

A SPECTROGRAPHIC METHOD FOR DETERMINING TRACE AMOUNTS OF LEAD IN ZIRCON AND OTHER MINERALS*

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ABSTRACT

Trace amounts of lead in zircon and in some other minerals have been spectrographically determined by the U. S. Geological Survey to provide data in a study of the age of the rocks that contained these particular minerals. Approximately 150 determinations have been made, and one reproducibility test (consisting of 25 observations) has been completed. The material used for the reproducibility test was a silica-base standard containing 30 ppm. lead. The average of the results was 30.4 ppm. lead. On the whole, standard spectrographic procedures were applied, including the split-filter method for calibrating the photographic emulsions.

The method is applicable to samples containing from 0.5 to 1,000 ppm. lead with an estimated accuracy of 6 to 10 per cent. No chemical separations or concentrations are required. The other minerals tested by the method are apatite, sphene, microlite, allanite, and perthite.

INTRODUCTION

The work of E. S. Larsen, Jr., (1952) in using the accessory minerals of granite to determine geologic age is based on ascertaining total radioactivity and total lead. This necessitated a precise and sensitive spectrographic method for the determination of lead in zircon and in other minerals and resulted in the development of a method that is sensitive to as little as 0.5 ppm. lead. To a great extent standard spectrographic procedures have been applied.

Various fluxes, sample weights, types of standards, electrodes, power sources, spectrographic emulsion types, and spectrographs were used in developing the method. The problem revolved around two difficulties, one of which was lead impurities in the chemicals and electrodes (especially in copper electrodes), and the other, the insensitivity of lead in very low concentrations. These problems were solved by systematic elimination and trial-and-error procedures. It was found that, using commercially available special graphite spectroscopic electrodes, an alkaline vapor (sodium carbonate) with type II-O Eastman spectrographic emulsion would record the 2833.1 Å line at a concentration of 0.5 ppm.

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PROCEDURE

A method is provided for determining the lead content of zircon samples in the range of 0.5 to 1,000 ppm. lead. It is thought that higher percentages of lead can be determined by applying the same procedure but with changes in transmission and line selection.

The method involves weighing a 12.5 mg. sample, mixing with three parts by weight of sodium carbonate, subjecting the sample and suitable standards to d-c arc excitation in the special graphite spectroscopic electrodes, processing the plate, reading with the densitometer, calibrating the emulsion, and making final calculations.

Apparatus

Excitation source	Multisource d-c arc.
Spectrograph	21-foot Wadsworth-mounted grating, dispersion 5 Å per mm. in the first order.
Intensity control	Neutral filters and split filter (stainless steel on quartz).
Developing equipment	Rocking developing tank, plate washer, and drier.
Electrode cutters	A. Lower electrodes, designed to cut $\frac{1}{4}$ -in. electrodes (outside diameter 0.22 in., inside diameter 0.19 in., depth of crater 0.24 in., depth of shoulder 0.24 in.). National special graphite spectroscopic electrodes. B. Upper electrodes, hemispherical 0.06-in. radius. National special graphite spectroscopic electrodes.
Densitometer	Nonrecording or recording.

Preparation of standards

Standards were prepared by adding solutions of pure lead nitrate to a lead-free base material (silicic acid). The mixtures were evaporated to dryness in platinum crucibles and ground in a boron carbide mortar to pass 100-mesh stainless-steel screen. The material was mixed by passing it through an 80-mesh stainless-steel screen approximately 15 times. The standards were prepared to contain the following concentrations of lead in parts per million: 1, 5, 15, 30, 50, 75, 100, 200, 500, 750, and 1,000. A blank of the base material was similarly processed to determine whether it was contaminated with lead.

A mixture of sodium carbonate and lead-free bismuth, as internal standard, was added to mineral samples, which were then excited in an alkali vapor. This mixture was prepared by adding 0.1 per cent bismuth¹ (or 0.05 per cent bismuth for determining low percentages of lead) to approximately 2 g. lead-free sodium carbonate (Sandell, 1944), and this was processed in the same manner as the standards. The electrodes were loaded with a mixture consisting of 12.5 mg. of the standard and 37.5 mg. of the sodium carbonate and bismuth mixture.

¹ Prepared by dissolving pure bismuth metal in lead-free nitric acid.

The mineral samples were ground in a boron carbide mortar to pass 100-mesh stainless-steel screen. In arcing, the loaded electrode contained 12.5 mg. of sample and 37.5 mg. of the sodium carbonate and bismuth mixture.

ANALYSIS OF UNKNOWNNS

The samples and suitable standards were placed in the electrode cups (positive) with the aid of a special glass funnel. The electrodes were arced for a period of 120 seconds, and the gap held constant at 6 mm. by manual adjustments. The following multisource conditions and photographic procedures were used:

Capacitance	60 microfarads
Inductance	400 microhenries
Resistance	15 ohms
Initiator	High
Phase	0
Strike	Strike position
Amperes	12 (± 0.5) (d-c arc)
Spectrograph	21-ft Wadsworth-mounted grating
Emulsion	SA-1 (Eastman)
Photographic development	4 minutes at 18° C. ± 0.5 , D-19
Slit	50 microns
Volts	300
Intensity control	Variable
Electrodes	Special graphite spectrographic electrodes

After the plates were processed the transmission values of the following lines were read by applying the nonrecording or recording densitometers:

<i>Bismuth</i> (Å)	<i>Lead</i> (Å)
2938.3	2833.1
2898.0	2823.2
	2802.0
	2663.2
	2614.2

After numerous tests the lead line 2833.1 Å and bismuth line 2898.0 Å were selected for use because these lines approach homologous-pair conditions.

Emulsion calibration

In calibrating the emulsion a two-step method was used. Similar methods, in which a split filter has been substituted for the rotating sector, have been described by Harvey (1950) and Churchill (1944). The split filter (stainless steel on quartz) is an improvement over the step sector because it minimizes or eliminates such well-known disadvantages as stroboscopic, intermittency, and target effects, which are prevalent in the step-sector method.

Calculations

The working curves prepared from the standards served as a check on the standards but were not used in the calculations of final results. The standards indicated reliability by the straightness of the line drawn through the points that were obtained by plotting the relative intensity against the logarithm of the lead concentrations.

By preliminary survey the parts per million of lead were estimated. Standards to bracket the lead content of the samples and the samples themselves were exposed on the same plate. The parts per million of lead were then calculated, employing the x and y coordinates of the relative intensities versus parts per million of lead. This method of calculation has the advantage of using on the same plate a short section of a curve with samples closely bracketed by standards.

TABLE 1. REPRODUCIBILITY DATA ON 30-PPM. LEAD IN SILICA BASE

Observation	Lead ppm.	Difference
1	31	1
2	30	0
3	33	3
4	30	0
5	34	4
6	30	0
7	29	1
8	30	0
9	28	2
10	28	2
11	28	2
12	29	1
13	30	0
14	30	0
15	32	2
16	28	2
17	31	1
18	30	0
19	35	5
20	32	2
21	30	0
22	29	1
23	30	0
24	31	1
25	32	2

No background corrections were necessary, as the background at the lead and bismuth lines was insignificant.

Reproducibility of results

Few data have been collected on the reproducibility of the results obtained by the method. The data on one test, consisting of 25 observations of the 30 ppm. lead standard in silica base, are shown in Table 1. The maximum variation is 5 ppm. lead in 1 observation, and there was no variation in 9 observations. The average of the 25 observations is 30.4 ppm. lead.

Reproducibility of results of lead determinations made at different times is shown in Table 2.

TABLE 2. REPRODUCIBILITY OF RESULTS OF LEAD DETERMINATIONS ON SOME OF THE ZIRCON SAMPLES

Sample no.	Parts per million of lead			
	1st run	2d run	3d run	4th run
Z- 1	86	89		
Z- 3	40	38		
Z- 5	50	49		
Z- 6	33	27	28	33
Z- 7	35			
Z- 8	18			
Z- 9	25	24	23	
Z-11	130	121	127	
Z-40	3			
Z-42	4			

A comparison of lead determinations made by the isotope dilution method, developed by Harrison Brown and his associates (personal communication), and by the method described in this paper gives the following results:

Minerals from Tory Hill, Haliburton area, Ontario	Lead (ppm.)	
	Isotope dilution	Spectrographic
Zircon	461	{ 462
Perthite	9.5	{ 437
Sphene	240	{ 5
		{ 245

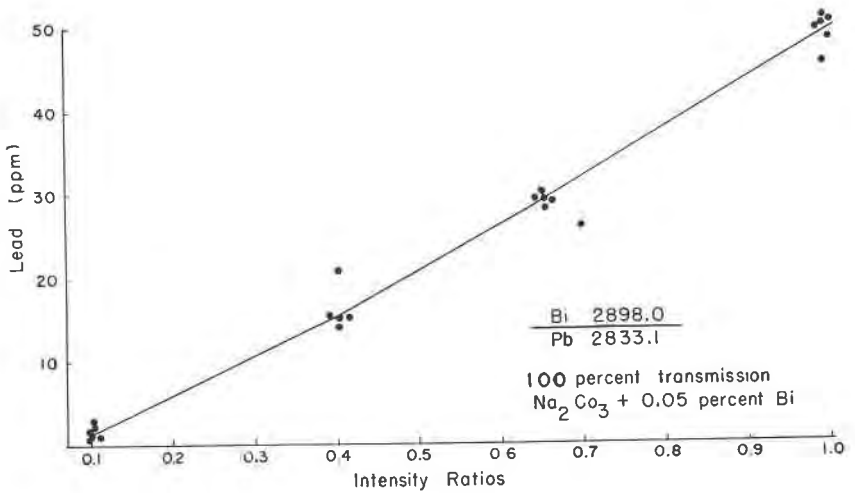


FIG. 1. Working curve for lead in zircon, applied in the range of 1 to 50 ppm. of lead.

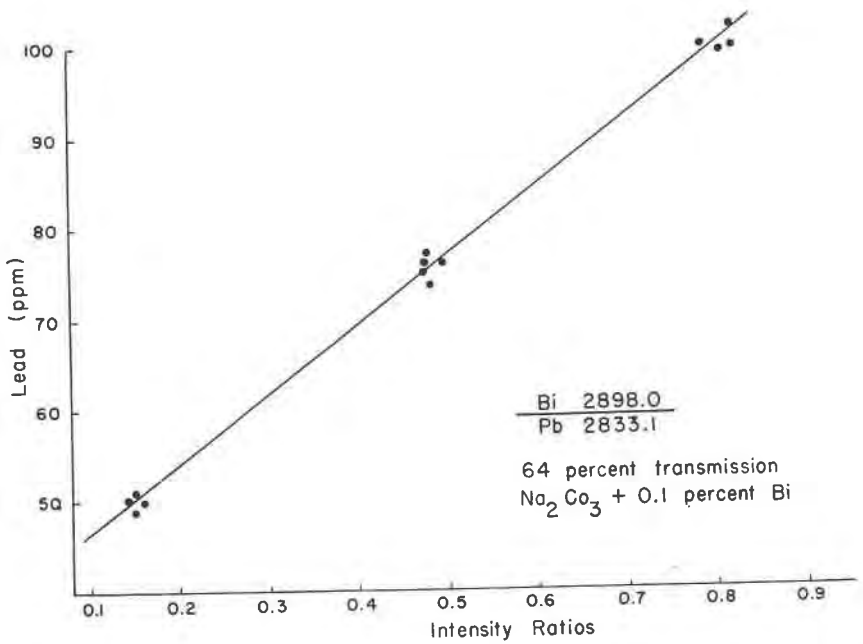


FIG. 2. Working curve for lead in zircon, applied in the range of 50 to 100 ppm. of lead.

It is hoped that microchemical and mass spectrographic techniques will be developed to provide further checks on this method. The precision of the method is estimated to be 6 to 10 per cent.

DISCUSSION

During the course of the analysis it was thought that certain lead results on zircon samples might be high. A microscopic examination of the samples showed foreign particles. Spectroscopic inspection of these particles indicated a high percentage of lead. As the lead in the zircon crystals was of primary interest, it became necessary to treat the samples with dilute aqua regia (1:1) to remove the foreign particles of high lead content that occurred naturally in the samples. This treatment with aqua regia is still in the experimental stage, but it will probably become a part of the standard procedures because it has yielded encouraging results.

Figures 1 and 2 are typical examples of working curves obtained by the described method. Some acceptable curves were also obtained by plotting transmission against lead (in parts per million); this leaves some doubt as to the necessity of an internal standard. Additional tests will be conducted before any conclusions are drawn.

As the chances of contamination are great, the method was designed to reduce the handling of samples to a minimum. It was found that grinding a sample in the agate mortar added a few parts per million of lead to the sample, but grinding a sample in a boron carbide mortar gave no lead contamination. Lead contamination was not detected from the stainless-steel screens, but screening through nylon cloth added a few parts per million of lead.

The d-c arc supplied by the multisource was selected for the tests because of its high degree of sensitivity with the added advantage of simple operation. It is probable that other excitation sources would also produce this sensitivity and could be applied to the trace lead determinations.

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