

Y 3. At7

AEC

RESEARCH REPORTS

221 y-1481

AEC RESEARCH AND DEVELOPMENT REPORT

Y-1481

Chemistry

SPARK-SOURCE MASS SPECTROMETRIC ANALYSIS
OF COMMON AND RADIOGENIC
LEAD

J. C. Franklin
E. B. Griffin

Y-12 PLANT
Oak Ridge, Tennessee

**UNION
CARBIDE**

UNION CARBIDE CORPORATION
NUCLEAR DIVISION

Operating the

- OAK RIDGE GASEOUS DIFFUSION PLANT
- OAK RIDGE Y-12 PLANT
- OAK RIDGE NATIONAL LABORATORY
- PADUCAH GASEOUS DIFFUSION PLANT

*For the Atomic Energy Commission
Under U.S. Government Contract W7405 eng 26*

UNIVERSITY OF
ARIZONA LIBRARY
Docu

metadc173338

Printed in USA. Price \$1.00. Available from the Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U.S. Department of Commerce, Springfield, Virginia

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Date Issued: June 11, 1965

Report Number Y-1481

Chemistry
TID-4500 (39th Edition)

UNION CARBIDE CORPORATION
Nuclear Division

Y-12 PLANT

Contract W-7405-eng-26
With the US Atomic Energy Commission

SPARK-SOURCE MASS SPECTROMETRIC ANALYSIS OF
COMMON AND RADIOGENIC LEAD

J. C. Franklin
E. B. Griffin

Oak Ridge, Tennessee
February 25, 1965

Report Number Y-1481Chemistry
TID-4500 (39th Edition)

Distribution:

Bailey, E. W.
Ballenger, H. F. (2)
Bell, B. B.
Bernander, N. K.
Briscoe, O. W.
Burkhart, L. E.
Center, C. E. (ORGDP)
Cowen, D. D. (ORNL)
Franklin, J. C. (8)
Griffin, E. B. (8)
Harwell, W. L. (ORGDP)(5)
Hemphill, L. F.
Huber, A. P. (ORGDP)
Keller, C. A. (AEC-ORO)(4)
Lewis, F. O. (ORGDP)
McLendon, J. D.
Mitchel, G. W.
Patton, F. S.
Whitson, W. K.
Winkel, R. A. (Paducah)
Y-12 Central Files (5)
Y-12 Central Files (Y-12RC)

In addition, this report is distributed in accordance with the category Chemistry, as given in the "USAEC Standard Distribution Lists for Unclassified Scientific and Technical Reports", TID-4500 (39th Edition), February 1, 1965.

ABSTRACT

Spark-source mass spectrography has been utilized to provide a method of analysis that is fast and has extremely low levels of detection for more than forty elements that may be present in lead.

CONTENTS

INTRODUCTION	5
SUMMARY	6
EXPERIMENTAL PROCEDURE	7
Discussion	7
Sample Preparation	8
CONCLUSIONS	10

INTRODUCTION

An Associated Electrical Industries MS-7 spark-source mass spectrograph is used in the analysis of metal samples for low levels of impurities. The samples are made into electrodes by machining, if necessary, or by support with tantalum clamps, or by twisting into a "cable" if the samples are fine. The samples are then vaporized with an approximately 40-kv RF spark to generate positive ions. These ions in the atomic-mass range between 8 - 270 are collected on a 2 by 10-inch Ilford Q-2 photographic plate. The ion beam is partially intercepted by a series of collimating slits so that 50% of the beam is accumulated by an electronic integrator and the remaining 50% is collected on the photographic plate. This combination of methods of recording ion-beam intensity enables subsequent concentration calculations to be performed.

SUMMARY

The spark-source method of mass spectrography provides a fast and extremely sensitive method of analysis for detecting more than 40 impurities in lead samples. No special sample preparation is required and samples in various forms can be handled.

EXPERIMENTAL PROCEDURE

DISCUSSION

Degreasing in methyl chloroform followed by acetone is the only sample preparation that is required. (a) This degreasing is followed by two 1-minute etchings in nitric acid. The samples are rinsed between each acid bath with deionized water ($\gg 1,000,000$ ohm; $\ll 0.1$ ppm NaCl). The final cleaning consists of three 5-minute rinses in running deionized water. Next, the samples are loaded wet into the instrument, the source is evacuated to 1×10^{-7} mm Hg or less, and the samples are presparked to remove any remaining surface impurities. Finally, a series of graded exposures are made.

The minimum exposure recorded has been 1×10^{-4} millimicrocoulombs (muc) and the maximum 1×10^2 muc. This exposure range of 10^6 for each sample yields a lower detection limit of about 0.01 ppm atomic when allowances are made for the isotopic composition of different elements. The limits vary from sample to sample but, in general, they are between 0.01 and 0.05 ppm atomic. The methods of calculation may be summarized in two equations:

$$\text{Plate Sensitivity (PS)} = \frac{E_{\min}}{E_{\max}} \times \frac{\% A}{100} \times \frac{\% I}{100} \times 10^6, \quad (1)$$

where:

E_{\min} is the minimum detectable exposure in millimicrocoulombs for the chosen internal standard isotope,

E_{\max} is the maximum exposure on the plate in millimicrocoulombs,

$\% A$ is the atomic percent of the element used as the standard ($\% A/100$ is usually 1), and

$\% I$ is the isotopic abundance of the standard.

$$\text{Element Concentration} = \text{PS} \times \frac{E_{\max}}{E_{\det}}, \quad (2)$$

where:

(a) Both are Mallinkrodt TransistAR-grade solvents.

E_{\max} is the same as before, and

E_{\det} is the minimum exposure in millimicrocoulombs at which the element in question is detected.

SAMPLE PREPARATION

When necessary, rod-like samples are machined to the desired size and then loaded into the sample holders which are simple clamps. Turnings or fine wire are twisted into a "cable" about one-eighth inch in diameter and this is clamped into the ion source. Small chunks of sample are supported by drilling and tapping on the back side of the sample and then mounted on a screw.

The following samples have been analyzed:

1. A common lead rod sample about one-eighth inch in diameter and 1.5 inches long.
2. Two radiogenic lead samples in the form of turnings from a larger body and four common lead samples of turnings.

The values obtained for the five common lead samples (A, B, C, D, E) are listed in Table 1. Concentrations in the table are given in parts per million on a metal weight basis.

In Table 1 and in those to follow, if a value is reported as $< (-)$ it means that on the most abundant isotope of that element no line was detected at the maximum exposure made on that plate.

In these samples, all concentrations are obtained by visual estimation of line densities and comparison with the Pb-204 isotope as an internal standard. The values are considered to be within a factor of two of the actual values.

In Table 2, two radiogenic lead samples are reported. In these samples the isotopic composition was such that the Pb-204 isotope provided a standard at approximately 0.04 and 0.05 atom percent.

At a later date, Samples A through G were analyzed by a conventional emission spectrographic method. These values are reported in Table 3.

CONCLUSIONS

The mass spectrograph is shown to be a valuable analytical tool for the estimation of trace impurities in lead even at the parts-per-billion range, using only a minor isotope as an internal standard. The data given from the analysis of these same samples by more conventional methods provide some indication of the reliability and accuracy of the spark-source method of analysis.

A comparison of the two methods of analysis is of interest. The emission spectrographic values were obtained by visual estimation and comparison with prepared standards, while the data from the mass spectrograph were obtained using a minor isotope as an internal standard.

The most striking feature of a comparison of the two methods is that 81% of the values reported by emission work are "less than" values with no value supplied.

There are differences in the two methods for some elements (Sb and Ag) but there are also excellent agreements (Fe, Cu, Ni, Au, Bi).

The lower limit of detection for the spark-source method is from 40 to 2000 times lower than that for the emission spectrographic procedure for all the 16 elements reported (Table 3). The spark source also detects 24 elements that are not seen by the conventional method.

The data given on these comparisons of the two methods show that the spark-source mass spectrograph is a valuable analytical tool for the estimation of impurities in lead and other metals at the parts-per-billion to parts-per-million concentration ranges. The method is fast, versatile, and has reasonable accuracy and reliability, particularly for low concentrations.

