THE AMERICAN MINERALOGIST, VOL. 45, NOVEMBER-DECEMBER, 1960

# SPECTROCHEMICAL DETERMINATION OF LEAD IN ZIRCON FOR LEAD-ALPHA AGE MEASUREMENTS*

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## ABSTRACT

A spectrochemical method is described for determining lead in zircon. A synthetic "zircon" standard is used to cover a range of concentration between 1 and 560 ppm. The method is designed for use in lead-alpha age measurements. Results of the analysis of 22 zircons indicate an overall 5% average deviation from isotope dilution and chemical values. This method differs from a spectrochemical method described previously in the composition of the standards and in the use of a full set of standards in preference to bracketing the samples.

## INTRODUCTION

The lead-alpha method for the determination of the geologic age of igneous rocks was described by Larsen, Keevil, and Harrison (1952). The age calculation is based on the determination of the lead content and alpha activity of certain accessory minerals, particularly zircon, separated from the rocks. A spectrochemical method was described by Waring and Worthing (1953) for determining lead in zircon and other minerals. These authors have since 1953 used opal glass (National Bureau of Standards, standard sample 91) diluted in silica as a lead standard (Gottfried, Jaffe, and Senftle, 1959). Until recently an evaluation of the accuracy of the method could not be made owing to the few available comparison analyses by independent techniques. Webber, Hurley, and Fairbairn (1956) reported lead values higher than results determined by C. L. Waring on four samples of zircon, but discarded the higher lead values. Some serious discrepancies between the spectrochemical lead values and the lead values determined by isotope dilution were noted by Gottfried, Jaffe, and Senftle (1959). A comparison of the spectrochemical results by the method of Waring and Worthing with the lead values determined by isotope dilution is given in Table 1. The variation in values ranges between 0.92 and 2.36 when expressed as the ratio of the isotope dilution values to the spectrochemical values. For reconnaissance age determinations, the agreement between five of the samples can be considered reasonably good, but the remaining samples indicate a bias greater than the precision of the spectrochemical method.

The magnitude of the differences between the lead values obtained by the two techniques prompted an interlaboratory study to determine the nature of the variation. This study includes an investigation of the behavior of zircon in the d-c arc, the preparation of a standard having arc-

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* Publication authorized by the Director, U. S. Geological Survey.

ing properties similar to the natural mineral, and a comparison of the determination of lead in 20 zircon samples by the method of Waring and Worthing (1953) and by the method described in this report.

## SPECTROGRAPHIC EQUIPMENT

A grating spectrograph with Wadsworth mounting is used with a 15,000 lines-per-inch grating having a dispersion of 5.0 Å per mm. in the first order. A 250 volt direct current motor generator is used to provide a current of 15 amperes during arcing of the sample. The current is controlled by a series resistance capable of providing current adjustments of 0.5 ampere. The resistance circuit is wired through a shorting switch that changes the amount of resistance and instantaneously increases the current from 5 to 15 amperes.

TABLE 1. COMPARISON OF SPECTROCHEMICAL VALUES (OPAL GLASS STANDARD) WITH ISOTOPE DILUTION RESULTS

| Sample | Spectrochemical[a] lead (ppm.) | Isotope dilution lead (ppm.) | Isotope dilution: Spectrochemical ratios |
|---|---|---|---|
| N-7 Oslo | 19 | 17.5[b] | 0.92 |
| S-2 Wemback | 31 | 46[b] | 1.48 |
| M-51 Cranberry gneiss | 39 | 59.5[c] | 1.53 |
| S-10 Halbmeil | 28 | 47[b] | 1.68 |
| B-4 Baltimore gneiss | 93.5 | 104[c] | 1.11 |
| 6-37 Natural Bridge[d] | 66.5 | 127[c] | 1.91 |
| S-7 Martinskapelle | 69 | 163[b] | 2.36 |
| Storm King | 346 | 337[c] | .97 |
| Wichita Mountains[d] | 351 | 376[c] | 1.07 |
| Z-22 Essonville[d] | 433 | 461[c] | 1.06 |
| SQ-81 Mountain Pass[e] | 1140 | 1760[c] | 1.54 |

[a] Analyses by Helen Worthing using method of Waring and Worthing (1953). National Bureau of Standards, standard sample 91, opal glass, diluted in silica as standard. The values reported are averages of all determinations.

[b] Isotope dilution by Henry Faul, U. S. Geological Survey, Washington, D. C.

[c] Isotope dilution by G. R. Tilton, Geophysical Laboratory of the Carnegie Institute of Washington.

[d] Gottfried, Jaffe, and Senftle (1959, p. 35).

[e] Gottfried, Jaffe, and Senftle (1959, p. 25).

A series of neutral filters is used in the optical path to control the amount of light entering the slit. Spectra are recorded on a 10-inch Eastman type III-O plate (10–560 ppm. lead) or Eastman type II-O plate (1–40 ppm. lead).

Open trays are used for developing and fixing solutions with continuous agitation. The temperature is maintained at 20° C. The emulsion is washed in running water and dried by a stream of warm air.

The transmittances of iron calibration lines and the lead line in standards and samples are measured with a projection comparator-microphotometer using a scanning slit at the plate.

## STANDARD SAMPLES

A synthetic "zircon" was prepared by thoroughly grinding together a high-lead glass, zirconia, and silica glass in proportions that were equivalent to the composition of zircon containing 5% lead. The mixture was sealed in a platinum crucible that was welded shut and heated to a temperature of 1450° C. for 12 hours in a platinum-wound electric furnace. After the material was cooled and mixed thoroughly by grinding in a boron carbide mortar a portion was analyzed chemically; gravimetric and colorimetric analyses by Frank Cuttitta of the U. S. Geological Survey of the material used in this study was found to contain 4.60% lead. Mineralogical and *x*-ray diffraction examination by D. B. Stewart and B. J. Skinner of the U. S. Geological Survey of a material prepared as described above revealed a mixture containing zircon, the high-temperature form of zirconia (baddeleyite), and a silicate glass. Although differential solution studies by Frank Cuttitta of the U. S. Geological Survey suggest that more than 90% of the lead was in the silicate glass, moving plate studies indicate that the volatilization pattern of lead from the synthetic "zircon" mixture was identical with the pattern established for the natural mineral.

A series of standards is prepared by diluting the synthetic "zircon" mixture with lead-free zircon base (68% zirconia and 32% silica) to cover a range of lead concentration from 1 to 560 ppm. A step-wise dilution of the lead by a factor of 0.562 is recommended to provide points sufficiently close to characterize the analytical curve. At each level the standard and zircon base are thoroughly mixed by hand grinding in a boron carbide mortar for half an hour.

Most sources of zirconia contain a few parts per million lead which requires a correction in the assigned lead content of the standard. We were fortunate in obtaining zirconia from the U. S. Bureau of Mines that contained less than one part per million lead. The source of silica is a ground silica glass (Corning glass no. 7940 lump cullet) that has no detectable lead.

## PREPARATION OF SAMPLE

The concentration of zircon from the rock prior to spectrochemical analysis is a specialized operation. The final yield of zircon is extremely small when compared to the initial rock sample. The general procedure, simply outlined, requires breaking up the rock in a jaw crusher and feeding the resultant chips into a roller-type grinder and passing the ground material through a 50-mesh sieve. The sample that passes through the sieve is concentrated over a Wilfley shaking table (Gottfried et al., 1959) for bulk removal of light-weight minerals (principally quartz and the feldspars). The heavy mineral fraction is passed through the Frantz isodynamic magnetic separator to remove the ferromagnetic minerals.

The sample is then further fractionated by treatment with bromoform and methylene iodide, and the heavier mineral fraction is passed through the magnetic separator repeatedly raising the current in small increments before each pass. The current at which the zircon will concentrate varies considerably for the metamict varieties. Fresh zircon concentrates as a nonmagnetic fraction.

The zircon-rich fraction is normally leached with hot concentrated nitric acid for 20 minutes to remove pyrite and apatite which may have been concentrated with the zircon.

The last and most important operation is a petrographic examination, accompanied by hand-picking to remove the last traces of impurities. The pure sample is ground in a boron carbide mortar to a very fine powder.

Fifteen milligrams of the sample is then mixed with 35 mg. of sodium carbonate and transferred to the electrode in the same manner as are the standards. Occasionally a sample will be submitted that has a lead content higher than the range of the standards. Such a sample is diluted with zircon base to bring it within the range.

## ELECTRODE SYSTEM

The lower sample-carrying electrode (anode) is a $\frac{1}{4}$ inch diameter pure graphite rod $1\frac{5}{8}$ inches in length with a cup at one end. The crater has a 0.144 inch inner diameter and a 0.020 inch wall thickness and has a depth of 0.238 inches with a 60° truncated cone ending in a 0.031 inch diameter base.

The upper electrode (cathode) is a pure $\frac{1}{8}$ inch graphite rod.

## EXCITATION

The samples and standards are arced so that single exposures of each are recorded consecutively in the upper part of the plate. An iron calibration spectrum is then recorded in the center of the plate. The same order of exposure of samples and standards initially recorded is repeated.

The samples and standards are arced in the above exposure pattern at an initial current of 5 amperes for 10 seconds. The current is then instantaneously raised to 15 amperes by a shorting switch that changes the amount of series resistance. The arc is continued for 80 seconds at 15 amperes. During this time the lead evolves, and the relatively low temperature of the sodium vapor prevents the zirconia from entering the arc.

An iron bead is arced at 5 amperes for 120 seconds through a 50 per cent two-step quartz filter at the slit. The resultant two-step spectra is used to calibrate the emulsion. To obtain more reproducible spectra from plate to plate, the iron bead should be subjected to a 2-minute preburn period.

Exposure conditions

The exposure conditions are given below:

| | |
|---|---|
| Spectral region, Angstroms | 2230–3480 |
| Slit width, microns | 25 |
| Slit height | 2 mm. for samples and standards,<br>4 mm. for iron bead exposures. |
| Image | Focus on grating |
| Arc preburn | None |
| Arc exposure | 10 seconds at 5 amp.<br>80 seconds at 15 amp. |

The exposure is adjusted to maintain the transmittance of Pb 2833.07 Å at 30 ppm. at approximately 60 per cent. An Eastman type III-O plate is used to give an effective lead concentration range between 10 and 560 ppm. The exposure may be adjusted by use of neutral filters in the optical path.

For low concentrations of lead the exposure conditions are adjusted to maintain a transmittance of approximately 50 per cent for Pb 2833.07 Å at a concentration of 5 ppm. lead. An Eastman type II-O plate is used for low concentration lead determinations between 1 and 40 ppm. lead. The exposure conditions for the two-step iron bead calibration are adjusted for each type plate to maintain a transmittance of approximately 20 per cent for Fe 3175.45 in the filtered step.

## EMULSION CALIBRATION

Calibration is accomplished by the two-step method (Harvey, 1950). The method is a modification of the procedure proposed by Churchill (1944). The series of homologous iron lines selected for calibration (Hodge, 1951) given below are convenient for this purpose.

Iron calibration lines, Å

| Fe | Fe |
|---|---|
| 3157.04 | 3205.40 |
| 3157.88 | 3207.09 |
| 3165.01 | 3215.94 |
| 3165.86 | 3217.34 |
| 3168.86 | 3230.97 |
| 3175.45 | 3248.20 |

The preliminary curve is established by plotting on log-log paper the per cent transmission of the lighter step of a given line as ordinate against the corresponding per cent transmission of the darker step as abscissa. The two steps of each spectral line obtained from a two-step filter give a single point. In like manner, points are plotted for each of the iron lines listed above.

The best curve is drawn through the points. The highest reliable point of the ordinate is selected from the preliminary curve, its value and its corresponding abscissa value are recorded. Using the abscissa value as the ordinate, its corresponding abscissa value is recorded, thus working down the curve recording all values to the end of the preliminary curve.

The emulsion calibration curve is established by plotting directly on log-log paper the above recorded values as ordinates against intensities as abscissa in intervals equal to the step ratio of the two-step filter. A two-step filter with a step ratio of approximately 1.50 is recommended; its exact ratio can be determined photometrically. For a 1.50 step ratio the interval points are 1.00, 1.50, $(1.50)^2$, $(1.50)^3$, $(1.50)^4 \ldots (1.50)^n$. A line drawn through these points constitutes the calibration curve.

## PHOTOGRAPHIC PROCESSING

The photographic processing procedure is altered slightly with a change in the emulsion.

| | |
|---|---|
| Emulsion | Eastman Type III-O<br>Eastman Type II-O |
| Development | Eastman D-19 with continuous agitation at 20° C. Type III-O for 5 minutes,<br>Type II-O for 3 minutes |
| Fixing | Eastman acid fixer, 6 minutes at 20° C. |
| Washing | Running water at 20° C. for 10 minutes |
| Drying | Blower-heater |

## PHOTOMETRY

Transmittance measurements for the Pb 2833.07 Å line and the iron lines for calibrating the emulsion are made on a projection comparator-microphotometer. No background correction is made for the high range emulsion (Type III-O). The low-range emulsion (Type II-O) requires a full background correction. The transmittances of the lead line are converted to relative intensities by means of the plate calibration curve. Where applicable, background transmittances are converted to relative intensities and subtracted from the line intensities. The standard samples serve to establish an analytical curve relating log intensity to log concentration. The intensities of the analytical lines of the unknown samples are converted to concentrations by reference to the analytical curve.

## PRECISION

The precision of this method is illustrated by the following data:

| Sample | Average conc. % | Coefficient of variation | Number of determinations |
|---|---|---|---|
| ZS-9 | 0.0306 | 4.9 | 10 |
| ZS-10 | 0.0048 | 3.5 | 8 |
| SR-1 | 0.00020 | 11.0 | 6 |

The coefficient of variation is calculated by the following formula:

$$\nu = \frac{100}{C}\sqrt{\frac{\Sigma d^2}{n-1}}$$

where

$C$ = average concentration, in per cent
$d$ = difference of the determination from the mean, and
$n$ = number of determinations.

## ACCURACY

A measure of the accuracy is obtained by comparing the spectrochemical results with those obtained by other techniques, most commonly by isotope dilution. The spectrochemical values gave an overall average deviation of less than 5 per cent. Table 2 gives data on 22 samples which were submitted as unknowns. The data given in the table are shown graphically in Fig. 1 by relating the spectrochemical lead values with the lead values obtained by isotope dilution and chemical analysis. Also shown in Fig. 1 is a comparison between the spectrochemical lead values obtained by the method of Waring and Worthing (Tables 1 and 3) with the lead values obtained by independent techniques.

## DISCUSSION

To determine the variation between the lead analyses by the method described here and the method of Waring and Worthing (1953), 20 zircons were analyzed by both methods. The results are given in Table 3. The 20 test samples were later revealed to be duplicate splits of each of 10 zircons. Six of the 10 samples were composites of 2 zircons prepared in the proportions given in the table. In addition to an analysis value, each composite sample has a value calculated by totaling the lead contribution of each component.

TABLE 2. COMPARISON OF SPECTROCHEMICAL (SYNTHETIC "ZIRCON" STANDARDS) LEAD ANALYSES WITH ISOTOPE DILUTION AND CHEMICAL RESULTS

| Sample No. | Description | Spectro-chemical[a] | Isotope dilution[b] | Chemical[c] | Chemical | Isotope dilution |
|---|---|---|---|---|---|---|
| | | Lead ppm. | Lead ppm. | Lead ppm. | Spectro-chemical | Spectro-chemical |
| ZS-10 | Zircon from syenite at Old Whitestone Farm, 1 mile east of Natural Bridge, N. Y. Collected by Arthur Montgomery. | 48 | | 47 | .98 | |
| ZS-6 | Zircon from a pegmatite, Pacoima Canyon, San Gabriel Mts., Calif. Collected by G. J. Neuerburg. | 33 | 35 | | | 1.06 |
| ZS-9 | Zircon from pegmatite, Quanah Mt., Okla. Collected by F. L. Hess and R. L. Dott. | 303 | 313 | 275 | .91 | 1.03 |
| NBS-197 | Zircon from beach sand, Jacksonville, Fla. National Bureau of Standards zircon ore sample. | 34 | | 34 | 1.00 | |
| ZS-4 | Zircon. A mixture containing 68% ZS-6 and 32% ZS-10. | 38 | | 38 | 1.00 | |
| ZS-12 | Zircon. A mixture containing 32% ZS-9 and 68% ZS-6. | 117 | | 109 | .93 | |
| S-10 | Zircon from granite, Halbmeil, Schwarzwald. Collected by Henry Faul. | 43 | 47 | | | 1.09 |
| N-7 | Zircon from Oslo nordmarkite, Oslo region, Norway. Collected by Henry Faul. | 18 | 18 | | | 1.00 |
| S-7 | Zircon from granite, Martinskapelle, Schwarzwald. Collected by Henry Faul. | 152 | 163 | | | 1.07 |
| G-5 | Zircon from Wilson Creek gneiss, Mortimer, N. C. Collected by G. R. Tilton. | 168 | 160 | | | .95 |
| SK | Zircon from Storm King granite, Bear Mt., N. Y. Collected by G. R. Tilton. | 335 | 337 | | | 1.01 |
| P-16 | Zircon from Baltimore gneiss, Spring Mill, Pa. Collected by G. R. Tilton. | 187 | 168 | | | .90 |
| Hybla | Zircon. Cyrtolite McDonald mine, Hybla, Ontario. Collected by G. R. Tilton. | 970[d] | 1045 | | | 1.08 |

[a] Lead values represent an average of all determinations.

[b] Isotope dilution analyses as follows: ZS-6 and R-200 by L. T. Silver, Calif. Inst. of Tech.; ZS-9, L. R. Stieff, U. S. Geological Survey; S-10, and S-7, by Henry Faul, U. S. Geological Survey. All other samples by G. R. Tilton of the Geophysical Laboratory, Carnegie Inst. of Wash., D. C.

[c] Chemical analysis of samples SQ-81 and 52Mt8 by R. A. Powell, U. S. Geological Survey. Other chemical analyses by Frank Cuttitta, U. S. Geological Survey.

[d] Samples diluted with 8 parts zircon base (68% $ZrO_2$ and 32% $SiO_2$)

TABLE 2 (*Continued*)

| Sample No. | Description | Spectro-chemical[a] | Isotope dilution[b] | Chemical[c] | Chemical | Isotope dilution |
|---|---|---|---|---|---|---|
| | | Lead ppm. | Lead ppm. | Lead ppm. | Spectro-chemical | Spectro-chemical |
| 52Mt8 | Monazite from placer, Warren Creek, tributary of Salmon River near Warren, Idaho County, Idaho. Collected by J. B. Mertie, Jr. | 1070[d] | | 1080 | 1.01 | |
| SQ-81 | Monazite from rare earth carbonate body, Mountain Pass. Calif. Collected by H. W. Jaffe. | 1760[d] | 1760 | 1770 | 1.01 | 1.00 |
| M-51 | Zircon from Cranberry gneiss, Deyton Bend, N. C. Collected by G. R. Tilton. | 57 | 59.5 | | | 1.04 |
| G-70 | Zircon from rare earth vein, Laurel Gap, Tenn. Collected by G. R. Tilton | 165 | 163 | | | .99 |
| G-15 | Zircon from granite, Crossnore, N. C. Collected by G. R. Tilton. | 33 | 32 | | | .97 |
| R-200 | Zircon from pegmatite, Pacoima Canyon, San Gabriel Mts., Calif. Collected by L. T. Silver. | 37 | 41.6 | | | 1.12 |
| G-64 | Zircon from Beech granite, West Roan Mts., Tenn. Collected by G. R. Tilton. | 54 | 58 | | | 1.07 |
| 6-37 | Zircon from Scarn, Old Whitestone Farm, 1 mile east of Natural Bridge, N. Y. Collected by A. F. Buddington. | 110[e] | 127 | | | 1.15 |
| B-15 | Zircon from gneiss, Mary's Rock Tunnel, Shenandoah National Park, Va. Collected by G. R. Tilton. | 78 | 83 | | | 1.06 |

[e] Analysis obtained on 4 mg. sample (diluted in zircon base) and the value reported is from a single exposure.

The precision of each method is indicated by comparing the lead analysis value of duplicate samples, and by comparing the values of the composite samples with the calculated values.

The variation in lead determinations between methods is reported in the table as a ratio of this method to the method of Waring and Worthing (1953). For the range of concentration of the analyses, the ratios range from 1.11 to 1.48, making an interpretation of the variation difficult and application of a single empirical correction factor impossible.

To determine the factors causing the variations in the lead values reported by the two spectrochemical methods, a study was made to investigate the chemical breakdown of natural zircon during its excitation in the d-c arc, and to compare the rate of volatilization of lead from the min-

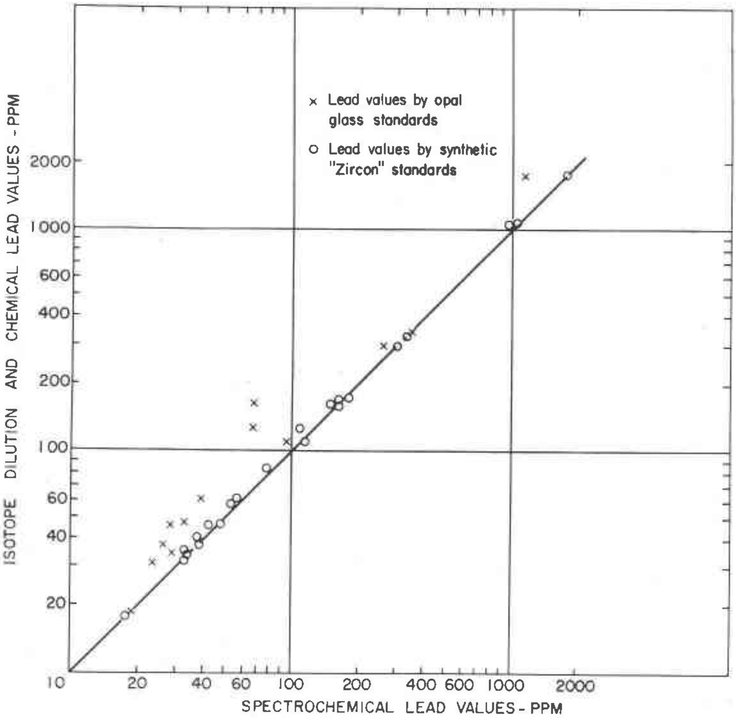

FIG. 1. Comparison of spectrochemical with isotope dilution and chemical analyses.

eral with the rate of volatilization of lead from the spectrochemical standards used by each method.

$X$-ray and mineralogical examinations of the material remaining in the crater of the electrode after excitation periods of 10, 20, 40, and 60 seconds disclosed that the decomposition products of zircon are baddeleyite and tridymite, high temperature forms of zirconia and silica, respectively. These oxides appear as a thin layer at the surface of the crater after 10 seconds of excitation. As excitation continues, the decomposition layer extends deeper into the electrode and after 40 seconds zircon is no longer identified in the remaining material. Examination of the crater material after 60 seconds of excitation indicated that only baddeleyite remained, the silica having volatilized from the crater. The above studies also reveal that the lead is released into the arc column during the decomposition of zircon. Lead can no longer be detected after the mineral has completely decomposed in the crater.

The rate at which lead volatilizes from the natural mineral, from synthetic "zircon," and from opal glass was observed by moving plate stud-

TABLE 3. COMPARISON OF PREVIOUS SPECTROCHEMICAL LEAD METHOD (WARING AND WORTHING, 1953) AND PRESENT METHOD ON 20 ZIRCON SAMPLES

| Sample No. | Source | Previous method | | | | Present method | | | | Ratio Present/ Previous |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Number of detns. | Range (ppm.) | Lead (ppm.) | Average of 2 samples[a] | Number of detns. | Range (ppm.) | Lead (ppm.) | Average of 2 samples[a] | |
| ZS-2 | NBS-197 Zircon ore | 4 | 27– 30 | 28.5 | 28.9 | 3 | 32– 34 | 33 | 32.9 | 1.16 |
| ZS-18 | | 4 | 28– 30 | 29.2 | | 3 | 33– 36 | 34.7 | | 1.19 |
| ZS-6 | Pacoima Canyon, San Gabriel Mountains, Calif. | 4 | 23– 25 | 24.3 | 23.5 | 6 | 31– 34 | 33 | 33 | 1.36 |
| ZS-17 | | 4 | 21– 24 | 22.7 | | 3 | 32– 34 | 33 | | 1.45 |
| ZS- 1 | 10% ZS-10, 90% ZS-6 | 4 | 22– 25 | 23.7 | 23.5 (24.5) | 2 | 34– 36 | 35 | 34.8 ( 34.5) | 1.48 |
| ZS-8 | | 4 | 22– 24 | 23.3 | | 2 | 33– 36 | 34.5 | | 1.48 |
| ZS-4 | 32% ZS-10, 68% ZS-6 | 4 | 26– 28 | 26.7 | 26.3 (26.6) | 3 | 37– 39 | 38 | 37.5 ( 37.8) | 1.42 |
| ZS-20 | | 4 | 25– 27 | 26.0 | | 3 | 36– 38 | 37 | | 1.42 |
| ZS-15 | 50% ZS-10, 50% ZS-6 | 4 | 27– 29 | 28.5 | 28.4 (28.5) | 2 | 39– 41 | 40 | 40.2 ( 40.5) | 1.40 |
| ZS-11 | | 4 | 27– 30 | 28.3 | | 2 | 40– 41 | 40.5 | | 1.43 |
| ZS-10 | Old Whitestone farm, Natural Bridge, N. Y. | 4 | 32– 33 | 32.5 | 33.5 | 5 | 46– 50 | 46.8 | 48 | 1.44 |
| ZS-16 | | 4 | 34– 35 | 34.5 | | 3 | 48– 51 | 49.3 | | 1.43 |
| ZS-7 | 10% ZS-9, 90% ZS-6 | 4 | 44– 46 | 45.0 | 46.1 (47.4) | 3 | 58– 62 | 60.3 | 60.3 ( 60.7) | 1.34 |
| ZS-19 | | 4 | 46– 48 | 47.3 | | 3 | 59– 63 | 60.3 | | 1.27 |
| ZS-3 | 15% ZS-9, 85% ZS-6 | 4 | 58– 62 | 60.0 | 60.7 (59.1) | 2 | 75 79 | 77 | 76 ( 74.5) | 1.28 |
| ZS-5 | | 4 | 59– 63 | 61.3 | | 2 | 74– 76 | 75 | | 1.22 |
| ZS-12 | 32% ZS-9, 68% ZS-6 | 4 | 94–100 | 97.5 | 97.3 (99.9) | 3 | 114–125 | 119 | 117.5 (121.6) | 1.22 |
| ZS-14 | | 4 | 94–100 | 97.0 | | 3 | 113–117 | 116 | | 1.20 |
| ZS-9 | Quanah Mountains, Wichita Mountains, Okla. | 4 | 255–265 | 260 | 262 | 7 | 280–325 | 310 | 303 | 1.19 |
| ZS-13 | | 4 | 260–270 | 265 | | 3 | 285–305 | 295 | | 1.11 |

[a] The values reported in parentheses were calculated by totaling the amount of lead contributed by each component of the mixture using the analysis value reported in the determination.

ies. The results indicate that while the lead volatilizes from the synthetic "zircon" in the same pattern rate as the natural mineral, opal glass releases lead into the arc column much more rapidly.

A series of each of the standard materials was exposed on the same plate, the emulsion calibrated, and the analytical curves constructed as illustrated in Fig. 2. The synthetic "zircon" standards form a straight line working curve. The opal glass curve, although shifted in the direction of lower lead analysis values, does not parallel the synthetic "zircon" curve. No single correction factor can be applied to align the curves.

It is apparent from the preceding studies that the most significant factor causing variations in the lead analyses is the difference in the chemical and physical properties of the spectrochemical standards. Because the relative intensities of analytical lines are influenced markedly by the reactions occurring in the electrode crater and in the arc column, the composition of the standards should be as nearly identical to the sample as possible. The tendency of the upper portion of the opal glass curve to flatten indicates that self-absorption is causing a decrease in the line intensities of the standards above 100 ppm. lead. The fact that the two

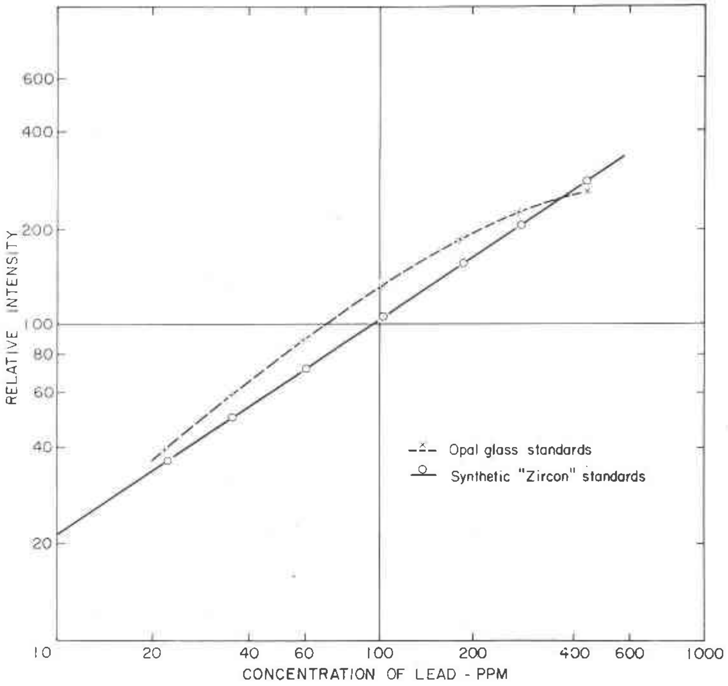

Fig. 2. Comparison of working curves of opal glass and synthetic "zircon" standards.

working curves cross at approximately 350 ppm. explains the favorable comparison of lead values by the Waring and Worthing method (1953) with the analyses of isotope dilution in this range of concentration, although only a limited number of samples are involved (Table 1).

The higher intensities displayed by the opal glass standards cause a shift in the analytical curve resulting in lower analytical values. Whether the increase in intensity is due to the more rapid rate of lead volatilization from opal glass affecting the vapor density of the arc gas at these concentrations is not known. It can only be concluded that in this range of concentration low analytical values result when opal glass is used as a standard. It should be mentioned that chemical analyses by several chemists and isotope dilution analyses by L. R. Stieff of the U. S. Geological Survey, indicate that the certificate value of 900 ppm. lead for opal glass (National Bureau of Standards, standard sample 91) is low.

This method is applicable to the determination of lead in monazite. Monazite is more radioactive and contains higher lead concentrations than zircon. Dilution of the sample in zircon base (68% zirconia and 32% silica) reduces the lead to a more suitable analytical range and at the same time creates a matrix similar to the standards. When sufficient quantities of monazite and zircon are concentrated from the host rock, lead-alpha ages can be determined by analysis of each of these minerals. The results of the analysis of two monazites by isotope dilution and chemical techniques and by this method are given in Table 2.

The spectrochemical method described for the determination of lead is a contribution to the lead-alpha method which is valuable for obtaining reconnaissance age estimates of zircon from igneous rocks. The present study emphasizes the importance of the composition of the standard and recommends the use of a full set of standards in quantitative spectrochemical analysis.

## ACKNOWLEDGMENTS

The authors express appreciation to G. R. Tilton, Carnegie Institute of Washington, L. T. Silver, California Institute of Technology, and Henry Faul, U. S. Geological Survey, who furnished samples on which they had made isotope dilution analyses. W. S. Connor and S. M. Young of the Statistical Engineering Laboratory, National Bureau of Standards, devised the controlled experiment given in the discussion.

We acknowledge the help of the following colleagues, all of the U. S. Geological Survey; D. B. Stewart and B. J. Skinner synthesized the material used as our standard and made numerous mineralogical and *x*-ray identifications. Frank Cuttitta, R. A. Powell, and L. R. Stieff analyzed some of the samples chemically or by isotope dilution. Helen Worthing

aided in the dilution of the standards and in the spectrochemical analysis of many samples.

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*Manuscript received March 4, 1960.*