

DEVELOPMENTS IN APPLIED SPECTROSCOPY

Volume 10

Selected papers from the
Tenth National Meeting of the Society for Applied Spectroscopy
and the Twenty-Second Annual Mid-America Spectroscopy Symposium
Held in St. Louis, Missouri, October 18-22, 1971

edited by

A. J. Perkins, E. L. Grove, Emmett F. Kaelble
and Joan E. Westermeyer

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**DEVELOPMENTS
IN
APPLIED
SPECTROSCOPY**

Volume 10

DEVELOPMENTS IN APPLIED SPECTROSCOPY

Selected papers from the Annual Mid-America Spectroscopy Symposia

- 1962: Volume 1 — Twelfth Annual Symposium, 1961
Edited by W. D. Ashby
- 1963: Volume 2 — Thirteenth Annual Symposium, 1962
Edited by J. Ziomek and J. R. Ferraro
- 1964: Volume 3 — Fourteenth Annual Symposium, 1963
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- 1965: Volume 4 — Fifteenth Annual Symposium, 1964
Edited by E. N. Davis
- 1966: Volume 5 — Sixteenth Annual Symposium, 1965
Edited by L. R. Pearson and E. L. Grove
- 1968: Volume 6 — Eighteenth Annual Symposium, 1967
Edited by W. K. Baer, A. J. Perkins, and E. L. Grove
- 1969: Volume 7A } Nineteenth Annual Symposium, with the
1970: Volume 7B } Seventh National Meeting of the SAS, 1968
Edited by E. L. Grove and A. J. Perkins
- 1970: Volume 8 — Twentieth Annual Symposium, 1969
Edited by E. L. Grove
- 1971: Volume 9 — Twenty-first Annual Symposium, 1970
Edited by E. L. Grove and A. J. Perkins
- 1972: Volume 10 — Twenty-second Annual Symposium, with the
Tenth National Meeting of the SAS, 1971
Edited by A. J. Perkins, E. L. Grove, E. F. Kaelble,
and J. E. Westermeyer

PREFACE

Volume 10 of Developments in Applied Spectroscopy presents a collection of twenty selected papers presented during the 10th National Meeting of the Society of Applied Spectroscopy held in St. Louis, Oct. 18-22, 1971.

The 10th National Meeting was sponsored by the St. Louis Section, Society of Applied Spectroscopy in cooperation with Baltimore-Washington, Chicago, Cleveland, Cincinnati, Houston, Intermountain (Idaho Falls), Kansas City, New England, Niagra Frontier, Northern California, North Texas, Pittsburgh and Rocky Mountain (Denver) Sections of the Society and combined with the 22nd Mid-American Symposium. Both theoretical and applied principles were presented in sessions on emission, atomic absorption, molecular, nuclear, mass, x-ray, flame, Massbauer, and magnetic resonance spectroscopy. In addition special symposia were held on on-line computers, spectra data processing and retrieval, application of spectrographic techniques for the museum, in environmental control, in space, in biomedical, sampling, the analysis and characterization of electronic materials and gas chromatography.

The members of the Program Committee, I. Adler, L. Beaver, J. E. Delmore Jr., J. Eichelberger, J. R. Ferraro, M. Fishman, C. L. Grant, X. W. Heitsch, W. M. Hickam, M. T. Jones, S. R. Koistychann, J. Kopp, D. W. Larsen, F. Pogge, W. Ritchey, M. E. Salmon, R. K. Skogerboe, J. J. Spijkerman, P. Urone, C. Veillon, M. S. Wang, and J. S. Ziomek, and the other meeting committee members are to be commended for the excellent program. Thanks are also extended to the exhibitors for their part in making the meeting a success.

A. J. Perkins
E. L. Grove
J. E. Westermeyer
E. F. Kaeble

CONTENTS

SPECTROSCOPIC TECHNIQUES FOR THE MUSEUM

Recent Interfaces between Mass Spectrometry and Art	3
Thomas Cairns and Ben B. Johnson	
The Use of EDX for Fragile and Refractory Objects	15
J. F. Hanlan	
Characterization of Medieval Window Glass by Neutron Activation Analysis	33
J. S. Olin, B. A. Thompson, and E. V. Sayre	

MOLECULAR SPECTROSCOPY

Infrared Spectra of Some Dimethylcyclohexanes at Very High Pressures	59
J. L. Lauer and M. E. Peterkin	
Raman Spectroscopy of High Pressure Phases of Solids	79
M. Nicol, Jane R. Kessler, Yukiko Ebisuzaki, William D. Ellenson, Mei Fong, and C. Sherman Gratch	
The Use of Pressure in Infrared Spectroscopic Studies of Hydrogen Bonding	107
R. J. Jakobsen and J. E. Katon	
High-Pressure, High-Temperature Spectrophotometer Cell for in situ Catalyst Identification	123
H. Burnham Tinker and Donald E. Morris	
Recent Developments in High Resolution Raman Spectroscopy of Gases	137
Alfons Weber	

ATMOSPHERIC AND SPACE SPECTROSCOPY

Measurement of Meteorological State Variables by Remote Probing	163
John A. Cooney	
Solar Spectroscopy from Space Vehicles	191
R. Tousey	
Spectroscopic Techniques in X-ray Astronomy	217
Herbert Gursky	

SPECTROSCOPY IN BIOMEDICINE

Surface Bioanalysis of Human Dental Enamel Using Infrared Internal Reflection Spectroscopy	235
David J. Krutchkoff and H. B. Mark, Jr.	
Nuclear Particle Spectroscopy: Applications of Neutron Activation Analysis and Gamma-Ray Spectroscopy in Biomedicine	247
David J. McKown and James R. Vogt	

SPECTROSCOPIC WEAR METAL
ANALYSIS IN LUBRICATING OILS

A Controlled Maintenance System Through Used Oil Analysis	261
Edward J. Forgeron	
A High Repetition Rate High Voltage Spark Source and Its Application to the Analysis of Wear Metal in Oils	269
W. W. Schroeder, A. Strasheim, and J. J. van Niekerk	
Wear Metal Analysis of Lubricating Oils	285
Bernard B. Bond	
An Improved Computer-Direct Reader System for the Analysis of Wear Metals in Lubricating Oils and Its Application to Other Types of Spectrographic Analysis	293
P. D. Coulter, N. L. Bottone, and H. W. Leggon	

X-RAY AND EMISSION SPECTROSCOPY

X-ray Diffraction Study of New Hafnium Compounds	307
Frank L. Chan and G. G. Johnson, Jr.	

The Annual Cycle of Some Minor Elements in Linsley Pond
(North Branford, Connecticut) as Determined by Optical
Emission 331
 Ursula M. Cowgill

Index 355

SPECTROSCOPIC TECHNIQUES FOR THE MUSEUM

RECENT INTERFACES BETWEEN MASS SPECTROMETRY AND ART

Thomas Cairns and Ben B. Johnson

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CHEMISTS have long been aware of the limitations imposed on their studies by the limits of sensitivity of many of those currently available analytical methods which permit a number of elements to be determined in one sample, e.g. optical emission spectrographic techniques, x-ray fluorescence analysis. This has led to the adoption of more sensitive methods for a restricted number of elements, e.g. neutron activation analysis. More recently, spark source mass spectrometry has provided the analytical chemist with the ability to cover the full range of elements in any sample in a single determination and the ability to detect those elements down to very low concentrations, i.e. parts in 10^9 . The advent of this technique was the product of semi-conductor technology where 10 parts per billion (ppb) of copper in germanium or 2 ppb of gold in silicon is reflected in the electrical properties of those semi-conductors.

EXPERIMENTAL

The AEI MS702 Spark Source Mass Spectrometer in the Conservation Center of the Los Angeles County Museum of Art was purchased with a grant from the Samuel H. Kress Foundation. This instrument like most other mass spectrometers consists essentially of three parts which are housed in a highly evacuated system (Figure 1):

- (a) the source for ionizing the sample - a radio frequency

- spark;
- (b) The analyzer to separate these ions according to their mass to charge ratio (m/e) - a combination of both electrostatic and magnetic;
 - (c) the detector to record the position and intensity of the ions - a photographic plate.

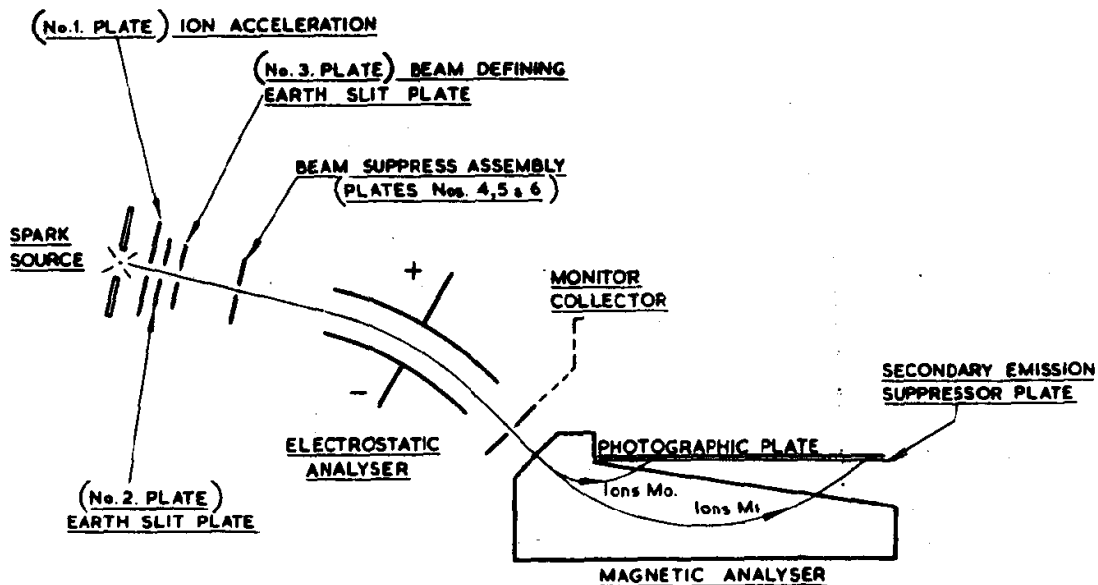


Figure 1. The AEI MS702 Spark Source Mass Spectrometer Schematic

A radio frequency (about one megacycle) voltage of several tens of kilovolts is applied in pulses across a small gap (a few thousandths of a centimeter) between the two sample electrodes in the source under high vacuum. The vacuum breakdown that occurs in this gap initiates an electrical vacuum discharge. The positive ions from this discharge which is representative of the sample under study are then accelerated through to the electrostatic analyzer, monitored and finally separated according to their m/e ratios. Usually a series of about fourteen graded

exposures (0.0001 nanocolumbs to 100 nC) per sample are recorded photographically on an Ilford Q2 plate.

With the radio frequency spark source, all elements are supposedly ionized with approximately equal sensitivity. Two factors must be taken into consideration; first that an ion beam with a large energy spread is produced, and secondly that the output from such a spark is somewhat variable. The large energy spread factor is overcome by using a double focusing instrument which gives the required resolution (3000) and the output variation from the mass spectrometer is corrected by using an integrator to measure the ion beam intensities. Advantages of the photo-plate method of detection are its simple integrating properties and the convenient record of the spectrum obtained.

SAMPLE PREPARATION

In the case of drillings taken from a cast bronze object or any other metallic artifact, electrodes (20 x 2 mm) can easily be formed by compressing such drillings in a specially designed polytetrafluoroethylene (PTFE) slug. Lack of sufficient material to form a whole electrode can be overcome by "topping up" with the necessary amount of ultra-pure silver powder. In many cases tipped electrodes such as these containing only a few milligrams can be prepared suitable for qualitative analysis.

Electrodes made by compressing pigment samples cannot be used because of their low electrical conductivity. The technique of incorporating a conducting powder must therefore be adopted. Silver powder and the sample are mixed together in a PTFE capsule, containing a pestle of the same material by means of a vibratory mixing machine. The resulting mixture is then compressed in the specially designed PTFE slug to form a solid electrode. Electrodes produced by this method have satisfactory mechanical strength and can be handled without difficulty.

More recently, in order to achieve very homogeneous electrodes the bronze drillings are dissolved in acid and then added to ultra-pure graphite powder. The resulting slurry is then taken to dryness and electrodes prepared in the normal manner. This new and novel technique can be used to prepare any concentration of the major components desired and so estimate them as if they were trace elements in the carbon matrix.

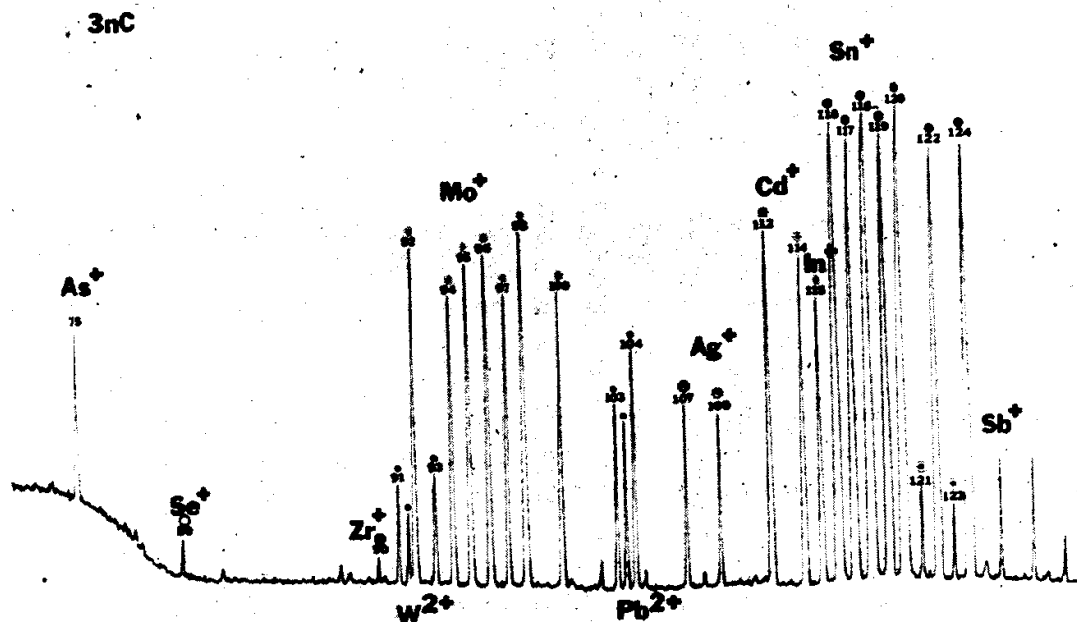


Figure 2b. Densitometer trace of 3nC exposure of a bronze sample over m/e 71 to m/e 130.

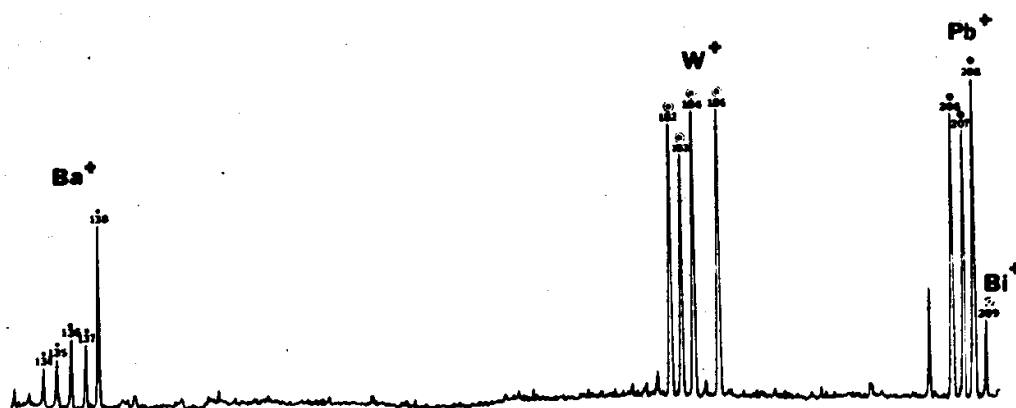


Figure 2c. Densitometer trace of 3nC exposure of a bronze sample over m/e 131 to m/e 210.

However, as the exposure is increased lines due to the lesser abundant components appear. At the 3nC level of exposure trace elements at the concentration level of 10 parts per million (ppm) are clearly visible, e. g. Bismuth at m/e 209 (Figure 2c).

- (b) Multiply-charged ions. Lines caused by multiply-charged ions are of much lesser intensity than those due

to the singly-charged species. In Figures 2a and 2b lines caused by the undermentioned multiply-charged ions can be seen - Cu^{2+} at m/e 31.5 and 32.5: Pb^{2+} at m/e 103.104.

The intensity of multiply-charged ions decreases with each degree of ionization (i. e. Pb^{3+} of less intensity than Pb^{2+}) and the ratio of intensities depends on the prevailing spark conditions.

- (c) Polyatomic ions. Polyatomic ions are usually a minor feature in most mass spectra, but carbon and silicon are exceptions to the rule.
- (d) Complex ions. Complex ions, composed of two or more different elements, are occasionally observed, in particular the types XO^+ and XOH^+ .

QUALITATIVE IDENTIFICATION OF ELEMENTS

Elements can usually be identified by their characteristic masses and isotopic patterns. In Figures 2b and 2c the elements Lead, Tin and Molybdenum may be identified by their characteristic groups of isotopes (Table 1) while the relative abundances of naturally occurring isotopes of these elements are given in Figure 3.

Table 1. Characteristic Isotopic Masses for Lead, Tin and Molybdenum

Element	Mass of isotopes
Lead	204, 206, 207, and 208
Tin	112, 114, 115, 116, 117, 118, 119, 120, 122, and 124
Molybdenum	92, 94, 95, 96, 97, 98, and 100

An element is reported as being present only when at least one of the following conditions is satisfied: