Rocky Mountain Conference on Magnetic Resonance

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Article 1

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20th ANNUAL ROCKY MOUNTAIN CONFERENCE
ON
ANALYTICAL CHEMISTRY

AUGUST 7, 8, 9, 1978

DENVER CONVENTION COMPLEX
DENVER, COLORADO

SPONSORED JOINTLY BY THE

ROCKY MOUNTAIN
SOCIETY FOR APPLIED SPECTROSCOPY

AND

ROCKY MOUNTAIN
CHROMATOGRAPHY DISCUSSION GROUP

The Rocky Mountain Conference an Analytical Chemistry presents an opportunity for chemists and spectroscopists to become aware and informed of new developments in analytical chemistry and spectroscopy.

The 121 papers include-internationally prominent scientists throughout the United States who will discuss the results of their work with conference attendees.

Exhibits of new chemical products and instruments will be on display during the three days.

Plan to attend the 20th Rocky Mountain Conference and take advantage of this opportunity to learn about new areas of research and maintain your expertise in your field.

While in Denver plan to enjoy beauty and the recreational facilities within the Rocky Mountains.

PROGRAM

ANALYTICAL CHEMISTRY - GENERAL
SYMPOSIUM OH ENVIRONMENTAL CHEMISTRY
SYMPOSIUM ON GAS CHROMATOGRAPHY/MASS SPECTROSCOPY .
SYMPOSIUM ON EPR
SYMPOSIUM ON NMR OF MACROMOLECULES
SHORT COURSE ON RECENT ADVANCES IN ION-SELECTIVE ELECTRODES

REGISTRATION

Admission.to all technical sessions requires a registration badge. Those planning to attend the conference are encouraged to preregister using the form provided.

Preregistration forms are to be mailed to:

Dr. Daniel A. Netzel
Laramie Energy Research Center
P.O. Box 3395, University Station
Laramie WY 82071

Valuable.time will be saved if you preregister. The registration desk will be located in the lobby of the Executive Tower Inn and at the Denver Convention Complex during the hours listed below.

REGISTRATION HOURS AND LOCATIONS

Sunday, August 6, Executive Tower Inn	*kzQQ* PM–8:00 PM
Monday, August 7, Denver Convention Complex	8:00 AH–4:00 PM
Tuesday, August 8, Denver Convention Complex	8:00 AM–4:00 PM
Wednesday, August 9, Denver Convention Complex	8:00 AM–12:00 PM

REGISTRATION FEE

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

VISITOR INFORMATION

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

SHORT COURSE

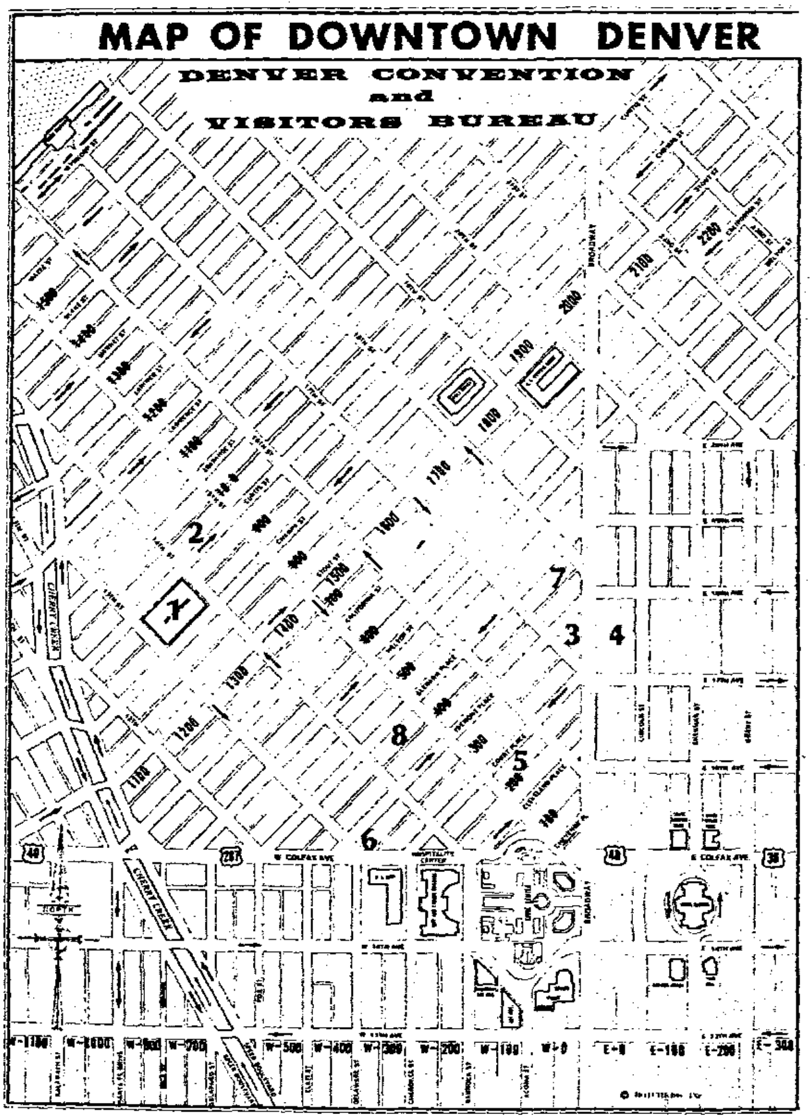
Orion Research, Inc. will present a free short course on "Ion-Selective Electrodes." The course will be 2 1/2-3 hours and will include an introduction to the subject of ion-selective electrodes as well as recent advances in the use of an ammonia electrode for rapid determination of high and low nitrogen concentrations in various types of samples.

SOCIAL FUNCTION

All Conference attendees are invited to a cash-bar mixer on Monday, August 7, from 5:00 PM to 7:30 PM at the Executive Tower Inn. The Conference banquet for all Conference attendees will be given Tuesday, August 8, from 6:00 PM to 9:00 PM at the Executive Tower Inn. Dr. Paul Rappaport, Director of the Solar Energy Research institute in Golden, Colorado has been invited as the after-dinner speaker. It is important that you check the box on the preregistration form if you are attending the banquet. Please include the banquet dinner cost of $7-00 per person with your registration fee.

HOTEL ACCOMMODATIONS

Hotel accommodations are the responsibility of the conference attendees. However, rooms at the Executive Tower Inn have been reserved for those attending the Conference. It is strongly urged that reservations be made as early as possible since Denver in August is abound with tourists. Approximate rates for the Executive Tower Inn and other hotels as well as a map of the downtown Denver area are given below:



	Single	Double/Twin
The Brown Palace Hotel **321 17th Street** **Denver CO** 80202 **Ph: (303) 825**-3111	**$33-53**	**$40-60**
Cosmopolitan 1780 **Broadway** **Denver CO 80202** *Ph:* **(303) 861-9000**	**$24-34**	**$30-40**
Denver Hilton Hotel **1550. Court Place** **Denver CO 80202** Ph: (303) 893-3333	**$31-42**	**$41-52**
Denver Marina Hotel 303 **West Colfax** **Denver CO . 80204** **Ph:** (303) 292-**9010**	$20-27	**$24-31**
Executive Tower Inn **1405 Curtis Street** **Denver CO 80202** **Ph:** (303) **571**-0300	$28 **up**	**$36 up**
The Fairmont **1755 Glenarm Street** **Denver CO 80202** **Ph:** (303) **534-3755**	**$35-55**	**$50-70**
Holiday Inn **Denver Downtown** **1450 Glenarm Place** **Denver CO 80202** **Ph:** (303) **573-1450**	**$26**	**$33**

1. Convention Complex
2. Executive Tower Inn
3. Brown Palace Hotel
4. Cosmopolitan Hotel
5. Denver Hilton Hotel
6. Denver Marina Hotel
7. The Fairmont
8. Holiday Inn — Downtown Denver

EXHIBIT HOURS

Monday, August 7	9:00 **AM**-5:00 **PM**
Tuesday, *August* 8	9:00 **AM**-5:00 **PM**
Wednesday, August 9	9:00 **AM**-12:00 **AM**

CONFERENCE EXHIBITORS (as of 5/15/78)

The exposition of products and services will be located on the first floor of the Denver Convention Complex. These exhibits will provide an excellent opportunity for your enjoyment and further *education and* enlightenment.

In order to take full advantage of the show we offer you an exhibit watcher's guide:

1. Plan to visit - set aside a special time in your busy conference schedule.
2. Browse - you'll surely miss something of value to you if you merely peek in.
3. Look - see them all; there's always something new under the sun.
4. Listen - the exhibitor is ready to talk with you about his display.
5. Get the facts - don't depend on rumors.
6. Follow up when you get home - exhibitors are glad to help throughout the year; not just during meetings.

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FOR ADDITIONAL BOOTH SPACE CONTACT:

Dr. Bill Beard
USDA-ARS
P.O. Box E
Fort Collins CO 80522
303-482-5733

OFFICERS OF THE ROCKY MOUNTAIN SECTION OF THE SOCIETY FOR APPLIED SPECTROSCOPY AND THE ROCKY MOUNTAIN CHROMATOGRAPHY DISCUSSION GROUP (1977-78)

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20Th ANNUAL ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

Chairman; Daniel A. Netzel

Committee Chairmen:

Publicity: Robert H. Heidel, Jerry Turbett
Printing: Roland Manning, Jerry Turbett
Banquet and Mixer: Duane Hunter, Steve Valente
Exhibits: Bill Beard
Facilities: Keith Grossaint
Visitors Information: Howard Taylor

Analytical Chemistry - General: Daniel A. Netzel
Symposia on Environment Chemistry: Howard Taylor, *Francis* McDonald
Gas Chromatography/Mass Spectroscopy: Frank D. Guffey, Michael Aaronson
EPR: Gareth Eaton
NMR: Daniel A. Netzel

21st Annual Rocky Mountain Conference Chairman: Howard Taylor

1978 PROGRAM SCHEDULE

		Monday	Tuesday	Wednesday
ANALYTICAL CHEMISTRY GENERAL PAPERS	AM	SESSION I 2nd Floor Rooms A,F	SESSION II 2nd Floor Rooms A,F	SESSION III 2nd Floor Rooms A,F
	PM			
SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY	AM	SESSION I Water Quality 2nd Floor Rooms B,E	SESSION II Air Quality 2nd Floor Rooms B,E	
	PM			
SYMPOSIUM ON GC/MS	AM	2nd Floor Rooms C,D		
	PM			
SYMPOSIUM ON EPR	AM		3rd Floor Rooms C,D	
	PM			
SYMPOSIUM ON THE NMR OF MACROMOLECULES	AM	SESSION I Macromolecules in the Solid State 3rd Floor Room A,F	SESSION I--Cont'd 3rd Floor, Rooms A,F	SESSION IV Polymers 3rd Floor Rooms A,F
	PM		SESSION II General NMR Techniques 3rd Floor, Rooms A,F	
	AM		SESSION III Biopolymers 3rd Floor Rooms B,E	
	PM			
POSTER SESSION	AM			
	PM		1:00 to 3:00 PM 1st Floor Exhibit Area	
SHORT COURSE ON ION SELECTIVE ELECTRODES	AM			2nd Floor Rooms B,E

ANALYTICAL CHEMISTRY

GENERAL PAPERS

D. A. Netzel, Chairman

GENERAL SESSION I Second Floor, Conference Rooms A,F

Monday Morning - Dale Lawlor, Presiding

9:00 Introduction - Daniel A. Netzel

9:05-1 RECENT ADVANCES IN LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL DETECTION, R. E. Shoup, C. S. Bruntlett, and P. T. Kissinger, Purdue University.

Thin-layer amperometric detectors for liquid chromatography were first devised six years ago and are now commonplace in many biochemical and pharmaceutical laboratories. The applicability of these detectors to trace analysis problems depends largely on the compatibility of the chosen chromatographic conditions (for the electroactive species of interest) with those of the electrode. In addition to yielding the desired separation, the mobile phase must also give very low residual currents, remain inert to the electrode surface, and be optimized (pH, ionic strength, dielectric constant) for maximum heterogeneous electron transfer. For these reasons, most separations have been performed with aqueous buffers or those containing only small amounts of CH_3OH or CH_3CN, at potentials of +1.2 V (vs. SCE) or less. The use of mobile phases with little or even no H_2O present would be advantageous for several reasons. These include the ability to elute electrochemically active, highly hydrophobic substances from reverse phase materials in a reasonable amount of time, the use of normal phase LC in addition to the reverse phase and ion exchange modes presently employed, and the ability, with rigorously dried solvents, to operate the detector at potentials as great as ±2.5 V (vs. SCE) without encountering detrimental background currents. The extension of LCEC to non-aqueous mobile phases will be discussed and the restrictions on the electrode materials and cell design will be reviewed. New thin-layer cell designs and the procedures necessary for successful non-aqueous LCEC operation along with several examples of typical separations will be presented.

9:35-2 OPTIMIZING RESOLUTION IN HIGH PERFORMANCE LIQUID CHROMATOGRAPHY BY SYSTEMATICALLY INVESTIGATING SECONDARY SOLVENT EFFECTS,

J. V. Greenwood, Spectra-Physics.

Recently, Bakalyar, McIlwrick, and Roggendorf [Journal of Chromatography, 142 (1977) 353-365] published a paper on Solvent Selectivity in Reverse Phase Chromatography. Selectivity was studied for eleven functional groups. Solvents were classified in terms of polarity and functional group selectivity. Their data indicated that solvent polarity does not accurately reflect eluting strength for all solutes. Strength is actually the sum total of three types of molecular interactions acting concurrently, e.g., dispersion, orientation, and hydrogen bonding. Following a brief discussion of solvent selectivity, general guidelines for optimizing resolution will be presented. Examples of how these guidelines can simplify method development will be shown.

10:05 Break

10:30-3 CHARACTERIZATION OF IMPURITIES IN BIDENTATE ORGANOPHOSPHORUS COMPOUNDS BY HPLC AND GC/MS, K. J. Grossaint, M. L. Grooms, J. D. Navratil, and L. L. Martella, Rockwell International.

Bidentate organophosphorus compounds, such as dialkyl-n,n-dialkyl carbamoyl phosphonate and the analogous carbamoyl methylene phosphonates, extract actinides well from 7M nitric acid solution. However, commercially available extractants contain impurities which interfere with back-extraction of the actinides from the organic phase.

The impurities largely resulted from residual reactants and thermal degradation of the product phosphonate during synthesis. The thermal stability problem also contributed to the difficulty of purification by standard distillation techniques.

The effort reported in this paper was concerned with developing methods for identifying and measuring concentration of the impurities. These methods could then be used to obtain correlations of extraction efficiency and purification technique with impurity content. The analytical problem was twofold: (1) to separate and identify the impurities, and (2) to develop standard response curves for the components.

High performance liquid chromatographic separation and gas chromatography-mass spectral characterization were selected to perform the required analyses.

The impurity components included several innocuous compounds, (e.g., hydrocarbon solvent and alkylhalide), which contributed only to a dilution of the extractant. Some potential complexing compounds such as phosphate and phosphonate esters, and alkylaminoamides were observed.

Response factors were obtained by injection of standard mixtures, where sufficiently pure compounds were available. For some impurities, the response factors were determined by injection of components recovered from the HPLC separation, or were inferred by difference calculations.

11:00-4 HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY IN THE ANALYSIS OF FATTY ACID COMPOSITION OF *VIBRIO PARAHAEMOLYTICUS* AND *VIBRIO CHOLERAE*,

L. D. Mell and S. W. Joseph, Naval Medical Research Institute.

Reversed-phase high performance liquid chromatography was used to identify cellular fatty acids isolated from *Vibrio parahaemolyticus*, an estuarine microorganism associated with diseases of marine and estuarine animals and seafood-borne enteritis in man, and *Vibrio cholerae*, a similar pathogenic microorganism. Liquid chromatography was chosen as an. aid for taxonomic identification of these bacteria since recent studies have shown that the fatty acid composition of bacterial cell envelopes can readily be identified using reversed-phase techniques and with greater sensitivity and selectivity than that observed with gas chromatography.

All analyses were conducted using a Waters Associates, Inc. Model 20k liquid chromatograph, Model 440 absorbance detector and Model 660 solvent programmer for gradient elution. Aliquots of saponified bacterial mixture were extracted with chloroform, dried under nitrogen and resuspended in DMF containing the UV tag p-bromophenacyl bromide. After dissolution, the reaction mixture was heated at 65°C for 15 minutes and aliquots of the reaction mixture injected into the liquid chromatograph. Derivatized fatty acids were separated using two mBondapak C_{18} reversed-phase columns in series with a Whatman ODS guard column. The solvent system consisted of deionized water and acetonitrile. The solvents were programmed from 40/60% to 100/0% acetonitrile/water over a three-hour period using curve 5 of the solvent programmer and a flow rate of 1 ml/min. The separation was continued for 60 minutes after reaching final conditions.

Derivatized fatty acids were detected at 25k nm and identified by comparison of retention times with standards. In the bacterial strains studied, C12, C14, C15, and C16 fatty acids had concentrations similar to those determined previously by gas chromatography. There was also evidence of CI8, Cl8:l, CI8:2, and C20 fatty acids which have not been reported. The high-performance liquid chromatographic technique showed improved sensitivity and selectivity over standard, gas chromatographic techniques and provided additional information for taxonomic identification of bacteria.

11:30-5 APPLICATION OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY TO THE RECLAMATION OF EMULSIFIABLE OILS, T. Osbourn and G. Mantelli, Coors Container Company.

With the rapid depletion of our natural resources and the associated rising costs for petroleum related raw materials, Coors Container Company decided to determine the feasibility of reclaiming emulsifiable oils used in our aluminum can manufacturing process.

The analytical requirements for reclaiming the oil under study required a number of quantitative determinations which were time consuming and not specific enough for this project. HPLC offered the advantage of determining the required information and in a much shorter time frame.

This paper discusses the HPLC procedure and presents the results obtained which enabled Coors Container Company to successfully reclaim our present source of emulsifiable oil.

Monday Afternoon - Steve Valente, Presiding

2:00-6 NEW "HIGH SOLIDS" ATOMIZATION SYSTEMS FOR ANALYTICAL ATOMIC SPECTROSCOPY, S. Hughes and R. C. Fry, Kansas State University.

The increasing use of atomic spectroscopy in the trace level monitoring and screening programs of clinical, environmental, and industrial laboratories has created a need for faster and more "preparation free" atomization systems. Sample preparation (drying, ashing, digestion, dissolution, etc.) of complex sample materials often proves to be the time consuming step for atomic absorption or ICP emission analysis.

This presentation will include the design and operational characteristics of new "high solids" atomization systems that provide faster and more "preparation free" assays of samples as complex as evaporated milk concentrate, tomato sauce, whole blood, urine, sea water, etc. Means of convenient sample introduction on a high sensitivity basis have been developed. The particle size behavior of suspended solids has been studied in these systems. The role of potentially interfering molecular spectra and light scattering induced by dissolved sugar and salt, and suspended solids concentrations as high as 50% will be discussed.

2:30-7 A METHOD FOR THE DETERMINATION OF COPPER, ZINC, AND COBALT IN PLANT MATERIAL BY ATOMIC ABSORPTION SPECTROSCOPY, D. R. Boline, M. J. Hall, and J. D. Parli, Emporia State University.

A method of analysis for copper, zinc and cobalt in plant material has been investigated. The residue from dry ashing of the sample is dissolved in a solution prepared by diluting 1 ml cone. HC1 to 100 ml with methanol. Each sample is diluted to 25 ml and aspirated directly into an acetylene-air flame for analysis by atomic absorption spectroscopy. The sensitivity and detection limits obtained for each metal are lower than those obtained using an aqueous solution. The amounts of metal found in the samples has been compared to the results obtained by the analysis of identical samples by the official A0AC colorimetric methods.

3:00 Break

3:30-8 DETERMINATION OF NANOGRAM AMOUNTS OF BERYLLIUM IN BIOLOGICAL SAMPLES BY FLAMELESS ATOMIC ABSORPTION SPECTROMETRY, J. A. Hurlbut, Metropolitan State College.

Methods for determining nanogram amounts of beryllium in urine, hair, fingernail and fecal samples by flameless atomic absorption spectrometry are described. A Perkin-Elmer Model 503 spectrophotometer equipped with an HGA-2100 graphite furnace was used. Group II cations, aluminum, cerium, silicon, chromium, molybdenum, tungsten, manganese, and lanthanum enhanced the absorption signal. The presence of 100 ug/ml of lanthanum yielded consistent absorption signals regardless of the cations present; so, lanthanum was used as a masking agent. Hydrofluoric, hydrochloric, and perchloric acids still interfered and had to be removed by evaporation. The tissue samples were digested using a nitric-perchloric acid mixture with the exception of the fecal and urine samples. A ferrous ion-hydrogen-peroxide digestion was used with the fecal samples, and a basic coprecipitation was used with the urine samples. Nanogram amounts of beryllium from the tissues and subnanogram per milliliter amounts of beryllium from urine were recoverable when the final samples were spiked with 100 ug/ml amounts of lanthanum. All recoveries varied from 90 to 110% with relative standard deviations of less than 13%.

4:00-9 INFRARED SPECTRA OF PERMETHYLATED HUMIC ACID FRACTIONS, R. L. Wershaw and D. J. Pinckney, U.S. Geological Survey.

The infrared spectrum of a humic acid normally consists of only a few broad absorption bands, the most prominent of which are the carbonyl stretching bands between 1720 cm^{-1} and 1630 cm^{-1} and the hydroxyl stretching, band in the region of 3400 cm^{-1} . After derivatization of the humic acid fractions, new bands appear in the so-called fingerprint region and the carbonyl bands are shifted. Infrared spectroscopy has also proved useful in monitoring the reaction of permethylated humic acid fractions with various derivatization and halogenation reagents. The moistening of the cast films of methylated humic acid fractions with deuterated water causes the quinone carbonyl bands to disappear. This effect is due either to hydrogen bonding between the quinone carbonyl groups and the protons in the water or to the actual formation of hydroquinones.

This study demonstrates that infrared spectroscopy may be used both for the elucidation of the chemical structure of humic acids and for the comparison of different humic acid fractions.

4:30-10 NITRITE AND NITRATE LEVELS IN PROCESSED MEATS, BY ION CHROMATOGRAPHY, R. Posner and A. Schoffman, United States Testing Company, Inc.

Increasing evidence that sodium nitrite can combine with secondary amines to form carcinogenic nitrosoamines in the human gut, along with the common usage of nitrite as a color enchancer and as a preservative in packaged meats, calls for improved methods of analysis.

Conventional wet methods for analyzing nitrite and nitrate in the presence of each other involves duplicate determinations under oxidizing or reducing conditions, and under as-received conditions. Each species is then calculated by difference. This procedure is cumbersome and suffers from many interferences.

Ion chromatography can be used to separate and quantitate nitrite and nitrate levels in meat products. In addition, a survey is made of nitrate:nitrite levels with respect to time, identification of other common additives such as ascorbate, benzoate, and citrate are accomplished.

GENERAL SESSION II Second Floor, Conference Rooms A,F

Tuesday Morning - Bill McCarty, Presiding

9:00-11 A COMPUTER NETWORK FOR THE AUTOMATION OF LABORATORY INSTRUMENTATION, D. DiLuzio, Eastman Kodak Company.

The Analytical Sciences Division of Eastman Kodak Research Laboratories is implementing a computer network to collect, analyze, and store data from various instruments. The concept upon which this network is planned includes a large central computer serving a number of smaller computers interfaced directly to laboratory instruments. The advantages of such a system are several, but included as particularly important are: (l) added computational power, (2) centralized use of costly peripherals, (3) use of specialized data acquisition software on the satellites, and (4) sophisticated, general purpose software on the central computer.

The first satellite computer is interfaced to 16 gas and liquid chromatographs. It is a PDP-11/10 running under Kodak software. The satellite collects data from 16 chromatographs, resolves peaks, and carries out other system utilities. The resulting data are transmitted to the central processor for analysis. The central computer is a PDP-11/40 running under DEC's RSX 11M.

The second satellite was developed using software and hardware comparable to the first satellite's. It collects and analyzes data from three multichannel analyzers.

Using the same approach, a third satellite is interfaced to 16 more chromatographs and an X-ray diffractometer.

Details concerning the philosophy, design, and future expansion of this network will be discussed.

9:30-12 FOURIER TRANSFORM INFRARED SPECTROSCOPY APPLIED TO ANALYTICAL PROBLEMS, K. Krishnan, Digilab Inc.

Fourier transform infrared spectroscopy has the advantages of high throughput and multiplexing. The data is collected under computer control, and this allows the mathematical manipulation of data, such as the subtraction of two absorbance spectra to look for small differences between the two spectra. Application of this technique of absorbance subtraction to the study of surface coatings, determination of impurities in semiconductors, and to the detection of environmental pollutants will be discussed. Interfacing of the Fourier Transform infrared spectrometer to a gas chromatograph enables the study of the spectra of gas chromatographic effluents. Examples of high sensitivity GC/IR spectra corresponding to a few nanogram levels of the sample will be presented.

10:00 Break

10:30-13 DYNAMIC MASS SPECTROMETRY TECHNIQUE AND APPLICATIONS, T. L. McFeeters, Rockwell International.

A mass spectrometric method for analysis of volatile components in terms of their flow-rates through the ionization region has been termed dynamic mass spectrometry.

The paper briefly describes theory, technique (including calibration) and applications (including examples) of the method.

Applications discussed include vacuum chamber residual gas analysis, contamination/cleaning studies, and determination of solvent permeation rates.

11:00-14 NEUTRON ACTIVATION ANALYSIS OF TRACE METALS IN SHALE OIL PRODUCTS, P. Shaw, Laramie Energy Research Center, and D. McKown and S. Manahan, University of Missouri.

Distillates, waxes, and residues from an in situ shale oil retort product were analyzed for selected trace elements by instrumental neutron activation analysis (1NAA). Selenium was analyzed by a special 5-second irradiation, 15-second decay, 15-second count. Short irradiations of 1 minute or less were employed for the determination of aluminum, vanadium, sulfur, manganese, iodine, chlorine, bromine, sodium, and arsenic. A 2-hour irradiation was employed for the determination of antimony, iron, cerium, copper, zinc, cobalt, molybdenum, chromium, and selenium. Standards employed included metal oxides and metals dissolved in nitric acid, ammonium salts of halides and sulfur compounds, and NBS fuel oil. The volumes of the standards were adjusted to simulate the geometry of the shale oil samples. Special techniques and precautions are described for the irradiation of shale oil products necessitated by pressure buildup due to gas production. Surprisingly, the waxes have especially strong tendencies to produce gases during irradiation.

In general, results obtained on elements analyzed thus far show enrichment of trace elements in the tars and depletion in the waxes. The waxes are much lower than the distillates in arsenic content. Distribution of other trace elements is discussed.

11:30-15 SYNCHRONOUS FLUORIMETRY OF ORGANIC WATER POLLUTANTS IN THE DENVER METRO AREA, G. Erickson and E. R. Weiner, University of Denver,

A major problem in water pollution control is identifying the source of a particular pollutant from among several possible sources. This is especially difficult when the pollutant is transported in groundwaters before entering a surface water body. The technique of synchronous fluorimetry was applied to oils and other organic water pollutants collected in the Denver area to evaluate its usefulness for identifying the pollutant sources. Spectra from stream samples were compared with effluent samples from possible sources.

Tuesday Afternoon - Bill Wiginton, Presiding

2:00-16 ROOM TEMPERATURE PHOSPHORESCENCE OF COMPOUNDS ADSORBED ON SODIUM ACETATE, R. J. Hurtubise and R.M.A. von Wandruszka, University of Wyoming.

The room temperature phosphorescence behavior of several compounds adsorbed on sodium acetate was studied. Comparisons of molecular structures and consideration of reflectance, fluorescence and infrared spectra allowed postulation of certain molecular requirements for room temperature phosphorescence. The interactions of p-aminobenzoic acid with sodium acetate were considered in detail. The adsorption process involved the formation of the sodium salt of p-aminobenzoic acid on sodium acetate surface and hydrogen-bonding. Only compounds dissolved in protic solvents showed the effect. It was also shown that the phosphorescent compounds are adsorbed flatly on sodium acetate.

Room temperature phosphorimetry of compounds adsorbed on sodium acetate has the analytical advantages of selectivity and relative insensitivity to moisture. In addition to p-aminobenzoic acid useful analytical results have been obtained for p-aminohippuric acid, 5-hydroxyindoleacetic acid, 5~hydroxytrytophan, p-hydroxybenzoic acid, and folic acid. Also, benzocaine which did not show room temperature phosphorescence when adsorbed on sodium acetate was hydrolyzed to p-aminobenzoic acid and the phosphorescence of p-aminobenzoic acid was measured on sodium acetate. A unique phosphorimetric method was developed for determining p-aminobenzoic acid in multicomponent vitamin tablets without separation.

2:30-17 THE APPLICATION OF ENERGY DISPERSIVE X-RAY FLUORESCENCE TO VETERINARY TOXICOLOGICAL SCREENING OF INORGANIC POISONS, J. D. Henion, G. A. Maylin, and J. G. Ebel, Jr., Cornell University.

The screening of biological samples for inorganic poisons has not experienced the growth and success that organic screening by thin layer chromatography has enjoyed. The wide variety of inorganic compounds with differing physical properties has precluded sensitive, specific analytical methods amenable to broad coverage at trace levels. Although there are a few multi-element analytical techniques suitable for screening inorganic elements, we have chosen the technique of energy dispersive X-ray fluorescence (XRF) as the most suitable method for screening veterinary biological materials with minimum sample preparation.

XRF allows us to screen animal tissues and plant materials for eighty-two possible elements which may be present at toxic levels. Since we are looking for significantly elevated amounts over the normal element profile (NEP) of the particular biological material, XRF can readily detect and identify the specific element present at a toxic level. Quantitation can then be accomplished either by XRF or other suitable methods.

Examples will be presented which demonstrate the analytical application of XRF for screening a variety of animal tissues from toxicological cases encountered in our veterinary diagnostic laboratory.

3:00 Break

3:30-18 DETERMINATION OF TOTAL ORGANIC CARBON (TOC) IN SODA ASH AND OTHER HIGH CARBONATE CARBON SAMPLES, A. E. King, Coulometrics, Inc.

The determination of organic Carbon in samples containing high levels of inorganic carbon has been a difficult analytical task. Conventional procedures require dissolution of solid samples in acid followed by purging to remove inorganic carbon. Organic carbon is then determined by wet oxidation with gravimetric or volumetric determination of evolved CO_2. A new method using coulometric titration of CO_2 following combustion in oxygen at 530°C has been developed.

Total organic carbon (TOC) was determined in several typical soda ash samples (as well as a Variety of other materials including NaHCO, and soda ash liquors). Interference from sodium bicarbonate was eliminated by preheating the sample at 160°C for 15 minutes for solid samples and by boiling for liquid samples. Agreement between the conventional and coulbmetric methods was within 10% for soda ash. Precision of the new method was ±2 ppm TOC for soda ash. Analysis time, excluding preheating to destroy bicarbonates, was less than 8 minutes for the coulometric method compared to 90 minutes for the conventional method. The coulometric method required minimal operator skill. The coulometric method will not detect organic carbon which is volatile under the pretreatment conditions or carbon which will not oxidize in an oxygen atmosphere at 530°C and therefore is only applicable to certain samples.

4:00-19 DEVELOPMENT OF METHODS FOR QUANTITATION OF NAPHTHIONIC ACID IN SERUM, B. Stavric, J. Craig, R. Klassen, and J. Ruddick, Health & Welfare Canada.

Recent controversy about the biological effect of Amaranth (F.D. & C. Red No. 2) prompted renewed interest in additional pharmacokinetic studies of this food azo-dye. An important parameter in these studies is to follow the serum concentration of Amaranth's major metabolite, naphthionic acid (NA).

Although an analytical procedure for quantitation of NA in serum, using thin layer chromatography, has been described, this method was not sensitive enough nor fast enough for our purposes.

A new, sensitive, reproducible and fast method (required for a few thousand samples) had to be developed. Attempts to use GLC techniques using different columns, and detectors, after various derivatizations of NA, had limited success.

The best results were obtained when the concentration of non-derivatized NA was measured by fluorescence spectrophotometry (excitation 328 nm, emission 420 nm) of the supernate, after precipitation of serum protein with absolute ethanol and heating (75°C; 30 min). About 100 determinations per day are possible with results available within 2 hours of sampling. Sensitivity of this method is 1 ng of NA in 20 ml of serum.

This is an unusual example where derivatization reduced the detectability of the original compound.

4:30-20 EVALUATION OF SELECTIVITY CHARACTERISTICS OF POLYSTYRENE-BASED PACKING MATERIAL, V. McKay, G. Hewett, and R. Stevenson, Altex Scientific, Inc., and R. Henry, Chemtest.

Polystyrene-based packing materials, familiar in classical ion exchange chromatography and size separation, are now gaining popularity in high performance liquid chromatography. The use of macroreticular resins in which the pore size is independent of the percentage crosslinking, offers several advantages. The uniformity of the pore structure leads to highly efficient packed columns (18,000 + theoretical plates/meter). The rigidity of higher cross-linking allows higher flow rates than is possible with microporous resins without compression of the bed. The resultant backpressure is low—comparable to that of silica based materials. The macroreticular character permits solvent changes without swelling and shrinking so there is no loss in efficiency. This flexibility with mobile phases allows size separations in a variety of eluents on a single column, or partition onto a neutral polystyrene stationary phase under certain other mobile phase conditions. Various moieties can be incorporated into the polystyrene base for operation in other modes. This paper will explore selectivity differences and similarities under various mobile phase conditions.

GENERAL SESSION III Second Floor, Conference Rooms A,F

^^crfgy Morning - Marvin Fishman, Presiding

9:00-21 SAMPLE PREPARATION FOR TRACE MULTI-ELEMENT ANALYSIS WITH EMPHASIS ON CONTAMINATION CONTROL, L. Jacobs, C. R. Wilson, and J. Oldham, Commercial Testing & Engineering.

Sample preparation for multi-element trace analysis has always been a problem for the analytical chemist. Therefore, we investigated two sample preparation techniques—low temperature plasma ashing and the Parr oxygen dissolution.

The sample types used in the investigation were coal, hair, and an organic resin XAD-2. A comparison of possible elemental contamination using the two different preparation techniques as well as various chemicals and reagents and the speed of operation will be shown.

Some analytical results using a Spark Source Mass Spectrometer as the multi-element analytical survey method will be shown.

9:30-22 DEVELOPMENTS IN ANALYTICAL HYDRIDE PRECONCENTRATIONS FOR SELECTED ULTRA-TRACE LEVEL GROUP IVA, VA, AND VIA ELEMENTS, S. J. Northway, University of Arizona; G. D. Dyke, J. D. Weishaar, and R. C. Fry, Kansas State University.

The use of strong reducing agents in acid media to convert oxidized forms of As, Sb, Bi, Se, Te, Ge, and Sn to the corresponding volatile covalent hydrides has been used for some time to effect a valuable gas phase preconcentration of these species for the purpose of concentration sensitivity enhancement in atomic absorption spectrometry.

This presentation will include new chemical reaction conditions, reducing agents, and means of reagent introduction that greatly improve the conversion of species previously not easily reduced [e.g., As(V)]. Reaction conditions and masking agents for the elimination of (otherwise) severe cationic and anionic interferences have been developed.

New experimental techniques for improving the efficiency of the low temperature entrapment approach to further preconcentration of the hydrides will be presented. A means of extending the low temperature entrapment to selected group VIA elements has been developed.

Evidence will be presented concerning the mechanisms by which several chemical inhibitions of hydride evolution proceed. Means of removing many of these interferences will be presented. The role of catalysis and kinetics in these reactions will be discussed. The varied contributions of transport vs. chemical interference have been studied. Several new detectors for the preconcentrated hydrides are being investigated.

10:00 Break

10:30-23 FUNDAMENTAL ARC PROPERTIES AND ACCURACY IN MULTIELEMENT SPECTROGRAPHIC ANALYSIS OF GEOLOGICAL MATERIALS, D. W. Golightly, A. F. Dorrzapf, Jr., and C. P. Thomas, U.S. Geological Survey.

The basic premise of accuracy in spectrographic analysis requires identical transport, ionization, and excitation of the sample and of the reference standard. These requirements are difficult to achieve in practice because of the complex inter-relationship between the physico-chemical properties of the material vaporized into the arc plasma and the thermodynamic properties of the plasma itself. The temperature and electron concentration in an arc-plasma are influenced by the ionization properties of the free-atom and free-molecule phases of samples, which contribute to the thermal and electrical conductivity of the arc-plasma. The complexity of this conventional electrical-arc model is furthered by the non-isothermal character of the discharge, and by the dynamic transport mechanisms for which only non-quantitative understanding exists. We have studied the matrix dependency of spectral emission for common geological materials to determine what correlations exist between measured effective temperatures, effective electron pressures, and matrix composition. A conventional source configuration for dc-arc analysis (AR-O_2 atmosphere, 4 mm gap, 15A) and a 3.4m Ebert spectrograph were used for moving-plate studies and regular exposures for computerized spectrographic analysis. Effective temperatures (5000-6500 K) and electron pressures (10-1000 Pa) were determined from relative spectral radiances of iron and titanium lines emanating from ions and neutral atoms in close proximity to the arc core. The correlations observed between fundamental arc properties and their implications for approaches to improved accuracy through calculations based on fundamental parameters will be discussed.

11:00-24 MULTI-ELEMENT ANALYSIS OF GEOCHEMICAL SAMPLES WITH A DIRECT READING EMISSION SPECTROMETER, P. J. Lamothe and J. L. Seeley, U.S. Geological Survey.

A computerized, multichannel direct reading emission spectrometer has been adapted for the rapid determination of 43 elements in a wide variety of geologic materials. Semi-quantitative trace element estimations on solid samples are accomplished using the DC-Arc in a current programmed mode, and the use of rubidium chloride as a spectroscopic buffer permits the concurrent quantitative determination of ail 10 major rock forming elements. Spectral interference corrections are made using the spectrometer's dedicated mini-computer, and two different background correction schemes have been evaluated for use with silicate rock samples. The results of this comparison will be summarized.

11:30-25 A SPECTROGRAPH IC METHOD FOR THE SIMULTANEOUS DETERMINATION OF LITHIUM, RUBIDIUM, AND CESIUM IN GEOLOGICAL MATERIALS, R. E. Mays and J. L. Seeley, U.S. Geological Survey.

Lithium, rubidium, and cesium are rapidly and accurately determined simultaneously in geologic samples by a spectrographic technique which requires little sample preparation and no equipment modification. Samples are prepared by mixing with a KC1 buffered quartz-graphite mixture. Standards were prepared by serial dilution of a well analyzed mineral (Lepidolite) which contained 2.50% lithium, 1.82% rubidium, and 0.075% cesium, by weight. To cover the wide range of concentrations typically found for these elements, a 3-step neutral density filter is used to optimize analytical conditions over a broad wavelength region. All 3 elements are detectable at the 0.5 to 5 part-per-million level. Excitation conditions and comparative results will be discussed.

Wednesday Afternoon - Bill Wigintoh, Presiding

2:00-26 USE OF AN INDUCTIVELY COUPLED ARGON PLASMA FOR MAJOR ELEMENT DETERMINATIONS IN VARIOUS MATRICES, A. F. Ward and L. F. Marciello, Fisher Scientific Company.

Since the introduction of the ICAP as an analytical technique, it has been primarily used for trace elemental analysis. Recently, however, there has been more emphasis on using the ICAP for total sample analysis which utilizes the unique ICAP property of highly linear calibration curves.

The use of the ICAP for the analysis of mineralogical, agricultural and metallurgical samples will be discussed. Correlation data with other analytical procedures and data obtained for the analysis of standard reference materials will also be presented.

2:30-27 CHEMISTRY IN A GLOW DISCHARGE PLASMA, D. A. McCamey and T. M. Niemczyk, University of New

For many years the glow discharge has been an important line emission, ion and atomization source. The mechanisms and reactions in the plasma which led to these utilizations are still not well known although they have been studied in different experiments by many workers. Recent work in our laboratory has provided a unique spectroscopic technique for studying the glow discharge plasma. The relative concentrations of all of the important species in the plasma can be monitored. These species include ground state neutral atoms and ions as well as metastable noble gas atoms. These metastables have been postulated to play an important role in excitation and ionization of the sputtered metal atoms according to the following reactions:

(1) $A^* + M \rightarrow M^* + A$ and

(2) $A^* + M \rightarrow M^+ + A + e^-$ (Penning ionization),

where A represents the noble gas atom and M is the sputtered metal atom. This paper will discuss results obtained from these experiments and the relative importance of the metastable species in glow discharge plasma reactions.

3:00-28 HOLLOW CATHODE EMISSION ANALYSIS OF NONMETALS, D. M. Mehs, Fort Lewis College, and T. M. Niemczyk, The University of New Mexico.

Trace analyses of nonmetals are frequently plagued by a variety of experimental difficulties. This is especially important for elements such as selenium and arsenic which present environmental health hazards even when present in trace quantities. Thus accurate and precise methods of analysis at the parts per million level are required. Atomic absorption spectroscopy is currently the most useful technique but it is necessary to contend with the problems associated with high excitation energies, highly volatile analytes, and the frequent necessity of using vacuum ultraviolet resonance lines. These difficulties can be circumvented by using the hollow cathode discharge directly as an emission source. Samples are introduced into the cathode of a demountable lamp, atomized and excited, and the spectrum conveniently analyzed. This highly energetic discharge easily excites the nonmetals while its confined nature counteracts volatility problems. A comparison of sensitivity, detection lim

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

H. E. Taylor and F. R. McDonald, Co-Chairmen

SESSION I - WATER QUALITY Second Floor, Conference Rooms B,E

Monday Morning,- Howard E. Taylor, Presiding

9:00 Introduction - Howard E. Taylor

9:05-29 Invited Paper - METHODOLOGY AND INSTRUMENTATION FOR COMPLIANCE MONITORING, J. F. Kopp, Environmental Protection Agency.

The Environmental Monitoring and Support Laboratory-CIN is charged with the development and adaptation of equipment and techniques to measure pollutants contained in surface and ground water; drinking water; sludges and soils; and the effluents from municipal, industrial and non-point sources. The objective of this effort is to provide the most efficient and effective monitoring techniques to meet the needs of EPA and related State monitoring programs. This includes the development, selection, modification, and adaptation of existing and proposed measurement technology specifically required to identify, characterize, and quantitate all environmental pollutants for EPA and State water monitoring techniques to improve the cost-effectiveness of monitoring operations; and the development of complete monitoring systems designs to establish and maintain the Agency's monitoring data bases. Emphasis is placed on methods and techniques necessary to establish and enforce standards and regulations already promulgated, now under consideration for promulgation or of specific interest to EPA as potentially harmful to the environment. Development of methods for toxic materials in industrial wastewaters, municipal wastes, public water supplies, fresh and marine waters and ground waters, and of techniques for the evaluation of hazards to human and aquatic populations from municipal and industrial discharges receive priority treatment.

Insight into method selection and approval, the alternate test procedure mechanism, and the need for a good laboratory quality control program to insure valid data will be discussed.

9:35-30 AUTOMATED ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF TIN IN WATER AND STREAMBED MATERIALS, G. Pyen, M. J. Fishman, U.S. Geological Survey.

An automated laboratory flow-through procedure was developed to determine tin in water and streambed materials. Sample solutions for streambed materials are obtained by a standard U.S. Geological Survey extraction procedure. The interferences from most trace elements are eliminated by addition of EDTA. Sodium borohydride is added to the sample stream to form tin hydride which is then stripped from the solution with the aid of nitrogen and decomposed at 850°C in a tube furnace that is in the optical path of an atomic absorption spectrometer. Twenty samples per hour can be analyzed. The detection limits are 1 mg/L and 0.1 mg/g for water samples and streambed materials, respectively.

9:55-31 THE DETERMINATION OF ORGANOTIN COMPOUNDS IN MARINE SAMPLES BY FLAMELESS ATOMIC ABSORPTION SPECTROSCOPY, G. R. Sirota, Dept. of Fisheries and Environment, Canada.

The organic compounds of tin are powerful biocides and are widely used in terrestrial and aquatic applications: Bis (tri-n-butyl tin) oxide is the major organotin compound, and is used in antifouling marine formulations. In this paper a method is described for the determination of bis (tri-n-butyl tin) oxide in a biological matrix. The method involves selective biphasic extraction with a polar/non-polar solvent system, chemical transformation of the extracted organotin, and analysis by flameless atomic absorption spectroscopy. Detection limits are 0.05 ng Sn and standard deviation is ± 12%.

10:15 Break

10:35-32 ANODIC STRIPPING VOLTAMMETRY FOR THE SIMULTANEOUS DETERMINATION OF ULTRA TRACE METALS: A DISCUSSION OF SCOPE AND INTERFERENCE EFFECTS, J. E. Bonelli and H. E. Taylor, U.S. Geological Survey; and R. K. Skogerboe, Colorado State University.

Anodic Stripping Voltammetry (ASV) is receiving increased attention as an alternate competitive technique to conventional atomic emission and absorption spectrometry for the determination of selected ultra trace metals. The scope of the ASV technique includes but is not limited to the determination of metals such as Bi, Cd, Cu, Ga, Pb, Sn, Tl, and Zn. Depending on analysis conditions and the nature of the sample to be analyzed, it is possible to determine one or more of these elements, simultaneously.

There are several types of interference effects including intermetallic compound formation in the mercury working electrode, and unresolved multiple oxidation peaks, that have significant impact on the practicality of analysis on "real" samples. Prior to choosing this method for routine analysis, a critical evaluation must be carried out on the prevalence and magnitude of these effects.

10:55-33 USE OF MODIFIED ELECTRODES FOR ANALYSIS OF METAL IONS AT ULTRA-TRACE LEVELS, R. F. Nelson, Gates Rubber Co.

Graphite powder has been chemically modified by bonding chelating agents to the surface via silanization and amidization reactions. The resulting powder, when made up into a carbon paste electrode, can be used to preconcentrate metal ions and carry out electroanalyses down to the picomolar region. The method of analysis involves uptake of the metal ion by the electrode through solution stirring for a preset time, followed by rinsing and subsequent immersion in an electrolyte solution containing a reagent that forms a sparingly soluble salt with the complexed cation. The deposited precipitate is then reduced cathodically to generate the free metal plated on the surface of the electrode. A subsequent anodic scan produces a stripping peak suitable for analysis. Using linear-sweep and differential-pulse voltammetry, Ag^+ has been analyzed down to 1.0×10^{-13} M and Cu^{++} down to 1.0×10^{-12} M with acceptable accuracy and precision. Applications to multi-element analysis have also been explored.

11:15-34 AUTOMATED COLORIMETRIC METHOD FOR DETERMINING DISSOLVED BORON IN WATER, R. R. Spencer and D. E. Erdmann, U.S. Geological Survey.

An automated colorimetric method to determine dissolved boron in water is described. The boron is complexed with azomethine-H which is readily available as the condensation product Of H-acid (8-amino-l-napthol-3,6-disulphonic acid) and salicylaldehyde. The yellow complex formed is then measured colorimetrically at 410 nm. Interference effects from other dissolved species are minimized by the inclusion of diethylenetriamine pentaacetic acid (DTPA) in the procedure; however iron, zinc, and bicarbonate interfere at concentrations above 400 mg/L, 2,000 mg/L and 150 mg/L, respectively. The bicarbonate interference can be eliminated by careful acidification of the sample with concentrated HC1 to pH 3-5. Thirty samples per hour can be routinely analyzed over the range of 0-400 mg/L boron.

11:35-35 CHARACTERIZATION OF LEACHATE PROPERTIES OF A COAL CONVERSION PROCESS SOLID WASTE, M. J. Carter, EPA, and R. G. Luthy and P. Vassiliou, Carnegie-Melton University.

Commercial-scale coal gasification facilities will generate large quantities of solid waste material. For example, a 250 million SCF/day Hygas process will produce about 1500 tons of solid waste char/day. The disposal of such large quantities of waste material presents unknown environmental problems. It was the purpose of this study to develop a methodology for assessing potential environmental problems associated with disposal of coal gasification solid waste char, and to apply this methodology to the case of pilot-scale Hygas coal gasification process char.

The major emphasis of this study was devoted to quantifying the extent and rate of release of 25 trace elements from the char when leached with eluants of varying qualities. Three different approaches to measuring the leaching potential of the char were investigated: (l) batch extraction and (2) continuous-flow column tests, both using six different leaching solutions and (3) intermittent flow column tests using a mixture of soil and char, using distilled water as the leaching solution. The leachate solutions were analyzed by ICAP emission and flame atomic absorption spectroscopy.

Only eleven of the twenty-five elements analyzed were found in significant concentrations with boron the most significant. In addition, it was found that the batch extraction studies were good indicators of what may be leached, but poor indicators of the total quantities leached. Specific methodology, significance of the results, and suggestions for further studies will be discussed.

Monday Afternoon - Howard E. Taylor, Presiding

1:30-36 A NEW CONCEPT FOR USING INDUCTION COUPLED PLASMA SPECTROMETRY FOR TRACE METALS ANALYSIS, J. R. Garbarino and H. E. Taylor, U.S. Geological Survey.

Many applications of water analysis do not require highly accurate quantitative results. Often, a very rapid semiquantitative survey is sufficient for reconnaissance purposes. An inductively-coupled plasma technique has been developed for the analysis of these types of samples for the following elements: Al, Sb, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Pb, Li, Ga, Ge, Mg, Mn, Mo, K, Ni, SiO_2, Ag, Na, Sr, Sn, Ti, V, Zn and Zr. Computer software has been developed to provide analysis results in a tabulated format with values rounded to the appropriate "reporting levels". "Reporting levels" are established in the ratio of 1, 3, 5, 7, and 10 over the range from the detection limit to the maximum concentration limit.

Suspended particulate matter often causes severe maintenance problems due to clogging with the conventional pneumatic crossflow nebulizer utilized in this system. Development of a new Babington type of nebulizer, insensitive to this problem, has been initiated. The sensitivity and precision of this new approach will be critically compared with the more conventional system.

1:50-37 A COMPARATIVE STUDY OF THE ISOLATION OF ORGANIC MATERIAL FROM WATER COLLECTED DURING THE IN SITU RETORTING OF TAR SANDS, T. E. Owen, F. D. Guffey, and F. A. Barbour, Laramie Energy Technology Center-DOE.

As the commercialization of in situ retorting of tar sands approaches, the contamination of water by organic compounds generated by the process becomes a concern. Whether one is looking at total organic content or individual species, it is important to know the quantity of organic material isolated. Previous methods of removing the organic material present in tar sands water have been limited to liquid/liquid extractions. For the purposes of this investigation, water collected from the in situ retorting of tar sands was treated by various methods to determine the most efficient in organic removal. These methods included liquid/liquid extraction, freeze drying and resin adsorption. The organic content in the water was determined before and after each isolation. Two methods of determining the efficiency of the organic carbon isolation were utilized and compared. The first method involved the conversion of carbon to methane followed by flame ionization detection and a second method converting the carbon to carbon dioxide followed by coulometric titration. The results of the various methods of isolation and detection will be discussed.

2:10-38 RAPID DETECTION AND MAPPING OF SUBSURFACE PETROLEUM OIL CONCENTRATIONS AT PROPOSED DEEPWATER PORT SITES, R. R. Hiltabrand, U.S. Coast Guard R & D Center.

A towed fluorometer was calibrated with a Louisiana Crude Oil and used to measure the background concentration of aromatic hydrocarbons present in the seawater at the proposed Deepwater Port Site "Loop" in the Gulf of Mexico.

The fluorometer was towed over a distance of 25 square miles at two separate depths during a sixteen-hour period by a Coast Guard Cutter and the oil concentration, turbidity, temperature and depth were constantly monitored during this period of time.

Results indicated that this technique can be used to detect and map oil spills and can give one a synoptic picture of the aromatic hydrocarbon concentration in the water column. The logistic support, time and effort required in gathering data by this method is greatly-reduced when compared to conventional means of obtaining samples for analysis.

2:30-39 A REVIEW OF SEDIMENT SURFACE REACTIONS IN NATURAL WATERS AND METHODS FOR STUDY, E. R. Weiner, University of Denver.

Sediments in natural waters acquire surface coatings by a variety of reactions with dissolved chemical species and play an important role in the transport of chemical substances through the aquatic environment. Sediments may be sources or sinks for dissolved species depending upon how water parameters such as pH, temperature, and ionic strength may change. Surface hydroxyl groups are involved in most of the sediment surface reactions. Surface species, reaction mechanisms, and surface bonding properties should be studied with sediments in a water environment. Some experimental approaches are discussed.

2:50 Break

3:10-40 APPLICATION OF EMISSION SPECTROGRAPHS TO THE DETERMINATION OF TOXIC ELEMENTS IN SILICATE MATERIALS, C.Heropoulos and J. L. Seeley, U.S. Geological Survey.

Any program dealing with the environmental impact of toxic elements must initially be directed toward determining the presence of those materials, with subsequent investigations to ascertain their points of origin. In many cases this type of investigation is hampered due to sample size limitations and lack of rapid, specific detection systems of adequate sensitivity. In the past, much of the data concerning the concentration levels of such elements as antimony, arsenic, cadmium, mercury, thallium, and selenium in silicate materials were accumulated one element at a time, involving time-consuming procedures and, in many instances, fairly large sample sizes. Optical emission spectrography, as applied to this problem, provides a means of simultaneously determining the above elements in milligram sized samples, rapidly and with detection levels at the 0.1 to 3 part-per-million concentration range. These levels of detectability are made possible by exciting the samples in a DC arc, at a high amperage, in an inert atmosphere. Data on all of these specific elements are recorded simultaneously on an ultraviolet-photographic emulsion (SWR), and may be treated either qualitatively, semi-quantitatively, or quantitatively. Additional information on other elements present is readily available, thus increasing the possibility of using elemental concentration ratios to track down pollution sources.

3:30-41 ANALYSIS OF HALO-ORGANICS AND ARENES IN WATER AT PPB LEVELS, R. S. Narang, NY State Hea

In recent years, few analytical methods have been developed to do the analysis of halo-organics present in water. These can be divided into four categories: Head space, direct aqueous injection (DAI) using an electron capture (EC) detector, gas sparging method of Bellar and Litchenberg, and closed system stripping followed by elution with a solvent-developed by Grob. The head space methods are relatively quick but cannot be automated and they also yield irreproducible results. The DAI method, although rapid, lacks sensitivity and also has the disadvantage that most EC detectors lose their sensitivity when water is injected on them. The gas sparging method is slow, not very flexible, difficult to reproduce retention times, and tends to yield ghost peaks. We describe a method which is based on Grob's closed system stripping with modifications on the use of absorbant and eluting solvent.

Absorption tubes are made by packing conditioned porapak N up to lengths of 1 to 1-1/2 sandwiched between two glass wool plugs in a 7" x 1A" glass tube. The sample to be stripped is poured in a graduated impinger immersed in a water bath kept at 40-45°C. The inlet of the impinger is attached to the outlet of the stainless steel diaphragm pump and the outlet to one end of the absorption tube. The second end of the tube is attached to the inlet of the pump to complete the cycle. The pump is run for fifteen minutes, the absorption tube is removed and placed in a 5 ml graduated test tube and eluted with methanol. A 1 to 1.5 ml fraction is collected which is then analyzed for halo organics on a modified chromosorb 102 column using an EC detector; for Arenes, on a 20% SE30 column using a photoionization detector; and for vinyl chloride on a porapak T column and a photoionization detector.

3:50-42 ANALYSIS OF AROMATIC AMINES AND PHENOLS IN AQUEOUS MEDIA BY HPLC, R. M. Riggin and C. C. Howard, Battelle Columbus Laboratories.

The use of HPLC for the determination of organic contaminants in aqueous media has numerous advantages over conventional gas phase separation techniques. Among these advantages are increased sample throughput (faster analysis time) and wider application. Aromatic amines and phenols represent two classes of compounds which are more easily separated by HPLC than GC.

This paper explores the advantages of using electrochemical detection to enhance the sensitivity and selectivity of HPLC analyses for phenols and aromatic amines. Applications in both the areas of waste water monitoring and biological monitoring (blood, urine) will be presented for a wide variety of phenols and aromatic amines.

SESSION II - AIR QUALITY   Second Floor, Conference Rooms B,E

Tuesday Morning - Francis R. McDonald, Presiding

9:30   Introduction - Francis R. McDonald

9:35-43   Invited Paper - DENVER'S URBAN PLUME, J. L. Durham, U.S. Environmental Protection Agency.

The City of Denver is located in the valley of the South Platte River, which flows northeast. The walls of the valley impose typical channel wind-flow behavior on the urban air mass associated with the Greater Denver area. During the night, the cold urban air mass flows down the river valley towards the northeast. After the sun rises and begins to heat the air, the wind reverses direction and flows up the valley towards the southwest. If low wind speeds and shallow temperature inversions persist, as they frequently do during the winter, Denver's morning urban plume returns at midday.- This situation often results in an air pollution episode within the city. One of the most prominent features of this urban plume is its brownish color, which can usually be observed from Denver looking toward the northeast during periods of stagnation. Field investigations were conducted in 1971 and 1973 to characterize the aerosols present during episode periods and to determine the reason for the brownish appearance of the urban plume.

The aerosol mass distribution was found to have modes at diameters of ~0.2 mm and ~10 mm, and a minimum at ~1 mm. Submicrometric aerosol mass concentrations at a. site 8 kilometers north of Denver were 25-50 mg/m^3, and the composition was sulfate, 30%; benzene soluble organic, 37%; nitrate, 10%; lead, 10%; silicon, aluminum, iron and calcium, 10%. The concentrations of lead, bromine, silicon, calcium, iron and carbon monoxide were found to have high pair-wise correlations, suggesting that they are associated with automobile traffic. Microscopy showed that the larger particles were principally quartz, with significant amounts of limestone, mica, and rubber tire dust. For visible light, the aerosol had high values for the ratios of backscatter/total scatter and absorption/total extinction. The visible light extinction due to aerosols was estimated to be greater than that of nitrogen dioxide by a factor of two or more. Visible light scattering by aerosols is most likely the cause of the brownish color of Denver's urban plume.

9:55-44 THE TRACE METAL ANALYSIS OF PLANTS COLLECTED IN THE PAGE, ARIZONA AREA, 1973-1978, L. Krecidlo, R. D. Foust, Jr., R. Herrin, C. Hooker, H. Fort, and W. Gaud, Northern Arizona University.

Samples of *Ephedra viridis*, *Orysopsis hymenoides* and *Gutierrezia sp*. have been collected at five sites adjacent to the Navajo Generating Station in Page, Arizona, and analyzed for cadmium, copper, vanadium, iron, manganese, chromium, and zinc. Soil samples were also collected at each site and weather data was recorded over the five year duration of the study. All data collected was treated in a multiple regression analysis in an attempt to identify statistically significant correlations. Trace element levels from *Ephedra viridis*, *Orysopsis hymenordes*, and soil show no correlation between sites, time or precipitation. The trace element levels from *Gutierrezia sp*., however, show very significant increases as a function of time at all sites studied. Chromium levels have been shown to increase an average of 1.0 PPM per year, cadmium levels have increased about 0.05 PPM per year, and iron has increased as much as 100 PPM per year at some of the sites studied.

10:15-45 IONIC STABILITY OF PRECIPITATION SAMPLES, M. E. Peden and L. M. Skowron, Illinois State Water Survey.

Event and weekly precipitation sampled with three types of collectors was stored under five different conditions and analyzed throughout a six-week time period to monitor changes in ionic composition. Ca^{++}, Mg^{++}, Na^{+}, K^{+}, H^{+}, NH_4^{+}, $S0_4^{-}$, $N0_3^{-}$ and Cl^{-} were the constituents under observation. Dramatic variations in the concentrations of some species are attributable to the sample particulate loading. Although cooling retarded changes in ionic composition, immediate filtering after wet-only collection was the most effective means of retaining sample integrity and preventing adsorption-desorption reactions.

10:35 Break

10:55-46 THE RECOVERY OF ALUMINUM FROM FLY ASH, R. Herrin, R. D. Foust, Jr., and N. Hood, Northern Arizona University.

The aluminum content of fly ash recovered from electrostatic precipitators averages about 14-15% for southwestern U.S. coals and about 10-11% for eastern U.S. coals. The aluminum present in fly ash is in a silicate matrix which complicates the aluminum recovery process. We have experimented with mixtures of sodium carbonate, calcium carbonate and fly ash to determine the optimum mixture composition for aluminum recovery when heated. The effect of heating times and temperatures on these mixtures were also investigated. After heating, the fly ash samples were cooled to room temperature, treated with an aqueous sodium carbonate solution, filtered, and treated with a slurry of calcium carbonate and CO_2 gas to precipitate the recovered aluminum. Typically, 55% of the available aluminum can be recovered from western fly ash and about 40% of the available aluminum is recovered from the eastern fly ash.

11:15-47 TRACE ANALYSIS FOR ELEMENTAL CHLORINE IN STRATOSPHERIC AIR SAMPLES, W. W. Berg, S. H. Gitlin, and F. E. Grahek, National Center for Atmospheric Research.

An extremely sensitive procedure is presented for the determination of total elemental chlorine in stratospheric air samples. Trace amounts of chlorine, in the ppbv range, were collected on ultra-clean coconut shell activated charcoal traps in both the particle and gas phase from the stratosphere. The charcoal traps were chemically cleaned and baked-out at 750°C and 10^{-4} torr for two weeks prior to sampling. Three traps of 1.5 g each constitute a single sampling train. The trapped chlorine is removed from each charcoal plug by passing helium at 250°C through the charcoal. Following separation the chlorine and helium carrier gas are passed through a helium microwave discharge and allowed to bubble slowly into a hot 1.0 n NaOH solution. This procedure insures the complete destruction of such stable chlorofluoromethanes as Freon 11 and 12. The chlorine determination is made spectrophotometrically by examination of an iron(III)-chloro complex at 353 nm. Instrumental neutron activation analysis (NAA

11:35-8 AMMONIA IN AIR MEASURED BY SECOND DERIVATIVE SPECTROSCOPY, W. S. Ferguson, R. G. Woodmansee, D. S. Bigelow, S. C. Torbit, Colorado State University.

We are using a Lear Siegler laboratory derivative spectrometer to measure ammonia concentrations in air. Diurnal variation in ammonia concentration was measured in ambient air in Fort Collins and at the Pawnee Site, Central Plains Experimental Range. Other applications to date include measuring the time profile of ammonia volatilization during laboratory experiments in drying bovine fecal paste, bovine urine-soaked soil, and soil litter.

Our data and interpretation from these initial studies will be presented along with a brief discussion of instrumentation, calibration procedures and practical operating problems.

Thursday Afternoon - Francis R. McDonald, Presiding

1:30-49 ULTRA SENSITIVE DETERMINATION OF CARBON OXIDES BY GAS CHROMATOGRAPHY, C. R. Beverly, Union Carbide Nuclear Corporation.

Catalytic hydrogenation of carbon monoxide and carbon dioxide is achieved by passing GC effluent through a heated nickel catalyst. Conversion of carbon oxides to methane permits the use of flame ionization detection, enabling ready determination of sub ppm concentrations of CO and CO2 in a wide variety of industrial and environmental samples. When this analytical scheme is used in conjunction with a carbon type molecular sieves separatory column, CO, CO2, CH^ and light hydrocarbon gases are determined sequentially in a single run. Typical applications include monitoring work areas, compressed gas cylinders, industrial stacks, and general environmental samples.

1:50-50 DIRECT MEASUREMENT OF CARBONYL SULFIDE BY CLASSICAL OR INSTRUMENTAL TECHNIQUES, A. G. Panson, Morgantown Energy Technology Center-DOE.

COS has been a major topic of interest in low-Btu gasification at the Morgantown Energy Research Center (MERC). MERC's Chemical Services Branch undertook the study for the direct measurement of COS in Producer gases by classical and instrumental techniques. Procedures for both methods are given and results are compared.

Literature reports, especially within recent years, have relied upon material balances to estimate COS concentrations in Producer gases. COS data have been reported by a number of workers; however, indications on how COS was measured either is not clear or, if stated, found to be questionable.

There have been surprisingly few direct measurements of COS in Producer gases. Measurements for COS have been reported for low-Btu gas as long ago as the 1930's in Britain, Germany and the USSR for a number of Lurgi plants. Typically, levels were reported in the range of 120-300 ppm. COS levels reported by MERC are in the 200-300 ppm level.

2:10-50 QUANTITATIVE ANALYSIS OF AIRBORNE POLYNUCLEAR AROMATIC HYDROCARBONS BY GLASS CAPILLARY GC AND HIGH PRESSURE LIQUID CHROMATOGRAPHY, D. R. Choudhury and B. Bush, New York State Department of Health.

Polynuclear aromatic hydrocarbons (PAHs) represent an important class of experimental carcinogens occurring in such diverse sources as atmospheric particulates, tobacco smoke, and liquid fuels. Conventional GC analysis of PAHs suffer from lack of capability to resolve isomeric compounds exhibiting a wide spectrum of carcinogenicity.

This paper describes a promising method for identification and quantitation of PAHs present in air particulates. The particulate samples analyzed have been collected from 23 sites representing a variety of industrial and rural areas in New York State and have been shown by us to possess mutagenic activity. The method involves isolation of the PAH fraction by TLC and analysis of the fraction by glass capillary GC, reverse phase HPLC using microparticulate column and capillary GC-mass spectrometry. The combined use of GC and HPLC helped to confirm identity of individual compounds. The simple TLC "clean up" helps to minimize interference due to a wide variety of non-PAH constituents of the crude sample. Resolution of many important isomeric PAHs that are not separable by conventional packed GC columns has been achieved. Such resolution is important for proper evaluation of toxicological hazard of any PAH containing sample.

B. Bush, D. R. Choudhury, T. L. Miller, R. Toombs, M. J. Wolin, Mutation Research, to be submitted.

2:30-52 APPLICATIONS OF GC/MS TO COAL GASIFICATION, K. B. Tomer, R. Zweidinger, C. Sparacino, and D. Smith, Research Triangle Institute.

The qualitative and quantitative analyses of the volatile and semi-volatile products from coal gasification reactors by means of high resolution capillary gas chromatography-mass spectrometry will be described. Quantitation of components is accomplished by the method of relative molar response values in which the system response of a selected ion extracted from full scan mass spectral data is related to the system response of a selected ion from an internal standard using the equation

$$\text{RMR} = \text{UNKNOWN/STANDARD} = \frac{\text{AREA}_{\text{UNK}}/\text{MOLES}_{\text{UNK}}}{\text{AREA}_{\text{Std}}/\text{MOLES}_{\text{Std}}}$$

Some typical RMR's relative to d_{10} anthracene are: naphthalene, 0.11(m/z 127); indan, 0.39(m/z 115).

Two ways of utilizing the quantitative data will be discussed. The first is to quantitate classes of compounds found and individual components in those classes which pose severe health hazards. The second is to follow the change in the chemical profile of the gasification stream as a function of time. For example, toluene and benzothiophene initially decrease and then pass through a maxima before arriving at the steady state level while others such as benzene and xylenes decrease steadily from the initial concentration to their final level.

This work is supported by EPA Grant #R804979010.

SYMPOSIUM ON GC/MS

Second Floor, Conference Rooms C,D

F. D. Guffey and M. Aaronson, Co-Chairmen

Monday Morning - Michael Aaronson, Presiding

8:30 Introduction - Frank D. Guffey

8:35-53 RECENT TRENDS IN GC/MS ANALYSIS, W. H. HcFadden, Finnigan Instruments.

The combination of gas chromatography and mass spectrometry was first proposed as a unified analytical system in 1967- Today, in the third decade of GC/MS, it is both interesting and instructive to review the growth of this important analytical technique. This paper will present an overview of the development of GC/MS and relate early methodology with that in practice today. The discussion will include the role of capillary columns, separators, chemical ionization, and selective methods of mass spectral operation. The dominant position assumed by the computer will be given special attention, particularly with respect to its part in future development.

9:05-54 A COURSE IN SEPARATIONS AND ANALYSIS BY GC, LC, MS AND GC-MS, A. M. Schoffstal1, University of Colorado at Colorado Springs.

A course in organic separations and analysis has been offered in which heavy emphasis is placed on laboratory practice. The content covers GC, MS, GC-MS, TLC, and HPLC. The course meets for one lecture hour and six lab hours per week. Instruments utilized are a Beckman 72-5 GC with Flame Ionization Detector, a Varian EM-600 Mass Spectrometer, a Hewlett Packard 5992A GC-MS with Membrane Separator (courtesy of F. J. Seller Research Laboratory, United States Air Force Academy), and a Solvent Programmable Altex HPLC System with Model 110 pumps. Emphasis is placed on deriving useful information from the separation and analysis techniques rather than learning about the inner workings of the instruments which is covered in the instrumental analysis course. Course examinations are take-home, and they are designed as learning experiences. The last portion of the course is a project based on a primary journal reference of each student's choice. Projects include GC and GC-MS or TLC and LC with MS. The main objective of the projects is to have students attempt to repeat work reported in the primary literature. Projects are not meant to be original research. At the conclusion of the project, students compare their data with that of their reference work. Texts, experiments and student data from the course will be presented.

9:50 Break

10:20-55 THE IDENTIFICATION AND MEASUREMENT OF ORGANIC POLLUTANTS IN HUMAN TISSUES BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY, G. W. Sovocool, L. H. Wright and Robert G. Lewis, U.S. Environmental Protection Agency.

Results are presented from the gas chromatography/mass spectrometry (GC-MS) examination of human adipose samples collected through the Environmental Protection Agency's National Human Monitoring Program for pesticides. Interference by fat-related species is discussed and methods used to remove fat from the samples are given. Foreign organic compounds found in human tissues and their possible origins are discussed. Species identified include: hexachlorobenzene, hexachlorocyclohexane isomers, DDT, chlordane-related components, polychlorinated biphenyls, mirex, hexabromobiphenyl and the recently discovered polychlorinated terphenyls. Artifacts such as cholesterol phthalate este

10:50-56 GC/MS ANALYSIS OF WATER AND WASTEWATER SAMPLES BEFORE AND AFTER OZONOLYSIS AND CHLORINATION, R. H. Shapiro, R. M. Barkley, K. J. Kolonko, L. J. Haack, J. C. Wallace, G. A. Eiceman, R. T. Binder, and R. E. Sievers, University of Colorado.

Combined GC/MS has been used to study the chemical changes occurring in water and wastewater which has been treated with either ozone or chlorine. Wastewater samples, both untreated and ozone treated, were obtained from the Upper Thompson Sanitation District treatment facility; untreated and chlorine treated samples were obtained from the Metro-Denver Sewage District plant. Major changes were observed with ozone treatment. For example, a large increase in aldehydes and saturated hydrocarbons was observed. Model compound studies revealed the origin of such species to be olefins which yield aldehydes; subsequent decarbonylation of the aldehydes yield the hydrocarbons. In other wastewater samples, heterocyclic compounds were identified before treatment with an oxidizing agent. Caffeine and uracil Were chosen as model compounds for determining products from the heterocyclic compounds and those substances were ozonized and chlorinated under laboratory conditions. The product mixtures were analyzed by GC/MS and products were identified by this as well as other techniques.

11:20-57 QUANTITATIVE DETERMINATION OF CHLORPHENIRAMINE IN SERUM BY SELECTED ION MONITORING GC/MS, J. A. Thompson, K. W. Panter and R. M. Barkley, University of Colorado.

Chlorpheniramine (CPA) has been a heavily used antihistaminic drug for many years; however, it has not been adequately studied with regard to its pharmacokinetic properties. The best explanation for this is that the drug is administered in very low doses (2-4 mg) and analytical methods with sufficiently high sensitivity and specificity to measure low nanogram to picogram amounts in physiologic fluids have only recently become available. Attempts were made to use GC with specific nitrogen detection of the column effluent for this work. The sensitivity is sufficiently high, but other compounds interfere with CPA quantitation. Alternatively, we have developed a GC/MS assay using tetradeuterated CPA (CPA-d_4) as the internal standard. CPA is efficiently and selectively labeled in the £-chlorophenyl ring by treatment with concentrated D_2SO_4 at 110°C in a sealed ampoule for several days. The base peak in the electron impact mass spectrum results from cleavage at the benzylic carbon with hydrogen transfer and charge retention in the ring system. This highly diagnostic ion occurs at m/e 203 with the analogous ion from CPA-d_4 occurring at m/e 207. Selected ion monitoring of these peaks (and the ^{37}CI isotope peaks at m/e 205 and 209) in samples spiked with known amounts of CPA and CPA-d_4 have resulted in the generation of standard curves to sub-nanogram quantities of CPA. Serum samples taken at various time points from pediatric patients under controlled CPA therapy have been quantitated by this technique.

Monday Afternoon - Frank D. Guffey, Presiding

1:30-58 FIELD-IONIZATION AND ELECTRON-IMPACT MASS SPECTROMETRIC CHARACTERIZATION OF RAW AND HYDR0TREATED ANTHRACENE OIL,* S. E. Scheppele and G. J. Greenwood, Oklahoma State University.

The effect of catalyst, reaction temperature, and hydrogen pressure on the upgrading of anthracene oil has been investigated using trickle-bed reactors by B. L. Crynes and associates in the Dept. of Chemical Engr. Samples of the feedstock and upgraded liquids were separated by our group using anion- and cation-exchange and complexation chromatography. Group-type analyses were obtained for each of the fractions using the technique of low- and high-resolution field-ionization and high-resolution 70-eV electron-impact mass spectrometry GC/MS was also employed to acquire compositional data for the neutral fractions. Compositional data will be presented for both feeds and products. Discussion will emphasize the effect of reaction conditions on both the production of hydroaromatics and reactivity of aromatic compound types containing sulfur, oxygen, and nitrogen. Carbon-number distributions for the sulfur-containing and basic-nitrogen-containing aromatics will be related to the available mechanistic data for desulfurization and denitrogenation.

*Research Supported by the Dept. of Energy; Contract Nos. EX-76-C-01-2011 and EX-76-S-01-2537.

2:00-59 USE OF COMBINED SIMULATED DISTILLATION AND GC-MS IN THE CHARACTERIZATION OF SHALE OILS, R. A. Heppner, Laramie Energy Techno1« Center-DOE.

The development and utilization of alternate fossil fuel sources such as oil shale requires the use of analytical techniques which provide both an accurate and an efficient characterization of the produced oil. Analysis of the product oil is necessary in order to evaluate both the in situ methods used for recovery of the fossil fuels and also their potential as feedstock materials. The simulated distillation GC-MS technique is attractive because it provides a relatively rapid sample analysis with minimal sample preparation. By operating the GC in a GC-MS system under conditions similar to those used in simulated distillation, mass spectra can be acquired as a function of distillation temperature. Summation of the mass spectra obtained within a certain distillate range results in an average mass spectrum representative of the sample material boiling in that temperature range. Various distillate cuts can be chosen, such as the naphtha, light, and heavy distillate fractions into which crude oils are conventionally separated. Application of a type analysis to the average mass spectrum for each distillate cut provides information about the distribution of compound types as a function of distillation temperature. Approximate carbon number ranges for the types can be inferred from the temperature information. The results obtained from the application of this technique to several produced oils will be presented.

2:30-60 GC/MS/DS CHARACTERIZATION OF HYDROCARBON AND POLAR FRACTIONS FROM CRUDE OIL DISTILLATE CUTS, T. R. Ashe and R. J. Pancirov, Exxon Research and Engineering.

Aside from mass spectrometric hydrocarbon type analysis, little data exists on the composition of petroleum liquids above the naphtha range. Compositional data of this type would be extremely valuable to the petroleum chemist involved in process development. In our laboratory GC/MS/DS has been used to partially characterize three column fractions obtained from crude oil distillate cuts in the 325-375°C range. The column fractions were prepared by eluting the crude from Attapulgus clay with n-heptane, toluene and acetone. The n-heptane fraction was further separated on silica gel to obtain an aromatic/saturate split. The aromatic fraction and toluene and acetone clay fractions were examined by GC/MS/DS for compositional information.

Data obtained indicates that this is an extremely powerful tool for determining the presence of compound types and their isomers.

In addition quantitative information can be obtained.

3:00 Break

GC/MS ANALYSIS OF ORGANIC MATERIAL ISOLATED FROM WATER PRODUCED DURING IN SITU RECOVERY OF FOSSIL FUEL RESOURCES,

F. A. Barbour, T. E. Owen, and F. D. Guffey, Laramie Energy Technology Center-DOE.

The production of fossil fuel by in situ techniques can yield large quantities of water. This water whether from intrusion, combustion, or process will be contaminated with water soluble organic compounds. The analysis of the organic material is important not only from the standpoint of selecting control technologies to purify the water but also in monitoring these technologies for efficiency. Combined gas chromatography/mass spectroscopy was used to analyze the extractable organic material in water produced during Laramie Energy Research Center's second in situ tar sand combustion.

Fractions of organic material defined as acid and base extracts were obtained by liquid liquid extraction using either trichlorotrifluorethane or ethyl ether. The acid extracts were directly analyzed by GC/MS which resulted in identification of individual components. The base extracts were found to be more complex and could not be studied directly with GC/MS. Fractions of the base extract were obtained by trapping intervals of the effluent from the GC separation of the base extract using an 0V-10I column. The fractions were chromatographed on an SP-1000 column for GC/MS investigations.

Combined gas chromatography/mass spectroscopy of these samples permitted the identification of individual components, but this is time consuming and not applicable to routine screening of samples. Using selected computer techniques, fewer mass spectrometric experiments were required for routine analysis of the samples.

4:00-62 A NEW MASS SPECTROMETER FOR QUANTITATIVE ANALYSIS OF GASES AND LIQUIDS, W. Henderson, G. A. Errock, D. J. Hoy, and S. Evans, Kratos Ltd.

The MS25Q is a high sensitivity double focussing mass spectrometer designed to provide the high linearity and reproducibility required in quantitative mixture analysis. With a resolution of 500 to >2500 and a mass range extending beyond m/e 300 at 4kV and m/e 1200 at IkV, the MS25Q is sufficiently flexible for adaptation to problems such as permanent gas analysis, isotope ratio measurements analysis of hydrocarbon gas mixtures, and analysis of petroleum liquids.

The use of the well established MS50 electron bombardment source and a control of ion chamber temperature to +_0.1°C contribute to the linearity and reproducibility of the instrument. The dual collector features a 16-stage electron multiplier for high sensitivity Operation and a retractable Faraday cage and electrometer with a noise level of 10 Amp for accurate ion beam intensity measurements free of mass effects.

The inlet systems comprise an all-metal inlet with accurate sample pressure measurement facilities, and an all glass heated inlet system for liquids.

The results of an analysis obtained with the MS25Q and the DS50 data system from a Cj to C^ hydrocarbon gas mixture, giving a mean coefficient of variation of less than 0.5%, and that of a saturate portion of a crude oil, giving a mean C.V. of 2.25%, will be discussed.

Examples of the analysis of permanent gases and of isotope ratio measurements will also be discussed.

SYMPOSIUM ON EPR

Third Floor, Conference Rooms C,D

G. R. Eaton, Chairman

- Gareth R. Eaton, Presiding

Introduction - Gareth R. Eaton

DETECTION OF FREE RADICALS IN AQUEOUS SOLUTIONS BY SPIN TRAPPING, E. G. Jaiizen, University of Guelph.

The usefulness of the spin trapping technique in aqueous solutions has been limited by the lack of suitable spin traps. The problems encountered with the use of nitroso-^-butane, PBN and DMPO in aqueous solutions around neutral pH's will be reviewed. Progress in the synthesis and development of differently substituted nitrones will be discussed with special reference to the detection of hydroxy and hydroperoxy radicals as a function of pH.

ESR STUDIES OF STABLE SPIN PROBES IN LIQUID CRYSTALS, G. V. Bruno and M. P. Eastman, University of Texas at El Paso.

EPR studies of vanadyl complexes and ionophore complexed potassium tetracyanoethylene ion pairs in nematic liquid crystals have been carried out. The purpose of these studies has been to investigate molecular motion and ordering in nematic solvents. The method of Polnaszek, Bruno, and Freed has been applied to slowly tumbling vanadyl spin probes in several nematic solvents. The effect on non-Brownian rotation and fluctuating torques on the rotation of the vanadyl probe is discussed. The ionophore complexed potassium tetracyanoethylene ion pairs are shown to be in equilibrium with free ions in certain liquid crystal systems. The effect of the ionophore on the order and motion of the complexed ion pair is demonstrated. The application of this work to biological systems is briefly explored.

Break

THERMAL AND SPIN LABEL STUDIES OF SCORPION CUTICLE, T. R. White and W. S. Glaunsinger, Arizona State University.

Cuticular phase transitions and molecular dynamics have been studied in the buthid scorpion, Ceritrurbides sculpturatus, and model systems using the techniques of thermogravimetric analysis (TGA), differential thermal analysis (DTA), and electron paramagnetic resonance (EPR). The data indicate that epicuticular lipids are very mobile and exhibit two phase transitions. The results are discussed with reference to current models of the structure of the arthropod cuticli

11:30-66 THE INTERNAL VISCOSITY OF SPINACH THYLAKOIDS, A SPIN LABEL STUDY
S. P. Berg, University of Denver, and P. D. Morse, II, Wayne State University.

The relative viscosity of the internal aqueous environment of spin thylakoids was measured with the spin label TEMPAMINE (2,2,6,6-tetr. methylpiperidine-N-oxyl-4-amine) and the spin broadening agent potassium ferricyanide. It was found: (l) that the 80 nM ferricyanide routinely used to attenuate the TEMPAMINE signal from the external aqueous environment of the thylakoids does not damage the thylakoid membranes as indicated by nearly normal electron transport (300 y eq/mg chlorophyll/hour) and phosphorylation efficiency (P/e_ of 0.8)-(2) that the attenuation of the TEMPAMINE signal by ferricyanide js ' highly dependent on the viscosity of the medium in which the spin label is present; (3) that the viscosity of the internal aqueous space of thylakoids is about 15—17 times that of water.; (4) that this viscosity value does not change substantially over a period of 30 minutes; (5) that ferricyanide enters the thylakoids slowly and broadens the TEMPAMINE signal over a period of 100 minutes, but that this does not alter the calculation of internal viscosity; (6) that the thylakoids were found to accumulate spin label by a factor of 3-5 relative to the concentration in the external aqueous medium; and (7) that the internal volume of the thylakoids is about 1.6 yl/mg chlorophyll at an osmolarity of 0.532.

Tuesday Afternoon - Gareth R. Eaton, Presiding

1:30-67 METAL-NITR0XYL INTERACTIONS, P. M. Boymel, G. A. Braden, J. R. Chang, D. L. DuBois, K. More, R. E. Smith, D. J. Greenslade, G. R. Eaton, and S. S. Eaton, University of Denver, University of Essex, and University of Colorado at Denver.

Electron-electron couplings ranging from 4 to ca. 2600 G have been observed in the room temperature solution EPR spectra of a variety of spin-labeled copper complexes. Ligand systems including Schiff bases, porphyrins, and acetylacetonates will be discussed.

2:10-68 ANALYSIS OF EPR SPECTRA OF SPIN-LABELED COPPER COMPLEXES, D. L. DuBois, G. R. Eaton, and S. S. Eaton, University of Denver and University of Colorado at Denver.

Electron-electron and electron-nuclear couplings in spin-labeled copper complexes have been analyzed as an ABMRY spin system. The off-diagonal matrix elements arising from electron-nuclear coupling were treated as a perturbation to second order. The simulated EPR spectra are in good agreement with the experimental spectra.

2:40 Break

•10-69 EPR STUDIES 0F [FeN°J COMPLEXES, R. D. Feltham, H. Crain, and
^ T. Ma lone, University of Arizona.

The electronic structure of transition metal nitrosyls has long been of interest to inorganic chemists because of the unusual chemical stability and wide range of geometry adopted by coordinated NO groups: linear, bent, and bridging. The [FeNO] group is known to form complexes in which its geometry ranges from linear to strongly bent, and thus provides a system par excellence for probing the relationship between electron distribution and MNO angle. Although a few [FeNO] complexes are high spin with S = 3/2, most are low spin with EPR spectra which are easily detectable at room temperature. Several of these iron nitrosyl compounds, including Fe(N0)[S CN(CHjJ , FeNO(tetraphenylphorphyrin), and Fe(N0)Cl [C,H$_{Ij}$(AstCH-)$_2$l$_2$**rCT0**$_{It}$**]** are isostructural with and form crystals which are Tsomorphous with the corresponding diamagnetic cobalt hosts: Co(NO)[S CN(CH_)J_, Co(NO)(tetraphenylporphyrin) and CoCl$_2$[C$_6$H$_{!t}$(As(CH$_3$)$_2$T$_2$]$_2$[CT0^]7 The FeNo bond angles for these complexes have been determined by X-ray crystallography and are 170°, 1*9°, and 157°, respectively. Single crystals of the dia- -, magnetic cobalt hosts containing 0.1-1% of the appropriate [FeNO] complex have been grown and their EPR spectra determined. The results of these studies will be discussed and related to the current descriptions of bonding in transition metal nitrosyls.

3:35-70 EPR LINEWIDTHS IN LINEAR CHAIN SYSTEMS, B. B. Garrett, Florida State University, and S. L. Holt, University of Wyoming.

In this paper we present a summary of the contributions of electron resonance lineshape studies to the understanding of spin dynamics in linear chain magnets. The existence of a characteristic lineshape has been used to identify linear chain behavior and some qualitative features of the *angu)ar* dependence and temperature dependence of these resonances have been explained but many features of the EPR data are not in accord with current theory. We examine, several such d^viatiojjis for AMnX_ compounds with A = (CH_)^N , RB , Cs and X = CI or Br . The implications of these deviations relative to linear chain correlations are described.

4:15-71 CHARGE COMPENSATION IN IMPURITY CENTERS OF DOPED IONIC CRYSTALS DETERMINATION BY EPR SPECTROSCOPY, G. L. McPherson, Wai-Ming Heung, D. Kay, and K. 0. Devaney, Tulane University.

The distribution of trivalent paramagnetic impurities in a series of doped ionic crystals has been investigated by EPR spectroscopy The particular crystals which were studied have a general formula of CsMX- or Cs^S^ (wheje. M is |g. or Cd and X is CI or Br). The divalent metal ions (Mg or Cd) in these solids are surrounded by approximately octahedral arrangements of halide ions. When trivalent impurities are introduced into these crystals, the foreign ions enter sites normally occupied by the magnesium or cadmium ions which creates a charge discrepancy. Analysis of the EPR spectra of crystals doped with trivalent chromium, molybdenum and gadolinium indicate that the most important factor governing the incorporation of trivalent impurities into these materials is the strict requirement of localized charge compensation. The dominant mode of charge compensation in these host lattices is dramatically affected by the presence of certain other impurity ions. In this paper the relationship of the mode of charge compensation to the structure of the host material as well as the details of the EPR analysis will be discussed.

SYMPOSIUM ON THE NMR OF MACROMOLECULES

D. A. Netzel, Chairman

ESSION I - MACROMOLECULES IN THE SOLID STATE   Third Floor, Conference Rooms A,F

^ ^ j l o j : r ^ - Gary E. MacTel, Presiding

8:30 Introduction - Daniel A. Netzel

^{13}C AND ^{31}P NMR OF MACROMOLECULES IN THE SOLID STATE, J. S. Waugh, Massachusetts Institute of Technology.

An introduction will be given to the principles of magic angle sample spinning in the presence of strong heteronuclear decoupling, emphasizing the obtaining of isotropic chemical shifts and also the anisotropies of various nuclear coupling parameters. These include . the chemical shift, heteronuclear dipole couplings, quadrupole couplings, and second order homonuclear dipole-dipole couplings. Illustrative applications will be given to small molecules, and also to industrial polymers and nucleic acids.

9:15-73 ^{13}C NMR IN CURED EPOXIES: THE ROLE OF MOLECULAR MOTION, A. N. Garroway, W. B. Moniz, and H. A. Resing, Naval Research Laboratory, and D. L. VanderHart, National Bureau of Standards.

Dipolar decoupling and magic angle spinning can produce high resolution C spectra from intractable polymers. For a model epoxy based on the resin diglycidyl ether of bisphenol A (DGEBA), the temperature dependent features of the spectrum signal the presence of large amplitude backbone motion, motions which may relate to the 3 transition in the mechanical loss spectrum. Practical limitations to spectral resolution in highly cross-linked materials will be discussed.

Molecular motion may also contribute to rotating frame relaxation (Tj_{ρ}) although interpretation of these measurements is complicated by the strongly interacting proton bath. Manifestations of dipolar ordering on rotating frame relaxation will be examined briefly for both homonuclear and heteronuclear systems.

9:55 Break

10:15-74 SOLID STATE ^{13}C NMR IN POLYETHYLENE: A QUEST FOR MOLECULAR INSIGHTS IN A STRONGLY COUPLED SYSTEM, D. L. VanderHart, National Bureau of Standards, A. N. Garroway, Naval Research Laboratories

The achievable modulus of highly drawn polyethylene (PE) is only about 25% of its theoretical, extended chain crystal modulus. Since PE is semicrystalline, the orientation and mobility of the non-crystalline regions is important in determining the modulus. Orientation and mobility have been investigated by proton decoupled C NMR in highly drawn PE samples prepared at different temperatures and having different draw ratios.

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C nuclei at natural abundance undergo C-C dipolar spin exchange only weakly so that dispersions of molecular motion are likely to evidence themselves.in C relaxation experiments as a superposition of individual C relaxation rates. This feature, along with the wide chemical shift range and the ability to^resolve different carbon resonances by magic angle spinning makes C relaxation studies potentially more informative-than proton relaxation studies. In a system like PE, T^ studies of C are very tedious due to the long Tj's of the crystalline-carbons. Therefore, C T.$_p$ measurements were performed. The C T^$_p$ measurements in PE were found to be very strongly influenced by the proton dipolar^system. This point will be discussed and ground rules for making C T^$_p$ measurements which can be interpreted in terms of molecular motion will be outlined.

CARBON-13 T EXPERIMENTS IN SOLID POLYMERS, J. Schaefer, E. 0. Stejskal, T. R. Steger, and R. A. McKay, Monsanto Company.

In a recent review of NMR of solid polymers, McCall pointed out that only T. or linewidth measurements have proven to be generally useful. Spin-lattice parameters (Tj and Tj) are severely complicated by spin diffusion processes so that only average values are observed (and these are often dominated by relaxation of uninteresting side groups, residual monomer, or impurities). Forcing main-chain relaxation to be more visible by varying temperature runs into the problem of describing and interpreting anisotropic motion analytically. Carbon-13 spin-lattice parameters are free from complications arising from spin diffusion, at least for most natural abundance experiments. In the study of main-chain motion in the mid-kHz frequency range, the C Tj is particularly useful. There are complications, however. First, the C Tj experiment is itself demanding. Second, the possibility exists of static H- C spin-spin interactions shortening T^ and so confusing its interpretation as a motional parameter. In order to evaluate quantitatively spin-spin contributions to C T. 's, we have measured a host of H and C parameters on a wide variety of glassy and partially crystalline polymers. These parameters include Tjg(ADRF), T.g(SL), Tj , Tjp, and W^- From these measurements we can show that at room temperature, for glassy, lossy polymers, with H linewidths of about 5 gauss, the C Tj (at 30 kHz) is predominantly spin-lattice of motional. This result is consistent with our previous qualitative conclusion. A dramatic demonstration of the spin-lattice character of T^ . is the comparison between the relaxation behavior of p,p-bisphenol-A polycarbonate (Lexan) and the asymmetric o,p-bisphenol-A polycarbonate, in both stationary and magic-angle spinning experiments. As might be expected, the C Tj parameter not only characterizes the room-temperature main-chain motion of glassy polymers, but also those physical and mechanical properties of the polymers which depend on this motion.

35-76 ^{13}C NMR STUDIES OF SOME NATURAL MACROMOLECULES, V. J. Bartusk* J.J.H. Ackerman, and G. E. Maciel, Colorado State University.

Many naturally occurring materials that consist of macromolecules are largely insoluble under conditions that will preserve the structural integrity of the macromolecules. Hence, standard nmr approaches on liquid solutions provide structural information only indirectly, via the small fraction of material that dissolves readily. Important examples of such naturally-occurring "intractable" materials are: coal, oil shale, and a variety of other organic geochemicals; humic acid; and lignin and many other animal or plant-related materials, including high-molecular-weight proteins and nucleic acids. We have obtained C nmr spectra on solid samples of these types of materials, using the magic-angle PENIS technique. Results on fossil fuels are presented in a separate talk. Our spectra are obtained at 15-1 MHz, using a proton Hj of 10 gauss and a ^{3}C H. of 40 gauss. Magic-angle spinning rates of about 2 KHz are obtained using air pressure of 14 lb/in .

This talk will present results on lignin, tannin, cellulose and seeds from a variety of sources and on humic acid samples that have been isolated or treated (e.g., with metal ions) differently. The structural implications of the spectra and their utility in practical studies will be discussed.

CARBON-13 NMR STUDIES OF SOLID POLYMERS: POLYMERS BASED ON p-HYDROXYBENZOIC ACID, J. Economy, C. A. Fyfe, J. R. Lyerla, W. Volksen, and C. S. Yannoni, IBM Research Laboratory.

High resolution carbon-13 NMR spectra have been obtained for the insoluble, highly crystalline homopolymer of p-hydroxybenzonic acid, for two methoxy derivatives of this polymer, and several aromatic copolyesters^by^se of proton dipolar decoupling, magic-angle spinning, and C- H cross-polarization techniques. Resolution is sufficient that the majority of carbons in the polymers repeat units appear as individual resonance lines. The width of resonance lines (<15Hz) are 3~6 times more narrow than obtained for glossy polymers—a result which is attributed to both the rigidity of these aromatic polyesters and the homogeneous local environment associated with crystal habit. Results from variable contact time cross-polarization experiments and variable temperature studies will be discussed relative to polymer structure.

2:00-78 DIPOLAR, QUADRUPOLAR, AND MAGIC ANGLE SPINNING NMR IN BIOLOGlCAl SYSTEMS, R. G. Griffin, Massachusetts Institute of Technology

Although the goal of multiple pulse and dilute spin double resonance NMR techniques is the suppression of dipolar broadening jn solids, the development of these methods has suggested means wh by dipolar interreactions may be retained as a source of structu^" data. That is, if spin pairs are present in magnetically dilute form, then well resolved dipolar spectra are observed and thus \nt nuclear distances and directions can be determined. We demonstrat^* this first with examples from C spectroscopy. In one case to be* discussed, the splittings are homonuclear in origin and consequent! solid state AB spectra are observed. *

We also show that ^{14}N can be an attractive nucleus for study of many problems from the standpoint of both sensitivity^and resolution. Specifically, because of its *33.6%* abundance N signals are easily observable and the large quadrupole couplings spread the lines over 4-5 MHz. The size of these splittings together with the relatively **narjjoWj** 1ines, results in spectral resolution of one part in 10-10 . N- H moiejjies constitute dilute spin pairsj and, consequently, undecoupled N spectra exhibit well resolved H dipolar splittings; thus, NH bond distances and directions can be determined in a straightforward manner. The possible application of N NMR to structural determinations of moderate size peptides will be discussed.

Finally, examples of magic angle spinning spectra at high magnetic fields (7.0 T) will be given. Contrary to conventional wisdom, the technique works well^at high fields and permits observation of high resolution P and C spectra of unsonicated model membranes. Thus, the decade old controversy concerning the effects of sonication on these systems can be circumvented.

APPROACHES TO NMR SPECTROSCOPY OF "BIG" MOLECULES IN THE SOLID STATE: FOSSIL FUELS AND POLYMER NETWORKS, J. L. Ackerman, A. Pines, and J. E. Mark, University of Cincinnati and University of California.

This talk will discuss the application of solid state NMR[1] spectroscopy to two types of extended molecular systems. In both instances, the macromolecular character prevents the isotropic molecular reorientation which would permit the NMR spectroscopist to obtain resolved chemical shift spectra of molecules in the liquid state by averaging away the strong dipole-dipole interactions.

Coal. A novel variation[1] of the magic angle spinning (MASS) technique is used to obtain high resolution isotropic chemical shift spectra of deuterium in solids. The experimental method as well as results for model compounds are presented. The potential application of this method to the study of the mechanism of hydrogenative liquefaction of coal is discussed. By using deuterium as an isotopic tracer and observing the undissolved sample directly, the procedure circumvents (1) the possible scrambling of hydrogen during preparation of a sample by dissolution, and (2) the task of searching for potentjally subtle changes in highly complicated C (double resonance) or H (multiple pulse) MASS spectra.

Elastomers. The molecular theory of rubberlike elasticity is based on the statistical mechanics of polymer chains and networks. Although established in the 1940's, the theory contains a key assumption, namely that of affine deformation, which has not been subject to direct experimental investigation,[2] except for very recent work using small angle neutron scattering, which requires highly sophisticated (and not widely available) experimental facilities. We present here a wideline solid state NMR experiment which might provide a test of the affine assumption.

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3:00 Break

3-30-80 ' JC NMR STUDIES OF SOLID FOSSIL FUELS, G. E. Maciel and V. J. Bartuska, Colorado State University; and F. P. Miknis, Laramie Energy Technology Center-DOE.

For oil shales and typical coals only a small fraction of the organic substances can be extracted from the solid under mild conditions that would be expected to preserve the primary structural integrity of the organic compounds. Hence, solid^ample C techniques are extremely valuable. We have obtained C nmr spectra of dozens of solid oil shale, kerogen and coal samples from around the world, using the magic-angle PENIS technique. Our spectra are obtained at 15.1 MHz, with a 10-gauss proton H., a 40-gauss *ic u* and magic-angle spinning rates of about 2 KHz (using 14 lb/in ^{1} air pressure). Results will be described for oil shale and coal before and after processing (e.g., retorting, reverse combustion, solvent refining). The most direct information obtained from the spectra are apparent ratios of aliphatic carbons to aromatic and olefinic carbons. Difficulties in quantitating the results and the need for intensity.standards are discussed. Various empirical correlations relating '3C-derived structural information to fuel data will be presented.

k:00-81 COAL, POLYMERS, AND THE TIME DEPENDENT SCHRODINGER EQUATION,
B. C. Gerstein, Iowa State University.

The use of transient techniques in nuclear magnetic resonance offers the possibility of selectively removing interactions which broaden solid state spectra. Applications include the use of multiple pulse NMR for determination of chemical shift anisotropics, a unique determination of crystallinity in polyethylene, determination of aliphatic fractions of protons and carbon in coals via combined multiple pulse homo- and heteronuclear decoupling and magic angle spinning, and determination of geometries of randomly oriented molecules in the solid state.

4:30-82 ANALYSIS OF PROTON TYPES IN SOLID PITCH SAMPLES, R. M. Pearson,
Kaiser Aluminum and Chemical Corporation.

Second moment analysis of wide line nmr spectra is used to calculate the relative concentrations of the major types of protons found in solid pitch samples. This method consists of measuring, by high resolution nmr, the chloroform soluble portion of a variety of pitch samples. The concentrations of aromatic protons, aliphatic protons and protons bound to a carbon atom adjacent to an aromatic ring are determined. These samples are then used to show that the second moment of the wide line nmr spectrum is a measure of aromatic protons when determined at liquid helium temperature, and a measure of aromatic protons plus protons on carbon atoms adjacent to the aromatic ring when determined at liquid nitrogen temperature. Thus, measuring the second moment of the nmr spectrum of a solid pitch sample at these two temperatures allows one to calculate the three major types of protons present in these materials.

SESSION 1 - MACROMOLECULES IN THE SOLID STATE—Continued

Tuesday Morning - Vic Bartuska, Presiding

8:30-83 HIGH RESOLUTION ^{13}C NMR IN SOLIDS USING VARIABLE TEMPERATURE MAGIC ANGLE SPINNING, C. A. Fyfe, J. R. Lyerla, and C. S. Yannnp,; IBM Research Laboratory.

Variable temperature isotropic high resolution NMR spectra of solids have been obtained using magic angle spinning, combined with cross-polarization and dipolar decoupling. The utility of temperature variation in NMR spectroscopy for kinetic measurements, derived both from spectral lineshape changes as well as spin lattice relaxation times is well known. The conglomerate NMR experiment pioneered by Schaefer and Stetskal makes this kind of study feasible in organic solids with carbon-by-carbon detail. A reliable spinning apparatus is necessary to be able to do variable temperature studies in both solids and frozen liquids. Such an apparatus, which is easily loaded into a standard NMR probe, will be described, along with results on a variety of materials: polymers, frozen organic liquids, charge transfer complexes and fluxional organometallic molecules. High resolution spectra have been obtained at liquid nitrogen temperature.

flli QUADRUPOLE EFFECTS ON HIGH RESOLUTION NMR OF SOLIDS: 'H NMR, RELAXATION AND C- N DIPOLAR SPLITTING IN MAGIC ANGLE SPINNING EXPERIMENTS,* M. Alia, R. Eckman, E. Kundla,** and A. Pines, University of California, Berkeley.

It was demonstrated recently that using relatively slow magic angle spinning of powder samples of inhomogeneously broadened NMR lines can be narrowed by several orders of magnitude. Preliminary applications to deuterium have been reported. We describe here some new developments. Using rotation-synchronized sampling together with an.improved spinner system (to be described) a narrowing factor of **10** was achieved for H, in favorable cases. This allowed determination of the isotropic chemical shifts of all deuterons for a series of parasubstituted benzenes. Selective Tj measurements suggest that spin diffusion which is effectively quenched by the orientation dependent quadrupole coupling, may be partially restored by the sample rotation.

The average of dipole-dipole interaction should not vanish under magic angle fast rotation conditions if one of the nuclei has a quadrupole coupj^ng. We investigated high resolution spectra of C coupled to N and indeed found a well resolved structure due to dipolar interaction. The splittings and the shapes of lines are determined by the internuclear distance, quadrupole coupling and the external magnetic field. Experiment and theory are in excellent agreement.

^Department of Chemistry and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 9**720.**

**Institute of Cybernetics, Estonian Academy of Sciences, Tallinn, Estonian SSR 200026.

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9:30-85 PULSE PROGRAMMER FOR HIGH RESOLUTION NMR IN SOLIDS, R. A. Monsanto Company. ;—

A pulse programmer for generating the pulse sequences required for a wide variety of solids NMR experiments is described. All pulses required for gating **4**-phase RF systems for both abundant (l) arvd rate (S) spins are included. Also, the pulse sequences required for the **4-8** pulse l-l decoupling schemes are included. The programmer can operate independently or under control of the spectrometer's computer.

10:00

10:15-86 A NEW TECHNIQUE FOR SELECTIVE HIGH RESOLUTION PROTON NMR IN SOLIDS, J. A. Reimer and R. W. Vaughan, California Institute of Technology.

Dipolar Difference Spectroscopy is a new technique in which dynamic double resonance pulse schemes which remove both heteronuclear and homonuclear dipolar interactions have been used to isolate the chemical shift spectra of specific protons within polycrystalline solids. While narrowing the proton, I, spectrum with the eight-pulse scheme,

we suppressed the heteronuclear l-S ('H-^^{3}C or ^H-^N) dipolar interactions with a four-pulse scheme every other acquisition. By alternately adding and subtracting acquisitions, we obtained by difference the proton chemical shift spectrum of the coupled I spin in a number of complex organic solids. Dipolar modulations of the proton chemical shift spectra were then created and furnish local geometric and motional characteristics in these solids. Applications of these techniques are discussed for several complex systems yielding information on hydrogen bonding, molecular motion and surface phenomenon.

— g7
10-.45- APPLICATION OF HIGH RESOLUTION SOLID STATE NMR TECHNIQUES TO FORMIC ACID ADSORBED ON Y ZEOLITES, M. T. Duncan and R. W. Vaughan, California Institute of Technology.

Cross polarization, proton decoupling, dipolar difference, and dipolar modulation spectroscopy have been applied to characterize the motional and chemical properties,of formic acid adsorbed on ultrastable-Y and ammonium-Y zeolites. C powder patterns obtained by cross polarization have line widths of 110 and **88 + 4** ppm on the ultrastable-Y and ammonium-Y, respectively, at room temperature, increasing to 155 and 120 + **4** ppm, respectively at -160°C. The center of mass and general shape of these lines_ compare with the C tensor in formate ions, such as $Ca(HC0_2)_2$ and NH^fHCO,,) as opposed to formic acid. The spectrum of the 'H bonded to the carbon obtained by dipolar difference spectroscopy is an asymmetric line, 10 ppm wide, also with a center of mass typical of protons bonded to a carbon in a formate ion. At least two different T^'s are observed for the formic acid, **4** msec and 90 msec, and they occur in a ratio of 1:2.**4** on both the ultrastable-Y and ammonium-Y zeolites.

11:**15**-88 DIPOLAR-NARROWED CARR-PURCELL MEASUREMENT OF MULTIPLE PULSE SPIN-LATTICE PARAMETERS IN NATURAL RUBBER, C. R. Dybowski, University of Delaware, and R. G. Pembleton, Iowa State University and DOE.

A technique for measuring the spin-lattice contribution to multiple pulse decays (e.g., associated with the REV**-8** sequence) via use of a 17-pulse sequence is demonstrated. The 17 pulse sequence has been applied to the determination of spin-lattice broadening in a sample of polyisoprene to estimate this contribution to the multiple pulse lineshape. The spin-lattice relaxation is exponential with a damping constant, Tj . This relaxation time is compared with Tj_p as determined by the' usual spin lock method, with a field of locking strength related to the pulse spacing of the sequence. T. depends on pulse spacing in a manner which is not in agreement ^*lin* calculations based on a model using a single correlation time.

A. Vega and R. Vaughan, J. Chem. Phys., **68, 1958** (1978).

45-89 MAGIC ANGLE SPINNING WITHOUT THE MAGIC, K. W. Zilm and D M **K**
University of Utah. * ran *,

Magic angle spinning is a well known technique for narrowing \\ broadened by dipolar interactions or chemical shift anisotropy "6S rigid solids. Equally well known are the difficulties associat'rt with spinning a polycrystal1ine sample at rotational rates of ma kilohertz. However, even with the experimental difficulties maa"^ angle spinning has gained greatly in popularity as an experiment^ technique in recent years. The combination of magic angle **spirm?** and cross polarization has yielded a wealth of high resolution ^ spectra of solids. Recently new approaches involving pulse seque and observation of the spins synchronous with the spinning have un-'* covered more applications for magic angle rotation. In our lab we have designed a magic angle spinner which is very easy to use. it is capable of speeds up to 15 kHz with helium as a driving gas. operation in the probe at anywhere from *h* to **8** kHz with air is almost trivial. The angle need only be found once during set-up with a standard sample such as hexamethylbenzene. Samples may be inserted and removed quite easily and without having to move either the probe or spinner base. In this fashion we assure that the magic angle is met from sample to sample without having to adjust it on each spectrum. This is especially useful in taking spectra of complex mixtures (e.g., coals, etc.) where there are no clear cut means of verifying that the angle is set or when the signal to noise is such that repeating the spectrum at different angles would require a prohibitive amount of time. Cross polarization and F.T. spectra of several compounds will be presented to demonstrate stability, sensitivity, resolution and reproducibility of the magic angle from sample to sample. Applications to complex systems such as coals and bile stones will be displayed along with photographs and drawings of the probe and spinner. Some of the problems in using such a set-up in variable temperature work will also be addressed.

II - GENERAL NMR TECHNIQUES Third Floor, Conference Rooms A,F

Afternoon - Roger Assink, Presiding

(5_q0 ^{13}C-^{1}H CROSS-POLARIZATION STUDIES OF ORGANIC LIQUIDS, R. D. Bertrand, A. N. Garroway, G. Chingas, and W. B. Moniz, Naval Research Laboratory.

The application of cross-polarization experiments to obtain proton decoupled C NMR spectra of liquid samples is presented. Compared to solid state cross-polarization, here the Hartmann-Hahn condition must be,more carefully matched. The observed sinusoidal variation of the C signal with cross-polarization time agrees with theoretical predictions for .CH, .Cl^, and CH, groups. Signal enhancements approach the four-fold value predicted. Conditions appropriate for rapid, accurate and precise quantitative analysis are presented. The efficiency of data acquisition is improved^through the use of paramagnetic relaxation reagents which reduce H T^'s. A novel compensation scheme is presented which makes the cross-polarization • process less sensitive to the Hartmaipn-Hahn condition. Results will also be given for the case in which H decoupling is not employed.

2-10-91 HIGH TEMPERATURE ^{13}C FT NMR STUDIES OF COAL PRODUCTS, H. C. jw
L. T. Taylor, and T. Glass, Virginia Polytechnic Institute anT"""'
State University.

The complexity of coal product mixtures represents an acute analytical problem for solution studies utilizing quantitative *C FT nmr techniques. The problem of solutjori homogenity for complex product mixtures in high resolution C FT nmr studies is the major focus of this presentation. One method of suppressing this problem is the use of C FT nmr high temperature nmr solvents and/or high temperature examination of "melts" of the coal products. Data will be presented which indicate the severity of the problem under typical conditions (e.g., room temperature studies). The variation of average molecular parameters (e.g., aromaticity) as a function of temperature for solvent refined coal (SRC) samples will be discussed. Results obtained for the SRC samples indicate a marked improvement in solution homogenity at elevated temperature.

2:35-92 A POSSIBLE PROTON NMR NOE REFERENCE MATERIAL, E. P. Mazzola and S. W. Page, Food and Drug Administration.

The nuclear Overhauser effect (NOE) involving spatially proximate protons within the same molecule has been recognized as a powerful tool in structural elucidation work for over a decade. This technique is, however, the most difficult to perform of the classical "double resonance" experiments such as spin decoupling and INDOR. Failure to observe an NOE may be due to a variety of experimental errors, but unlike the latter methods no reference material such as 2,3-dibromopropionic acid (INDOR) exists for the determination of NOE's.

2,5-Dichloro-4-nitroanisole may fill this need. It appears to be a promising reference material for the following reasons: (i) all three of the resonance signals are single lines which allow facile irradiation and integration, (ii) H-3 can serve as an internal control whose integrated intensity should not increase upon irradiation of the methoxyl protons, (iii) the chemical shifts of the two aromatic protons are sufficiently separated (*ca*. 1.1 ppm) to permit easy integration, (iv) substantial enhancement *(>3Q%)* has been observed for H-6 upon irradiation of the methoxyl protons, and (v) the compound is easily prepared and may eventually be commercially available.

The subject anisole may prove to be a useful reference material for the determination of proton homonuclear NOE's in both the CW and FT nmr modes.

3:00 Break

3:15-93 COMPLEXATION STUDIES OF MERCURY COMPOUNDS WITH NITROGEN CONTAiu LIGANDS USING ^{yy}Hg NMR, M. J. Albright, R. H. Obenauf, and K ^{G}

JEOL Analytical Instruments, Inc. ' '^{G}°to,

Complexation of the Group MB metals has been studied in detail Zinc compounds that are complexed with nitrogen or oxygen conta* ing ligands are numerous. Cadmium is not as well known, but me'-" cury compounds with phosphorous containing ligands are quite common. However, mercury complexes with nitrogen ligands are virtu unknown since the nitrogen donating orbitals (2p hybrid) and the empty 6p orbitals on mercury do not overlap well.

Previous ^{199}Hg NMR studies hav^ |ound large changes of the chemical shift with donor solvents. ' A Lewis acid-base mechanism appeared to be contributing significantly to the chemical shift. AlsOg^he binding of Hg(II) ions to carbonic anhydrase was observed by Hg NMR.

Since the interaction would be solvent sphere in nature a nitrogen containing ligand in a non-nitrogen containing solvent should compete for available sites on the mercury, and some measure of the nitrogen binding should be available from the Hg chemical shift. This is true for nitrogen containing ligands such as pyridine, bipyridal, dipyridal amine and EDTA. To confirm that some nitrogen-mercury binding was really responsible for this effect, the N NMR of the dipyridal amine was monitored as mercury concentration increased. Only the ring nitrogen, not the amineqnitrogen, displayed the change in chemical shift. Other than the Hg chemical shift, the Tj's of the mercury were greatly affected by the nitrogen ligand concentration. Complexation would affect both the spin rotation and the chemical shift anisotropy mechanisms.

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M. A. Sens, N. K. Wilson, P. D. Ellis, and J. D. Odom, J. Magn. ,Resonance, 19, 323 (1975).
J. L. Sudmeir and T. G. Perkins, J. Am. Chem. Soc., 99, 7732 (1977).

3:40-9* CARB0N-13 FTNMR OF SUB-MILLIGRAM AMOUNTS, T. H. Mareci and K. N. Scott, University of Florida.

Carbon-13 NMR spectra of sub-milligram amounts have been obtained by the repetitive pulse Fourier transform technique with careful consideration given to optimizing spectrometer operating conditions. We will discuss in detail the factors affecting the sensitivity of observation, such as type of sample cell, solution volume, insert sensitivity, sample temperature, pulse duration, rf power, repetition rate, relaxation times, digitization and data collection conditions.

i>:05-95 13c AND 19pNMR SPECTROSCOPY OF HALOCARBONS, A. Foris, E. I. du Pont de Nemours and Company.

C NMR is an excellent technique for the isomer identification of pure compounds and of components in simple mixtures. The technique readily yields information about the number of different-C nuclei and the numbers of H and F nuclei attached to each C. ^C NMR spectra of complex mixtures, however, may be difficult to interpret. Often such mixtures can still be analyzed by F NMRjSince the F spectral range is much wider than the corresponding C range.

Quantitative^analysis of C^-chlorofluorocarbon isomers is best achieved by F NMR. The limit of detection of a given isomer varies with the type and number of isomers involved, their absolute concentrations in the mixture and the equipment available. Relative concentrations of 99.9 and 0.1 percent have been determined for some isomer pairs. The method is simple, direct, specific and requires no calibration.

4:30-96 THE STUDY OF PHASE SEPARATION IN BLOCK AND SEGMENTED COPOLYMPD ERS BY NMR,* R. A. Assink, Sandia Laboratories.

Block or segmented copolymers often undergo microphase separ f with the resultant formation of hard and soft domains. Many f¹ unique mechanical properties of segmented polyurethanes can b ^ understood on the basis of their microphase structure. The ex* ence of domains, the glass transition temperature of each type'^* main, and the kinetics of domain formation were studied by obse °" ing the two component behavior of the proton-free induction deca*" A series of polyurethanes was investigated in which the relative^* composition of rigid and flexible segments was systematically varied. The glass transition temperature of the hard domain was found to increase as the percent of rigid segments increased while the polyurethane with the lowest percentage of rigid segments did not undergo phase separation. Polyurethanes crosslinked at elevated temperatures were found to undergo less complete phase separation. The mobility of the soft domain decreased as the extent of cross-linking increased. Recently obtained hydrogen decoupled spectra of block and segmented copolymers has permitted the chemical composition of each phase to be determined. Evidence for an interface region could be seen.

*Work supported by U.S. Department of Energy.

SESSION HI**H** **I** - BIOPOLYMERS   Third Floor, Conference Rooms B,E

^5^yjtorn]n£ - Michael Burke, Presiding

8-30-97 HIGH-FIELD NMR OF MEMBRANES AND PROTEINS, E. Oldfield. University of Illinois.

Combined application of high-field NMR, neutron diffraction and Raman spectroscopic techniques permit detailed evaluation of the structure of deuterium labelled membranes. Results will be presented on the lecithin-cholesterol system, and progress in the study of intact biological membranes will be reported.

Results obtained using a recently constructed sideways-spinning 20 mm tube probe, designed to optimize signal-to-noise ratios in superconducting magnet geometries, will be presented on the following proteins: hemoglobin, lysozyme and cytochrome £. A C NMR investigation of the denaturation of lysozyme will be discussed.

9:00-98 NMR RELAXATION AND DIFFUSION OF PHOSPHOLIPIDS IN MODEL MEMBRANES, A. Kuo and C. G. Wade, University of Texas.

The lipid-water binary system when oriented forms multibilayers which resemble natural membrane structures. The lipid diffusion coefficients have been determined by pulsed gradient spin echo NMR techniques. In order to minimize the dipolar interactions, the lipid-D^O samples were macroscopically oriented, and all experiments were carried out with the bilayer normal at the "magic angle" (54°7V) with H_q. The results on pure lipid multibilayers are temperature dependent, ranging from 10 to 10 cm /sec at temperatures from the transition temperature, T , to 62°C. The diffusion coefficients show a slight water concentration dependence. Cholesterol content has a strong effect on the transition temperatures but not on the diffusion coefficients. A strong reduction of the transition temperature is observed from 0-12.1 mole percent cholesterol. At *k$* mole percent cholesterol a sharp transition is no longer observed. Cholesterol at high cholesterol concentrations reduces the diffusion coefficients above the phase transition.

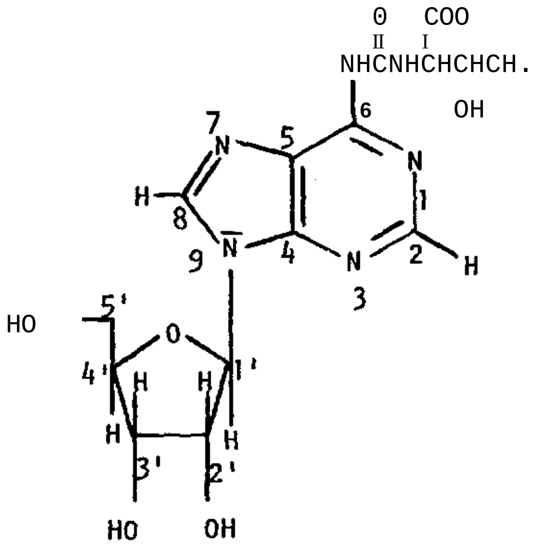
9:30-99 NMR OF TRANSFER RNA, M. P. Schweizer, University of Utah.

We will discuss several nmr studies on structure and function of transfer RNA (tRNA) and several of its unusual constituents.

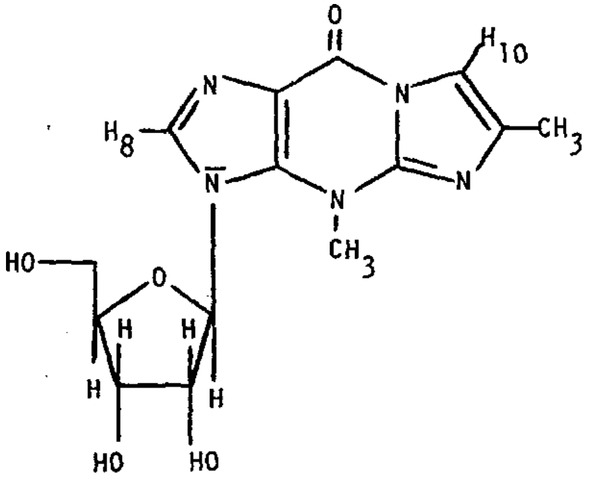
I. N-[9-(B-p_-ribofuranosyl)purin-6-ylcarbamoyI] threonine, t^{6}A, appears next to the anticodon in tRNAs breeding codons beginning with adenosine. Previous results indicated a possible magnesium ion coordination to this residue. We have probed the binding of manganese ion to t^{6}A using ^{13}C NMR at 25 and 75 MHz. We conclude that metal coordination occurs between the carbonyl function at either N$_1$ or N^ on the purine ring.

II 360 MHz pmr studies on a hexanucleotide from the anticodon loop of torula yeast tRNA^{phe} have revealed that the Yt (torula wyosine) is the site for conformation flexibility and base-base destacking in this fragment. This situation is contrasted to the findings on a similar fragment from baker's yeast tRNA containing a more complicated wyosine.

III. The conformational dynamics of tRNA^{glu} and its interaction with glutamic acid synthetase (gluRS) are being investigated using site specific C enrichment. Latest findings will be described.



t^{6}A



10:00 Break

30-100 DEVELOPMENT OF NMR TECHNIQUES FOR DELINEATING CONFORMATIONS OF PEPTIDES AND PROTEINS, J. D. Glickson, N. R. Krishna, R. E. Lenkinski, and D. G. Agresti, University of Alabama in Birmingham.

We wish to report the adaptation and refinement of a number of techniques which hold considerable promise for defining conformational details of peptides, proteins and other biopolymers.

Paramagnetic Metal Probes. A generalized formalism based on the Marquardt or Simplex algorithm has been developed for the analysis of nmr shift and relaxation data. This method was employed^ to fit data on hen-egg-white lysozyme complexes with lanthanides and with transition metals to the following equations:

$$Sd = K_x(3 \cos^2 6 -])Jr^3 + K_2(\sin^2 e \cos 2<j>)/r^3 \qquad (l)$$

$$AV'' + Virr_{2M} = cf(x)/r^6 \qquad (2)$$

where 5 is the electron-nuclear dipolar contribution to the chemical shift, and *K* are constants related to the elements of the magnetic susceptibility tensor of the metal, (r,8,(|>) are the spherical polar coordinates of a given hydrogen in a coordinate system in which the metal **jjS** at the origin and the susceptibility tensor is diagonalized, AV, is the increment in the^roton nmr linewidth associated with binding of a metal such as Gd , r is the corresponding transverse relaxation time, c is a constant which contains electronic terms of the metal ion and ***f(r)*** is a function of the correlation times of the complex. Statistical hypothesis tests employing the Hamilton R-factor ratio method led to rejection of the commonly assumed "axial model" (i.e., ***K*** = 0 or ***K*** <^ ***K)*** with a confidence level in excess of 97.5%. $_1$

Intramolecular Nuclear Overhauser Effect (NOE). We have recently demonstrated that the intramolecular NOE of peptides originates from a predominantly dipolar mechanism and have derived a set of equations suitable for the analysis of NOE data of peptides and other complex biomolecules which do not satisfy the "extreme-narrowing" limit. The effects of conformational averaging, anisotropic rotation, and spin diffusion on NOE measurements have been considered. Transient NOE experiments involving selective excitation of resonances have been suggested for overcoming problems resulting from spin diffusion in macromolecules. The utility of NOE experiments was demonstrated by an analysis of NOE data on the valinomycin-K complex which indicated that the solution conformationgcorresponds to the structure determined by X-ray crystallography.

10:30-100 **P**-ntUat^^

Continued nffSt^in changes in the intensifies^
thetr correspondtng resonances when the solvent ,s saturated,
the r OTJrir?P°"a'j2BCts can be accomplished by combining the transfer
of lS»r.t.**on**'mea"reSnS (for NH protons) and internalecular ^
measurements (for CH hydrogens) with appropriate T experiments. For
measurements v^4 X ' teofproton exchange with the,**sol-**
vent y^rn Fo CH do en^thf theory of Krishna and Gordon^1 Y| elds
t • * rmn w uar dipolar relaxation. The above rates serve as]„.
the mtermoe^^* ofNHand CH hydrogens, respectively. To
f1 lustrate*Z* e **Sods** we have employed intermolecular NOE experi-
illustrate tnese e f lvent exposure of the aromatic CH
ments to compa™ J jxttn . of5 (^T) {ndimethylsulf
hydrogens of cyclo ^ ™e pr * t£)nexcnange rates of the NH hydrogens
3-pep. ^ — ^
identify NH hydrogens which are snieiaea

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01 NMR STUDIES OF BLEOMYCIN INTERACTION WITH NUCLEIC ACIDS AND METALS,

P. M. Chen, R. E. Lenkinski, N. R. Krishna, J. L. Dallas, T. T. Sakai, D. J. Patel , E. S. Mooberry, G. C. Levy, and J. D. Glickson, University of Alabama in Birmingham, Bell Telephone Laboratories, North Carolina A S T State University, and Florida State University.

The bleomycins (BLM) are glycopeptide antibiotics employed in cancer chemotherapy. Complexes of the BLM's with radioactive polyvalent metals are employed in the scintigraphic detection of various solid tumors and malignant lymphomas. Our laboratories have been employing H and C FT-nmr spectroscopy to characterize the structure and dynamics of these molecules and of their complexes with polyvalent metals and nucleic acids. Essentially all of the H and C nmr resonances of these complex macromolecyles (M.W. ~ 1,500) have been assigned. ' Chemical shifts of the C resonances were employed to monitor the acid-base titrations of the BLM's, yielding the pK 's of the various ionizable groups. Carbon-13 spin-lattice relaxation times and nuclear Overhauser effects (NOE) were measured at 37-73 MHz and 67.89 MHz at various pH's. Relaxation data for the backbone carbons of the polymer were analyzed in terms of the Woessner model, which applies to an isotropically rotating sphere with one degree of internal rotational freedom per carbon atom. Proton nmr was employed to monitor the binding of BLM-A^ to poly dA-dT and dC-dC-dG-dG, self-complementary poly- and oligonucleotides which serve as models for A-T and G-C base pairs, respectively, of DNA. Selective broadening and shifting of the bithiazole resonances of BLM-A2 and the adenine H-2 resonance of poly dA-dT indicated that these hydrogens are intimately involved in the drug-nucleic acid interaction. Broadening of the positively charged dimethylsulfonium group of BLM-A_2 at low ionic strength also indicated probable association of this group with the anionic phosphate group of poly dA-dT. Qualitatively similar results were obtained in studies of BLM-A_2 binding to dC-dC-dG-dG. Complexes of BLM-A^ with lanthanides, transition metals and gallium were studied by both multinuclear nmr and fluorescence spectroscopy. Nuclear magnetic resonance transfer of saturation experiments yielded estimates of the exchange lifetimes of some of these complexes.

References

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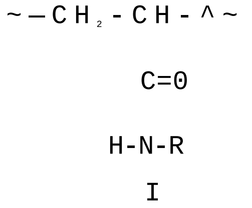
11:30-102 STUDIES OF POLYMER-SUPPORTED a-CHYMOTRYPSIN, J. T. Gerig and D Loehr, University of California. "

A series of N-substituted polyacrylamides (l) has been prepared • which the substituent is either neutral, positively charged or 'n tively charged at pH 7. Light scattering data show that la and"?!!9* are random coils in aqueous solution while the neutral polymer



$$\sim\!-CH_2-\underset{\substack{|\\ C=O\\ |\\ H-N-R\\ \mathrm{I}}}{CH}-\sim$$

a_ R = $-CH_2CH_2COOH$

b R = $-CH_2CH_3$

£ R = $-CH_2CH_2CH_2\overset{+}{N}(CH_3)_3Cl^-$

has anomalous light scattering behavior and appears to exist as a microgel. The proteolytic enzyme a-chymotrypsin has been covalentlv linked to these materials by means of Woodward's reagent K. The kinetic properties of the enzyme-polymer conjugates toward neutral and charged substrates will be briefly described.

Fluorine nmr techniques have been used to examine the active site of the polymer-bound enzyme. Studies of reversible complexes formed with p-fluoro-cinnamic acid and of enzymes irreversibly inactivated with p-trifluoromethylbenzenesulfonyl fluoride will be described. The nmr results suggest that the structure of the enzyme's active site can be appreciably modified by attachment to charged polymers, although the kinetic manifestations of these changes are not large.

Tuesday Afternoon - Martin P. Schweizer, Presiding

1:45-103 COORDINATED CARBON MONOXIDE AS A PROBE OF THE HEME POCKET, J. D. Satterlee and J. H. Richards, California Institute of Technology.

The nmr and ir spectroscopic parameters for the CO-hemoglobins from G. d?branchiata have been obtained. Carbon-13 nuclear magnetic resonance spectra of most '^normal" mammalian CO-hemoglobins exhibit resonances for heme bound CO between -206 and -207 ppm from tms. However, the rabbit CO-hemoglobin and for the hemoglobin from G. dibranchiata the heme coordinated CO resonances occur outside this region of "normal" appearance. A summary of the pH dependence of these spectroscopic parameters for three species of hemoglobins will be presented. This data is interpreted in terms of an ionization process involving the distal histidine (E-7) which suggests a specific role for this ubiquitous amino acid residue.

-104 270 MHz NMR STUDY OF INSULIN, K. L. Williamson, Mount Holyoke College, and R. J. P. Williams and G. Bentley, Oxford University.

Insulin, the hormone responsible for regulating blood sugar levels, consists of a 51 amino acid monomer divided in two chains held in place by disulfide bonds. Insulin is stored in the pancreas as a hexamer, MW 36,000, which derives its stability and conformation by complexing with two zinc atoms. Only at exceedingly low concentrations does this hexamer dissociate into the monomer. We have *carried* out one of the first high field nmr investigations of insulin at physiological pH. The object of the study is to determine whether and how insulin binds to more than two zinc atoms, a matter of clinical interest, in that it governs the duration of action of insulin administered to a diabetic.

Assignments of key resonances of 270 MHz (and some 360 MHz) ^H spectra of native 2-Zn insulin hexamer have been made. Spectra of zinc-free insulin titrated with Zn are unchanged after the addition of • one equivalent of zinc per insulin_hexamer and resemble 2-Zn spectra. Titration of 2-Zn hexamer with SCN or other ions high on the Hofmeister series causes marked changes in the spectra owing to major conformational changes leading to a new hexameric form capable of binding six zinc atoms. Analysis of difference spectra indicates this new hexamer binds two equivalents of SCN at two sites which are assumed to be identical and independent.

2:45-105 APPLICATION OF NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY TO THE CHEMICAL STRUCTURE OF HUMIC ACID, R. L. Wershaw and D. J. Pinckney, U.S. Geological Survey, and L. Cary, Stanford Research Institute.

Nuclear magnetic resonance (NMR) spectroscopy has proven to be a particularly useful tool for the study of the chemical structure of both small molecules and macromolecules. The success that has been achieved by NMR in other fields of chemistry has encouraged several investigators to try the technique on humic acids. These workers have used two different types of NMR: proton NMR and natural abundance C. NMR on unfractionated and underivatized humic acid preparations. The spectra that have been obtained in these studies contain very broad lines which only provide very general structural information. In addition to proton and natural abundance C NMR, we have employed two other NMR approaches to obtain additional structural information. In one of these we prepared methyl derivatives of humic acid fractions in which the.methyl groups added to the humic acid molecules were enriched in C. The NMR spectra obtained on these derivations clearly demonstrate that ester and ether linkages are formed. In the-other approach the humic acid fractions were fluorinated and the F NMR spectra measured. It appears that aromatic substitution has taken place in these experiments. These results show that it is possible to identify definite structural elements in the humic acid molecules.

3:15 Break

3:45-106 STRUCTURAL STUDIES OF A. VARIABILIS CYTOCHROME c**-553**, J. L. Markley, and D. W. Krogmann, Purdue University.

The small soluble photosynthetic cytochrome from the cyanobact • Anabaena variabilis has been structurally characterized by *H !!RIUM spectroscopy. In spectra of the reduced cytochrome resonances r lated to the heme methyl and meso protons, the methionine and h*"6" dine iron ligands, and several aromatic amino acid ring protons h*'* been tentatively assigned. Only one of the three tyrosine resid ^ present exhibits pH titration behavior with a pK of ll.**o**. The ble cytochrome from M. aeruginosa contains a single tyrosine at D ^ tion 80 which is also conserved in all cyanobacteria soluble cyto- '* chromes. This tyrosine also titrates and allows the Anabaena titrat ing tyrosine to be assigned to position 80. The tyrosine ionization* affects the chemical shift of one heme meso proton suggesting a clos spatial relationship between these groups. A temperature study has been carried out on the oxidized cytochrome from Anabaena. Heme methyl resonances are identified in the extreme low field region of • spectra of the oxidized cytochrome. The resonance positions indicate an asymmetric distribution of the unpaired electron density over the heme ring. Structural mechanisms responsible for variations in c-typ« cytochrome mid-point potentials will be discussed in light of the H nmr data presented. (Supported by NSF grant PGM 76-01956.)

4:15-107 STRUCTURE OF XANTH0VIRIDI CAT IN D, A METABOLITE OF PENICILLIUM VIRIDICATUM. APPLICATION OF PROTON AND CARBON**-13** NUCLEAR MAGNETIC RESONANCE, E. P. Mazzola and M. E. Stack, Food and Drug Administration.

Penicillium viridicatum is one of the most frequently occurring mold species in foods and feeds and has been implicated as the causative agent in many instances of animal illness and death. This mold produces numerous metabolites including xanthomegnin, viomellein, rubrosulphin, and viopurpurin (Mac Millan and Simpson, **1975** and 1**977)•** Another P. viridicatum metabolite, designated xanthovi ridicatin D, has been found by proton and carbon**-13** nmr to have the following structure:

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SESSION »v .nu iv - POLYMERS Third Floor, Conference Rooms A,F

^ j ^ H a y Morning - Fran P. Miknis, Presiding

fl.30-IO8 THE POTENTIAL OF ^{17}O FOR THE STUDY OF MACROMOLECULES AND SOME PRELIMINARY RESULTS, D. Fiat and B. Valentine, University of Illinois at the Medical Center.

The ubiquity of oxygen in biomolecules makes it particularly useful forjObtaining information by nuclear magnetic resonance. The use of O as a nuclear probe for studying solvation, correlation times, and hydrogen bond formation is facilitated by the size of chemical shifts observed and the length of its relaxation times. For O the dominant relaxation mechanism is due to the time dependent perturbation (resulting from molecular motion) of the interaction between the nuclear electric quadrupole moment and the intramolecular field gradient so that relaxation studies can yield insight into the motional freedom of the molecule studied. The O chemical shifts are sev-> eral orders of magnitude larger than the proton chemical shifts thus enabling the extension of exchange studies to faster rates than obtainable by proton magnetic resonance. This ability to study faster exchange rates can be applied to rapid tautomerization from which information can be derived concerning stability of various tautomeric forms of macromolecule side chains and substituents in solution. The ability of oxygen to form both proton donating and accepting hydrogen bonds and the distinct chemical shifts of the various hydrogen bonds formed allows the distinction to be made between intra- and intermolecular hydrogen bonds importantjto macromolecules in various solvents. We have been studying the O nmr of amino acids, oligopeptides, and are extending these studies to macromolecules as well as the oxygen containing solvents of these molecules. The goal of the study is to obtain information pertaining to solvation, motional freedom, hydrogen bond formation, and conformation. Because of the wide occurrence of oxygen in biological molecules and the omnipresence of H^O in physiological systems, information obtained should prove invaluable to the study of such systems.

'^O spectrum at natural abundance have been obtained of proline, alanylglyclyglycine and poly-D-L-glutamic acid all in aqueous solutions. The carboxylate resonance of 1 M proline solution was found to be 267 + 2 ppm downfield from H_2O with a half width at half height of 130 + *kHz* at 27°C and pH = 7.8. The oxygen-17 resonance of 1 M solution of alanyl-glyclyglycine was found to be 351 + 3.5 ppm downfield from water with a half width at half height of 187 ±_ 3Hz at 42°C and pH = 5-4. The signal obtained for poly-D-L-glutamic acid (100 mg/ml) had a chemical shift of 359 ±.2.5 ppm downfield from water with a linewidth of 170 + 6Hz at 42°C and pH = 3.4.

9:00-109 ^{13}C NMR STUDIES OF ^{13}C ENRICHED MACROMOLECULES, N. Matwiyoff, Los Alamos Scientific Laboratory.

9:30-110 THE ^{13}C NMR STUDY OF POLYSULFONES, F. A. Bovey, Bell Laboratories

Whereas a-olefins can form only 1:1 alternating copolymers (po] fones) with sulfur dioxide, monomers which can add their own fresu'~ radicals are capable of giving copolymers of varied composition Styrene and 2-chlorobutadiene (chloroprene) yield nearly alternat" polysulfones at low polymerization temperature. As the temperatu'"9 is increased, the tendency to form alternating structures is reduc^ and the sulfur dioxide content becomes smaller. The styrene-SO s tem exhibits a "ceiling" at 40°C above which alternating sequences^" not formed. In the chloroprene copolymers, 1,4-trans_ structures ^ strongly predominate; 1,4-c?s units can be detected but no 1,2 or 3 t units. Head-to-head tail-to-tail chloroprene linkages are prominent even in the polymers prepared at low temperatures. Various strateqi for the assignments of carbon resonances in complex macromolecular *s spectra are discussed. The solution dynamics, as observed by T and NOE measurements, are discussed. Sulfone units stiffen the chains but not as much as was once believed on the basis of dielectric measure-, ments.

10:00 Break

10:30-111 A ^{13}C SPIN RELAXATION STUDY OF CHAIN MOBILITY IN SOME TEREPHTHALIC ACID POLYESTERS, R. A. Komoroski, Diamond Shamrock Corp.

Carbon-13 spin-lattice relaxation times (T^), nuclear Overhauser enhancements (NOE), and resonance linewidths(Av) have been measured for a series of terephthalic acid polyesters containing ethyl, butyl, hexyl, and isopropyl groups between neighboring terephthalate units. The relaxation parameters of all carbons in the terephthalate groups are independent of the length of the separating alkyl chain. Reduced NOE's ajje seen for all carbons. The data are interpreted in terms of a log X distribution of correlation times of constant width, but variable average mobility. The average mobility in the alkyl chain increases with increasing distance from the terephthalate group in a given polymer. For a given position in the chain, mobility increases with increasing chain length. The above behavior is consistent with the presence of independently-reorienting, highly-solvated terephthalate groups.

,-112 EVALUATION OF COMPLEX MOLECULAR DYNAMICS IN POLYMERS FROM VARIABLE FREQUENCY ^{13}C RELAXATION MEASUREMENTS, G. C. Levy, D. Wright, and D. Axelson, Florida State University.

Variable temperature studies of viscous polymer solutions at several frequencies have revealed that a model containing a nonexponential autocorrelation function, or its mathematical equivalent, a distribution of correlation times, must be used to describe the NMR parameters obtained for the polymer backbone carbons. However, frequency-dependent spin-lattice relaxation time (T_1) and nuclear Overhauser effect (NOE) behavior observed for all side-chain carbons, including the terminal methyls, with NT_1's of the order of 20 s, could not be described in terms of present theoretical approaches.

A model which retains the distribution of correlation times for the backbone carbons and incorporates the effects of multiple internal rotations about the carbon-carbon single bonds for the side-chain carbons predicts a substantial frequency dependence for broad distribution widths which can quantitatively reproduce most of the observed data. The predictions of this modified theory are compared with experimental variable temperature studies of poly (*n*-butyl methyacrylate) solutions at three frequencies (67-9, 37-7 and 22.6 MHz) and at various concentrations. The value of variable frequency experiments to understand molecular motions in complex systems is discussed.

Wednesday Afternoon - Gary E. Maciel, Presiding

1:30-113 CARBON-13 FT NMR ANALYSIS OF PHENOL-FORMALDEHYDE RESINS: STRUCTlio AND REACTION MECHANISMS, S. A. Sojka and R. A. Wolfe, Hooker Res earct> Center.

Carbon-13 FT NMR was used to analyze phenol/formaldehyde resins The structure and composition of resins could be elucidated. Inf0rmation such as phenol content, end groups, branching centers, aver " molecular weight and distribution of structural units could be ob- 9* tained from the C-13 spectrum. The resin forming reaction was stud! A in the probe of the spectrometer. This provided insight into the reaction mechanism and time dependence of products and reaction intermediates.

2:00-1IV SEQUENCE DISTRIBUTIONS IN PROPYLENE-BUTENE-1 AND ETHYLENE-PROPYLENE COPOLYMERS, J. C. Randall, Phillips Petroleum Company.

The desired information in structural characterization of copolymers includes the comonomer content, sequence distributions and mean sequence lengths. Such information is readily available from C-13 NMR studies of propylene-butene-1 copolymers where the monomer additions are uniformly head-to-tail and isotactic. The corresponding information cannot be so easily extracted from C-13 NMR data of ethylene-propylene copolymers which contain monomer unit inversions and stereoirregular sequences. If the ethylene-propylene copolymers are described in terms of methylene, methine sequences as opposed to ethylene, propylene sequences, a comonomer distribution and methylene sequence distribution can be obtained. These two types of analyses will be discussed and data presented for a series of both types of copolymers.

30-115 RELAXATION STUDIES IN THE SYSTEM POLY(ETHYL METHACRYLATE)CHLOROFORM BY CARBON-13 AND PROTON NMR, L. J. Hedlund, W. G. Miller, and R. M. Riddle, University of Minnesota.

The polymer-solvent system PEMA-CHC1, has been studied as a function of polymer concentration ranging from the neat solvent to highly viscous, polymer-rich preparations with the goal of analyzing the concentration dependence of both polymer and solvent motion. Unlike most polymer-solvent systems which have been investigated, the relaxation of the solvent carbon-13 and proton exhibits a concentration dependence at less than five percent polymer. However, polymer concentration does not affect carbon-13 relaxation in PEMA until higher concentrations are reached and, then, the various polymer carbons are affected differently. The results are analyzed and compared, when possible, to other motional studies on polymer-diluent systems.

3:00 Break

3:15-116 THE USE OF NMR SPECTROSCOPY IN THE ANALYSIS OF POLYESTER POLYMER SYSTEMS, M. J. Vaickus and D. G. Anderson, DeSoto, Inc.

Of the many techniques suggested for the qualitative and quantitative analysis of polyester polymer systems, proton magnetic resonance (pmr) spectroscopy has been demonstrated to have the most utility. In addition, the availability of carbon -13 magnetic resonance (cmr) spectroscopy has helped to expand the qualitative analysis of acid and polyol species. However, NMR does have limitations, especially in the qualitative determination of polyol components. Monomeric polyhydric alcohols can generally be determined using chemical degradation, derivitization and gas chromatography. When polymeric polyols are used, most techniques fail to determine the molecular weight of the species present. Gel permeation chromatographic techniques have been developed which permit the determination of these polymeric polyols following chemical degradation with butyl amine.

Examples illustrating the application of pmr, cmr and several chromatographic techniques in the qualitative and quantitative analysis of several polyester polymer systems will be presented.

3:45-117 NMR STUDIES OF CHARGED POLYMERS AND COPOLYMERS, A. C. Watterson, Jr., J. C. Salamone, C. C. Tsai, M. Mahmud, A. Olson, and S. F. Krauser, University of Lowell.

Structural studies of charged polymers via nmr techniques has provided considerable insight into the mechanism of spontaneous polymerization of vinylpyridines and vinylpyridinium salts. Recently we have extended our structural studies to polymerization products of cationic-anionic monomer pairs. These novel polyampholytes have been characterized by proton and carbon nmr as well as other techniques. These nmr studies will be discussed in terms of the mechanism of polymerization of the cationic-anionic monomer pairs.

POSTER SESSION

First Floor Exhibit Area

OPEN Monday and Tuesday, 9:00 AM-5:00 PM
Authors will be present from 1:00-3:00, Tuesday

URANIUM ISOTOPIC ANALYSIS USING A MOMENTARY PEAK SWITCHING MAGNETIC MASS SPECTROMETER, H. G. King, Jr., W. T. McBryde, E. R. Rogers, and J. R. Ferguson, Oak Ridge Y-12 Plant.*

A 60-degree (TT/3 radians) magnetic sector, 6-inch (152.4 mm) mass spectrometer has been designed and built for uranium isotopic analyses. The instrument uses a Nier-type geometry and has several improvements, both optically and electrically, which makes it rapid and precise. Instrument control is good and the analytical results for uranium isotopes are excellent.

Outstanding features in the function of the instrument are rapid (millisecond) peak switching and an integrating circuit for signal accumulation in four channels, one for each uranium isotope measured. Calculations and readout are obtained from a Hewlett-Packard programmable calculator, Model 9825A.

The instrument is currently in use in the Oak Ridge Y-12 Plant Laboratory The relative precision in the 90 to-95 percent U range is +0.04 percent. The sample throughput capability is about forty (40) samples in an eight (8) hour day.

*Operated for the U.S. Department of Energy by Union Carbide Corporation-Nuclear Division, under contract W-7405-eng-26.

DIGESTION TUBE DIFFUSION AND COLLECTION OF AMMONIA FOR TOTAL NITROGEN AND ISOTOPE RATIO ANALYSIS, W. A. O'Deen and L. K. Porter, U.S. Department of Agriculture.

Block digested Kjeldahl nitrogen samples were made alkaline, sealed, and heated to stimulate ammonia diffusion into small HC1 collection vials within the digestion tubes. This ammonia collection system eliminates the time-consuming steam distillation of ammonia. Diffusion was studied as a function of temperature, time, nitrogen level, and volume of sample solution. Minimal fractionation was noted. Total nitrogen can be determined on NH.C1 from evaporated HCl vials gravimetrically, by solid state CI electrode, or by autotechnicon.

120 REMOVAL AND PRECONCENTRATION OF SURFACTANTS FROM WASTEWATER WITH OPEN-PORE POLYURETHANE, C. M. Smith and J. D. Navratil, Rockwell International

A column of ?n-situ polymerized open-pore polyurethane (OPP) was evalu for removing and concentrating linear alkylate sulfonate (LAS) from synthetic waste water. The OPP can be used to effectively remove LAS from waste water for treatment as well as a preconcentration step prior to analysis. Results of comparisons of breakthrough capacities and elution rates for LAS on OPP, active carbon and macroreticular resins are presented.

121 METHODOLOGICAL PROBLEMS IN THE MEASUREMENT OF THE OPTICAL ACTIVITY OF SHALE OIL, R. 0. Asplund, University of Wyoming, and D. L. Lawlor, Laramie Energy Research Center-DOE.

Shale oils from a number of sources and obtained by a variety of processes are optically active, an observation which is quite surprising in view of the thermal requirements for extraction. The quantitative measurement and characterization of this activity is beset by a number of difficult problems. These include location of the relevant Cotton effects in the vacuum UV region of the spectrum, optical opacity of shale oils and their various fractions, and false readings caused by light-scattering from colloidal suspensions in the oils. Solutions to these problems include special handling and fractionation of the oils, modification of standard instrumentation and the application of mathematical analysis to the experimental abbreviations. This has made possible the identification of the molecular sources of optical activity and has indicated the potential for the use of optical activity in understanding the chemical dynamics of shale oil.

122 A NEW MICROPROCESSOR BASED PROGRAMMABLE PEAK SELECTOR, J. D. Burden and M. Soursa, UTI.

This presentation will describe the value of a new microprocessor based Programmable Peak Selector in extending the utility and increasing the ease of operation of quadrupole mass spectrometers. The unit provides preselection of up to 8 mass peaks for direct monitoring of up to 8 gases during an experiment—for example, in process monitoring applications. Examples presented will include process monitoring during sputter deposition and plasma etch. An alternate storage version of this unit meets the needs of a user with an extremely fast experiment (flash desorption) or an experiment where data is taken over a relatively long period of time. In either case the various gas concentrations as a function of time for the entire experiment are acquired and stored and then later plotted sequentially w,t an x-y plotter.

ID STATE ^{J}C NMR STUDIES OF SICKLE CELL HEMOGLOBIN, W. Egan, D. A. Torchia, A. N. Schechter, and W. J. Sutherland, National Institutes of Health.

•'C- H nuclear magnetic double resonance techniques have been used to study the polymerization of deoxy hemoglobin S molecules, both in solution and within sickle erythrocytes. Only isotropically mobile hemoglobin molecules (**T** < 10 sec) are detected in a scalar decoupled ^{13}C NMR spectrum, whereas only motionally restricted molecules of polymerized hemoglobin are detected in a proton-enhanced C spectrum. The latter spectrum is obtained using a matched Hartmann-Hahn contact to transfer polarization from protons to carbon. Both isotropically mobile and polymerized hemoglobin are detected in a dipolar decoupled C spectrum. A comparison of integrated intensities obtained from the various decoupled spectra show that at **37**°C» approximately 0.4 of the molecules in a **28** g/dl preparation of deoxy hemoglobin S enter the polymer phase, while at **37** g/dl a significantly higher fraction, ca. 0.6, of the hemoglobin is in the polymer phase. As much as 0.8 of the hemoglobin is polymerized in deoxy sickled erythrocytes. The rigid nature of the polypeptide backbone in the polymerized molecules is indicated by the width of the signal (> |50 ppm) observed in the carbonyl-aromatic region of the proton-enhanced C spectrum.

SHORT COURSE

Second Floor, Conference Rooms B,E

Wednesday Morning - 9=00-12:00

ION SELECTIVE ELECTRODES, S. Lichtenstein, Orion Research, Inc.

The course will be 2-1/2 to 3 hours and will include an introduction to the subject of ion-selective electrodes as well as recent advances in the use of an ammonia electrode and a microprocessor specific ion meter for rapid determination of high and low nitrogen concentrations in various types of samples. Results are delivered directly in any units of nitrogen or protein concentration with a better than 2% coefficient of variation.

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