

Robert K. Munns, Jeffery A. Hurlbut, Jose E. Roybal, and Wilbert Shimoda. Food and Drug Administration, Animal Drug Research center, 500 U.S. Customhouse, Denver, Colorado 80202.

Three electro-active derivatizing reagents have been synthisized for labeling organic acids that have week chromophoric properties. The esterfication of certain drugs and metabolites allow for their determination at less than 2.5 p mole level. The results of a comparitive study of the three compouds show that the dihydroxyphenyl ester will form at room temperature and is oxyidized at a potential as low as +0.4 volts. The conditions of reaction, and LC retention data as well as the detection properties for a variety of organic acid are given. Special emphasis was paied to antibotics drugs.

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HPLC DETERMINATION OF TETRACYCLINE RESIDUES IN ANIMAL FEEDS. Elizabeth E. Martinez and Wilbert Shimoda. Food and Drug Administration, Animal Drug Research Center, 500 U.S. Customhouse, Denver, Coloraso 80202.

The tetracyclines (TCs) are antibotics commonly used in animal feed for medication and growth promotion. A liquid chromatography method for the multiresidue determination of tetracyclines in feeds is described. The levels of quantitation are 10 ppm in each for Tetracycline HCl (TC), Oxytetracycline (OTC), and Chlortetracycline HCl (CTC); and the detection limit is 40 ppb for each. The method shows linearity between 2.5 and 100 ppm. The procedure involved double extraction with pH 2.0 and pH 4.5 McIlvain buffers, a Sephadex LH-20 column purification, a Nova-Pak, C18 column separation and 370 nm detection. The recoveries for 10 ug/g of each Tetracycline in multiresidue feed samples ranged between 55.8-75.5% for OTC, 71.6-100% for TC, and 22.4-60.6% for CTC. The TCs are confirmed by Thin Layer Chromatography.

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HIGH PRESSURE LIQUID CHROMATOGRAPHIC DETERMINATION AND CAPILLARY GC/MS CONFIRMATION, USING MULTIPLE ION DETECTION OF DIMETRIDAZOLE (DMZ) AND IPRONIDAZOLE (IPR) IN SWINE FEEDS. Jose E. Roybal and William Morris. Food and Drug Administration, Animal Drug Research Center, 500 U.S. Customhouse, Denver, Colorado 80202.

A simple and rapid method is described for the determination if dimetridazole (DMZ) and ipronidazole (IPR) in swine feeds at various levels (0.11-110 ppm). The drugs are released from feed by prewetting with buffer, followed by extraction with either methanol or methylene chloride, depending on the drug level; if necessary, an acid-base cleanup is used before the liquid chromatographic analysis. The analytes are separated on a C18 column and monitored at 320 nm for detection and quantitation.

Capillary GC/MS analysis with MID provides EI mass spectral confirmation for low level (0.1) residues of DMZ and IPR. Consistency in the ion ratios (5 ions in DMZ and 6 in IPR) permits identification of these compounds by electron ionization MS.

Quantitative results obtained by capillary GC/MS with MID are comparable for both compounds to results obtained by liquid chromatography.

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DETERIORATION OF COQUINA BY ACID RAIN AT CASTILLO DE SAN MARCOS NATIONAL MONUMENT. Joni A. Simms. USG Corporation, 700 N. Highway 45 Libertyville, Illinois 60048. David G. Rands. Southern Illinois University at Edwardsville, Chemistry Dept. Box 65C, Edwardsville, Illinois 62025.

The Castillo de San Marcos is a National Parks Services monument located in St. Augustine, Florida. The monument was constructed from 1672 to 1695 and was built using coquina, a natural mineralogical composite. Recently, park officials, alarmed by degradation of walls of the monument, have been led to believe that acid rain is one of the causes of the severe damage. Increasing rainfall acidity and reports of damage of this type led to this study on the effects of acid rain. Because the monument was constructed of a very porous composite, a great amount of rainfall seeps through the walls of the structure and runs into the interior rooms. Observation of weathered coquina at the Castillo site indicates that the deterioration of coquina leaves loose Donax shells, due to the dissolution of the calcite which binds these shells. This dissolution of $CaCO_3$ appears to be the main effect of acid rain's action on the coquina at the monument. For this reason, our data are interpreted on the basis of $CaCO_3$ solubility in various acidic solutions. This presentation will give the results of our study on the solubility of calcite in these acidic solutions.

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IMPLEMENTATION OF A LABORATORY INFORMATION SYSTEM ON A UNIX DRIVEN FT-IR.

Joseph J. Rafalko. Hoechst Celanese Research Company, 86 Morris Aveune, Summit, NJ 07901

One of the advantages of using a Unix operating system for FT-IR is the ability to run third party software. We have integrated Informix, Relational Database Systems, Inc., and Mattson's FT-IR software package with Unix shell programming to form a laboratory information system for a high volume industrial laboratory. The primary benefits have been time savings and increased productivity. Time savings have resulted from fewer data entries, faster information retrieval, and templated reports. The menu driven system has also led to fewer mistakes. The system has the following additional capabilities: 1) reports can be electronically mailed to customers (via a mainframe VAX) and 2) Informix database information can be combined with spectral library searching. In this talk a detailed description of the operation and implementation of this system will be given.

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SURFACE ACOUSTIC WAVE VAPOR DETECTION OF ORGANOPHOSPHORUS COMPOUNDS.

Raymond E. Miller, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423; John A. Parsons, Geo-Centers Inc., 4710 Auth Place, Suitland, MD 20746

Results will be reported on an investigation of the detection of dimethyl methylphosphonate (DMMP) using a Surface Acoustic Wave (SAW) vapor detector. The principle upon which the SAW concept is based is the reversible absorption of various chemical species by absorbent coatings that are sensitive to a given vapor. This device incorporates 158 MHz dual delay line oscillators coated with various polymeric films. A screening effort was undertaken to determine which coatings may be effective in DMMP detection. It will be shown that DMMP vapors may readly be detected at concentrations as low as 0.5 ppm. Experimental equipment and techniques, a method for vapor generation and analysis, and results obtained, will be presented. Detection data, consisting of calibration curves that define the device sensitivity and selectivity, will also be presented.

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SPECTROPHOTOMETRIC STUDIES OF THE IRON(III)-THIOCYANATE COMPLEXATION REACTION IN MIXED SOLVENTS.

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The complexation reaction of iron(III) with the thiocyanate ion in aqueous/mixed solvent media has been the subject of numerous studies published that (1) determined the stoichiometry of the complex species present in various solution environments and (2) developed spectrophotometric analyses procedures for iron applicable to various water samples. In spite of this, considerable uncertainty remains regarding the reproducibility of existing analytical procedures and the optimum conditions for complex formation in aqueous/mixed solvent media. This study was conducted to ascertain the optimum conditions under which the iron(III)-thiocyanate complexation could be more reliably accomplished and, thus, a more reproducible spectrophotometric analysis procedure devised. The study results to be presented include: (1) the effects of variables such as solvent composition, time, acid used, reagent concentration, etc., (2) determination of the stoichiometry of the complex species present, (3) tentative conditions for an improved spectrophotometric analysis procedure, and (4) recovery studies involving both synthetic and natural water samples.

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THERMODYNAMICS OF PROTON TRANSFER EQUILIBRIA OF TRIFLUOROACETYLPINACOLONE IN AQUEOUS DIOXANE MEDIA.

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Thermodynamic proton-ionization constants, $^{T}pK_a$, of *1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione*, also commonly called as trifluoroacetylpinacone (TFAP) have been determined pH-metrically in 20-70% dioxane-water mixtures at 25 and 35 ± 0.01°C applying an empirical pH correction for mixed hydro-organic media. The pK_a's in aqueous medium (at 0% dioxane) are obtained following the method of extrapolation and least-squares. TFAP is found to be very weak monoprotic acid. $^{T}pK_a$'s do not vary linearly with the reciprocal of dielectric constant of the medium, but a plot of $^{T}pK_a$ vs. the mole fraction of dioxane is linear at a given temperature. The 'true constant' K_a' and the solvation number, n, in the expression $[H^+][A^-]/[HA] = K_a'[S]^n = K_a^*$ for this diketone have been evaluated by analyzing the experimental data mathematically. Values of ΔG°, ΔH° and ΔS° are also computed. Positive value of ΔH° found in aqueous-dioxane media for this fluorinated derivative indicates the endothermicity of the relevant proton enolization reactions. Temperature, medium as well as substituent effects are briefly discussed.

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TECHNOLOGY FOR THE MEASUREMENT OF TRACE METALS IN ATMOSPHERIC PRECIPITATION USING ICP-MS,

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Inductively coupled plasma-mass spectrometry was used to evaluate the accuracy and collection performance of two recently developed rain collector prototypes. The collectors employ a funnel-shaped collecting surface, trace metal preconcentrating resin, and a sample collection and storage vessel. The collectors were designed to operate unattended and to assemble composite rain samples over a 2 to 4 week period. The major difference in the collector designs was the preconcentration process; one employed a cartridge preconcentrator while the other used a batch preconcentrator. Concentration factors were dependent on the volume of the composite sample. Sample volume losses due to evaporation were eliminated using a correction based on field control samples. Trace metals were preconcentrated in the field on 50-100 mesh Chelex 100 resin and subsequently eluted using less than 20 mL of 2 M HNO_3 prior to analysis. Isotope dilution or concentration calibration methods were used to quantitate Ba, Be, Cd, Co, Cu, Mn, Ni, Pb, Sr, and Zn in the eluent. Recovery efficiencies were nearly 100 percent in laboratory experiments and results from field experiments comparing samples collected with and without preconcentration correlated within experimental error. Precipitation collectors employing preconcentration techniques enables analyte determinations at part per trillion concentration levels in composite rain samples.

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PHOTOLYSIS OF AMINO ACIDS SORBED ONTO IRON-OXYHYDROXIDE (Goethite).

Marvin C. Goldberg and Kirkwood M. Cunningham, U.S. Geological Survey, P. O. Box 250446 MS 424, Lakewood, CO 80225.

When photolyzed, several amino acids sorbed to Goethite, were shown to be able to reduce iron(III) from the Goethite lattice. The lyotropic series of iron production is: aspartine > glutamine > serine > aspargine > arginine > glycine > alanine. Mechanistically, the carboxyl group on the amino acid sorbs to the surface of goethite. During photolysis sufficient activation energy is imparted to the system to allow the adsorbed amino acid to donate an electron to the kernel iron(III) atom. This results in reduction of lattice Fe(III) to Fe^{+2} and the formation of a carboxy radical on the amino acid which is easily oxidized to CO_2. The $RHC{\cdot}NH_2^+$ radical is simultaneously formed and rearranges to the RHC=NH imine, which is rapidly hydrolyzed to the equivalent aldehyde. Analyses of samples, taken at regular intervals over a six hour period for the aldehyde product, shows a linear production with respect to the lattice Fe^{+2} released to solution. The ratio is not unity indicating more than one reaction sequence takes place. The reaction pathways and the kinetics of each reaction step are given.

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THREE DIMENSIONAL CHROMATOGRAMS OF A LASER FLUORESCENCE SPECTROPHOTOMETRIC DETECTOR IN HPLC, Yuko Arai and Toshihiko Hanai, Gasukuro Kogyo Inc., 237-4 Sayamagahara, Iruma 358 Japan.

The analysis of three dimensional chromatograms of an ultra-violet absorption spectrophotometric detector is a very powerful tool for optimization of separation conditions, and for qualitative analysis of components in effluent. About 60 spectra of the components in urine were automatically displayed after their separation by reversed-phase mode liquid chromatography and several peaks were identified from their spectra. Fluorescence detectors, on the other hand, are sensitive and selective monitors for HPLC. A helium-cadmium laser (325nm, 10 mW) was used as an excitation source to obtain strong fluorescence spectra, and the spectra were measured by a photodiode array monitor. When this instrument was applied to the analysis of vitamins, the sensitivity of the detector was similar to that measured by a conventional fluorescence detector. This laser fluorescence detector was also applied to the analysis of the components in urine separated by reversed-phase mode liquid chromatography.

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ANISOTROPY IN THE PROTON NMR PARAMAGNETIC SHIFT OF CYCLOOCTATETRAENE AND CYCLOPENTADIENE ANIONS COORDINATED TO U(IV). Bruce R. McGarvey and Steven T. Nagy. Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9G 3P4, Canada.

Variable temperature proton NMR studies at 90 MHz were made on solid powders of uranocene and tris-cyclopentadienyl chloro-uranium(IV). Anisotropies were observed in the spectrum of uranocene at all temperatures which became very pronounced at the lowest temperatures ($\sim$90K). The anisotropies are too large and of the wrong shape to be assigned to the dipolar shift portion of the paramagnetic shift. It will be shown that the bulk of the large anisotropy must be due to a large anisotropy in the transferred spin component of the paramagnetic shift. This is the part of the paramagnetic shift that most investigators have called the "contact shift" and have assumed to be isotropic in nature. Our results demonstrate in a dramatic fashion that the "isotropic contact shift" is in fact very anisotropic in uranocene. A pronounced anisotropy of similar magnitude but opposite sign has also been found in tris-cyclopentadienyl-chloro-uranium(IV).

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DETERMINATION OF LOW AMOUNTS OF CARBOXYLATE IN POLYACRYLAMIDE USING FT-IR. James E. Tackett. Marathon Oil Company, Exploration and Production Technology, P.O. Box 269, Littleton, Colorado 80160.

Several different methods have been used for measuring the relative amounts of amide and carboxylate groups in polyacrylamide and partially hydrolyzed polyacrylamide samples. Acid titration, the Dow color test, C/N ratios, infrared spectroscopy and C13NMR are among the techniques discussed in the literature. While some of these techniques provide adequate results when the carboxylate content is greater than 5 to 10%, their use is limited when less than 3% carboxylate groups are present. We have developed an FT-IR method that can provide useful data when the carboxylate content is as low as 0.2%. To accomplish this low level of detection it is necessary to cast uniform films on AgCl disks, and carefully control the spectral subtraction step. Calibration is perhaps the most difficult task.

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ACETYLCHOLINE RECEPTOR—AGONIST BINDING: RESULTS FROM PROTON NMR T_1 MEASUREMENTS AND 2D-NOE'S,

Ronald W. Behling, Tetsuo Yamane, Gil Navon, Michael J. Sammon, and Lynn W. Jelinski, AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Selective proton NMR T_1 measurements were used with nicotine titrations to determine relative binding constants for nicotine, acetylcholine, muscarine, and carbamylcholine binding to purified acetylcholine receptors from *Torpedo californica*. The results show that (1) binding to the receptor can be measured rapidly and directly with T_1 measurements; (2) specific and nonspecific agonist binding can be distinguished if a specific inhibitor is available; and (3) the receptor-ligand interaction produces a large change in the selective T_1 even at agonist concentrations 100x greater than the receptor concentration. These measurements provide a rapid way to measure drug binding when only small amount of receptor is available. The conformation of acetylcholine (ACh) has been determined in the free and bound states by proton NMR 2D-NOE's. The conformation of ACh is distinctly different in the free and bound states with the conformational change probably resulting from a rotation about the ester bond from the *anti*-planar conformation in the free state to *syn*-planar in the bound state. The significant difference between the free and bound state conformations implies that structure-activity studies based solely on molecular modelling strategies must be approached with caution.

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SOLUTION OF THE ^{14}N-^{15}N SPECTRAL OVERLAP PROBLEM USING PULSE EPR.

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Short pulse saturation recovery (SR) electron spin resonance (ESR) methods have been used to measure lateral diffusion of a nitroxide-labeled cholesterol analog (cholestane spin label, CSL) in multilamellar liposomal dispersions. Nitroxides with ^{14}N and ^{15}N isotopes introduced together were employed. SR experiments were performed on samples containing $^{14}NCSL$:$^{15}NCSL$ pairs, and recovery signals were analyzed for initial conditions and multiexponential time constants by computer simulation. Rate equations describing the system were written and solved. We have investigated the complication that occurs from overlap of ESR spectral fragments from ^{14}N and ^{15}N moieties. The interesting result is that the time constants of the multi-exponential signals are independent of ESR line shape and position. The time constants contain the combinations of electron spin lattice relaxation time T_{1e} for both isotopes, and the Heisenberg exchange rate constant K_x. From K_x the lateral diffusion constants of CSL in DMPC were calculated ($D = 1.7 \times 10^{-8}$ at 27°C and 2.7×10^{-8} cm^2/s at 37°C). It is shown that short pulse saturation recovery methods are able to overcome the ESR spectral overlap problem that is encountered in conventional ESR and CW ELDOR studies of spin-spin interactions. The present method can be directly extended to more complex situations involving spin labels in different environments with physical and perhaps chemical exchange.

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RECENT EPR STUDIES OF INDIAN COALS

S.K. De, Dr. S.K. Srivastava

By obtaining EPR Spectrum, the following subjects have been studied. (a) Characterisation and Irradiation effect on coal, (b) Catalyst effect for gasification of coal. One EPR Spectrometer with a rectangular cavity in TE102 mode has been used for the above work. Different types of Indian coals e.g. Bituminous, Sub-bituminous and lignites are treated with Nickel Nitrate, vapour HNO_3, liquid HNO_3 and with -ray and EPR spectrum were recorded before and after the above treatments. In the case of coals/lignites when treated with Nickel nitrate (which was found to be very much efficient for low temperature steam gasification to yield H_2) show that the free radicals concentration and g-value decrease and H_o increase on addition of Nickel to Coal/Lignites. The raw lignites contain free radicals. When these raw lignites are treated with vapour HNO_3, the free radical concentration increase and H_o, Line width and g-values change. When the lignites are treated with liquid HNO_3, free radicals increase still further. It is observed that in ordinary Indian Samla coal free radical concentration is very high (comparable to DPPH concentration). The above results have been interpreted by EPR.

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A 9 GHZ LOOP-GAP ENDOR SPECTROMETER, R. A. Isaacson and G. Feher, University of California, San Diego, La Jolla, CA 92093

A sensitive ENDOR spectrometer capable of operation down to 1.3 K is described. For a fixed sample volume, typically $\leq 30\lambda$ its sensitivity is more than 10X that of a Bruker TM_{110} system. Very low ENDOR background baseline and drift characteristics are obtained from a silyered-quartz 2 gap loop-gap resonator (LGR). The EPR enhancement factor, Λ^2, for a non-saturating point sample in the LGR compared to a standard TE_{102} cavity (1) is 5 to 7 for an LGR length of 1 cm. Optimum ENDOR signals for protons in aqueous samples at room temperature can be obtained typically with a 100W RF amplifier instead of a 500W unit needed with TM_{110} cavities. This spectrometer has been used to study proton, deuteron, and nitrogen hyperfine couplings in photosynthetic reaction centers of Rb. sphaeroides (2).

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AN ESR STUDY OF THE CONFORMATION OF THE TRANSIENT GERMANIUM-CENTRED TRIS-(2-PHENYL-2-METHYLPROPYL)GERMYL RADICAL.

Manfred Lehnig, Wilhelm P.Neumann, und Elisabeth Wallis. FB Chemie, Universität Dortmund, Postfach 500 500, D-4600 Dortmund 50

ESR data are given for the tris-(2-phenyl-2-methylpropyl)germyl (trineophyl) radical. At T 60°C, the spectrum shows a septet due to the interaction of the unpaired electron with the six methylene protons, indicating their equivalence on the ESR time scale. As the temperature is lowered to -120°C, an alternating linewidth effect is observed, indicating the equivalence of the two protons of the methylene groups. This inequivalence shows that the radical has a pyramidal structure which is rigid on the ESR time scale at low temperatures. The exchange of the methylene protons between the two inequivalent positions is caused by hindered rotation around the C-Ge bonds. The preferred conformation of the radical has been determined and compared with those of similar tin-centred radicals. From the line broadening an activation energy of 5.4± 0.8 kcal/mol for this exchange and a lifetime of the conformation of $3.6 \pm 0.3 \cdot 10^{-10}$ s at 23°C are determined.

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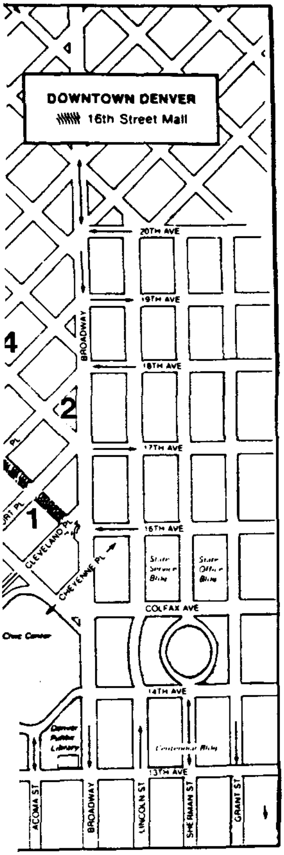
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