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August 1971

13th Annual Rocky Mountain Spectroscopy Conference

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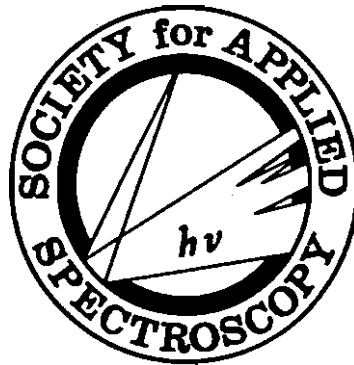


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PROGRAM

THIRTEENTH ANNUAL ROCKY MOUNTAIN SPECTROSCOPY CONFERENCE



August 9-10, 1971
New Albany Hotel *
Denver, Colorado

WELCOME

TO THE

THIRTEENTH

ANNUAL

ROCKY MOUNTAIN

SPECTROSCOPY

CONFERENCE

HOST

Rocky Mountain Section

SOCIETY FOR

APPLIED SPECTROSCOPY

New Albany Hotel

August 9-10, 1971

SOCIETY FOR APPLIED SPECTROSCOPY

1971 ROCKY MOUNTAIN SPECTROSCOPY CONFERENCE COMMITTEE

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The Dow Chemical Company
Golden, Colorado

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Denver, Colorado

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1971 ROCKY MOUNTAIN SECTION OFFICERS

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The Rocky Mountain Section of the Society for Applied Spectroscopy is pleased to present this program for the Thirteenth Annual Rocky Mountain Spectroscopy Conference to be held at the New Albany Hotel, Denver, Colorado, August 9-10, 1971. This year's program consists of 43 technical papers chosen to represent the various disciplines of spectroscopy. It is our earnest hope that you will find this a most informative and worthwhile meeting.

Registration

Registration will be held throughout the conference starting at 7:45 a.m. Monday, August 9.

Registration badges are required for admission to all sessions of the conference. Registration fees are as follows:

Members and Nonmembers . . .	\$10.00
Students*	\$ 2.00
Banquet	\$ 5.00

*defined as those attending school on a full time basis.

Accommodations

All conference functions will be held at the New Albany Hotel, 17th and Stout Streets.

Visitor Information

Information on the Denver area may be obtained from the Denver Convention Bureau, 225 West Colfax Avenue, Denver, Colorado 80202.

Conference Mixer and Banquet

The conference banquet will be held Monday evening, August 9, at 7:00 p.m. The banquet will be preceded by a hosted cocktail hour from 6:00 to 7:00 p.m. Banquet tickets may be purchased at the registration desk until 12:00 noon, Monday, August 9 (\$5.00 per person).

The Outstanding Service Award will be presented to Marvin W. Skougstad in recognition of his service to the Rocky Mountain Section of the Society for Applied Spectroscopy.

Monday Evening

AUGUST 9, 1971
6:00 P.M.

CONFERENCE MIXER and SOCIAL HOUR sponsored by the Rocky Mountain Section of the Society for Applied Spectroscopy. The serving bar will be located in the EXHIBIT ROOM adjacent to the CROWN JEWEL ROOM. PLEASE WEAR YOUR REGISTRATION BADGE.

7:00 P.M.

CROWN JEWEL ROOM

CONFERENCE BANQUET

DINNER

FRESH FRUIT SUPREME, HAWAIIAN

ASSORTED ICED RELISHES

ROAST PRIME RIB OF BEEF AU JUS

BAKED POTATO, SOUR CREAM & CHIVES
ASPARAGUS MILANAISE

NEW ALBANY DINNER ROLLS

HEARTS OF LETTUCE SALAD
THOUSAND ISLAND DRESSING

CHOICE OF PIE

COFFEE - TEA - MILK

BANQUET SPEAKER:

Charles C. Macnamara, M.P.H.
Senior Health Educator
Air Pollution Control Division
State of Colorado Department
of Health
Denver, Colorado

Title: **AIR POLLUTION CONTROL IN COLORADO**

The banquet talk will feature slides to illustrate sources, effects, and devices used to control air pollution.

Charles c. Macnamara received his B.A. degree from the University of Illinois in 1942. He then served in the U. S. Navy through both World War II and the Korean conflict, retiring from the Naval Reserve program in 1962 with the rank of Lieutenant Commander. In 1955 he received his M.P.H. degree (Health Education) from the *University of Michigan*. He has held the position of Executive Director of Tuberculosis and Health Associations in Lake County, Illinois, Contra Costa County, California, and the Island of Oahu, Hawaii. Since 1967, he has been Senior Health Educator, Air Pollution Control Division, at the State of Colorado Department of Health.

Equipment Exhibits

The latest in spectroscopy instrumentation and supplies will be on display in the Exhibit Room adjacent to the Crown Jewel Room, and rooms 5 and 6 on the Mezzanine Floor.

Exhibitors

Beckman Instruments, Inc.
Blake Industries
Buhrke Company
Canberra Industries
Fisher Scientific Company - Rm. 5
Instrumentation Laboratory, Inc. - Rm. 6
Kevex Corporation
Labtest Equipment Company, Inc.
Northern Science
Nuclear Data, Inc.
Nuclear Equipment Corporation
Picker Industrial
Varian Anaspect
Varian Techtron
VWR Scientific

DRI X-Ray Conference

The 20th Annual Denver Conference on Applications of X-Ray Analysis will be held August 11-13, 1971 at the New Albany Hotel, Denver, Colorado.

Coffee Breaks

Coffee and rolls will be served at the morning recesses, and coffee and cokes at the afternoon recesses. The serving tables will be located in the main Exhibit Room.

Inquiries

For further information contact:
George M. Pachelo
The Dow Chemical Company
Bldg. 559. P. O. Box 888
Golden, Colorado 80401

Monday Morning Session

Crown Jewel Room

August 9, 1971

Session Chairman—M. L. Salmon
Fluo-X-Spec Analytical
Laboratory
Denver, Colorado

- 8:50** WELCOME—H. N. *Barton*, The Dow Chemical Company, Golden, Colorado, Chairman, Rocky Mountain Section of the Society for Applied Spectroscopy.
- 9:00** (1) X-RAY SPECTROCHEMICAL DETERMINATION OF TUNGSTEN, HAFNIUM AND RHENIUM IN TANTALUM ALLOYS, J. S. Rudolph, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania.
- 9:20** (2) PRECISION IN TRACE-ELEMENT ANALYSIS BY X-RAY EMISSION SPECTROGRAPHY, J. H. Howard III, The University of Georgia, Athens, Georgia.
- 9:40** (3) SENSITIVITY MEASUREMENTS—A METHOD OF EVALUATING ELECTRON MICROPROBE X-RAY DATA FOR QUANTITATIVE ANALYSIS, R. H. Heidel, U. S. Geological Survey, Denver, Colorado.
- 10:00** (4) AN EVALUATION OF A CAPILLARY ARC PLASMA AS AN ANALYTICAL TOOL IN TRACE ANALYSIS, J. L. Seeley and R. K. Skogerboe, Colorado State University, Fort Collins, Colorado.
- 10:20** RECESS
- 10:40** (5) NON-FLAME ABSORPTION CELL TECHNIQUE AND ITS APPLICATIONS TO THE ANALYSIS OF ENVIRONMENTAL POLLUTANTS, J. Y. Hwang, Instrumentation Laboratory Inc., Lexington, Massachusetts.
- 11:00** (6) SOME ADVANTAGES OF FURNACE ATOMIC ABSORPTION OVER FLAMES R. Woodriff, Montana State University, Bozeman, Montana.
- 11:20** (7) ELECTRODELESS DISCHARGE LAMPS AS ATOMIC ABSORPTION SPECTROSCOPY LIGHT SOURCES, K. E. Smith and W. G. Schrenk, Kansas State University, Manhattan, Kansas.
- 11:40** (8) EVALUATION OF LIGHT SCATTERING AND MOLECULAR ABSORPTION INTERFERENCES IN ATOMIC ABSORPTION ANALYSIS OF BIOLOGICAL MATERIALS. W. A. Abbott and R. K. Skogerboe, Colorado State University, Fort Collins, Colorado.
- 12:00** LUNCH

Monday Afternoon Session

Crown Jewel Room

August 9, 1971

Session Chairman—S. E. Valente
Regis College
Denver, Colorado

- 1:30 (9)** ZINC AND MANGANESE ANALYSIS IN PLANT MATERIAL BY ATOMIC ABSORPTION SPECTROSCOPY, D. L. Smith and W. G. Schrenk, Kansas State University, Manhattan, Kansas.
- 1:50 (10)** LUMINESCENCE AND POLARIZATION SPECTRA OF COUMARINS AND FURCOUMARINS, P. S. Song and M. L. Harter, Texas Tech University, Lubbock, Texas.
- 2:10 (11)** LUMINESCENCE DETERMINATION OF CHLORINATED BIPHENYLS, C. M. O'Donnell and T. S. Spencer, Colorado State University, Fort Collins, Colorado.
- 2:30 (12)** PHOSPHORIMETRY UNDER AMBIENT CONDITIONS, E. M. Schulman, A. R. Lepley, and C. Walling, University of Utah, Salt Lake City, Utah.
- 2:50 (13)** REMOVAL OF STATISTICAL SCATTER FROM GAMMA-RAY SPECTRA WITH HIGH ORDER POLYNOMIALS, H. P. Yule, National Bureau of Standards, Washington, D. C.
- 3:10** RECESS
- 3:30 (14)** MEASUREMENT OF OZONE CONCENTRATION IN HYPERSONIC WAKES, C. P. Dyjak, Massachusetts Institute of Technology, Lexington, Massachusetts.
- 3:45 (15)** PHOTOMULTIPLIERS FOR SPECTROSCOPY, D. E. Persyk, RCA, Lancaster, Pennsylvania.
- 4:05 (16)** APPLICATIONS OF SELF-BEAT SPECTROSCOPY, C. T. Meneely, C. Y. She, and D. F. Edwards, Colorado State University, Fort Collins, Colorado.
- 4:25 (17)** TRACE ANALYSIS BY MICROWAVE INDUCED EMISSION SPECTROSCOPY, F. E. Lichte and R. K. Skogerboe, Colorado State University, Fort Collins, Colorado.
- 4:45 (18)** ENERGY TRANSFER IN THE HYDROGEN-BONDED CARBAZOLE-BENZOPHENONE COMPLEX, T. S. Spencer and C. M. O'Donnell, Colorado State University, Fort Collins, Colorado.

Monday Afternoon Session

Pine and Spruce Room

August 9, 1971

Session Chairman—J. H. Weber

Laramie Energy Research
Center
Laramie, Wyoming

- 1:30** (19) SOLVENT EFFECTS ON THE CARBON-13 CHEMICAL SHIFTS OF TETRAMETHYLSILANE AND CYCLOHEXANE, M. R. Bacon and G. E. Maciel, Colorado State University, Fort Collins, Colorado.
- 1:50** (20) TEMPERATURE EFFECTS ON THE NMR LINE SHAPES OF OIL SHALE, A. B. Denison, F. P. Miknis, A. W. Decora, and G. L. Cook, University of Wyoming, Laramie, Wyoming.
- 2:10** (21) CARBONYL CARBON-13 CHEMICAL SHIFTS AND TRANSANNULAR INTERACTIONS, T. T. Nakashima and G. E. Maciel, Colorado State University, Fort Collins, Colorado.
- 2:30** (22) PARAMETERS AFFECTING THE ANALYSIS OF OIL SHALES USING WIDE-LINE NMR SPECTROSCOPY, F. P. Miknis, A. B. Denison, A. W. Decora, and G. L. Cook, Laramie Energy Research Center, Laramie, Wyoming.
- 2:50** (23) CARBON-13 CHEMICAL SHIFTS IN 1 - SUBSTITUTED - 4 - METHYLBICYCLO - (2.2.2) OCTANES, H. C. Dorn and G. E. Maciel, Colorado State University, Fort Collins, Colorado.
- 3:10** RECESS
- 3:30** (24) CHARACTERIZATION OF SELECTED HIGH MOLECULAR WEIGHT PETROLEUM SATURATE FRACTIONS BY NMR SPECTROSCOPY, F. D. Guffey, F. R. McDonald, and J. H. Weber, Laramie Energy Research Center, Laramie, Wyoming.
- 3:45** (25) CARBON-13 CHEMICAL SHIFTS AND ADDITIVITY RELATIONSHIPS IN 1, 2-DISUBSTITUTED ETHANES, L. Simeral, G. E. Maciel, R. Elliott, B. Kaufman, and K. Cribley, Colorado State University, Fort Collins, Colorado.
- 4:05** (26) TUNABLE GUNN-EFFECT DIODE EPR SPECTROMETER, A. B. Denison, K. W. Pontinen, and J. P. Cruts, University of Wyoming, Laramie, Wyoming.
- 4:20** (27) ^{13}C - ^{13}C COUPLING CONSTANTS IN ISOPROPENYL COMPOUNDS, G. E. Maciel and V. J. Bartuska, Colorado State University, Fort Collins, Colorado.

Tuesday Morning Session

Crown Jewel Room

August 10, 1971

Session Chairman—A. J. Johnson
The Dow Chemical Company
Golden, Colorado

9:00 (28) A WAVELENGTH-TUNABLE LASER SYSTEM FOR INFRARED SPECTROSCOPY, C. F. Dewey, Jr., Massachusetts Institute of Technology, Cambridge, Massachusetts.

9:20 (29) RAMAN SCATTERING APPLIED TO SOLID STATE PHYSICS, T. W. Broberg, C. Y. She, and D. F. Edwards, Colorado State University, Fort Collins, Colorado.

9:40 (30) APPLICATIONS OF MULTIPLE INTERNAL REFLECTANCE SPECTROSCOPY TO AIRCRAFT MATERIALS EVALUATION, T. T. Bartels, McDonnell Aircraft Company, St. Louis, Missouri.

10:00 (31) INFRARED DETERMINATION OF CARBOXYL AND HYDROXYL CONTENTS OF FUNCTIONALLY TERMINATED POLYBUTADIENES, A. S. Tompa, Naval Ordnance Station, Indian Head, Maryland.

10:20 RECESS

10:40 (32) HYDROXYL GROUPS ON THE SURFACE OF MgO, S. Akhtar, University of Nevada, Reno, Nevada.

11:00 (33) INFRARED SPECTRA OF PLUTONIUM AMMINE COMPLEXES, R. S. Cichorz, The Dow Chemical Company, Golden, Colorado.

11:15 (34) CHARACTERIZATION OF FATTY ACID POLYMORPHIC MODIFICATIONS BY X-RAY AND INFRARED TECHNIQUES, A. V. Bailey, D. Mitcham, V. W. Tripp, and G. Sumrell, U. S. Department of Agriculture, New Orleans, Louisiana.

11:35 (35) A CORRELATION OF HAMMETT SUBSTITUENT CONSTANTS AND HYDROGEN BONDING BETWEEN SUBSTITUTED BENZYL ALCOHOLS AND ALKYL AMINES, M. A. Taylor, K. E. Kolb, and E. I. Stout, Bradley University, Peoria, Illinois.

11:55 LUNCH

Tuesday Afternoon Session

Crown Jewel Room

August 10, 1971

Session Chairman—A. B. Denison
University of Wyoming
Laramie, Wyoming

- 1:30** (36) STABLE ISOTOPE RATIO MEASUREMENTS: MASS SPECTROMETER TECHNIQUES AND PROBLEMS, H. L. Dequasie, University of Utah, Salt Lake City, Utah.
- 1:50** (37) SPARK SOURCE MASS SPECTROMETRY AS AN ANALYTICAL TECHNIQUE. R. Brown, Accu-Labs Research, Inc., Arvada, Colorado.
- 2:10** (38) SUBSTITUENT GROUP PARTICIPATION IN COMPETING CLEAVAGE AND REARRANGEMENT PROCESSES FOR THE N-ETHYL N¹-(R-PHENYL) UREA MOLECULAR ION, R. A. Adams and D. D. Rosebrook, Midwest Research Institute, Kansas City, Missouri.
- 2:25** (39) OPTICALLY MODIFIED MASS SPECTROSCOPY—A NOVEL WAY TO STUDY EXCITED IONIC STATES, R. E. Ellefson, A. B. Denison, and J. H. Weber, University of Wyoming, Laramie, Wyoming.
- 2:40** RECESS
- 3:00** (40) MASS SPECTROMETRIC CHARACTERIZATION OF THE ISOMERIC DIMETHYLNAPHTHALENES, F. G. Doolittle and D. G. Earnshaw, Laramie Energy Research Center, Laramie, Wyoming
- 3:15** (41) RESOLUTION OF THE FINE STRUCTURE IN THE IONIZATION EFFICIENCY CURVES FOR CeHe⁺ AND CeDc⁺ J. H. Weber, R. E. Ellefson, and A. B. Denison, Laramie Energy Research Center, Laramie, Wyoming.
- 3:30** (42) MASS SPECTROMETRIC INVESTIGATION OF THE DISSOCIATION ENERGIES OF THE MOLECULES Pd₂ AND CePd, D. L. Cocke, and K. A. Gingerich, Texas A&M University, College Station, Texas.
- 3:50** (43) DEUTERIUM LABELING IN THE ANALYSIS OF LINEAR OLEFINS FROM SHALE OIL, D. G. Earnshaw, F. G. Doolittle, and A. W. Decora, Laramie Energy Research Center, Laramie, Wyoming,

ABSTRACTS

(1) X-RAY SPECTROCHEMICAL DETERMINATION OF TUNGSTEN, HAFNIUM AND RHENIUM IN TANTALUM ALLOYS, J. S. Rudolph, Westinghouse Research Laboratories, Pittsburgh, Pa. 15235.

Industrial demands for high strength and corrosion resistant *materials* which *retain* their *properties* at temperatures greater than 2000°F and in the presence of alkali metal vapors have resulted in the development of tantalum alloys containing tungsten, hafnium and rhenium. As the metallurgical processes for producing these alloys were being developed, analyses of numerous samples were required to determine melting losses and homogeneity of the ingots. An x-ray spectrochemical method will be described which is used for these analyses since chemical methods for the determination of tungsten, hafnium and rhenium in the presence of tantalum are complex and expensive.

The chemical composition of the tantalum alloys is ideal for x-ray fluorescence analysis since hafnium, tantalum, tungsten and rhenium are adjacent elements in the periodic table, 272-275, and matrix effects are minimal. In the procedure, the sample is dissolved in hydrofluoric and nitric acids because dissolution simplifies the preparation of calibration standards and a representative sample can be obtained from chips or drillings. Also, wire samples can be analyzed without difficulty. Tantalum-tungsten alloys other than those described in this paper, i.e. 80% Ta-20% W, can be analyzed by adding sufficient tantalum to the sample solution to match the calibration standards. The solutions are analyzed using a 100 KV Philips X-ray Spectrometer. Hafnium and rhenium fluorescence is obtained with a tungsten x-ray tube, Superior sensitivity for tungsten is obtained by excitation with a molybdenum x-ray tube. X-ray measurements are converted to concentration by processing the data through a time-sharing computer (On-Line-Systems).

A brief description of the Basic program for data processing written by R. Gabler, et al, of the Bureau of Mines will be presented. The calibration data shows a linear relationship between x-ray intensity and concentration for all elements. Comparative chemical and atomic absorption data show that rapid and accurate determinations of tungsten, hafnium and rhenium in T-1 11, T-222, ASTAR 811C and ASTAR 1211C can be obtained by x-ray fluorescence.

(2) PRECISION IN TRACE-ELEMENT ANALYSIS BY X-RAY EMISSION SPECTROGRAPHY J. Hatten Howard III, Department of Geology, University of Georgia.

Analysis of the error in two analytical methods for the determination of trace elements by x-ray emission illustrates application of the theory of error. Data obtained by analytical work are expressed by an equation representing the method of analysis, and errors are propagated according to this equation.

The concentration of an element can be calculated from measured net intensities (I and I_c) of the unknown sample and of the sample to which a known concentration, c , has been added, by the equation

$$C = \frac{c}{\frac{I_c}{I} - 1}$$

The value for the unknown concentration is in error by an amount which results from the errors in the quantities c , I_c , and I in the formula. The general rule for propagation of independent errors is applied to this function of C , so that the relative standard error of the standard-addition method.

$$S_c = \frac{C}{c} \cdot \frac{I_c}{I} \sqrt{\frac{(I_p + I_b)}{t \cdot I^2} + \frac{(I_{pc} + I_{bc})}{t \cdot I^2}}$$

where I_p and I_b are peak and background intensities and t is the counting time. Precision of the analysis varies in a complex way with both the unknown amount of element in the sample and the concentration of that element added.

Random emission of x-ray quanta introduces an important and unavoidable error into x-ray analysis: the standard counting error. Yet the counting error which results from four intensity measurements (standard-addition method) does not adequately evaluate the relative standard error of the standard-addition method.

An analytical method by which the effect of sample matrix on net peak intensity can be defined from measurement of scattered background permits calculation of the unknown concentration by the equation

$$C = \frac{I}{R}$$

where R is the sensitivity ratio (in cps/ppm) determined from the scattered background. Precision in the element concentration results from errors in the net peak intensity (two measurements, background and peak) and in the empirical equation by which R

is determined. This error is the differential

$$dC = \frac{N_p + N_b}{tR} + \frac{N_p - N_b}{tR^2} \cdot (sR)$$

where N_p and N_b are quanta counted for the peak and background. The error in sensitivity ratio, sR , is determined by error analysis of the element calibration curve.

Comparison of the relative errors of these two analytical methods aids in the choice of method on the basis of precision as well as upon time of analysis or sample preparation.

(3) SENSITIVITY MEASUREMENTS — A METHOD OF EVALUATING ELECTRON MICROPROBE X-RAY DATA FOR QUANTITATIVE ANALYSIS, Robert H. Heidel, U. S. Geological Survey, Denver, Colorado 80225.

In quantitative electron microprobe analyses, sophisticated computer-based correction factors are commonly used to reduce the first approximation of the concentration, k_s (X-ray intensity of unknown/X-ray intensity of standard), to "true" concentration. This procedure is somewhat dubious because the values of the constants used in correcting the formulas are not precisely known. A different procedure for obtaining "true" concentration is based on *sensitivity*, S (where $S = \text{counts/weight concentration}$). Sensitivity has been used to evaluate analytical precision, detectability limits, influence of operating voltage on atomic number and absorption corrections, and linearity between concentration and X-ray intensity. The factors of counting precision and sample homogeneity have also been studied.

(4) AN EVALUATION OF A CAPILLARY ARC PLASMA AS AN ANALYTICAL TOOL IN TRACE ANALYSIS, J. L. Seeley and R. K. Skogerboe, Colorado State University, Department of Chemistry, Fort Collins, Colorado 80521.

Freeze dried blood is introduced as a fine aerosol into a highly stabilized d.c. arc plasma in argon. The capillary arc assembly, the means of producing the aerosol, and a number of parameters used in the method will be discussed. Detection levels of several trace elements and the relative precision data will be reported.

(5) NON-FLAME ABSORPTION CELL TECHNIQUE AND ITS APPLICATIONS TO THE ANALYSIS OF ENVIRONMENTAL POLLUTANTS, Jae Y. Hwang, Ph.D.,

Instrumentation Laboratory Inc., 113 Hartwell Avenue,
Lexington, Mass. 02173.

Conventional flame-aspiration type atomic absorption spectrophotometer has been extensively used in trace analysis of the environmental pollutants. The method, however, has some disadvantages such as lack of sensitivities at nanogram or picogram levels and large sample consumption rate. In non-flame absorption cell technique less than 100uJ of sample solution is used and yet the improvement of sensitivity is made up to 100 to 1000 folds over the conventional atomic absorption technique. The present technique employs an electrothermal heating of the sample in an enclosed cell to produce atomic vapors. Atomization takes place in an argon atmosphere which not only increases the atomic population of the analyte, but also eliminates the oxidation of the tantalum strip used as the sample boat. Among the elements studied are Ag, Cd, Cu, Mg, Mn, Pb and Zn. Sensitivities are usually 10^{-12} gr with precision of + 5% at 10^0 gr levels by this technique.

(6) SOME ADVANTAGES OF FURNACE ATOMIC ABSORPTION OVER FLAMES, Ray Woodruff.

Furnaces ordinarily have a long path length, no dilution of the sample with flame gases, no combustion or turbulence, and the sample is confined to the light path for a relatively long time. Memory effects are minimized by having the chamber walls hotter than the flushing gas stream. Our work, unlike most furnace work, is confined to constant temperature furnaces. The only perturbation is that due to the sample. The temperature of several hundred grams of graphite core is affected only slightly by a few milligrams of sample and a light graphite cup.

Our sample introduction system is also unique. The solid sample is introduced from the atmosphere against a flushing stream of argon. Liquid samples dissolved in methanol or other solvents with a carbon to oxygen ratio of one to one are nebulized and carried into the furnace with argon. Liquid samples give less sensitivity than solids, but the sensitivity is still considerably better than flames and they promise to give much better accuracy and precision, especially when nebulized ultrasonically. The nebulizer was obtained from Tomorrow Enterprises of Portsmouth, Ohio.

Since our first paper in 1966 many models of furnaces have been built and tested. The advantages and uses of the latest models will be discussed.

(7) ELECTRODELESS DISCHARGE LAMPS AS ATOMIC ABSORPTION SPECTROSCOPY LIGHT SOURCES,

K. E. Smith and W. G. Schrenk Department of Chemistry, Kansas State University, Manhattan, Kansas 66502.

Microwave excited electrodeless discharge lamps (EDL) provide intense line spectra for atomic species, making them feasible as source lamps for atomic absorption spectroscopy (AAS). To be useful in this capacity the lamps should be relatively easy to prepare, give intense, relatively sharp lines, possess good stability (both instantaneous and long term) and remain in service for a reasonable lifetime.

In addition to the evaluation of the above characteristics, the effect of fill gas pressure on intensity will also be discussed for the zinc lamps which have been prepared. This effect varies depending on whether the lamp is jacketed or non-jacketed. The jacketing, either evacuated or static air was used to increase the stability of the lamps since air currents were found to profoundly affect the lamps.

The line widths obtained from these lamps did not seem to be affected by the input power to the lamp, allowing the use of the maximum power available (100 watts). This, consequently, permitted the electronics to be operated well within their limits thus reducing the noise of the output.

(8) EVALUATION OF LIGHT SCATTERING AND MOLECULAR ABSORPTION INTERFERENCES IN ATOMIC ABSORPTION ANALYSIS OF BIOLOGICAL MATERIALS, W. A. Abbott and R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521.

Light scattering and molecular absorption interferences are now widely recognized as a problem in atomic absorption analyses and several means have been developed to compensate and/or correct for these. An evaluation of these corrective measures with particular reference to the determination of trace elements in blood, plant tissue, and excreta will be presented.

(9) ZINC AND MANGANESE ANALYSIS OF PLANT MATERIAL BY ATOMIC ABSORPTION SPECTROSCOPY, D. L. Smith and W. G. Schrenk, Kansas State University, Manhattan.

The increasing importance of determining trace elements in agricultural plant material has led to many published analytical methods. Zinc and manganese are usually determined by colorimetric methods. These methods require considerable pre-

liminary chemical treatment of the sample and therefore are rather time consuming.

The need for a rapid and simple method of analysis for determining zinc and manganese in plants has led to an investigation into the application of atomic absorption spectroscopy. The results of this study are presented.

Operating conditions for performing the analyses have been established for the Jarrell-Ash Tri-Flame burner and the Beckman total consumption burner. The Tri-Flame burner was operated using either air-acetylene or nitrous oxide-acetylene and the Beckman burner was operated with oxygen-acetylene.

Variations of gas flow to the burner did not significantly affect the absorption signal. However, the current applied to the hollow cathode was found to be quite important for zinc but not for manganese.

No significant interference was noted from other ions present in plants when using the Tri-Flame burner. The signal obtained from the Beckman burner was affected by the presence of certain ions. Potassium, sodium, and sulfate ion caused slight decreases in the zinc absorption while the phosphate ion produced as much as a 20% decrease in the signal.

Wet and dry ashing techniques produced similar results. Variations in results from one day to another were somewhat greater than desirable; however, one method was not consistently higher or lower than the other.

Results from the atomic absorption analysis of plant samples have been compared to accepted AOAC methods. The manganese data is incomplete at this time but zinc analyses compare favorably. The atomic absorption method is much simpler and faster than the AOAC method.

(10) LUMINESCENCE AND POLARIZATION SPECTRA OF COUMARINS AND FUROCOUMARINS, Pill-Soon Song and Marian L. Harter, Department of Chemistry, Texas Tech University, Lubbock, Texas 79409.

The lowest excited singlet and triplet states of coumarins and furocoumarins have been assigned to the ($n\pi^*$) type on the basis of luminescence and polarization (photoselection) data in ethanol at 77°K. Two lowest $\pi\pi^*$ bands in these molecules are polarized essentially along the long molecular axis, except for 8-methoxy psoralen which has the second lowest transition polarized nearly along the short axis. The polarization assignments have been deduced from photoselection, linear dichroism, and SCF MO CI results. Emphasis of the present paper will be on the nature of the triplet excited state which plays an

important role in photodermatitis, photomutagenesis, and related photodynamic actions sensitized by coumarins. Surprisingly, coumarins and furocoumarins showed their 0-0 phosphorescence bands at essentially the same location regardless of size and substituent of these molecules. It should be pointed out that the absorption and fluorescence bands show strong red shifts upon extension of the conjugated system and by CT substituents. Phosphorescence lifetimes were found to be 0.5-1.2 sec. These results can be interpreted in terms of highly localized triplet states in the region of the pyrone double bond. Photobiological reactivity of coumarins is attributed to such a highly localized triplet excitation. The concept of the localized triplet state may be extended to carcinogenic polycyclic aromatic hydrocarbons which undergo photocycloaddition to DNA. (This work was supported by Robert A. Welch Foundation (D-182) and by National Science Foundation (GB-21266)).

(11) LUMINESCENCE DETERMINATION OF CHLORINATED BIPHENYLS, C. M. O'Donnell and T. S. Spencer, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521.

We have determined a method to distinguish between DDT (p,p') and chlorinated biphenyls in water by the use of luminescence spectroscopy. In addition, data will be presented to demonstrate how phosphorescence spectra coupled with phosphorescent lifetimes may be used to distinguish between a series of chlorinated biphenyls. The application of phosphorescence as an analytical tool for the analysis of organic pollutants will be discussed.

(12) PHOSPHORIMETRY UNDER AMBIENT CONDITIONS, E. M. Schulman, A. R. Lepley and C. Walling, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

Low temperature matrices and exclusion of oxygen have been essential in obtaining phosphorescence spectra. We have now developed a technique for measurement of phosphorescence which is not significantly influenced by oxygen or temperature. The phosphorescence spectra produced show sharp, intense bands readily utilized for fingerprint characterization of compounds. Our technique simply involves absorption of salts of acidic organic materials on a solid support and measurement of the spectra with a commercial spectrophotophosphorimeter. Materials studied include biphenyl carboxylic acids, polynuclear aromatic phenols, carboxylic and sulfonic acids, and

amides; and the biologically important class of porphyrins. These long-lived emissions are readily detected visually, with discernable color variation, when intermittently irradiated with black light. A variety of applications from air pollution analysis to physical-organic chemistry are apparent for the new technique because of quick and easy sample preparation and the use of standard equipment.

(13) REMOVAL OF STATISTICAL SCATTER FROM GAMMA-RAY SPECTRA WITH HIGH ORDER POLYNOMIALS, Herbert P. Yule, Activation Analysis Section, Analytical Chemistry Division, National Bureau of Standards, Washington, D. C 20234.

Various mathematical methods of removing statistical scatter from gamma ray spectra have been published. One of these is the simplified least squares data convolution technique proposed by Savitzky and Golay (1). It has the advantage of being extremely rapid so that many spectra may be smoothed quickly and inexpensively. Briefly, the method involves fitting a polynomial of order p to n channels of data to generate the height of the smoothed spectrum at the center of the interval. Repeating the process for different groups of n channels permits the entire spectrum to be smoothed.

Proper choice of the parameters, n and p , is very important. It has been shown (2) that the best results are obtained when n is approximately the resolution of counting system (FWHM). In the past, it has been assumed that second or third order polynomials would give the best results, since the top of a photopeak is roughly quadric in shape and the side is roughly cubic. Studies of distortion introduced by smoothing indicates that higher order polynomials introduce less distortion, especially when there are overlapping peaks.

Examples of smoothing of different spectral configurations will be shown.

(1) A. Savitzky and M. J. E. Golay, *Anal. Chem.* 36. 1627(1964).

(2) H. P. Yule, *Nuclear Instr. Methods* 54, 61 (1967).

(14) MEASUREMENT OF OZONE CONCENTRATION IN HYPERSONIC WAKES*, Charles P. Dyjak, Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173.

The time-resolved concentration of ozone in turbulent hypersonic wakes has been measured by firing a projectile through a multi-pass absorption cell and measuring the change in intensity of transmission of

the mercury 2537 Å line which passed through the wake. The projectile, a non-ablating copper-plated aluminum sphere of 4.76 cm diameter, was fired at a velocity of about 5.8 Km./sec. into pure dry air at pressures of 20 to 80 torr. The ozone is formed in situ from fast chemical reactions which take place in the hot wake, with a nearly steady state concentration being reached in about 10 milliseconds after projectile passage. The measured concentrations are compared with those predicted by a detailed chemical model to test the model's validity.

Similar measurements were also made using ablating projectiles of teflon and delrin to study the effect of ablation on wake chemistry and to serve as inputs for more complicated models which include ablation. Both fluorine and hydrogen ablated from teflon and delrin respectively, tend to inhibit the ozone formation by depleting the atomic oxygen in the wake.

*This work was sponsored by the Advanced Research Projects Agency of the Department of Defense.

(15) PHOTOMULTIPLIERS FOR SPECTROSCOPY, Dennis E. Persyk, RCA, Electronic Components Division, Photomultiplier Product Development Group, Lancaster, Pennsylvania 17604.

Recent advances in III-V compound photoemissive materials have been incorporated into photomultipliers for spectroscopic applications. Photocathodes with luminous sensitivities in excess of 1000 uA/lumen are now available in photomultipliers. Data are presented on the C31034A photomultiplier which utilizes a GaAs (Cs-O) photocathode having high quantum efficiency from the UV to approximately 900 nanometers. A discussion on selection guidelines for photomultipliers is given. Emphasis is placed on new detectors with negative electron affinity photocathodes which afford significant improvements in signal-to-noise ratios over conventional detectors. The photon counting technique for low signal-level detection is discussed, and an applications guide to the selection of photomultipliers for photon counting is presented.

(16) APPLICATIONS OF SELF-BEAT SPECTROSCOPY, C. T. Meneely¹, C. Y. She¹, David F. Edwards², Quantum Electronics Laboratory, Colorado State University, Fort Collins, Colorado 80521.

Self-beat spectroscopic methods are analogous to the superheterodyne or homodyne mixing techniques used in the rf and microwave region of the electromagnetic spectrum. The theoretical basis of the opti-

cal self-beat spectroscopic method will be given including the advantages of the system over more conventional methods. Using the self-beat technique the average random velocity was measured for polystyrene spheres in an aqueous solution undergoing Brownian motion. The measured results will be compared with calculated values assuming hydrodynamic relations. The average translational velocity of a water vapor stream was measured using this same technique. This experiment will also be described. The possible application of self-beat methods to problems of engineering and biological interest will be briefly discussed.

1. Physics Department
2. Electrical Engineering and Physics Department

(17) TRACE ANALYSIS BY MICROWAVE INDUCED EMISSION SPECTROSCOPY, Fred E. Lichte, R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521.

An on-line chemical generator designed to produce volatile metal chlorides will be described. The metal chlorides are vaporized and swept into a 2450 MHz microwave plasma, for excitation of the metallic species. Dynamic background correction is used to eliminate interference caused by the HC1: metal chloride band spectra. Determination of some elements of current environmental interest at the nanogram and subnanogram level will be discussed.

(18) ENERGY TRANSFER IN THE HYDROGEN-BONDED CARBAZOLE-BENZOPHENONE COMPLEX, T. S. Spencer, C. M. O'Donnell, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521.

A study of the absorption and emission spectra of carbazole and benzophenone in polar and non-polar solvents at 77°K. has shown that carbazole emission is quenched by benzophenone, but only in non-polar solvents. Triplet lifetime measurements indicate that the quenching results from triplet-triplet energy transfer from carbazole to benzophenone in a hydrogen-bonded complex.

(19) SOLVENT EFFECTS ON THE CARBON-13 CHEMICAL SHIFTS OF TETRAMETHYLSILANE AND CYCLOHEXANE* by Mark R. Bacon and Gary E. Maciel, Department of Chemistry, Colorado State University and Department of Chemistry, University of Cali-

fornia, Davis.

Carbon-13 shifts of tetramethylsilane and cyclohexane dissolved in about fifty halobenzenes and halocyclohexanes were obtained relative to the hydrogen signals of the two solutes. Hydrogen shifts in more than half of the solvents were obtained by means of the technique of Beconsall, Daves, and Anderson. These results indicate that cyclohexane is somewhat more immune to solvent effects than tetramethylsilane. The experimental results were subjected to a factor analysis procedure similar to that of Malinowski and co-workers.

*Supported by a grant from the National Science Foundation.

(20) TEMPERATURE EFFECTS ON THE NMR LINE SHAPES OF OIL SHALE, A. B. Denison, Physics Department, University of Wyoming, Laramie, Wyoming 82070 and F. P. Miknis, A. W. Decora, and G. L. Cook, U. S. Department of the Interior, Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming 82070.

Recent work attempting to characterize the organic material in oil shale and the way in which this material is combined with the inorganic matrix of the shale has brought about a need for intercorrelation of several measurement techniques. One of these methods, variable temperature wide-line NMR, appears to offer information as to the molecular motion and onset of the mobility of the organic material itself. We present data which clearly show the increased molecular mobility of the organic material as the temperature of the oil shale is heated and the reverse effect as the sample is cooled. Attempts are currently being made to correlate specific molecular motions or fluid flow over specific temperature ranges.

(21) CARBONYL CARBON-13 CHEMICAL SHIFTS AND TRANSANNULAR INTERACTIONS*, T. T. Nakashima and G. E. Maciel, Department of Chemistry, University of California, Davis, and Department of Chemistry, Colorado State University.

Carbon-13 magnetic resonance spectra were obtained in natural abundance on cyclooctanone and three cyclic ketones that have been studied previously for evidence of transannular interactions with the carbonyl group. Each of the three substituted ketones, 1-oxacyclooctan-5-one, 1-thiacyclooctan-5-one and 11-methyl-11-azabicyclo [5.3.1] hendecan-4-one, was studied in chloroform solution and in cyclohexane solution. Both continuous wave and Fourier transform

methods were employed. The measured ^{13}C chemical shifts will be discussed in terms of the strength of the interactions in question.

*Supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

(22) PARAMETERS AFFECTING THE ANALYSIS OF OILSHALES USING WIDE-LINE NMR SPECTROSCOPY, F. P. Miknis, U. S. Department of the Interior, Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming 82070, and A. B. Denison, Physics Department, University of Wyoming, Laramie, Wyoming 82070, and A. W. Decora and G. L. Cook, U. S. Department of the Interior, Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming 82070.

Previous studies in our laboratory have shown that wide-line nuclear magnetic resonance spectrometry has potential applications in areas such as the estimation of oil yields and organic carbon contents of oil shales. In a *continuation* of this study, *parameters* affecting the analysis of oil shales using the NMR technique will be discussed, with emphasis on universal *quantification* of the *method*. Such *parameters* include relaxation times, hydrogen-carbon ratios, sample density, and amount of water present in the sample. Data obtained from samples taken from different geographical locations, but yielding approximately the same number of gallons of oil per ton of shale will be presented.

(23) CARBON-13 CHEMICAL SHIFTS IN 1-SUBSTITUTED-4-METHYLBICYCLO-[2.2.2] OCTANES*, by H. C. Dorn and G. E. Maciel, Department of Chemistry, Colorado State University.

^{13}C magnetic resonance spectra were obtained in natural abundance on 4-substituted-1-methyl bicyclo [2.2.2] octanes, in which the 4 position is occupied by the following groups: F, Cl, Br, I, H, OCH_3 , OCOCH_3 , and CO_2H . Fourier transform methods were employed to obtain the spectra. Off-resonance decoupling and comparison with the characterized spectra of 1-substituted bicyclo [2.2.2] octanes were used in making the spectral assignments. The resulting chemical shifts are discussed in terms of the concepts of field effects and inductive effects.

*Supported by a grant from the National Science Foundation.

(24) CHARACTERIZATION OF SELECTED HIGH MOLECULAR WEIGHT PETROLEUM SATURATE FRACTIONS, BY NMR SPECTROSCOPY, F. D. Guffey, F. R. McDonald, and J. H. Weber, U.S. Department of the Interior, Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming 82070.

The characterization of high boiling petroleum fractions is an objective of American Petroleum Institute Research Project 60. We have performed extensive NMR studies on selected high molecular weight saturate fractions from several crude oils. Structural characterization in terms of the amount of naphthenic carbon (inferred from the amount of naphthenic hydrogen) has been made and these results are compared with the mass spectral analyses of these fractions. To arrive at a more complete picture of the petroleum fractions, the importance of combined MS-NMR analyses of the fractions will be shown.

(25) CARBON-13 CHEMICAL SHIFTS AND ADDITIVITY RELATIONSHIPS IN 1,2-DISUBSTITUTED ETHANES*, G. E. Maciel, L. Simeral, R. Elliott, B. Kaufmann, and K. Cribley, Department of Chemistry, University of California, Davis, and Department of Chemistry, Colorado State University.

Carbon-13 magnetic resonance spectra were obtained on natural abundance samples of nearly fifty 1,2-disubstituted ethanes covering a variety of substituents, Cl, Br, I, OH, OCH₃, N(CH₃)₂, COCH₃, CH = CH₂, C = CH and C₆H₅. Both continuous wave and Fouriertransform methods were employed in obtaining the data. The ¹³C chemical shifts were analyzed in terms of additivity relations. The results are discussed in terms of various contributions to substituent effects on ¹³C chemical shifts.

*Supported by Grant GP-8799 from the National Science Foundation

(26) TUNABLE GUNN-EFFECT DIODE EPR SPECTROMETER, K. W. Pontinen, J. P. Cruts, and A. B. Denison, Physics Department, University of Wyoming, Laramie, Wyoming 82070.

It has been demonstrated that one can build an EPR spectrometer using the Gunn-Effect Diode. Signals have been observed in our scheme which uses a Gunn-Diode sitting in a tunable re-entrant cavity. The basic designs involved are unsophisticated and economic to build. Several different types of schemes involving the Gunn-Effect Diode will be discussed.

(27) ^{13}C - ^{13}C COUPLING CONSTANTS IN ISOPROPENYL COMPOUNDS*, V. J. Bartuska and G. E. Maciel, Department of Chemistry, University of California, Davis, and Department of Chemistry, Colorado State University.

^{13}C - ^{13}C spin-spin coupling constants were obtained on twelve specially synthesized compounds of the type $\text{CH}_2\text{-}^{13}\text{C}(\text{CH}_3)\text{X}$, where X covers a representative range of substituents. The mono-labeled compounds provided adequate ^{13}C sidebands in continuous wave experiments using time averaging for both the $\text{CH}_2=\text{C}$ and C-CH_3 coupling constants to be measured. The results are compared with previously reported J_{CC} data on $\text{CH}_3\text{CH}_2\text{X}$ and CH_2COX compounds, and discussed in terms of the nature of substituent effects on C-C coupling constants.

*Supported by Grant GP 8119 from the National Science Foundation.

(28) A WAVELENGTH—TUNABLE LASER SYSTEM FOR INFRARED SPECTROSCOPY*, C. Forbes Dewey, Jr., Associate Professor of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

For many years it has been apparent that the use of lasers in spectroscopy would be enormously enhanced by systems in which the laser wavelength was continuously variable. This tunability has been achieved by dye lasers in the visible, near ultraviolet, and near infrared (approximately 0.34 to 1.06 μm). Parametric oscillators have been used to provide high-power tunable radiation at wavelengths below about 4 μm .

A laser system will be described which offers the potential of producing narrow-band emission tunable through the infrared from 2 μm to 20 μm . A ruby laser and a dye laser are used to produce infrared difference frequencies in a nonlinear crystal (1). Changing the dye laser wavelength alters the difference frequency and effects continuous wavelength tuning. The system parameters (linewidth, intensity, wavelength stability, tuning ranges for each dye, etc.) will be described, and several examples of absorption spectroscopy using this system will be presented.

*This research was supported in part by the Office of Naval Research and the Advanced Research Projects Agency under Contract No. N00014-0204-0040, ARPA Order No. 322.

(1) C. F. Dewey, Jr. and L. O. Hocker, *Appl. Phys. Lett.*, 18, 58 (1971)

(29) RAMAN SCATTERING APPLIED TO SOLID STATE PHYSICS, T. W. Broberg; C. Y. She' and David F.

Edwards², Quantum Electronics Laboratory, Colorado State University, Fort Collins, Colorado 80521.

The use of the laser as an excitation source for Raman scattering measurements has renewed a great interest in Raman Spectroscopy. The application of laser excited Raman scattering techniques for the determination of Raman-active vibrational modes of KH_2PO_4 will be presented. This crystalline molecule is an example of a class of molecular systems in which the tetrahedral $(\text{PO}_4)^{3-}$ ion remains essentially as an "individual" molecule in the crystal with its vibrational modes split by the local crystalline field of S_6 symmetry. The lattice modes responsible for the ferro-electric phase transition in KDP have been measured and the results will be reported.

1. Physics Department
2. Electrical Engineering and Physics Department

(30) APPLICATIONS OF MULTIPLE INTERNAL REFLECTANCE SPECTROSCOPY TO AIRCRAFT MATERIALS EVALUATION, T. T. Bartels, McDonnell Aircraft Company, St. Louis, Mo.

Multiple internal reflectance (MIR) spectroscopy is primarily used to define the composition of surface coatings. Typical applications include the study of effects of weathering on a surface, chemical aging, identification of coatings without prior removal from the substrate, and the absorption of contaminants on surfaces. This paper reports another application of MIR spectroscopy, the quantitative determination of the mix ratio and chemical composition of polymeric materials currently used in aircraft construction. The speed and convenience of MIR sampling enables rapid recording of the spectrogram with minimum sample pretreatment, sample orientation allows the internal composition of the material to be defined, and the absorbance ratio method provides quantitative information of interest. Therefore data obtained is more representative of the quantitative bulk composition of the specimen rather than the qualitative surface condition, MIR spectroscopic methods applicable to silicone and polyester potting compounds and to advanced composite materials are discussed.

(31) INFRARED DETERMINATION OF CARBOXYL AND HYDROXYL CONTENTS OF FUNCTIONALLY TERMINATED POLYBUTADIENES, Albert S. Tompa, Science Directorate, Naval Ordnance Station, Indian Head, Maryland 20640.

A concentration dependent infrared study of the

carboxyl and hydroxyl group of functionally terminated polybutadiene (CTPB and HTPB) was made. As the concentration exceeds one gram/liter, intermolecular effects become more noticeable. Deviation from a Beer's law plot shows that hydrogen bonding affects the hydroxyl group to a greater extent than the carbonyl in the carboxyl group. The carboxyl band at 1708 cm^{-1} was analyzed in CCl_4 solution, and as a film using the vinyl band at 1638 cm^{-1} or the methylene band at 1435 cm^{-1} as internal standards. The free hydroxyl band at 3615 cm^{-1} and the total hydroxyl absorption in the 3700 to 3200 cm^{-1} region was analyzed in CS_2 using peak height and graphical integration methods. Primary, secondary, and saturated HTPB could be distinguished by the band shape of the hydroxyl band. The shape of the hydroxyl band appears to be influenced by the unsaturation of the polymer backbone. HTPB with less than 10% cis and trans unsaturation had a narrower monomer absorption band at 3615 cm^{-1} . Phenolic antioxidant present in HTPB interferes, but may readily be corrected. Pre-polymer samples from different vendors had slightly different absorptivities which may depend upon the method of preparation. The accuracy of the infrared analysis was within a mean error of +0.03% of the titration value.

(32) HYDROXYL GROUPS ON THE SURFACE OF MgO, Salim Akhtar, University of Nevada, Reno, Nevada.

Hydroxyl groups on the surface of MgO are investigated using transmission and ATR spectroscopy. In contrast to a single sharp band at 3698 cm^{-1} for the OH stretching in $\text{Mg}(\text{OH})_2$, two intense and two weak bands in the range 2840 cm^{-1} to 2950 cm^{-1} are observed for the hydroxylated MgO. Tentative assignments of the bands are discussed.

(33) INFRARED SPECTRA OF PLUTONIUM AMMINE COMPLEXES, Roger S. Cichorz, Mass Spec Laboratory, The Dow Chemical Company, Rocky Flats Division, P. O. Box 888, Golden, Colorado 80401.

Several air-sensitive plutonium ammine complexes were prepared by reacting plutonium (III) and (IV) halides with liquid and gaseous ammonia in a dry, inert-atmosphere glove box, and their infrared spectra (4000 to 400 cm^{-1}) were recorded. Because of the α -radio-activity and toxicity of plutonium and of the extreme reactivity of these ammines with air and moisture, special sample-handling and transfer techniques were employed in the infrared spectroscopy investiga-

tions.

The spectra of the Pu (III) complexes are similar to those of the metal (III) halide hexammine complexes of the transitional metals Co, Cr, and Ni. The Pu (IV) complexes are characterized by a shift of ν^* Pu-N to higher frequencies, indicating stronger metal-nitrogen bonding than in the case of the Pu (III) complexes.

Representative infrared spectra of Pu (III) and (IV) ammine halides and a discussion of sample handling techniques will be presented.

(34) CHARACTERIZATION OF FATTY ACID POLYMORPHIC MODIFICATIONS BY X-RAY AND INFRARED TECHNIQUES, 1 D. Mitcham, A. V. Bailey, V. W. Tripp, and G. Sumrell, Southern Regional Research Laboratory 2] New Orleans, Louisiana.

Many important properties of fatty acids and their derivatives are primarily dependent upon crystal structure. Whereas x-ray diffraction data are available for the different polymorphic forms of both the saturated odd and even carbon numbered long-chain fatty acids, little effort has been directed toward the characterization of these various polymorphs by infrared techniques. Moreover, x-ray diffraction data and infrared spectra for the more common low melting unsaturated long-chain fatty acids is almost non-existent. Techniques and procedures devised and worked out for obtaining x-ray diffraction patterns and infrared spectra for both saturated and unsaturated long-chain fatty acids in the solid phase at sub-ambient temperatures are discussed. X-ray diffraction data are correlated with infrared spectra for polymorphic modifications of both saturated and unsaturated fatty acids.

(35) A CORRELATION OF HAMMETT SUBSTITUENT CONSTANTS AND HYDROGEN BONDING BETWEEN SUBSTITUTED BENZYL ALCOHOLS AND ALKYL AMINES, Max A. Taylor, Department of Chemistry, Bradley University, Peoria, Illinois 61606, K. E. Kolb, Department of Chemistry, Bradley University, and E. I. Stout, Northern Regional Research Laboratory, 1815 North University, Peoria, Illinois 61604.

Data such as that of Goulden¹ demonstrate a shift in the O-H stretching frequency with different substituents in phenol and benzoic acid derivatives. However, in inert solvents such as carbon tetrachloride and benzene the substituted benzyl alcohols unexpectedly show no shift in the O-H stretching frequency as substituents are changed. When the hydroxyl group is hydrogen-bonded with various alkyl amines, the hydrogen-bond shifted O-H stretching frequency will

be shown to correlate well with the Hammett substituent constants generally accepted for correlation of thermodynamic and kinetic data in aromatic systems. Correlation of the shifted O-H stretching frequencies with Hammett substituent constants and amine base strengths enables estimates to be made of the magnitude of substituent inductive effects on the benzyl alcohol group.

¹J.D.S. Goulden, *Spectrochim. Acta* 6, 129 (1954).

(36) STABLE ISOTOPE RATIO MEASUREMENTS: MASS SPECTROMETER TECHNIQUES AND PROBLEMS, Henry L. Dequasie, University of Utah, Salt Lake City, Utah.

The discovery and measurement of isotopes was one of the first applications of the mass spectrometer. Recent applications of the stable isotopes of carbon, nitrogen, oxygen, and sulfur in mining, pollution, and medical studies have renewed interest in their ratio measurements.

Ratio measuring mass spectrometers must be equipped with dual collectors and special inlet systems to perform with the necessary precision. Results are expressed in terms of a sample's deviation from a standard gas in order to reduce errors from long-term instrumental variations. Gas switching systems are used to rapidly compare gases to reduce errors from short-term instrumental variations. Careful observation of the mass spectrometer's operation can prevent malfunction of these systems from also introducing errors.

Elements under consideration must be converted to a pure gas sample that is compatible to the mass spectrometer. Samples must be prepared by an isotopically non-fractionating process or by a process of a known and stable amount of fractionation that makes corrections possible. Experience has shown that the presence of impurities in samples can be detected without analysis, by indirect means, when ratio measurements are attempted.

(37) SPARK SOURCE MASS SPECTROMETRY AS AN ANALYTICAL TECHNIQUE, R. Brown, Accu-Labs Research, Inc., and Associated Electrical Industries, Ltd.

The applications of spark source mass spectrometry in trace element analysis will be surveyed. New instrumentation features such as electrical detection, peak switching and computer data treatment will be described. In addition, some new innovations in sampling, instrument operation and data evaluation will be discussed.

(38) SUBSTITUENT GROUP PARTICIPATION IN COMPETING CLEAVAGE AND REARRANGEMENT PROCESSES FOR THE N-ETHYL N'-(R-PHENYL)UREA MOLECULAR ION, R. A. Adams and D. D. Rosebrook, Midwest Research Institute, Kansas City, Missouri 64110.

A series of 5 mono- and di-substituted N-ethyl N'-(R-phenyl)ureas (R denotes the various substituents) have been investigated at a high and low voltage electron bombardment energy. An energetic and kinetic approach was employed in the interpretation of the mass spectra. Rearrangement reactions with competing simple cleavage have been studied. The rearrangement process showed a more intense metastable peak than the competing, simple cleavage process, which is consistent with Chupka¹ and McLafferty and Fairweather.²

Williams and Cooks³ have reported another method for studying rearrangement process based on the simplified form of the basic rate equation of the quasi-equilibrium theory (QET). The basic equation is given by $K(E) = \frac{j}{N} \exp\left(-\frac{E - Q}{h\nu}\right)$ here K is the rate constant, E is the internal energy, Q is the activation energy, j is the frequency factor and N is the number of oscillators.

For two competing reactions, one being a simple cleavage and the other a rearrangement process, the terms E and N-1 are constant for the two reactions. The frequency factor j for a rearrangement reaction is lower than the frequency factor (j_c) for a simple cleavage, and it has been experimentally determined that the activation energy for many rearrangement processes is lower than the activation energy for a competing simple cleavage. At high ionizing energies the simple cleavage is expected to occur to the greatest extent, since the large differences between E and E_c allow the frequency factor to rule the rate expression. As the ionizing energy is decreased, the activation energies begin to control the rates of the competing reactions, and the rearrangement process should become progressively more important.

We employed these two methods to investigate the rearrangement and competing simple cleavage processes that lead to the observed mass spectra at the various electron bombardment energies.

1. W. A. Chupka, *J. Chem. Phys.*, **30**, 191 (1959).

2. F. W. McLafferty and R. B. Fairweather, *J. Am. Chem. Soc.*, **90**, 5915 (1968).

3. D. H. Williams and R. G. Cooks, *Chem. Comm.*, 663 (1968).

(39) OPTICALLY MODIFIED MASS SPECTROSCOPY — A NOVEL WAY TO STUDY EXCITED IONIC STATES, R. E. Ellefson and A. B. Denison, Physics Department, University of Wyoming, Laramie, Wyoming 82070 and J. H. Weber, U.S. Department of the

Interior, Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming 82070.

A technique has been developed in our laboratory for reducing or increasing fragment ions in a mass spectrum by changing the population of the excited states of the ions that lead to fragmentation. The population of excited ionic states are changed by stimulated emission or absorption of photons. The effect produced is an optically modified mass spectrum (OMMS). Comparisons of the wavelengths that produce the OMMS effect with known UV absorption spectra of some small molecular ions will be presented. Knowledge of the wavelengths that modify fragmentation patterns provides further insight into the fragmentation mechanisms occurring in the mass spectrometer.

The theory of OMMS will be presented along with predictions of uses of the technique as analytical aids.

(40) MASS SPECTROMETRIC CHARACTERIZATION OF THE ISOMERIC DIMETHYLNAPHTHALENES, F. G. Doolittle and D. G. Earnshaw, U.S. Department of the Interior, Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming 82070.

A portion of the work at the Laramie Energy Research Center involves the characterization of oil shale. Recent studies indicate that a series of dimethylnaphthalenes (DMNS) are present in some of the fractions isolated from the Green River oil shale. Because of the small quantities of DMNS present, normal separation techniques are not sufficient to resolve the isomers.

Field and Franklin state that in general, isomeric compounds give spectra which are very difficult to distinguish from one another because of similar fragmentation patterns. Our mass spectral study shows that although the fragmentation patterns for the isomeric dimethylnaphthalenes are similar, significant differences exist in certain peak ratios to distinguish the compounds presently available. Studies on the overall fragmentation patterns have been made and fragmentation routes are hypothesized.

(41) RESOLUTION OF THE FINE STRUCTURE IN THE IONIZATION EFFICIENCY CURVES FOR $C_nH_m^+$ and $C_nD_m^+$, J. H. Weber, U.S. Department of the Interior, Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming 82070 and R. E. Ellefson and A. B. Denison, Physics Department, University of Wyoming, Laramie, Wyoming 82070.

Deconvolution of an ionization efficiency curve reveals the fine structure (appearance potential and excited appearance potentials) of the ion studied. We have deconvoluted the ionization efficiency curves of $C_6H_6^+$ and $C_6D_6^+$. The energy breaks determined from these deconvoluted curves are compared with the results from photo-electron and photo-ionization spectroscopy. Furthermore, reliable relative transition probabilities for ionization were obtained from our deconvolution studies.

(42) MASS SPECTROMETRIC INVESTIGATION OF THE DISSOCIATION ENERGIES OF THE MOLECULES Pd_2 AND $CePd$, D. L. Cocke and K. A. Gingerich.

The combined Knudsen effusion and mass spectrometric techniques have been used in the investigation of the molecules Pd_2 and $CePd$. Under conditions of solid phase-gas phase equilibrium, appropriate reactions involving these species have yielded enthalpy data which allows their dissociation energies and heats of formation to be determined.

These dissociation energies will be discussed in terms of the Pauling model of a polar bond and the Brewer-Engel theories.

(43) DEUTERIUM LABELING IN THE ANALYSIS OF LINEAR OLEFINS FROM SHALE OIL, D. G. Earnshaw, F. G. Doolittle, and A. W. Decora, U.S. Department of the Interior, Bureau of Mines, Laramie Energy Research Center, Laramie, Wyoming 82070.

This paper describes the analysis of a set of linear vicinal dideuterioalkane samples. These samples were obtained by the homogeneous deuteration of shale-oil olefins with subsequent separation into unbranched, single-carbon-number fractions in the C_{10} to C_{20} range. The analysis of the dideuterioalkanes can be related directly to the precursor olefins.

The analyses are performed using matrices produced from predicted spectra of all possible linear vicinal dideuterio isomers for a given carbon number. The spectra are predicted by the method of Earnshaw, Doolittle, and Decora as reported in Organic Mass Spectrometry (in press).

The spectra cannot be predicted exactly so that each predicted value lies within some plausible range. Several different matrices are produced for each carbon number using different values within the range. Each carbon number sample is then analyzed using the different matrices to give some indication of accuracy.

Results of these analyses will be presented in detail.