

# Rocky Mountain Conference on Magnetic Resonance

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Article 1

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## 16th Annual Rocky Mountain Spectroscopy Conference

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## 16th Annual Rocky Mountain Spectroscopy Conference

### Abstract

Final program and abstracts from the 16th annual meeting of the Rocky Mountain Spectroscopy Conference, sponsored by the Rocky Mountain Section of the Society for Applied Spectroscopy. Held in Denver, Colorado, August 5-6, 1974.



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**16th Annual  
Rocky Mountain  
Spectroscopy  
Conference**

*FINAL PROGRAM — ABSTRACTS*

**August 5—6, 1974**

**Brown Palace Hotel  
Denver, Colorado**

*Sponsored by the*

**ROCKY MOUNTAIN SECTION**

*of the*

**SOCIETY FOR APPLIED SPECTROSCOPY**

## **General Information**

### **Sponsor**

Again, the Rocky Mountain Section of the Society for Applied Spectroscopy extends a warm welcome to all conferees, confident that the program offered will be diverse and comprehensive, and hopeful that it will prove to be of value to everyone attending. This year, the program has been oriented around a "symposia" concept, with selected topics assigned to several sessions. We hope you'll find this useful in planning your attendance and participation, and we invite your comments for its improvement.

Also new in concept this year is the social event, which will be held at Central City (Blackhawk). We have arranged transportation for those of you wishing to attend, and we hope to see you all there.

### **Registration**

Registration will be at the head of the stairs, on the mezzanine floor, (old bldg) and will be available throughout the conference. Checks should be made payable to the Rocky Mountain Section, Society for Applied Spectroscopy (RMS-SAS). Registration badges will be necessary for admission to all sessions. Registration fees are as follows:

All conferees (except students).....	\$15.00
Conference plus SAS membership (including journal).....	\$30.00
Students (full time).....	\$3.00

Abstracts will be available at registration.

### **Accommodations**

The Brown Palace Hotel has a number of rooms reserved for the conference. Other nearby hotels are the New Albany, Cosmopolitan, and Hilton.

### **Conference Social**

This year, the dinner will be held at the Black Forest Inn in Blackhawk, August 6, at 7:30 p.m. Following the dinner and presentation of the Outstanding Service Award, there will be an opportunity for everyone to absorb some of the local culture. A choice of menu will be offered with an anticipated average charge of \$7.00 per person. Transportation to and from Blackhawk will be provided for those who desire it for a modest fee of \$2.00.

### **Outstanding Service Award**

This year, the Rocky Mountain Section is presenting its annual service award to N. Cyril Schieltz, retired Colorado School of Mines Professor of Chemistry, and past chairman of the RMS-SAS. The presentation will be made at the Black Forest Inn.

### **Exhibits**

Current state-of-the-art instruments and equipment will be on display outside the auditorium. Exhibitors are:

- Analytical Development Associates Corporation
- Beckman Instruments
- ORTEC
- Canberra Industries
- Diano Corporation
- KeveX Corporation
- Scientific Resources, Inc.
- Wilks Scientific Corporation
- Technical Equipment Corporation
- Buhrke Co.
- Lear Siegler
- US Geological Survey

### **Coffee Breaks**

Refreshments for scheduled recesses will be furnished courtesy of Van Waters and Rogers and Varian Instruments.

### **DRI X-Ray Conference**

The 23rd Annual Denver Conference on Applications of X-Ray Analysis will be conducted at the hotel August 7, 8, and 9. For additional information contact C.O. Ruud, Metallurgy and Materials Science Division, Denver Research Institute, University of Denver, Denver, Colorado 80210. Telephone: (303) 753-2141.

### **Inquiries**

For additional information on the RMS-SAS Conference, address inquiries to: Roland R. Manning, Ball Brothers Research Corporation, Box 1062, Boulder, Colorado, 80302, or call: (303) 441-4529.

### **Conference Schedule**

All morning sessions will begin at 9:00 and afternoon sessions at 1:30.

### **Monday Morning — General**

#### **9:00 Welcoming Remarks**

Steve Valente, 1974 RMS-SAS and Session Chairman, Regis College, Denver, Colorado.

**9:10 (1) Comparison and Discussion of Chemical and Mineralogical Data from Four Laboratories**

D. B. Roberts, Geological Consultant, Denver, Colorado.

The practical aspects of the use of analytical data frequently involve the comparison of laboratory results obtained by different methods, by different methods, by different laboratories, and over significant periods of time. The investigator is faced with the necessity of selecting the best or most likely value from several analytical results. This selection must normally be made on the basis of less information than would be desired in the ideal case.

Mineralogical data obtained by X-ray diffraction, and elemental data obtained by X-ray fluorescence, atomic absorption, and optical emission are presented as examples of typical situations in data treatment and interpretation. Discussion and comment are invited, recognizing that in some cases more work would have been necessary to resolve the observed discrepancies, and such additional analytical work was not economically justified in this case.

Missing data points and "less than" values are handled differently for different elements. In averaging data, equal weight is normally given to each of the available values, but in some cases the result from one analytical method is favored over that from another.

**9:30 (2) Interferometry and Low Frequency Vibrations**

Ernest Tuazon and W. G. Fateley, Department of Chemistry, Kansas State University, Manhattan, Kansas, and A. S. Manocha, Department of Chemistry, University of Maryland, College Park, Maryland.

Fourier Transpose Spectroscopy (FTS) is now making a great impact on the measurement of the infrared region and very especially the far infrared (i.e. below  $200\text{ cm}^{-1}$ ). Data will be presented on the measurement of samples by FTS. A description of the investigation of torsional frequency, those vibrations below  $400\text{ cm}^{-1}$ , and their relation to a new chemical parameter, similar to the Hammel sigma will be presented.

**9:50 (3) Selectivity in Inorganic Probes for the Analysis of Nucleic Acids**

**I. T. Urasa and C. M. O'Donnell**, Department of Chemistry, Colorado State University, Fort Collins, Colorado

The use of phosphorimetry as an analytical technique has, in the past few years, proved to be a powerful technique particularly in the analysis of trace quantities of organic and biological molecules.

Iodide, as an external heavy ion, and silver, as an internal heavy ion, have been utilized as probes by Lukasiewicz et al. (1) and Rahn et al. (2), respectively, in the analysis of nucleic acids and other organic molecules particularly those of biological interest. Such inorganic probes have been found to produce significant enhancement in phosphorescence intensity and a corresponding reduction in phosphorescence lifetimes of the excited molecules. (3,4)

This paper will be concerned with the use of silver, mercury and gold as inorganic probes for the analysis of nucleic acids and related biological compounds. We will demonstrate that tremendous sensitivities and/or selectivities can be achieved if such probes are coupled with other parameters such as the pH of the system.

**References**

- (1) Lukasiewicz et al., Anal. Chem., 40, 963 (1972).
- (2) Rahn, et al., Photochem. Photobiol. 18, 29 (1973).
- (3) G.D. Boutiller and C. M. O'Donnell, Submitted for publication, Anal. Chem. (1974).
- (4) R.E. Sheridan, C.M. O'Donnell and E.L. Pautler, Anal. Biochem. 52, 657 (1973).

**10:10 (4) Circular Dichroism of Tetracycline Complexes**

**E. C. Newman and C. W. Frank**, Department of Chemistry, University of Iowa, Iowa City, Iowa, 52242.

Because the mode of action of the tetracycline family of antibiotics has been established as involving the metal ion complexes of these compounds, the study of these complexes has been the subject of numerous investigations. The complexes of tetracycline and related compounds with:  $Al^{+3}$ ,  $B^{+2}$ ,  $Ca^{+2}$ ,  $Cd^{+2}$ ,  $Co^{+2}$ ,  $Fe^{+2}$ ,  $Mg^{+2}$ ,  $Mn^{+2}$ ,  $Ni^{+2}$ ,  $Sr^{+2}$ ,  $An^{+2}$ , and other metal ions have been studied, either by analysis of the isolated chelates or by direct observation of the complexes using primarily potentiometry, uv-visible, or fluorescence spectrometry.

The conclusions derived from these investigations are often conflicting both as to the stoichiometry of the complexes and the complexation sites.

In this study the determination of the stoichiometry and the binding sites of the tetracycline complexes which have the most biological importance, are discussed. Modified tetracyclines were prepared which had a blocked site (or sites) and the metal ion complexes of these compounds were then studied by spectrometric techniques, particularly circular dichroism. The CD spectra were used to determine whether a particular modified tetracycline, blocked at a certain site, still formed a complex and if that complex was similar to that of tetracycline.

#### **10:30 Coffee Break**

#### **10:50 (5) Effect of Hydrogen-Bonding on the Emission of N-Heterocyclic Compounds**

Thomas S. Spencer, Robert L. Cunico, and C. Michael O'Donnell, Department of Dermatology Research, Letterman Army Institute of Research, San Francisco, California.

The total emission spectra of hydrogen-bonded N-heterocyclic complexes of carbazole with quinoline or isoquinoline have been studied. Both quinoline and isoquinoline at  $2 \times 10^{-3}M$  completely quench carbazole emission in non-polar solvents, but not in polar solvents. Stern-Volmer plots indicate a 1:1 complex of donor:acceptor. The triplet lifetimes of carbazole and the fluorescence-phosphorescence ratios for carbazole were determined. The mechanism for quenching is related to radiationless deactivation processes rather than energy transfer followed by emission from the acceptor.

#### **11:10 (6) Tryptophane Emission as an Intrinsic Environmental Probe of Human Skin**

Robert L. Cunico and Thomas S. Spencer, Department of Dermatology Research, Letterman Army Institute of Research, San Francisco, California.

Stratum corneum, the thin outer layer of the skin, represents the principal barrier to penetration of substances into the body. The fluorescence and phosphorescence spectra of human stratum corneum have been studied *in vitro*. The spectra and lifetimes are characteristic of tryptophane residues



in intracellular proteins. Spectra of tryptophane in solution with  $I^-$ ,  $OH^-$ , and  $H^+$  are compared to the emission of tryptophane residues within the stratum corneum. When substances such as  $I^-$  are allowed to penetrate the skin, changes in the emission spectra indicate changes in the microenvironment of tryptophane residues. These changes are related to the degree to which the substance has penetrated the protein macromolecule.

**11:30 (7) Flame Spectroscopy Applied to High-Intensity Continuous Combustion with NO<sub>x</sub> Formation**

P. C. Malte, Department of Mechanical Engineering, Washington State University, Pullman, Washington, 99163.

Flame spectroscopy, as a diagnostic, has led over the years to an understanding of one-dimensional flame structure and reaction kinetics. On the other hand, continuous combustion, with recirculation of burned gases and turbulent mixing for stabilization, has until very recently received scant spectroscopic attention.

To fill this void, a few investigators have initiated flame spectroscopic measurements in continuous combustion reactors employing high-intensity recirculation and mixing. Impetus for this recent research has been the kinetics of pollutant formation and decomposition, particularly for nitrogen oxides "NO<sub>x</sub>".

In our initial work, a special jet-stirred combustion reactor (figure 1) fitted with optical access sapphire windows has been used. Gas radiation was focused on the entrance slit of double pass prism monochromator fitted with a 1P28 photomultiplier. With near-sonic feed-jets of cold, premixed fuel ( $H^2$ , CO, or  $CH^4$ ) and air, the reactor gave near-homogeneous volume burning with nearly uniform temperature and composition. Local flames were not observed because of the intense mixing.

by observing and measuring chemiluminescent emission in the range 3000 to 6000Å, it has been possible to study at the fuel-lean conditions the effect on NO<sub>x</sub> formation of active pyrolysis and combustion intermediates such as O-atoms and Ch-radicals. The experiments were aided by gas sampling for CO and NO<sub>x</sub> and by thermocouple temperature measurements. Super-equilibrium O-atom concentrations were determined by direct spectroscopic measurement of "blue" continuum

chemiluminescence due to  $\text{CO} + \text{O} \rightarrow \text{CO}^2 + h\nu$ . The O-atom measurements explained  $\text{NO}_x$  formation only for CO/air combustion (figure 2 and 3), strong chemiluminescence due to the CH (0,0) band at  $4315\text{\AA}$  was also monitored. A strong correlation between CH emission intensity and  $\text{NO}_x$  concentration was observed.

Discussion of this new application of known and routine flame spectroscopy will hopefully stimulate further and more sophisticated optical diagnoses of high-intensity continuous combustion.

**11:50 (8) Second Derivative Spectra of  $\text{AsH}_3$ ,  $\text{PH}_3$ , and  $\text{SbH}_3$  in the Region of 1950-2200  $\text{\AA}$**

Victor T. Jones, Geophysical Laboratories, Houston, Texas, and A. M. Garcia, Lear Siegler, Inc., Englewood, Colorado, 80110

Previous work on the spectra of  $\text{AsH}_3$ ,  $\text{PH}_3$  and  $\text{SbH}_3$  indicate three diffuse bands for  $\text{PH}_3$  in the region 200-240 nm. In the case of  $\text{SbH}_3$  and  $\text{AsH}_3$  only continuous absorption has been observed in the region 1900-2400.

This paper will discuss the second derivative absorption bands of  $\text{PH}_3$ ,  $\text{AsH}_3$  and  $\text{SbH}_3$ . In all three cases sharp second derivative bands emerge from the absorption continuum. The use of these bands for identification and measurement of these compounds will be discussed.

**12:10 (9) Spectrophotometric Determination of Nitrate with 4,4'-Diaminodiphenylsulfone**

W. I. Winters, Atlantic Richfield Hanford Co., Richland, Washington.

Nitrate reacts with 4,4'-diaminodiphenylsulfone (DDS) in concentrated sulfuric acid to form a yellow dye whose absorbance at 410 nanometers has been used for the spectrophotometric determination of nitrate in synthetic nuclear waste. The optimum sample volume and sulfuric acid and DDS concentrations for color development were determined. Twenty-three potential interfering ions were studied and their tolerance limits measured. Sodium hydroxide, acetic acid, and urea did not seriously interfere even at high levels. The effect of nitrite on the determination of nitrate was established and methods to destroy nitrites in acidic and basic media using urea are described. Even though a method for the total removal of nitrite was not found, a technique for measuring nitrate in the presence of five times more nitrite is discussed. Halide interference

is removed by the addition of silver sulfate. The method has a molar absorptivity of approximately  $2400 \text{ liter mole}^{-1} \text{ cm}^{-1}$ . The method has been used to analyze synthetic nuclear waste and has a standard deviation of  $\pm 7.3$  percent at the  $100 \mu\text{g}$  nitrate level and  $\pm 2.4$  percent at nitrate levels greater than  $200 \mu\text{g}$ .

**12:30 Lunch**

**Monday Afternoon — Mass Spectrometry**

**1:30 Opening Remarks**

Jim H. Weber, Session Chairman, U.S. Bureau of Mines, Laramie Research Center, Laramie, Wyoming.

**1:40 Keynote Address: An Overview on the Growth and Development of Mass Spectrometry**

G. L. Cook, U.S. Bureau of Mines, Laramie Research Center, Laramie, Wyoming.

**2:00 (10) Applications of GC-MS to Problems in Clinical Research**

S. P. Markey, Department of Pediatrics, University of Colorado Medical Center, Denver, Colorado, 80220.

Over the past 6 years, a GC-MS computer system has been applied to problems in clinical research—principally, the analysis of inborn errors of metabolism. A description of the design and construction of this system will be presented along with examples of its ability in the diagnosis of unknown neurological disorders.

**2:20 (11) Optically Modified Mass Spectra of  $\text{CO}_2$**

A. B. Denison, B. A. Osterlitz, J. Phillips, Department of Physics, University of Wyoming, and J. H. Weber, U.S. Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming.

A large enhancement of the  $\text{CO}_2^+$  peak intensity is observed upon optical irradiation of the ionization chamber in our time-of-flight mass spectrometer. For moderately low sample pressures, the beam from a 250-watt Hg lamp is able to increase the  $\text{CO}_2^+$  peak intensity by a factor of two for an electron impact energy of 60 eV. We report the systematic observation of the  $\text{CO}_2^+$  peak intensity as the optical excitation is scanned in frequency for a series of electron impact energies. With this technique one is able to obtain detailed information about energy

levels which are of importance in the ionization process of  $\text{CO}^2$ .

#### **2:40 Coffee Break**

#### **3:00 (12) Mass Spectra Aided Structural Elucidation of an Amino Acid Amide and Synthetic Oligopeptides**

Dominic M. Desiderio, Institute for Lipid Research and Marrs McLean Department of Biochemistry, Baylor College of Medicine, Houston, Texas, 77025.

Mass spectra of a series of stable isotope derivatives aided a structure elucidation study of an amino acid amide ( $\text{Tyr-NH}_2$ ) and the following family of synthetic oligopeptides:  $\text{Gly-Tyr-NH}_2$ ,  $\text{Gly-Gly-Tyr-NH}_2$ ,  $\text{Gln-Gly-Gly-Tyr-NH}_2$ ,  $\text{Gln-Gln-Gly-Gly-Tyr-NH}_2$ ,  $\text{Ala-Gln-Gln-Gly-Gly-Tyr-NH}_2$ ,  $\text{Ser-Ala-Gln-Gln-Gly-Gly-Tyr-NH}_2$  and  $\text{Lys-Ser-Ala-Gln-Gln-Gly-Gly-Tyr-NH}_2$ . This series of peptides was synthesized by classical methods. *N*, *O*-permethylated, *N*-acetylated derivatives were synthesized to provide sufficient volatility for mass spectrometry. Various combinations of stable isotope derivatives ( $\text{CH}_3\text{CO} + \text{CH}_3$ ,  $\text{CD}_3\text{CO} + \text{CH}_3$ ,  $\text{CH}_3\text{CO} + \text{CD}_3$ ,  $\text{CD}_3\text{CO} + \text{CD}_3$ ) confirmed proposed fragmentation pathways and corroborated hypothetical ion structures. This family of oligopeptides corresponds to the C-terminus of scotophobin. To date, nobody has synthesized such a family of oligopeptides and a combination of stable isotope derivatives, recorded and examined mass spectra of the derivatives, correlated fragmentation patterns and corroborated proposed ion structures. Such a study is necessary in order to provide a firm foundation to understanding the electron impact-induced fragmentations and rearrangements of derived oligopeptides. Understanding these processes facilitates the structural elucidation of unknown peptides of biological origin.

#### **3:20 (13) Some Recent Applications of Spark Source Mass Spectrometry to Environmental Studies.**

R. Brown and H. E. Taylor, Accu-Labs Research, Inc., Wheatridge, Colorado, 80033.

Increased exploitation of the earth's natural resources in the West has resulted in an upsurge of investigations into the impact of combustion of fos-

sil fuels on the environment. The increase in the use of previously uncharacterized fossil fuels necessitates an examination of the potentially hazardous trace elements indigenous to the fuel. The authors have expended considerable efforts in the examination of fuels with an emphasis on coal, and shale oils, naturally the known toxic trace elements such as mercury, thallium, cadmium, arsenic, selenium, etc., have demanded special attention. A description will be given of the method of analysis and results obtained. A description of the analysis of biological tissue will be given to illustrate the effects of environment on human tissue.

**3:40 (14) Polar Constituents Isolated from Green River Oil Shale.**

D. E. Anders, F. G. Doolittle, and W. E. Robinson, U.S. Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming, 82070.

The oil shales of the Green River Formation of Colorado, Utah and Wyoming are a vast, potential energy source. Numerous investigations of these carbonaceous deposits have been made by the Bureau of Mines, academic departments, research centers and petroleum laboratories in an effort to effectively utilize this sedimentary material as a fuel source. Research concerned with the characterization of the organic material indigenous to Green River shale has, in the past decade, produced dozens of articles. Most of these articles have focused on the nature, distribution and/or the post-depositional fate of the carbonaceous materials deposited in this sedimentary rock.

In spite of numerous articles describing the organic composition of Green River shale, few studies have ventured more than a cursory look at compound types other than hydrocarbons, amino acids, fatty acids and fatty alcohols. This is particularly true of the heterocyclic structures. Heterocyclic compositional types shown to be present in Green River shale include carbohydrates, porphyrins, and certain nitrogenous compound types such as quinolines, tetrahydroquinolines, pyridines and indoles.

This report interprets the mass spectrometric, infrared absorption and nuclear magnetic resonance data for 24 compounds obtained from a polar fraction of Green River shale. The major constituents analyzed are believed to be of the following compositional types:  $C_nH_{2n-2}O$  (cyclohexanols and chain isoprenoid ketones),  $C_nH_{2n-10}O$  (tet-

ralones),  $C_n H_{2n-1} NO_2$  (hydroxypyrrrolines),  $C_n H_{2n-5} NO_2$  (maleimides),  $C_n H_{2n-7} N$  (tetrahydroquinolines),  $C_n H_{2n-11} N$  (quinolines),  $C_n H_{2n-8}$  (tetralins),  $C_n H_{2n-12}$  (naphthalenes) and  $C_n H_{2n-14}$  (benzylbenzenes). This work expands the present information about nitrogen, oxygen and aromatic constituents indigenous to Green River shale.

#### **4:00 (15) Terpane and Sterane Released from Kerogen by Pyrolysis GC-MS**

E. J. Gallegos, Chevron Research Company, Richmond, California, 94802.

Analysis by pyrolysis GC-MS and GC-MS of the pyrolysate of solvent-extracted Green River shale showed pyrolytic release of many identifiable terpanes and steranes, some of which are known present in the extractable oil from this shale. These include among others gammacerane,  $17\alpha$ -H hopane, and  $C^{27}$ ,  $C^{28}$ , and  $C^{29}$ ,  $5\alpha$ - and  $5\beta$ -cholestane, ergostane and stigmastane, respectively.

#### **4:20 (16) Mass Spectroscopic Investigation of Biologically Significant Saturate Fractions of Petroleum**

F. D. Guffey and J. H. Weber, U.S. Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming.

Hydrocarbon fractions of petroleum boiling between 400 to 600° C are felt to be most representative of the primordial material of petroleum. The saturate hydrocarbon fractions being the most characteristic class of compounds from an oil were investigated by high- and low-resolution mass spectroscopy. Four separate oils, each divided into two distillate fractions (370 to 535° C and 535 to 675° C), were studied. The compound types present in each fraction as defined by z-number and carbon-number range are compared. The biological significance of these compound types in relation to the origin of petroleum is discussed.

### **Tuesday Morning — Atomic Absorption and Emission**

#### **9:00 Opening Remarks**

Rodney K. Skogerboe, Session Chairman, Colorado State University, Fort Collins, Colorado.

**9:10 (17) A Microsampling Cup System for Determining Less Volatile Elements by Atomic Absorption Spectrometry**

D. Mitchell, M. Kahl, A. Ward, K. Jackson, and K. Aldous, New York State Department of Health, Division of Laboratories and Research, Albany, New York.

This system is built up from a slot burner without a nebulization chamber, cup and enclosed ceramic absorption tube. Liquid or homogenized tissue sample for analysis is pipetted into a cup, dried, and injected into a nitrous oxide-acetylene flame.

This system has a number of important advantages:

(a) it extends the range of microsampling cup (Delves) analysis from volatile metals such as Pb, Cd, Zn and Hg to metals such as Fe, Co, Ni and Cr.

(b) with biological samples, matrix effects are substantially reduced.

(c) the burner gives high gas exit velocity and has a low mixing volume. This substantially reduces the probability of flashback, and the severity of any flashback.

Analytical data for the determination of iron in serum will be presented.

**9:30 (18) A Study of Two Atomic Absorption Methods for the Determination of Sub-microgram Amounts of Arsenic and Selenium**

Brick B. Mesman and Thomas C. Thomas, USAF Environmental Health Laboratory, McClellan AFB, California, 95652.

Arsenic and selenium analyses by the most commonly used wet chemical methods provide results down to microgram levels but have many drawbacks. Not only do these methods involve tedious procedures, but they sometimes utilize apparatus which is expensive, fragile, and difficult to clean after analysis. In the arsenic analysis, the solvent is pyridine, which, used on a frequent basis and under careless conditions, could lead to detrimental effects on the health of the analyst.

The determination of arsenic and selenium by conventional atomic absorption spectrometry does not come close to providing the required sensitivities most commonly desired in analyzing waters, soils, and biological materials. However, in recent years, accessories have been developed which

when coupled to atomic absorption systems, provide results down to submicrogram levels for these elements. In our laboratory two such accessories are available; the Perkin-Elmer Heated Graphite Electrode and the Fisher Trace Metal Analyzer. Since one involves a flame and the other a flameless operation, both were compared in our study for common interferences, detection limits, coefficients of variation in analyses and ease of operation.

### **9:50 (19) Application of Atomic Absorption Spectroscopy to Trace Element Analyses in Plants**

W. G. Schrenk, Chemistry Department, Kansas State University, Manhattan, Kansas.

This paper will focus attention on the methods used to develop atomic absorption procedures for use in the determination of trace elements in plant tissue.

The development of any new methods of analysis follows a certain sequence of events such as are included in the following outline.

- A. Preliminary investigations
  - 1. Need for a new method
  - 2. Criteria for selecting the technique
    - a. detection limits
    - b. interference problems
- B. Development of the method
  - 1. typical calibration curves
  - 2. operating parameters
  - 3. sample preparation
  - 4. statistical evaluation
  - 5. comparison with existing methods
- C. Application of the method
  - 1. evaluation by other laboratories
  - 2. standardization of the technique
  - 3. collaborative study
  - 4. acceptance of the method

The steps involved in the development of a new method of analysis, as given in the above outline, will be illustrated with examples from our laboratories.

### **10:10 (20) Determination of Copper, Iron and Cadmium in Plant Materials by Atomic Absorption Spectroscopy**

Duane Boline and W. G. Schrenk, Chemistry Department, Kansas State University, Manhattan, Kansas, 66056.

A method of quantitative determination of cop-



per, iron and cadmium in grain that does not require concentration enhancement by complexation and extraction is proposed. The use of a methanol-water solvent system increases the sensitivity for the metals by a factor of 1.5 or greater over an aqueous solution.

Optimum instrumental parameters are reported using a Jarrell Ash 82-500 MVAA with a premix laminar flow burner, and an acetylene-air flame.

Wet and dry ashed samples of corn, alfalfa and soybeans are analyzed by the proposed method and the results compared with values obtained by standard A.O.A.C. colorimetric methods.

#### **10:30 Coffee Break**

#### **10:50 (21) Another Look at Sample Solution Techniques for Analysis of Rocks by Atomic Absorption**

O. Karmie Galle, University of Kansas, Lawrence, Kansas, 66044.

The fusion of silicate and carbonate rocks with lithium meta-borate as a means of sample solution for atomic absorption analysis has been reported in the literature. The ability to obtain consistent results for the analysis of silica and aluminum in concentrations above 70% have not always been successful when using this technique. This report deals with some variations of the reported methods. Ammonium nitrate is added to the fusion mixture and the fusion is carried out in graphite crucibles. The molten fusion is added directly to 50ml of H<sub>2</sub>O containing 5ml HCl. The fusion button is then brought into solution in about 15 minutes. Interferences by Si, Al, and Ti are also reviewed. A description of how the use of large dilution factors and the lower portion of the standard curve statistically improve the precision of analytical results is included. Statistical evaluation of all data will be presented.

#### **11:10 (22) The Determination of Several Elements in Samples from a Filter Bed of Sewage Sludge by Optical Emission Spectrography**

Truman C. Waugh, Kansas Geological Survey, University of Kansas, Lawrence, Kansas, 66044

A 1.5 Meter Wadsworth Mount Spectrograph is used with commercial semi-quantitative standards in a routine optical emission spectrographic examination of sewage sludge. Several problems encountered will be discussed.

**11:30 (23) The Determination of Organic Lead Components in the Atmosphere by GC combined with OE Detection**

Brian Andreen, Research Corporation, Minneapolis, Minnesota, P. L. Dick and R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado, 80521.\*

Several procedures for the determination of alkyl lead compounds in gasoline by gas chromatography have been developed. Atmospheric samples pose a more difficult situation due to interference from the dihalide scavenger compounds and the requirement of high sensitivity. The use of a highly selective, sensitive optical emission detector for this purpose will be described.

\* Research supported under NSF grant and by the Research Corporation

**11:50 (24) An Automated Background Correction System for a Direct Reading Emission Spectrometer**

P. J. Lamothe and R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado, 80521.

The development of an automated background correction system for a multichannel optical emission direct reading spectrometer provides a flexibility that is impossible to achieve through the traditional direct reader program circuits. Some of the unique advantages associated with such a system are: (1) background correction for each channel, (2) improved limits of detection, (3) extended intensity ratio measurements, (4) individual pre-burn and exposure times for each channel, (5) ability to perform time resolution studies.

**12:10 (25) Computerized Flame Spectrochemical Analysis**

M. Bonner Denton and M. W. Routh, Department of Chemistry, University of Arizona, Tucson, Arizona.

Many of the interactions occurring in multiparameter-dependent flame spectrochemical systems can be investigated more effectively through the use of interactive computer control. The determination of optimum flame compositions, readout parameters, and area of the flame viewed can be rapidly carried out for various elements by utilizing computer control techniques. Interference effects can be easily evaluated and often minimized.

A computer-controlled flame spectrometer will be described for studying flame processes. Considerations into the design of such systems, including hardware and software requirements, will be presented as well as data from a number of recent studies. The relative merits of computer control will be evaluated and contrasted to conventional techniques.

**12:30 Lunch**

**Tuesday Afternoon — NMR, X-Ray**

**1:30 Opening Remarks**

Gary E. Maciel, Session Chairman, Department of Chemistry, Colorado State University, Fort Collins, Colorado.

**1:40 (26) Nuclear Magnetic Resonance with Metal Nuclides**

Jerry L. Dallas and Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, Colorado, 80521.

Pulse fourier transform techniques have been developed and applied in our laboratory to a variety of metal nuclides in natural abundance samples. The general nature of these techniques will be presented in perspective with similar techniques which have been applied to  $^1\text{H}$  and  $^{13}\text{C}$ . A brief summary of recent instrumental innovations will be discussed along with the relationship of these efforts to experimental investigations. Particular attention will be focused on developments in recent studies of the  $^{207}\text{Pb}$  and  $^{195}\text{Pt}$  nuclides. Applications to the chemistry of liquid and solid samples will be discussed.

**2:00 (27) The Application of NMR to Problems in Tetracycline Chemistry**

G. L. Asleson and C. W. Frank, Department of Chemistry, University of Iowa, Iowa City, Iowa, 52242.

The application of nuclear magnetic resonance spectroscopy to problems in tetracycline chemistry has been limited because the spectra obtained are fairly complex and the solubility properties of tetracyclines limit the choice of solvents. However, nmr has been used to elucidate stereochemical and structural features, to determine microscopic dissociation constants, and to monitor the kinetics of epimerization at the 4-position.

Both  $^1\text{H}$  and  $^{13}\text{C}$  nmr were employed in the investigation of tetracycline hydrochloride. A number of model compounds and modified tetracyclines were used to facilitate the assignment of signals in both the proton and carbon spectra. The application of nmr to the determination of the sites of metal ion complexation is also discussed.

#### **2:20 (28) Nuclear Magnetic Resonance Studies of Tissue Water Protons: Effects of DMSO on Observed Line Widths**

Theodore I. Malinin and Ray L. Nunnally, Miami Veterans Administration Hospital and University of Miami School of Medicine, Miami, Florida, 33152.\*

The physical state of water in isolated rat myocardium has been examined by proton nuclear magnetic resonance (NMR). Isolated rat hearts were perfused through the aorta with a standard tissue culture medium and with standard medium containing various cryoprotective agents. Samples of left ventricular myocardium perfused with media containing 15% dimethyl sulfoxide (DMSO), 10% polyvinylpyrrolidone (PVP, M.W. 50,000) and 10% D-glucose, were obtained at 1 min. and 30 min. post-perfusion. Additionally, tissue samples were also taken at the prescribed intervals and quick-frozen by immersing in small vials in a dry ice-acetone bath. The frozen samples were subsequently thawed and analyzed by NMR. In all cases, line widths reported for water proton resonance in tissue samples varied by  $\pm 2$  Hz for determination of three-to-five specimens in each group. All spectra were obtained on Varian and Perkin-Elmer 60 M Hz instruments.

For all observed spectra, DMSO had the greatest effect on the observed line widths. In the 1 min. myocardium samples, average line widths for DMSO perfused hearts were three times those observed in the samples prepared with the standard perfusate, 60.0 Hz vs. 20.5 Hz respectively. In the 30 min. samples a marked reversal of line width was observed for the DMSO perfusion when compared with the 1 min. sampled perfusion, 12.0 Hz vs. 60.0 Hz respectively. In comparison with non-frozen samples, line widths of frozen myocardium samples were narrowed by 10-20%, indicating probable cellular damage and release of bound water. The initial broadening of the water proton line width in the DMSO perfused samples (non-frozen) taken at 1 min. was not observed in the frozen samples taken at 1 min.

A simple correlative study was made of the effect of DMSO on agar gels. A standard preparation of 2% agar in triply-distilled water was made, and another agar gel was prepared using 15% DMSO in distilled water. The observed line widths were 8 Hz and 4 Hz respectively.

These results tend to support the view that DMSO acts as a cryoprotective agent by dehydration. This data also raises the possibility that DMSO may be a useful solvent as a "probe" for paramagnetic ions and magnetic field gradients within tissue samples. Deuterated solvent and double resonance studies are currently in progress in this laboratory in an effort to further examine this potential use of DMSO as a tool in elucidating water interactions in biological systems by NMR.

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#### **2:40 (29) Experiments Using a Parallel Plate Screen-Waveguide Stark Cell**

James E. Wollrab, Anderson, Wollrab and Wilson Attorneys At Law, St. Louis, Missouri, 63103.

A microwave absorption cell has been designed to permit the observation of rotational transitions in flowing reaction mixtures as a function of distance from the point of initiation of the reaction. The waveguide consists of three parallel fine-mesh metallic screens; the central screen is used to carry a Stark field similar to conventional microwave absorption cells. The reaction flows normal to the screen surfaces with the mesh of the screen optimized to permit maximum transmission of the microwave field and minimum interference with the flowing gas mixture. The screens are unequally spaced to permit increased spatial resolution in those cases where discrete Stark lobes can be detected on low J rotational lines. Several experiments which utilize the characteristics of this cell shall be described.

#### **3:20 (30) Determination of Trace Uranium in Plutonium by X-Ray Fluorescence Spectrometry**

W. I. Winters and S. G. Metcalf, Atlantic Richfield Hanford Co., Richfield, Washington.

A method for the determination of trace levels of uranium ( $200\mu\text{g}$  of U per gram of Pu) in plutonium oxide and plutonium nitrate used in fabrication of nuclear fuels has been developed. The method employs 0.1M tri-n-octyl phosphine oxide (TOPO) to separate the uranium from the plutonium and the

uranium content is measured by X-ray fluorescence. Plutonium oxide is dissolved in concentrated HCl and HF, and evaporated to dryness. The residue is dissolved with 2M NH<sub>2</sub>OH·HCl in 4M HCl and AlCl<sub>3</sub> is added to complex any residual fluoride. The NH<sub>2</sub>OH·HCl reduces the Pu(IV) to Pu(III). After the plutonium reduction, the solution is allowed to cool to room temperature and 0.1M TOPO in cyclohexane is used to extract the uranium. Plutonium nitrate solutions are pipetted directly into the NH<sub>2</sub>OH·HCl solution used for the reduction. The TOPO containing the uranium is mounted and dried on a paper pad and the uranium content is determined by X-ray fluorescence spectrometry. For plutonium nitrate solutions a thorium internal standard is useful.

The relative standard deviation for the analysis of a plutonium oxide standard supplied by Los Alamos Scientific Laboratory as part of the quality assurance program for the Fast Flux Test Facility project was 8.9 percent. Two other extraction systems, TOPO extraction from 2M NH<sub>2</sub>OH·HCl, in 2M HNO<sub>3</sub> and triisooctylamine (TIOA) extraction from 2M NH<sub>2</sub>OH·HCl in 4M HCl, were studied. Their advantages and limitations will be discussed. X-ray fluorescence permits the use of a faster separation of the uranium from the plutonium, than the commonly used spectrophotometric methods and provides the required sensitivity, accuracy, and precision for analysis of plutonium used for fabrication of FFTF fuels.

### **3:40 (31) Energy Dispersion X-Ray Fluorescence Analysis with a Siemens SRS-1 Crystal Spectrometer**

Colin G. Sanderson and Norman Lutner, Health and Safety Laboratory, USAEC, New York, New York, 10014.

The analysis of trace elements in environmental samples by wavelength dispersion x-ray spectrometry is a slow and tedious procedure since each wavelength of interest must be measured separately. Although energy dispersion systems using Si(Li) x-ray detectors and multichannel analyzers have greatly increased the rate of data acquisition, the crystal spectrometer is capable of providing for superior spectral resolution. Therefore, complex multi-element samples can best be resolved by a crystal spectrometer, while less complex samples, free of interferences from adjacent elements can be most efficiently analyzed by energy dispersion.

A large (80 sq. mm.), high resolution (175 ev FWNM at 5.9 KeV) Si(Li) detector has been inter-

faced to a Siemens SRS-1 x-ray fluorescence crystal spectrometer. This detector, mounted at  $0^\circ$  (2 theta), is used independently of the crystal, thereby producing a single instrument capable of both wavelength and energy dispersion x-ray fluorescence analysis.

This paper will describe the installation of the solid state Si(Li) detector in the Siemens spectrometer, and compare the analysis of environmental samples such as air particulates on filter paper, air filters and NBS standard reference materials (orchard leaves and bovine liver), by both wavelength and energy dispersion using a 3KW tungsten x-ray tube. "Thin Film" sample preparation methods and pure metal calibration techniques will be discussed.

#### **4:00 (32) A Highly Stable, Dual Anode X-Ray Tube for Optimum Broad Range Excitation with Energy Dispersive Fluorescence Analyzers**

E. Elad, D. Gedeke, and D. Schlafke, ORTEC, Inc., Oak Ridge, Tennessee, 37830.

Intrinsically, energy dispersive fluorescence analysis can be a broad range analytical technique; both in terms of concentration range, and in the range of elements which can be simultaneously analyzed. Full realization of this potential requires an excitation source which meets the following criteria:

- (1) Efficient simultaneous excitation of a broad range of elements.
- (2) A lack of interfering characteristic lines.
- (3) Efficient excitation of trace element concentrations.
- (4) High stability of the X-ray flux.
- (5) Sufficient flexibility to enhance the excitation for specific elements.
- (6) The ability to quickly change excitation conditions and take reliable data.

X-ray tubes hold the best promise for meeting these requirements. The paper describes the novel design of a dual anode X-ray tube, and its ability to meet the above criteria with the addition of regenerative monochromator filters.

The simultaneous excitation of a broad range of elements is best achieved by using the bremsstrahlung X-ray continuum from an anode material with a high atomic number. In many cases the characteristic lines from such an anode interfere with the elements to be analyzed in the specimen. A convenient solution to this interference is provided by incorporating a second anode of different atomic

number within the same tube. Electrostatic deflection with a strongly focused electron gun provides quick anode selection. In addition to solving the interference problem, a judicious choice of the two anode materials can lead to a greater flexibility in exciting specific elements. Improved trace element excitation is obtained through the use of regenerative monochromator filters. Design choices of such filters will be described. Optimum excitation conditions for a variety of elements require a wide range of operating parameters for the X-ray tube. The described dual anode tube operates over such a wide dynamic range of currents (1-200  $\mu$ A) and voltages (10-50kv). Design criteria for the tube, which differ from those of high power X-ray tubes, will be described.

Proper instrument design and operation can limit medium and long term fluctuations to within  $\pm 1\%$  for sample position variations, and  $\pm 0.25\%$  for generator stability with a low power tube. The ability of low power tubes to achieve settling times of the order of 10 seconds will be described.

#### **4:20 (33) Applications of a Dual Anode X-Ray Tube to Major And Trace Element Analysis by Energy Dispersive X-Ray Fluorescence.**

L. S. Albrecht, ORTEC, Inc., Oak Ridge, Tennessee, 37830.

Effective use of the simultaneous multielement detection capability of the energy dispersive x-ray spectrometer for x-ray fluorescence analysis requires the use of a flexible method of excitation. A low power, dual anode x-ray tube with stable emissions over an operating range of 200:1 together with a variety of regenerative monochromator filters (RMF) provides the flexibility needed for analysis of a wide variety of samples.

The emission spectrum from an x-ray tube is composed of a continuum of x-rays (bremsstrahlung) along with the characteristic lines of the anode material. Since the cross section of x-ray production is greatest when the exciting radiation is just above the absorption edge energy of the elements of interest, direct excitation from the x-ray tube efficiently excites a wide range of elements simultaneously. Direct excitation from an x-ray tube is typically used for the analysis of metal alloys where the x-rays from the elements of interest cover the energy range from 1 to 20 keV. Direct excitation is also used for the simultaneous analysis of elements from sodium through iron in geological sam-



ples. An example is given contrasting direct excitation with monoenergetic excitation for this application.

Analysis of the heavier trace elements in many types of samples is not possible with direct excitation because the bremsstrahlung from the tube is scattered by the sample and forms a high background in the spectrum. Since the cross section for x-ray scattering is highest for samples containing large amounts of low atomic number material, this problem is most noticeable for the analysis of liquid samples, biological samples, and geological samples. In these cases a regenerative monochromator filter is used between the x-ray tube and the sample to filter out the unwanted bremsstrahlung and provide a low background for the analysis of selected elements of interest. Proper selection of RMF material, anode material, and tube voltage result in two low background regions for trace element analysis, thus maintaining the advantage of the energy dispersive spectrometer for multielement analysis. Examples are given showing application of a variety of RMF materials to different anode materials. Detection limits and typical analytical results are given for samples of interest in industry and environmental sciences.

The use of regenerative monochromator filters for background reduction and trace element analysis is compared with other techniques for trace element analysis that are currently being studied for use with the energy dispersive x-ray spectrometer. For most types of analysis, the use of regenerative monochromator filters is shown to have the same detectable limits as other techniques while giving the advantage of more elements detected simultaneously.

### **Conference Social**

At approximately 5:30, the "Blackhawk Express" (a double-decker bus) is scheduled to leave for the Brown Palace for the Black Forest Inn in Blackhawk, Colorado, where the conference dinner and a brief award ceremony have been scheduled to commence at 7:30. The bus is tentatively scheduled to return from the Central City area at 10:00 p.m.

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