

# Rocky Mountain Conference on Magnetic Resonance

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Volume 19 *19th Annual Conference on Analytical Chemistry*

Article 1

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## 19th Annual Conference on Analytical Chemistry

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## 19th Annual Conference on Analytical Chemistry

### Abstract

Program and abstracts from the 19th annual meeting of the Conference on Analytical Chemistry, co-sponsored by the Rocky Mountain Section of the Society for Applied Spectroscopy and the Rocky Mountain Chromatography Discussion Group. Held in Denver, Colorado, August 1-3, 1977.

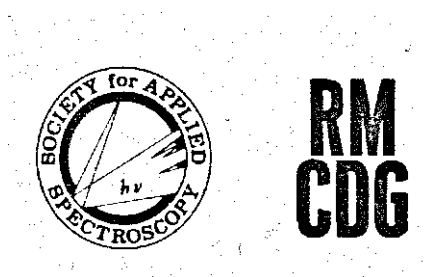
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**19TH ANNUAL  
CONFERENCE  
ON  
ANALYTICAL CHEMISTRY**

**AUGUST 1-3, 1977**

**RADISSON DENVER HOTEL**

**DENVER, COLORADO**

**Sponsored jointly by the**

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## GENERAL INFORMATION

### Sponsors

The Rocky Mountain Section of the Society for Applied Spectroscopy and the Rocky Mountain Chromatography Discussion Group welcomes you to the 19th Annual Conference on Analytical Chemistry (formerly Rocky Mountain Spectroscopy Conference). The technical program promises to be an excellent one, covering a broad spectrum of analytical chemistry and including symposia on DC-Arc Analysis of Geological Samples and Modern Chromatographic Techniques. Some of the latest developments in instrumentation, laboratory equipment, and analytical aids will be exhibited during the conference. An opportunity for a relaxing and enjoyable social evening will be provided for the conferees and their guests attending the conference banquet.

### Location

The conference is located at the Radisson Denver Hotel, which is in downtown Denver. The address is 1790 Grant Street, Denver, Colorado. Technical papers and exhibits, as well as the poster session on Tuesday, will be in various rooms of the Radisson Denver. Arrangements have been made for free parking for conferees at the hotel parking lots, and there are several municipal parking facilities in the immediate vicinity of the hotel.

### Accommodations

Conferees from outside the immediate Denver area must arrange housing facilities for their stay in Denver. The conference committee has arranged for a block of rooms to be held for conferees, and a reservation form for the Radisson Denver Hotel is included with this pamphlet.

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#### Visitor Information

Information on the Denver area may be obtained from the Denver Convention and Visitors Bureau, 225 West Colfax Avenue, Denver, Colorado 80202. (Phone: 303/982-1505)

#### Conference Social

The conference banquet will be held at the Denver Petroleum Club, Monday evening, August 1. There will be a cash bar at 6:00 p.m., with the meal being served at 7:15 p.m. The meal will be a buffet, and will offer a choice of meat. The guest speaker will be John Goodlette, Executive Director of Technical Operations, Viking Program, Martin Marietta Aerospace Denver Division. Mr. Goodlette will speak about the results of the Mars Viking Lander Mission. The title of his talk will be The Viking Mission to Mars. Admission will be by ticket (\$7.00) which will be available at the conference registration desk.

#### Exhibits

The following exhibitors will have the latest in instrumentation and equipment on display.

|                              |                          |
|------------------------------|--------------------------|
| Alcatel Vacuum Products      | Finnigan Corp.           |
| Beckman Instruments          | Hewlett Packard          |
| Denver Valve and Fitting Co. | Nuclear Data, Inc.       |
| Digilab, Inc.                | Perkin-Elmer             |
| Drummond & Associates        | Sargent-Welch Scientific |
| Dupont Instruments           | Spectrometrics           |
| Extranuclear Labs, Inc.      | Uthe Technology, Inc.    |
| Farrand Optical Co., Inc.    | Whale Scientific, Inc.   |
|                              | Waters Associates, Inc.  |

#### Inquiries

For additional information on the 19th Annual Conference on Analytical Chemistry, contact Kelly R. O'Keefe, Department of Chemistry, Colorado

**State University, Fort Collins, Colorado 80523.  
(Phone: 303/491-5204 or 493-8503, home).**

**Registration Information**

See inside back cover.

**CONFERENCE SCHEDULE**

**Monday, August 1, 1977**

Welcome: *K.R. O'Keefe*, Department of Chemistry  
Fort Collins, Colorado

Technical Program:

**SESSION (I)**

New Techniques in Analytical Chemistry, **Chairman:**  
Cordell Brown, Colorado Bureau of Investigation,  
Denver, Colorado.

9:20 Keynote Address - **Photoacoustic Spectroscopy  
of Solids.**

*Dr. A.M. Schaffer and J. Favre*, Phillips Petroleum  
Company, Research and Development, Bartles-  
ville, Oklahoma.

A photoacoustic spectrometer consisting of a modulated monochromatic light source, sealed sample cell, microphone and preamplifier, lock-in detector, and data collection system has been constructed and tested. The effects of chopping frequency, microphone type, cell volume, and coupling gas on the photoacoustic signal have been determined. The unique advantages of the photoacoustic technique to problems in analytical chemistry and catalysis will be discussed.

10:05 **Quantitative Determination of the Solution Configurations of Paramagnetic Metal Complexes.**

*William B. Tucker*, D.F.S. Natusch, Department of Chemistry, Colorado State University, Fort Collins, Colorado, and K.P. Li.

Although the precise configurational determination of compounds in the crystalline state has become almost commonplace by the use of X-ray and neutron diffraction, the configurational determination of compounds in solution has proven much more difficult. One method with great potential which has been used in a few instances utilizes the extremely sensitive distance dependence of dipolar paramagnetic relaxation produced by ions such as  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$ . We have shown the general utility of this technique, as well as some of its limitations, using 8

amino acid ligands as model compounds. The technique is simple, requiring only a standard **NMR** spectrometer, fast, and in many cases extremely precise. Histidine was also examined, resulting in a more exact knowledge of its solution configuration. In addition, the utility of this technique was demonstrated for a **macromolecular** structure, lysolecithin micelles.

—BREAK—

**10:30 Applications of Laser Light Scattering Techniques to Suspended Sediment Analysis.**

*Neil J. Asting* and Marvin C. Goldberg, U.S. Geological Survey, Lakewood, Colorado, and Eugene R. Weiner, Department of Chemistry, University of Denver, Denver, Colorado.

The interaction on an incident laser beam with a suspended sediment sample produces **Mie**, Rayleigh dipole and **Franuhofer diffraction** scattering. The intensity of each of these scattering phenomena is a function of the Laser excitation wavelength and the particle mean size. By ratioing the scattered intensity at two angles in the forward lobe, the size of each of the components of the sediment mixture responsible for Franuhofer diffraction scattering can be determined. If the illuminating source is linearly polarized then when viewing the sample at a back angle, usually greater than **150** degrees, a depolarization effect is observed. This is attributed to multiple **reflections** within the sample and is an indirect measurement of the sediment concentration. The effect is independent of particle size. Our measurements indicate **that** a curvilinear relationship exists between the sediment concentration and the light depolarization ratio in the range from 50 to 8000 parts per million.

**10:55 Analysis of Air Contaminants Using Coated Piezoelectric Detectors.**

*R.C. Faris*, and R.K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado.

Piezoelectric quartz crystals have previously been shown to be extremely sensitive devices for detecting weight changes. Such crystals, coated with selective reacting substrates, are being investigated as a means of collecting and determining trace levels of several air contaminants. This method offers several unique advantages including: very low cost, high portability, and excellent sensitivity. The results of this work and possible applications will be discussed.

**11:20 A Proposed Design for a Rapid Scanning Spectrometer Involving a Novel Comparison of a Vidicon Detector and a Moving Mirror.**

*Patrick MacCarthy*, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado.

The current major limitation on the rapid-scanning ability of a vidicon spectrometer results from the difficulty in rapidly moving the interrogating electron beam in a controlled manner. The purpose of this paper is to outline the principles of a new vidicon spectrometer design which circumvents this limitation and which also presents some other interesting features. A simple method for implementing the concept is described and some possible problems will be considered. The concept and basic features of the proposed spectrometer are illustrated by using an example of laser-excited fluorescence.

**—LUNCH—**

**SESSION (II)**

New Techniques in Chromatography, Chairman: Dr. H.F. Walton, Department of Chemistry, University of Colorado, Boulder, Colorado.

**1:10 The Effect of Stirred-Slurry Packing Techniques on Silica Used for HPLC.**

P.Y. Howard and J.C. Hodgins, Micrometetics Instrument Co., Norcross, Georgia.

A new stirred slurry technique for packing HPLC columns has been developed based on existing techniques.

A series of **microparticulate** silica gels has been exposed to various stirring times and pressures for determining the extent of crushing resulting from the packing procedures used. Different particle sizes were stirred for various periods of time, and then subjected to particle size analysis. These materials were then used for packing HPLC columns via a stirred-slurry technique described previously. After packing, particle size distribution studies were repeated. Particle size distributions were obtained using classical sedimentation techniques and selected samples were observed using electron microscopy to confirm indications from distribution studies.

The results demonstrate that for the times employed during this HPLC column packing technique, there is no measurable degradation of particle size.

**1:30 Synthesis and Properties of Novel Ion Exchangers for HPLC, based on Polyorganosiloxanes.**

K.K. Unger, M. Engler and H. Kramer, Technische Hochschule, Darmstadt, Germany.

In two consecutive steps rigid porous **microbeads** of polybenzylsiloxane were synthesized by means of cohydrolysis and cocondensation of tetraethoxysilane and **benzyltriethoxysilane** <sup>1,2</sup>). The procedure permits the control and variation of (i) the mean particle size (ii), the swelling properties and the pore structure parameters of the microbeads and (iii) the concentration of surface benzyl groups. The resin structure can be considered as a homogeneously crosslinked network of siloxane groups, which contains benzyl groups that are attached to silicon atoms via a Si-C bond.

By corresponding substitution reactions (sulphonation; chlormethylation and **amination**) cation and anion exchangers, respectively, were obtained exhibiting a maximum effective capacity of about 2 **mequivalents/g**. The **pH-stability** was found to be reasonably well in the pH-range between 1.0 and 8.5. **Due** to the favourable pore structure of the resin the ion-exchange equilibrium is rapidly attained. In order to understand the selectivity behaviour of the novel ion exchanger in HPLC organic compounds such as carboxylic acids, amines, amino acids etc. were used (<sup>3,4</sup>). On the basis of the results which are obtained up to now one can conclude that the selectivity is not only affected by electrostatic forces between the charged surface sites and the organic ions but also by adsorption interactions.

Separations were carried out on columns packed with 10 **µm** particles of these supports using the well-known slurry technique.

**1:50 HPLC-Fluorescence Detection of Biogenic Amines.**

P.M. Froehlich, North Texas State University, Denton, Texas.

Analytical techniques for biogenic amines in tissues and body fluids are extremely useful to the medical and biochemical community in the detection of disease and for an understanding of the mechanism of the central nervous system. An assay for the biogenic amines must consider their low levels and chemical similarities. We have used high performance liquid chromatography coupled with **post-elution** derivatization and fluorescence detection to separate and identify various catecholamines. Various metabolites of tryptophan can be readily detected via the native fluorescence of the indole ring system. Catecholamines and indole amines can be separated using a cation exchange column with an

acetate-citrate buffer system. Although the separation can be performed via an isocratic mode, a gradient separation of the **indoleamines** permits more rapid elution. Detection of the catecholamines was effected by forming the **fluorescamine** derivative or the **o-phthaldehyde (OPT)** derivative in the flow stream after separation. It was found that the OPT derivatives were more fluorescent and the fluorescence was higher in a borate buffer (pH = 9) than in a pyrophosphate buffer. The fluorescence of the derivative from dihydroxyphenylalanine was increased by heating the eluant stream to **45°C** to obtain a more sensitive procedure for the amino acid. A typical analysis for three catecholamines could be performed in about 10 minutes, with a sensitivity of 30 p mole, and a linear range of **500-1000**. A major advantage of the OPT fluorescence assay is that the presence of **O<sub>2</sub>** is not a major concern, as it is with electrochemical detection.

#### 2:10 **Evaluation of Anion Exchange Resins for Pre-Analysis Separations of Actinides.**

**J.D. Navratil**, Rockwell International, Golden, Colorado.

Anion exchange is the technique usually employed to separate **plutonium** and neptunium from actinides and other sample constituents prior to radiochemical determinations of the actinides. For **plutonium-neptunium** separations, neptunium (IV) is sorbed on an anion exchanger and the plutonium (III) allowed to pass with the effluent and wash streams from a **5M HNO<sub>3</sub> -0.66M A1 (NO<sub>3</sub>) -0.2M Fe (SO<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>** feed solution. Plutonium is separated from plutonium-uranium solutions by sorbing plutonium (IV) on the resin from a **7M HNO<sub>3</sub>** feed and permitting the uranium (VI) to follow the effluent and wash streams. In both cases, plutonium and neptunium are eluted from the resins with dilute nitric acid.

For the actinide separations, pellicular, **macroreticular**, and microreticular (gel-type) anion exchange resins were compared. The pellicular and macroreticular (porous gel) resins showed faster elution and washing properties for the **non-sorbable** ions than the microreticular resins. However, the actinide breakthrough capacities of the pellicular and macroreticular resins were less than the microreticular resins but the breakthrough capacities for the macroreticular resins were dependent on actinide feed concentrations.

#### 2:30 **Gas Chromatographic Analyses of Antihistaminic Drugs and Metabolites, using Glass Capillary Columns and a Specific Nitrogen Detector.**

*J.A. Thompson, K.W. Panter and G.A. Eiceman,*  
University of Colorado, Boulder, Colorado.

Pharmacokinetic and metabolic studies of several **antihistaminic** drugs are complicated because of the very small therapeutic doses used. Chlorpheniramine (CPA), brompheniramine (BPA), **carbinoxamine** (COA) and tiproldine (TPI) are usually administered as individual doses of 2-5 **mg** (as maleate or hydrochloride salts), or daily doses of 3-15 **mg**.

The analytical capability must be available to measure plasma levels of unchanged drugs in the range 1-5 **ng/ml**, and trace metabolites in urine. Extracts of physiologic fluids contain many endogenous metabolites which can interfere with analyses of low levels of drugs or drug metabolites. Standard GC procedures utilizing packed columns and flame ionization detection do not provide the necessary degree of sensitivity or selectivity. Combined **GC/MS/computer** methods (especially selected ion monitoring) can be applied to this work, however in many cases analyses of routine pharmacokinetic samples are more efficiently performed by GC alone. A specific nitrogen-phosphorus (N-P) GC detector has been used with antihistamines to increase the sensitivity of detection by factors of **5-10**, and to eliminate many of the interfering GC peaks. This detector has been used in conjunction with wall-coated glass capillary columns to further resolve nitrogen-containing compounds and yield highly reproducible retention-time values. Once peaks have been identified by GC/MS, this GC method is a reliable procedure for generating kinetic and metabolic data on **anthistamines** and other nitrogenous drugs.

**—BREAK—**

### **3:00 New Developments in Gas Chromatography Detectors.**

L.S. Ettre, M.J. Hartigan and B. Welton, The Perkin-Elmer Corp., Norwalk, Connecticut.

While quantitation is its prime analytical attribute, gas chromatography is also used as a qualitative tool in spite of the fact that the use of gas chromatographic retention data for component identification is never equivocal. Recognizing this shortcoming, many procedures specify the use of two or more dissimilar liquid phases in order to improve the qualitative integrity of retention data. This generally requires that multiple analyses be performed with a corresponding increase in total analysis time. This increased analysis time has been overcome with the use of parallel column systems in conjunction with dual detectors operated simultaneously. This configuration provides dissimilar liquid phase data with a single

injection.

**Substance-selective** detectors such as the electron capture, flame photometric and nitrogen/phosphorus thermionic detectors have been widely used in the past few years. Their application has been mainly restricted to the determination of low level components with specific characteristics in complex mixtures such as the determination of pesticide residues in foodstuffs, water, soil, etc. Recent advances in instrumentation greatly improved the operation of these detectors. In addition, new spectroscopic detectors extend the **specificity** of gas chromatography to certain compound classes which up to now could not be selectively detected.

While the thermal conductivity and flame ionization detectors retain their position as universal detectors, their linearity, sensitivity and operation has also been **improved**.

The paper will survey the new advances in detector technology and illustrate their advantages for the practical gas chromatographer.

### 3:20 **The Development of a Practical Microwave Emission Spectrometric Detector for Gas Chromatography.**

*J.E. Gebhart*, C.W. Frank and Don Gay, University of Iowa, Iowa City, Iowa and Environmental Protection Agency, Las Vegas, Nevada.

Increased interest in the presence and nature of heavy metal contaminants in the environment has generated a demand for analytical methods for these materials which are rapid, sensitive and selective. A microwave induced plasma coupled to the outlet of a gas chromatographic column answers this demand for volatile metal compounds.

Initial work by **McCormack**, Tong and Cooke, and **Talmi** have led to the development of the element-selective microwave emission spectrometric (MES) detector for G.C. In general, this detector consists of a quartz capillary tube attached to the outlet of a gas chromatographic column. Carrier gas (argon or helium) containing effluent material is excited in a plasma sustained by a microwave cavity in a defined area of the tube. Radiation from this plasma is focussed, normally by means of a large **plano-convex** lens, on the slits of a spectrophotometer which is set to the appropriate wavelength for the element of interest. This general detector suffers from several major problems, including: lack of long term stability, low sensitivity, and high noise.

In these laboratories, these difficulties have been largely eliminated by altering the plasma confinement system and introducing a lensless collimating device.

With these developments in the GC-MES system, long term stability of several weeks and absolute detection limits of less than 10 pg have been achieved.

**3:40 Chemical Analysis by Gas Chromatography Coupled to Fourier Transform Infrared Systems.**

A.W. Mantz, D.L. Wall and W.H. Chan, Digilab, Inc., Cambridge, Massachusetts.

The combination of FT-IR and GC techniques has rendered unambiguous results in complex chemical analysis. A high sensitivity, minicomputer-controlled system has been developed in this laboratory. **Data** on the detection of 10 nanogram of isobutyl **methacrylate** will be discussed. Results on some higher molecular weight compounds will also be presented. Design of the system, software capability and ultimate sensitivity of detection will be discussed.

**4:00 Gas Chromatographic Determination of Airborne Particle Nitrate and Nitric Acid Vapor in the Lower Troposphere.**

*J.W. Tesch* and R.E. Sievers, University of Colorado, Boulder, Colorado.

Gas chromatography with electron capture detection has been used for the determination of particulate nitrate and nitric acid vapor collected by two-stage selective filtration. Particulates are collected on a Millipore FHL P filter (reinforced Teflon with 0.5 $\mu$  pore size) which allows NO, NO<sub>2</sub>, and HNO<sub>3</sub> vapor to pass while maintaining a high efficiency of collection for particulate nitrate. The second stage, which is a cotton fiber filter, collects nitric acid vapor while allowing NO and NO<sub>2</sub> to pass. The lengthy extraction step normally employed in the determination of particulate nitrate is replaced by simple chemical pretreatment consisting of adding water, sulphuric acid, and a suitable aromatic compound such as benzene to the filter. The collected nitrate in the reaction mixture is converted to a volatile organic compound such as nitrobenzene, which is subsequently measured by gas chromatographic analysis. The excellent sensitivity of the electron capture detector for nitro-aromatic compounds (e.g., detection limit ca. 1 picogram for nitrobenzene) enables sub-ppb determinations to be made with air samples collected for less than 30 minutes. A substantial but variable fraction of nitric acid vapor may be adsorbed on glass fiber filters which are widely employed in high volume air sampling. Nitric acid vapor may also be adsorbed on the collected particulate matter. These problems are minimized through the use of Teflon filters and short sampling times.

**Tuesday, August 2, 1977**

**SESSION (III)**

DC-Arc and Spectrochemical Analysis of Geological Samples, Chairman: Dr. R.F. Jarrell, Jarrell-Ash Division, Fisher Scientific Co., Waltham, Massachusetts.

9:00 Introductory Remarks

**General Advantages of DC-Arc Analysis.**

9:05 **DC-Arc Spectrographic Analysis of Geologic Materials with a High-Precision Scanning Microphotometer.**

*Anthony F. Dorzopf, Jr., and Catharine P. Thomas,*  
U.S. Geological Survey, Reston, Virginia.

Computer analysis of transmittances recorded by a precision scanning microphotometer allows maximal utilization of the information available on a photoplate. Concentrations of 64 elements in geologic materials are reported within five minutes of completion of the recording. Geologic materials (15 mg), mixed with graphite (1:2) are arced under controlled conditions in an argon-oxygen (70:30) atmosphere. Cadmium fiducial lines are co-exposed within each spectrum using a camera-mask system. Recording fidelity is achieved by driving the microphotometer bed with a lead screw coupled to a shaft encoder which gates an A/D converter. During a 70 second scan transmittance readings over the wavelength region, 2300-4750 Å are sampled every 5µm at 1.3 KHz. A32K minicomputer simultaneously acquires the transmittances and locates preselected spectral lines. A 2-step iron arc exposure is used to calibrate the emulsion at 250 Å intervals on each plate. Concentration calculations are based on stored coefficients from 6-step synthetic or natural standards and interference corrections are compiled from examination of the spectra of well-characterized reference materials representing a variety of geologic materials. A dynamic concentration range for each element is achieved through spectral line switching using a predetermined priority scheme based on sensitivity and freedom from interference. Precision is enhanced by intercomparison and averaging of results from up to 7 lines per element. A permanent record of all the preliminary information calculated for all analytical lines and calibration lines is available microfiche. Because this system is software controlled, a wide variety of potential applications is possible using various stored wavelength tables and analytical coefficient data.

9:25 **Multi-Element Analysis of Geochemical, Mineral, and Soil Samples with a Direct Reading, Emission Spectrograph.**

*Jack Woodyard*, Keith Stever, Benjamin Piper,  
Reno Metallurgy Research Center, Reno, Nevada.

The Federal Bureau of Mines has developed a rapid, semi-quantitative, **emission-spectrographic** procedure for the analysis of geochemical, mineral, and soil samples. These samples originate from the Bureau's engineering sampling program for proposed candidate areas for the National Wilderness Preservation System, and from mineral reconnaissance sampling of Indian reservations. A computerized, **direct-reading** spectrograph is used to simultaneously determine 42 elements. A special computer program and a **timeshared** CDC 6400 computer are used to calibrate the instrument, and another timesharing program controls the print out of the concentration data. Simple background and spectral **interference** corrections can be made either through the dedicated minicomputer housed in the instrument, or through the output program. This system eliminates the need for reading photographic plates and prevents many forms of "human" error. One operator can easily analyze about 30 samples per day, and all data are machine-printed without operator intervention.

9:45 **A General Spectrochemical Direct Reading Technique for Geological Samples Using a Germanium Buffer.**

*W. Harold Champ*, Geological Survey of Canada,  
Ottawa.

Abstract not available.

—BREAK—

10:10 **Direct Reader Analysis of Major and Trace Elements in Geological Samples Using a Graphite Buffer.**

*James Seeley* and Paul Lamothe, U.S. Geological Survey, **Menlo** Park, California.

A multichannel direct reading emission spectrometer, specifically adapted for rapid analysis of geologic materials, will be described. The instrument has been designed to incorporate the advantages of two separate photographic procedures which involve excitation in different atmospheres (argon and argon/oxygen) and recording on photographic emulsions of different sensitivities (**III-O** and **SWR**). The excitation sources available are the DC arc, spark, and induction coupled plasma. Trace element determinations on solid samples are accomplished using the DC arc; however, all the

sources are being evaluated for the major element determinations. Instrumental operations are computer controlled, with data being reduced and reported (in concentration) on up to 50 elements within 30 seconds after completion of the sample burn. Matrix corrections are programmable with dynamic background evaluations being made either using dedicated slits for such measurements or wavelength modulation to affect all slits.

**10:30 Automated Electrode Interchanger and Gap Adjustment for the DC-Arc.**

J.D. Caylor, W.T. McBryde, and R.T. Goodpasture,  
Union Carbide, Oak Ridge, Tennessee.

Automatic electrode changers which position the electrodes in the arc chamber have been in use at the Oak Ridge Y-12 Plant Laboratory for more than a decade. Up to 40 loaded sample electrodes (6.35 mm dia.) may be placed in the linear magazine at a time. A corresponding number of counter electrodes (3.17 mm dia.) are placed in the upper carousel magazine. Pneumatic cylinders activate the movement which dispenses with the burned electrodes and locate the next unburned electrodes into the prefire position. During the arcing the arc gap is maintained relatively constant by a photocell-controlled servo-motor mechanism.

**—LUNCH—**

**SESSION (IV)**

Atomic Spectroscopy and Chemical Analysis, Chairman:  
H.E. Taylor, U.S. Geological Survey, Denver, Colorado.

**1:30 Capabilities of a D.C. Plasma-Echelle Spectrometer System for Multielement Analysis of Natural Waters.**

H.E. Taylor, U.S. Geological Survey, Denver, Colorado; and R.K. Skogerboe and G. Johnson, Department of Chemistry, Colorado State University, Fort Collins, Colorado.

A commercial **d.c. plasma-echelle** spectrometer system has been evaluated for the simultaneous determination of **19** elements in samples of natural water. The operational features of the system have been examined and optimized; the occurrence and extent of potential interference effects have been studied; and the general analytical capabilities of the system defined. The results of these studies show that for most of the elements considered, analyses comparable to those using atomic absorption techniques are easily achieved.

1:50 **Examination of Aerosol Nebulization and Transport in Flame and Plasma Spectrometry.**

*Stephen J. **Freeland*** and R.K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado.

Sensitivity in flame/plasma sources is limited by the concentration of analyte in the flame or plasma per unit time. The factors governing nebulization and transport of the analyte aerosol to the source are being examined and the parameters affecting aerosol vaporization in the source are being determined. The results will be discussed in terms of defining means of enhancing analytical sensitivity and reducing interference effects.

2:10 **A background Correction and Parameter Optimization System for the Inductively-Coupled Plasma.**

*Paul J. **Lamothe*** and J.L. Seeley, U.S. Geological Survey, Menlo Park, California.

A dynamic background correction system based upon a wavelength modulation technique has been developed for an inductively-coupled plasma. Wavelength modulation is accomplished by placing a scanner motor mounted refractor plate behind the entrance slit of the **monochromator**. The refractor plate is scanned in a square wave manner so that in one orientation of the plate the detector will measure the intensity of the analytical line, while in the alternate orientation the **detector** will measure the background in the immediate vicinity of the line. The use of a lock-in amplifier tuned to the second harmonic of the modulation frequency allows the net line intensity to be displayed on a recorder or other read out device. Since only the net line intensity (line minus background) is displayed, plasma operating parameters such as carrier gas flow rate, r.f. power, and observation height can be optimized very efficiently. Examples of the application of this system to the analysis of **geochemical** samples will be presented.

2:30 **Evaluation of a Low Pressure Argon Microwave Induced Plasma for Atomic Spectroscopy.**

*P.L. **Sulik*** and R.K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado.

Low pressure microwave induced plasmas have been shown to have certain advantages as spectral excitation sources. Most of these studies have concentrated on helium as the support gas. There has been only one report on the use of a low-pressure **MIP** as an atomic absorption medium. The present study has concentrated on

comparing the atomic absorption and atomic emission characteristics of a low-pressure **MIP** in argon. The results of this comparison will be summarized.

**2:50 A Critical Comparison of Pneumatic Nebulizers Used with Induction Coupled Plasmas.**

*H.E. Taylor* and *J.R. Garbarino*, U.S. Geological Survey, Denver, Colorado.

A critical comparison is presented between the performance of the concentric flow glass bead **iminger** type nebulizer and the cross flow Ames type nebulizer on a 27 MHz, argon, induction coupled plasma. Characteristics such as sensitivity detection limits, long and short term stability, precision and memory effects are discussed. Data is presented for 20-30 elements to illustrate these characteristics. In addition, the relative magnitude of interference effects between the two nebulizers is discussed and data is presented to substantiate conclusions. Finally, the general applicability of each of the nebulizers for quantitative analysis of trace metals in natural waters is discussed.

**—BREAK—**

**3:10 Matrix Effect Studies in Hollow Cathode Atomic Absorption Spectroscopy.**

*David A. McCamey* and Thomas M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, New Mexico.

It can be stated that the weakest link in the atomic absorption spectroscopy experiment is the sample **atomization** step. Among other problems, atomizers in use today, both flame and nonflame, suffer from sample matrix interferences. The hollow cathode discharge has attracted investigation as an atomizer for many reasons, including the suggestion that atomization caused by a sputtering mechanism, as in this discharge, would lead to reduced matrix effects. This proposition is being investigated in this laboratory in conjunction with other work involving the hollow cathode atomizer. The apparatus used in these experiments includes a hollow cathode atomization cell and associated atomic absorption spectroscopy equipment interfaced with a PDP-8/e minicomputer. The results of these experiments are reported.

**3:30 Electron Temperatures in Hollow Cathode Discharges.**

*Doreen M. Mehs* and Thomas M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, New Mexico.

An apparatus has been designed to conveniently measure the electron temperature in the plasma discharge of a hollow cathode lamp. A floating double probe technique utilizing an assembly specially built for insertion into standard-sized hollow cathode discharges was employed. The electron temperatures thus determined allow a partial characterization of the discharge in hollow cathode lamps. The plasma electron temperatures in these light sources are compared with similarly measured temperatures in electrodeless discharge lamps.

**3:50 Automated Atomic Absorption Determination of Inorganic and Organically Bound Arsenic in Water and Streambed Materials.**

*Marvin Fishman* and Roberto Spencer, U.S. Geological Survey, Denver, Colorado.

An automated method to determine both inorganic and organic forms of arsenic in water, water-suspended mixtures and streambed materials is described.

Organic arsenic-containing compounds are decomposed by either ultraviolet radiation or by sulfuric acid-potassium persulfate digestion. The ultraviolet radiation procedure is applicable only to the determination of organic arsenic compounds in samples that have been filtered. Water-suspended sediment samples and bed materials must be analyzed by the sulfuric acid-potassium persulfate digestion. The arsenic so liberated, with inorganic arsenic originally present, is reduced to arsine with sodium borohydride. The arsine is stripped from the solution with the aid of nitrogen and is then decomposed in a tube furnace heated to 800°C which is placed in the optical path of an atomic absorption spectrometer. Thirty samples per hour can be analyzed to levels of 1 microgram arsenic per liter.

**4:10 Application of a Two Channel Atomic Absorption Spectrometer to Geochemical Analysis.**

*Timothy Corum*, Anthony Rattonetti, and David Leighty, Instrumentation Laboratory, Inc., Houston, Texas.

A new two-channel double-beam atomic absorption spectrophotometer, equipped with a microcomputer, has been developed, and has been applied to a series of geochemical analyses with the intent of making improvements in the conventional analytical procedures. Among the materials that were analyzed are waters, ores, and cement.

EPA Water Quality Controls were analyzed, two elements at a time, by flame atomic absorption. The following pairs were determined simultaneously: AL-Be,

**Ni-Co**, Fe-Cu, **Pb-Co**, and **Zn-Mn**. With a temperature-controlled furnace (CTF) atomizer employed to give higher sensitivity, As-Se and Pb-Cd were determined.

Many laboratories are charged with analyzing sequences of hundreds or even thousands of ores, so that the ability to determine two elements simultaneously can produce significant time savings. "Standard" ore materials were successfully analyzed for Cu-Mn and **for Zn-Ni**. Large (1,000-fold) differences in Cu and Mn concentrations could be measured by the use of secondary, less sensitive, resonance lines.

Calcium was determined in cement, with copper used as an internal standard. Before the cement was dissolved, a measured amount of copper was added, and both materials were carried through the sample preparation procedure. The use of the internal standard made the analytical results independent of possible dilution errors. NBS and PCA standard cements were analyzed with very high accuracy.

### **Wednesday, August 3, 1977**

#### **SESSION (V)**

Geochemical Analysis, Chairman: Marvin **Fishman**, U.S. Geological Survey, Denver, Colorado.

#### **9:00 Analysis of Phosphatic Rocks by Infrared Spectroscopy.**

*S.N. Ghosh* and *S.P. Ghosh*, Cement Research Institute of India, New Delhi, India.

The application of infrared spectroscopy (**IR**) in the estimation of mineral assemblages in phosphatic rocks recently discovered in large quantities and with varying **mineralogical** compositions in certain parts of India has been demonstrated as a first-hand quality check for rapid industrial uses.

A **Perkin-Elmer** model 621 spectrometer has been used in this study. Both absorption (**KBr-Pellet**) and reflection (ATR) techniques were tried for the above study in line with our previous study of quantitative estimation of dolomite and calcite in limestone. Complementary studies by XRD, DTA and microscopy have also been carried out.

Under microscope, the rocks show fine grained heterogranular texture and phosphate is represented by amorphous collophane, **dahlite** and **francolite** and the former very often shows partial or total **recrystallination** into the latter. The phosphate minerals show integrowth with fine grained carbonate giving rise to a mosaic structure.

The IR spectra of the phosphate samples indicate departure from tetrahedral symmetry of  $\text{PO}_4$  ion arising out of substitution and solid state interaction and this is evident in band splitting in  $\nu_3$  ( $1092\text{ cm}^{-1}$ ) and  $\nu_4$  ( $604$  and  $577\text{ cm}^{-1}$ ) and the appearance of the Raman active mode  $\nu_1$  ( $960\text{ cm}^{-1}$ ). Samples containing dolomite, calcite, quartz and phosphate could be readily identified independently. A semi-quantitative estimation of some of these minerals is possible in certain cases. Several samples showed bands at  $1455$ ,  $1428$  and  $864\text{ cm}^{-1}$  in their spectra. The origin of these bands has been assigned to 'carbonate' on the basis of studies (thermal and acid treatment). The absence of  $711\text{ cm}^{-1}$  ( $\nu_4$ ) band in their spectra and higher than normal temperature of dissociation of carbonate indicate participation of carbonate in phosphate structure.

**9:20 Rare Earth Elements Distribution in Cassiterite and Bauxite Ores by Neutron Activation Analysis.**

*Harjoto Djojosubrato*, National Atomic Energy Agency, Bandung, Indonesia.

Rare earth elements have nearly identical chemical properties and exhibit a close geochemical coherence. The distribution of individual lanthanides elements in cassiterite and bauxite ores was determined by neutron activation analysis. One of the main features of the neutron activation analysis is the possibility of simultaneous, highly selective and sensitive multi-elements analysis, regardless the chemical behavior of the elements in the sample. Although the induced radioactivity was counted by a high resolution gamma-ray spectrometer system, a group separation was needed due to the presence of interfering activities, e.g. spectral interference by  $^{182}\text{Ta}$ . The group separation was conducted by acid dissolution of the sample (for cassiterite ore, the sample was fused with sodium peroxyde prior to dissolution), precipitation of cerium carrier with fluoride, redissolution of the precipitate in nitric acid. The resulting solution was converted to chlorides and then passed through a Dowex 1X10 anion exchange resin column. The rare earth elements chlorides in the eluate was precipitated and then counted. In quantitative analysis the interference by gamma-ray peak from rare earth element radionuclide was minimized by proper choice of the peak and cooling time. The result in the utilization of a large coaxial semiconductor detector in gamma-ray spectroscopy was compared with that of low energy photon detector.

**9:40 The Use of Emission Spectroscopy in Exploration Geochemistry.**

*James A. Domenico*, U.S. Geological Survey, Golden, Colorado.

Emission spectrographic analyses are particularly useful in preliminary and large-scale geochemical surveys. Spectrographic analyses enable a large number of elements and their concentrations in various geologic materials to be determined rapidly and inexpensively.

Semiquantitative emission spectrographic procedures are uncomplicated and can be easily adapted to the needs of individual geochemical surveys. The precision of the analyses and the levels of detection are adequate for diagnostic geochemical appraisals of the elements analyzed. Emission spectrographic procedures require only a small sample; thus a geologic sample can often be separated into its mineral components for further analysis and examination.

The spectrographic apparatus can be placed in truck-mounted mobile laboratories. These laboratories supply rapid on-the-spot analytical data, which are useful to geochemical field parties for daily evaluation.

**10:00 Assessment of a Modified Addition Method for Multiple-Element Trace Analysis of Silicate Rocks by DC-Arc Spectrography.**

*D.W. Golightly* and *A.F. Dorrzopf, Jr.*, U.S. Geological Survey, Reston, Virginia.

In the past, high accuracy and precision in spectrographic trace analysis were achieved through the use of sample fusions or solution techniques. These techniques effectively dilute the concentrations of trace elements, require considerable time and handling of samples, and significantly increase the probability of contamination. The standard addition methods reported in the literature require fusions or solutions, with their associated problems. Although d.c. arc spectrography enables high sensitivity by methods requiring minimal sample handling, the attendant accuracy problems arising from matrix- and interelement effects require the skills and insights of an experienced analyst. To circumvent the matrix effect problems and simultaneously achieve multiple-element analysis capability we have adopted a matched-matrix addition approach that fully utilizes the desirable sensitivity of the d.c. arc and that virtually eliminates the problems arising from matrix effects. The approach entails dilution of a pulverized silicate rock with a geochemical reference standard of similar type. Matrix similarity is determined from rapid semiquantitative spectrographic analysis by a computerized microphotometer. Relative

line intensities from **d.c.** arc spectra of the sample, standard, and mixtures define a least-squares fitted functional relationship between concentration and intensity. Spectra produced **by a 3.4 m Ebert** spectrograph are recorded on 102 x 508 mm (**III-0**) plates. Buffered sample/standard mixtures are stomized and excited by a 15 A arc in an **Ar-O<sub>2</sub>** atmosphere. Small quantities (approximately 250 mg) of sample and standard are required in each analysis for 20-30 elements, and computerized microphotometry enables rapid estimates of trace element concentrations. The success of the modified addition method depends totally on a diversified assemblage of standards that have been well characterized for trace element content. The concepts of matched-matrix addition, effects of non-linearity of calibration functions, and successes and problems in the accurate analysis of selected rhyolites and granites will be discussed.

**10:20 Multielement Trace Metals Analysis in Natural Waters by Differential Pulse Anodic Stripping Voltammetry.**

*H.E. Taylor* and *J.E. Bonelli*, U.S. Geological Survey, Arvada, Colorado; and *R.K. Skogerboe*, Department of Chemistry, Colorado State University, Fort Collins, Colorado.

The simultaneous analysis of multiple trace metals in natural water samples was performed by differential pulse anodic stripping voltammetry. An evaluation of the accuracy and precision that can be obtained for the elements cadmium, copper, lead, and zinc in a multiple element routine analysis mode indicates that results similar to those achieved by single element determinations are obtained. Comparative data based on the analysis of reference standards of natural water from the United States Geological Survey Standard Reference Water Sample program are used to illustrate the practical limits of accuracy and precision that can be obtained in the multielement mode.

—BREAK—

**SESSION (VI)**

**10:45 Air Sampling for Pesticides.**

*David L. Spencer*, Department of Microbiology, Colorado State University, Fort Collins, Colorado.

During the past few years there has been an extensive effort to monitor the environment for pesticide residues.

The various sources of the pesticide residues detected in air have been summarized by several investigators;

however, comparatively little data are currently available on residue incidence and levels largely due to the lack of adequate air sampling methods.

Several ambient air sampling devices are available and each has its advantages and disadvantages. Some of the more commonly used samplers include:

1. **Greenburg-Smith impingers**
2. Midwest Research Institute Sampler (**MRI**)
3. High Volume Air Sampler
4. Nylon Cloth Screen

We are currently evaluating an air sampler developed by the Syracuse University Research Corporation (SURC).

A discussion of results from an air sampler comparison and evaluation study conducted by the Colorado Pesticide Center will be presented.

**11:05 The Mathematical Analysis of Metal-Multiligand Equilibria.**

**Garon C. Smith** and Patrick **MacCarthy**, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado.

The equilibria which exist between a metal ion and a complicated mixture of ligands is of relevance in many situations, for example in soil, biological and geochemical studies. A mathematical treatment of such systems is naturally more complicated than that of a single ligand system. We have been developing an analysis of such systems by (i) generating the mathematical equations to describe **metal-multiligand** equilibria and (ii) solving these equations by means of a digital computer to give the distribution of all species present in simulated systems. A mathematical model will be presented.

**11:25 Trace Elemental Analysis of Cosmetics by Spark Source Mass Spectrometry.**

**M.L. Jacobs**, and **S.. Sweeney**, Instrumental Analysis Division of Commercial Testing and Engineering, Golden, Colorado.

In the past, emphasis has been placed predominantly on the potentially hazardous organic constituents in facial and body cosmetics. Very little information on trace elemental composition is available and access to such information is hindered by the proprietary nature of the product. However, recent consumer and governmental regulatory agency interest has stimulated trace elemental investigations into facial cosmetic products in our laboratory.

Presentation of the samples to the spark source mass spectrograph taxed the imagination of the analyst. Cosmetic samples were rarely presented in the original

formulation since oils, waxes, and perfumes are generally contained in the formulation and must be removed. In our study this was accomplished by low temperature thermal ashing, generally **350°C** for one hour. Comparative analysis by neutron activation and atomic absorption techniques show the loss of some of the more volatile trace elements using the thermal ashing at **350°C**.

An A.E.I. **MS7**, modified for increased resolution and higher speeds, utilizing an **Ilford Q2** photoplate as an ion detector was used for the trace analysis in this study.

Several brands of iridescent eye shadows were examined by spark source mass spectrographic techniques initially as a survey for potentially hazardous trace elemental content and secondly to compare trace composition between individual manufacturers. A face powder, body powder, eye mascara and lipstick were also examined for trace element composition.

Lead, arsenic, selenium and chromium were found in several cosmetic products in potentially detrimental concentrations.

Sample preparation and spark source preparative techniques, as applied to this survey will be discussed.

#### 11:45 **Luminescence in Metal Flames Irradiated with a CO<sub>2</sub> Laser.**

*John C. Moulder*, National Bureau of Standards, Boulder, Colorado.

In an earlier paper presented at this conference in 1975, we reported the observation of unusual peaks in the continuum radiation emitted by calcium and magnesium flames irradiated with a **CO<sub>2</sub>** laser. In the present paper it is suggested that these emission peaks are due to **candoluminescence** of metal oxide smoke particles. The luminescence is apparently excited by the heterogeneous oxidation of metal vapor on the surface of growing oxide particles. The experimental results suggest that infrared radiation stimulates one or more steps of the complicated process leading to luminescence. Although the exact mechanism for this infrared stimulation remains unclear, some of the ways in which laser radiation can affect surface reactions are discussed.

—LUNCH—

#### **SESSION (VII)**

Analytical Chemistry in Energy Related Fields, Chairman: Marvin Goldberg, U.S. Geological Survey, Denver, Colorado.

**1:30 Chemical Characterization of Sulfate Aerosols Associated with Coal Fly Ash.**

*R.P. Conway* and R.K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado.

The very sharp renewed interest in coal as an alternative source of energy has spurred increased concern over atmospheric pollution from sulfur dioxide, sulfates and airborne particulate matter. The behavior and interaction of these species in the environment is not clearly understood.

A separation/analytical scheme will be described which allows identification of chemical species of sulfate and determination of the factors which are important in the conversion mechanism of sulfur compounds in the atmosphere.

**1:50 Carbon-13 NMR Studies of *In Situ* Oils from Shale, Tar Sands and Coal Gasification.**

*Daniel A. Netzel*, Laramie Energy Research Center, Laramie, Wyoming.

It is well known that both carbon-13 and proton NMR spectroscopy can be used in identifying directly pure and/or simple mixtures. Difficulties are encountered, however, when using NMR to characterize materials such as oils that contain many hundreds of compounds. Research at the Energy Center is in progress in which both carbon-13 to the determination of the olefinic content in shale oil, phenolic **identification** in coal tars and the identification of the components in the **paraffinic, aromatics**, acids, bases and olefinic fractions of the various oils will be discussed.

**2:10 New Methods for Uranium Analysis.**

*B.B. Jablonski* and D.E. Leyden, Department of Chemistry, University of Denver, Denver, Colorado.

The chemistry of uranium is well known and as a result, there exist numerous analytical methods for uranium. Despite this fact, there is still considerable interest in developing new methods which are sensitive to trace levels of the element. Three new techniques which are rapid and simple, yet sensitive, have been devised in our laboratory.

A photometric flow monitor for uranium based on the reactions between uranium and 2,3 dihydroxy-naphthalene-6-sulfonic acid has been developed. The reaction occurs at alkaline pH and the presence of ammonium carbonate helps to free the system from interference. The lower limit of detection is 2 **ppm** with 1.1% precision at 60 ppm uranium.

Two methods of sample enrichment prior to x-ray analysis have also been developed. One technique takes advantage of the insolubility of the double salt of uranium,  $\text{Ba}(\text{NH}_4)_2\text{UO}_2(\text{CO}_3)_3$ . The lower limit of detection is 2 micrograms uranium.

Uranium can be recovered from solution as the carbonate complex by a chelate immobilized on silica gel. The concentration of carbonate in the uranium sample must be well controlled to achieve quantitative removal of the element from solution. A precision of 0.8% at 0.8 mg of uranium has been observed with a calculated lower limit of detection of 2 micrograms uranium. A brief comparison of the three methods will be given along with a discussion of possible application to alkaline leach operations.

#### 2:30 **X-Ray Spectrometric Determination of Technetium in Nuclear Fuels Processing Wastes.**

*S.G. Metcalf*, Atlantic Richfield Hanford Co., Richland, Washington.

Technetium is formed in high yield by thermal neutron fission of  $^{235}\text{U}$ , has a long half-life, and emits beta radiation. An alternative method to beta counting is desirable because for beta counting other beta emitting isotopes, which are present in large amounts, interfere and give high analytical results. The method is based on extraction of Tc from strongly basic solutions with 30 percent, by volume, methyltricaprylammonium chloride (MTC) in xylene. All samples are at least 4M in NaOH. Re, which coextracts with the Tc, is added as an internal standard. The MTC containing the Tc and Re is pipetted onto a filter pad, dried and the amount of Tc and Re is determined by use of standard X-ray spectrometric techniques. The detection limit for typical nuclear fuels reprocessing waste solutions is 90 PPb. The average recovery, at the 95 percent confidence level is  $101 \pm 9$  percent. A series of experiments with various cations and anions present at levels normal to fuels reprocessing waste solutions shows no interference for this method. Sample volumes of up to 100 ml can be employed if desired. The separation reduces the radiation level emanating from the sample, which is handled by the operator, by more than a factor of 200. The method has been successfully employed on actual waste solutions.

#### 2:50 **Instrumentation for the Detection and Analysis of Uranium and Other Radioactive Materials.**

*John P. Salsgiver*, R.D. Stetson, and R.L. MacLure, United Technical Corporation, Leominster, Massachusetts.

The need to determine small amounts of uranium and other radioactive materials is essential for their proper understanding, management and control. **For** many years Oak Ridge National Laboratories has been concerned with this problem. As a result of the technology transfer program initiated by Oak Ridge, this instrumentation is now available commercially for the first time. The instrumentation has been updated where required and features precision and the professional quality needed to make the most accurate analysis possible in accordance with the state of the art. Further, the instrumentation is readily adaptable for completely automatic operation.

For the determination of uranium by ultraviolet fluorescence, the most sensitive known, the Model FP-3500 **Fluorophotometer** has been constructed. Either a fluoride or carbonate pellet is prepared with the aid of the Model FF-1500 Fusion Furnace at a rate of 40 samples per hour. This method, **by the way**, provides sample melts 30% more sensitive than previous open-flame techniques. The pellets are then inserted into the rotary sample tray (capacity 24 samples) of the Fluorophotometer where the uranium present in the sample is displayed digitally in nanograms. The sample range of the instrument is 2 to 1500 nanograms at an accuracy of better than 2%. Sample reading time is 5 seconds so that screening analyses can be accommodated.

For the determination of uranium by controlled potential titration, the Model CTA-2500 **Coulometric** Titrator has been prepared. Here, either one of two standard titration cells is selected by the titrator for analysis. The cells may be located up to 50 feet away **from** the titrator control unit. This solid state instrument, constructed in standard **NIM** bin fashion, measures uranium in the range of 0.595 to 59.5 milligrams with a relative standard deviation of only 0.005% per day.

For the accurate pipetting of samples containing uranium, the Model ADP-1100 Remote Control Pipetter has been built. Constructed of corrosion resistant materials, the instrument features a sample range of 1 to 1000 microliters with a relative standard deviation of 0.06% at **80%** of capacity. Sample size is selected by a digital dial on the solid state control unit where operation of the pipetter is accomplished by push buttons. The control unit may be located up to **50 feet** from the pipetting stand.

Color slides of the instrumentation will be shown.

**—BREAK—**

### SESSION (VIII)

Chairman: Jan Howard, Natural Resources Ecology Lab,  
Colorado State University, Fort Collins, Colorado.

#### 3:15 Selective Photodestruction of Amino Acids.

*Nissim Levi* and James G. Lawless, NASA-Ames  
Research Center, Moffett Field, California.

One of the main problems in analysis of amino acids in  
chemical evolution experiments and in extracts of  
meteorites is the large number present.

In Murchison meteorite for example were found  $\alpha$  amino  
acids,  $\beta$  amino acids,  $\gamma$  amino acids, mono n-substituted  
a amino acids and dicarboxylic a amino acids. The  
chromatogram of the amino acids in Murchison is very  
complicated and there are many more amino acids than  
were positively identified by computerized GC-MS.

We discovered an analytical method to selectively  
destroy the  $\alpha$  amino acids leaving in solution the  $\beta$  and  $\gamma$   
amino acids.

$\text{Cu}^{+2}$  is known to complex with amino acids with the  
order of stability  $\alpha$  amino acids  $< \beta < \gamma$ ,  $\delta$ ,  $\epsilon = \text{o}$ .

Aqueous solutions of  $\alpha$  amino acids - Cu chelates are  
known to be decomposed by 254 mμ light as well as by non  
monochromatic uv light, yielding a precipitate of  $\text{Cu}_2\text{O}$ .

We found that at 254 mμ (Ligand metal charge transfer  
band) the rate of destruction of amino acids in  $\text{Cu}^{+2}$   
aqueous solutions is in the following order:

Dicarboxylic a amino acids  $> \alpha$  amino acids  $>$  mono n-  
substituted a amino acids  $>> \beta$  amino acids  $\approx \gamma$ - amino  
acids

Thus by irradiation with 254 mμ light in the presence of  
 $\text{Cu}^{+2}$  all the amino acids can be destroyed except the  $\beta$  and  
 $\gamma$  amino acids. When almost 100% of the  $\alpha$  amino acids are  
destroyed 80% of the  $\beta$  and  $\gamma$  amino acids still exist in  
solution.

By this analytical procedure a very complex mixture of  
amino acids can be simplified to make identification by  
GC-MS easier.

#### 3:35 Analytical Chemistry and Pediatrics.

*P.V. Fennessey*, E.R.B. McCabe, S.I. Goodman,  
Donough O'Brien, and Barbara Miles, Department  
of Pediatrics, University of Colorado Medical  
Center, Denver, Colorado.

The real time analysis of physiological fluids from our  
failure-to-thrive population in Colorado and the sur-  
rounding states poses a number of problems to the  
analyst. In this paper we will present the methods we use  
for the initial screening, the gas chromatograph/mass  
spectrometer/computer (gc/ms/com) system we use for

detailed analysis and the data we routinely obtain. We will then show how this methodology was used to detect the chemical basis of the disease in three patients who were not growing and how this data has affected their treatment.

**3:55 PCB's and Chlorinated Pesticides in Human Milk.**

*John D. Tessari*, Department of Microbiology, Colorado State University, Fort Collins, Colorado.

In 1975-76 the Colorado Epidemiological Pesticide Studies Center (the Center) under contract with the EPA, determined levels of chlorinated pesticides and PCB's in human milk among nursing mothers giving birth in U.S. hospitals.

Use of the **organochlorine** compounds started in 1936 when DDT was first used as a moth-proofing agent. Because of their broad spectrum activity, low cost, and stability, the chlorinated hydrocarbon insecticides have been of great agriculture and public health importance.

Prior to 1970, medical and public health interest in polychlorinated biphenyls (PCB's) in the United States was meager. It was not until 1966 when Soren Jensen of Sweden discovered that PCB's were **confused** analytically with chlorinated hydrocarbon pesticides that the toxicology literature on PCB's broadened beyond the level of articles on patents, industrial aspects, and hygienic implications.

In the past, an indication of a person's exposure to a particular pesticide has been documented through residues in human adipose tissue and blood. When these pesticides were found in mother's milk, concern arose as to what effect, if any, this must have on breast fed infants.

The population that was sampled consisted of approximately 1600 samples collected from 783 hospitals participating in the "Acute Pesticide Poisoning Study" which had nursery facilities. These hospitals were randomly selected from a list of approximately 7000 general hospitals according to the protocol for "Field Studies System for Characterization of Acute Pesticide Poisonings." Each hospital was classified according to pesticide usage levels (geographic area) and state.

**4:15 Fluorescence and Electrogenated Chemiluminescence of Dimethyl Benzo(a)pyrenes.**

*Su-Moon Park*, Department of Chemistry, University of New Mexico, Albuquerque, New Mexico.

Fluorescence spectra, fluorescence quantum yields, electrogenerated chemiluminescence, and electrode potentials of **5-dimethylbenzo(a)pyrenes** are reported. Singlet excited energy levels of these compounds in

benzene solutions at room temperature were approximately  $3.0 \pm 0.1$  eV in all cases and 0-0 fluorescence bands were found to be concentration quenched at higher concentrations than  $10^{-4}$  M, resulting in formation of excimers, which mostly emit at approximately 520 ~ 540 nm. When radical anions and cations of these compounds were generated by the double potential step methods at the oxidation and reduction potentials at the platinum wire electrode alternately in the benzene-acetonitrile (50:50) solution, electrogenerated chemiluminescence (ecl) was obtained in all cases. All these ecl systems were energy sufficient and ecl spectra were characterized by the intense and broad longer-wavelength emission centered around 520 ~ 550 nm with the very low intensity fluorescence shoulder at around 450 nm. From the various experimental observations, the shorter wavelength peaks at approximately 450 nm were identified to be the fluorescence emission from the parent molecules and the longer wavelength emissions are originated from the electrode reaction products. Detailed mechanisms involved in the light generating stages will be discussed.

#### 4:35 **Chronopotentiometric Determination of Pseudo-First-Order Decay Rate Constants of Electro-generated Species.**

Donald A. Tryk and Su-Moon Park, Department of Chemistry, University of New Mexico, Albuquerque, New Mexico.

In current reversal chronopotentiary (CRCP), a problem has been how to compute, efficiently and to any desired precision, the pseudo-first-order decay rate constant,  $k_d$ , for the decay of the electrogenerated radical species. The problem arises from the implicit nature of the relationship:  $2 \operatorname{erfc} k_d \tau_2 = \operatorname{erfc} k_d (t_1 + \tau_2)$ , where  $t_1$  = time elapsed before current reversal, and  $\tau_2$  = transition time after current reversal.

A method has now been devised to use an explicit expression for  $t_1$  and to use Newton-Raphson iteration to determine  $k_d$  knowing  $t_1$  and  $\tau_2$ . A FORTRAN IV (IBM 360) program has been written incorporating this method into the standard method for determining  $k_d$  using a  $k_d t_1$  vs.  $t_1$  plot [Testa and Reinmuth, *Anal. Chem.*, 32, 1512 (1960)], in which a least-squares fit is run on the data points.

This method is employed to obtain a  $k_d$  value for a previously well-characterized system.

### Registration

Conference registration will be in the lobby of the Radisson Denver Hotel. Preregistration using the form provided is urged. The registration desk will be open from 7:45 a.m. to 3:00 p.m. August 1, and from 7:45 a.m. to 10:30 a.m. on August 2 and 3. Please make checks payable to the 19th Annual Conference on Analytical Chemistry. Registration badges will be necessary for admission to all technical program sessions. Registration fees are as follows:

|                                                                   |         |
|-------------------------------------------------------------------|---------|
| Pre-registered conferees<br>(except full-time students) . . . . . | \$15.00 |
| Conferees who do not pre-register                                 | \$20.00 |
| Full-time students . . . . .                                      | \$ 5.00 |
| Banquet . . . . .                                                 | \$ 7.00 |



### 1977 Conference Chairman

Dr. Kelly R. O'Keefe, Department of Chemistry,  
Colorado State University, Fort Collins, Colorado.

### 1978 Conference

Next year's conference will be entitled the 20th Annual Rocky Mountain Conference on Analytical Chemistry and Spectroscopy, and is tentatively scheduled for August 7, 8, and 9, 1978.

The Conference Chairman will be Dr. Dan A. Netzel, ERDA, Laramie Energy Research Center, Laramie, Wyoming.