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DETERMINATION OF THORIUM IN ZIRCON*

By

Frank Cuttitta

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DETERMINATION OF THORIUM IN ZIRCON

By Frank Cuttitta

ABSTRACT

A method is presented for the separation and spectrophotometric determination of thorium in zircon and other associated minerals. The organic reagent 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid (thoron) is used to develop the color for the final optical measurement. The method covers a range of 3 to 230 micrograms of thoria with a precision within 10 percent in the 3-microgram range and 2 percent in the 230-microgram range. The steps necessary for the separation of interfering ions are discussed, and a study of the effect of various cations and anions is presented.

INTRODUCTION

The work of E. S. Larsen, Jr., (1952) in using the accessory minerals of igneous rocks to determine geologic age is based on ascertaining the amounts of uranium, thorium, and lead in a rock. Methods for the determination of trace amounts of lead and uranium have already been reported in an investigation by Waring and Worthing (1953). There was need of a precise and sensitive method for the determination of thorium in zircon and in other associated minerals.

The problem of determining thorium in minerals such as zircon, sphene, and apatite presents many difficulties when undertaken by classical methods. Usually the difficulties increase progressively as the concentration of thorium in the sample decreases. Carriers are often

added to insure complete precipitation of the thorium and many analytical steps may be involved. In addition, relatively large amounts of sample may have to be taken for analysis. Efforts were made therefore to find a method that was applicable at low levels of thorium in small samples containing macro amounts of zirconium.

The most sensitive of the methods surveyed is that originally reported as a visual method by Kuznetsov (1944) utilizing the organic reagent 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid (thoron) to form a colored complex with thorium. Later the method was developed into a spectrophotometric procedure by Thomason, Perry, and Byerly (1949). Thomason's procedure was combined with a modification of the mesityl oxide extraction method of Levine and Grimaldi (1954) to extract thorium nitrate selectively. Use of Na_2HPO_4 as a retainer effects the separation of thorium from zirconium.

It has been found that the method covers a range of 3 to 230 micrograms of ThO_2 per 25-ml volume with a precision within 10 percent in the 3-microgram range and 2 percent in the 230-microgram range.

Thoron has also been used as a reagent for the spectrophotometric determination of thorium in monazite (Banks and Byrd, 1953), black sands (Banks, Klingman and Byrd, 1953), and water (Taylor and Dillon, 1952). Horton (1953) used the bleaching effect of fluoride on the thorium-thoron complex as a method for the determination of fluoride. However, none of the available methods has adequately solved the problem of the serious interference of zirconium. As zirconium is the major constituent of the silicate mineral zircon, the present investigation was undertaken principally to determine micro amounts of thorium in small quantities of

zircon and to extend the method of analysis to other mineral associates in igneous rocks:

The method consists of the following steps:

The silicate is decomposed by a carbonate-borate fusion (Ampt, 1935) and most of the salts are separated from thorium by precipitation of $\text{Th}(\text{OH})_4$ with ammonium hydroxide. The thorium is then precipitated as the fluoride using lanthanum as a carrier. The fluorides are separated by centrifuging and dissolved in a saturated aluminum nitrate solution acidified with nitric acid (final acidity is 9 percent v/v). The thorium nitrate is extracted into mesityl oxide, the extraction of zirconium being prevented by using Na_2HPO_4 as a retainer. The thorium nitrate is then stripped from the solvent with water. An oxalate precipitation is made using Ca as a carrier (Taylor and Dillon, 1952; Waring and Mela, 1953) and the resultant oxalates wet-ashed with $\text{HNO}_3 \cdot \text{HClO}_4$. The thorium is then determined spectrophotometrically with thoron. The procedure has been worked out using synthetic mixtures of known composition and zircon, and it yielded satisfactory results.

The author wishes to express appreciation to his associates of the U. S. Geological Survey, especially to Dr. Esper S. Larsen, Jr., for providing many of the samples and offering valuable suggestions. This work was done on behalf of the Division of Research of the U. S. Atomic Energy Commission.

REAGENTS AND APPARATUS

The absorbancy measurements were made with a Beckman DU spectrophotometer equipped with 1.00-cm and 5.00-cm corex cells. The blank

in the reference cell consisted of a solution containing the same amount of perchloric acid, hydroxylamine hydrochloride, and thoron as was used with the thorium in the other cell. All pH measurements were made with a continuous indicating line-operated pH meter. For centrifugal separations, a clinical centrifuge with 15-ml Lusteroid tubes was used.

Solutions used in the determination of interfering cations were prepared from reagent grade chloride or nitrate salts of the metals and doubly distilled water. The anion solutions were prepared from the sodium salts. Spectrographic analysis of the lanthanum nitrate reagent disclosed no traces of thorium.

The thorium nitrate used was spectrographically free of significant quantities of rare earths and all common cations. Appropriate amounts of this nitrate were then dissolved to make the stock solutions containing approximately 10 mg of thorium per ml. These solutions were standardized by evaporating 10-ml aliquots to dryness and igniting (to ThO_2) to constant weight at 1000°C . The standardization was also checked by the precipitation of thorium with carbonate-free ammonium hydroxide and also by precipitation with mandelic acid. The stock solutions were diluted to obtain solutions containing 10, 46, 50, and 57.5 micrograms of thorium dioxide equivalent per milliliter.

Hydroxylamine hydrochloride was used as the reducing agent. The 10 percent solution of hydroxylamine hydrochloride was prepared by dissolving the C.P. reagent in doubly distilled water.

In accord with other investigators who have based their nomenclature on the analytical selectivity of the arsonic acid group, naming the

thorium reagent as a benzene arsonic acid derivative is preferred instead of the substituted naphthol, 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid. The reagent, although complex, requires little preparation and is now commercially available. The reagent can be synthesized in the laboratory according to directions given by Kuznetsov (1944). A more complete and detailed procedure for the synthesis of the organic reagent was published by Margerum and associates (1953). Solutions of thoron, 0.1 percent and 0.02 percent, were prepared by dissolving the reagent in doubly distilled water.

Commercially available mesityl oxide was found to be satisfactory and comparable to mesityl oxide purified by distillation at 128° to 130°C in the laboratory. The aluminum nitrate scrub solution was prepared by dissolving 950 g of reagent grade aluminum nitrate nonohydrate in 500 ml 15:85 HNO₃. The carbonate borate flux was prepared by mixing equal portions by weight of anhydrous sodium carbonate and anhydrous sodium borate. Carbonate-free NH₄OH was prepared by saturating ice-cold, doubly distilled, CO₂-free water with tank ammonia gas.

PROCEDURE

Preparation of sample solution.--Grind the samples to -200 mesh and mix thoroughly. Small particle size is necessary to insure complete fusion in a reasonable time. Accurately weigh 0.1000 g sample into a 15-ml platinum crucible and add 1 g of the carbonate-borate flux. (Ampt, 1935). Mix thoroughly. Cover the crucible and place in a moderately heated furnace to drive off any moisture. Gradually increase temperature until the mass is a viscous liquid (approximately 1000°C). Keep the

crucible at this temperature for 20 to 30 minutes. Cool to room temperature and place crucible and melt in a 100-ml beaker, add 30 to 40 ml 3:7 HNO_3 , cover, and digest on a steam bath to effect solution.

Precipitation with ammonium hydroxide.--Thorium is separated from most of the salts by means of a carbonate-free ammonium hydroxide precipitation as described below.

Add a few drops of methyl red (0.2 percent alcoholic solution) and heat to boiling for one minute. Carefully add carbonate-free 1:2 NH_4OH dropwise until the color of the solution changes to a distinct yellow. Boil the solution for 1 to 2 minutes, and filter at once on a number 41 Whatman paper or equivalent. Wash the precipitate thoroughly with hot ammonium nitrate solution (2 percent) made basic with ammonia. Dissolve the hydroxide precipitate with 15 to 20 ml hot 1:1 HNO_3 directly into a 50-ml platinum dish. Add 2.0 ml of $\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ solution [approximately 20 mg $\text{La}(\text{NO}_3)_3$] and evaporate the solution to incipient dryness on the steam bath.

Separation and solution of fluorides (Banks and Byrd, 1953).--Add 25 ml of 1:1 HF, cover the dish with a platinum cover, and digest the solution on the steam bath for at least 1 hour, stir occasionally. The sample is allowed to stand half an hour at room temperature. Transfer a portion of the material in the dish to a 15-ml Lusteroid centrifuge tube and centrifuge at full speed for 3 to 5 minutes. Carefully pour off and discard the supernatant liquid and continue the transfer of the material from the platinum dish into the Lusteroid tube until the separation is complete.

After the last of the soluble fluorides has been discarded, wash the insoluble fluorides with 5:95 HF, centrifuge once again, and reject the washings. Transfer the fluorides quantitatively into a 50-ml beaker with 15 ml of 15:85 HNO₃ used in small portions. Add 28.5 g of Al(NO₃)₃·9 H₂O to the beaker containing the fluorides and place on a hot plate. As the mixture is warmed, the fluorides will dissolve because of the formation of the stable fluoaluminate ion. Add 0.5 g of Na₂HPO₄ and heat to dissolve the salt. Do not heat longer than necessary to effect solution of the phosphate. Cool to 15° C or less and transfer to a 125-ml separatory funnel using small portions of the aluminum nitrate scrub solution to effect the transfer.

Extraction with mesityl oxide (Levine and Grimaldi, 1954).--Keep temperature of all components at less than 15° C. Silica interferes in the extraction of thorium nitrate with mesityl oxide by causing emulsification of the two phases. If the preceding HF separation has been omitted, the sample solution must not contain more than 10 to 15 mg of soluble silica. After the sample solution has been poured from the beaker into the 125-ml separatory funnel, wash the beaker twice with 10-ml portions of mesityl oxide and add washings to the separatory funnel. Shake separatory funnel for 30 seconds. Drain off the aqueous phase into a second separatory funnel. A white suspension or emulsion may form at the interface during the extraction. It should be carried along with the solvent phase. The nature of this effect is not known. However, it does not seem to affect the results in any way. Add 20 ml of solvent to the second separatory funnel and shake for 30 seconds. Drain off the aqueous phase into a third separatory funnel and repeat the extraction

with a fresh 20-ml portion of mesityl oxide. Discard the aqueous phase. Combine all three portions of the solvent phase in one separatory funnel and add 20 ml of scrub solution. Again shake for 20 seconds and discard the aqueous phase. Repeat the scrubbing operation until the aqueous phase is clear (2 to 4 scrubblings). The solvent turns brown during the extraction and scrubbing due to some oxidation by HNO_3 . This is unimportant but can be minimized by working rapidly and with cold solutions. Add 20 ml of water to the mesityl oxide extract and strip the thorium from the solvent by vigorous agitation for 30 seconds.

Drain the water layer into a 150-ml beaker and repeat the stripping twice more. Occasionally the strip solution will have a yellow tinge because of the oxidation effect of nitric acid on the mesityl oxide. This will not affect subsequent work.

Evaporate the solution to a volume of about 5 to 10 ml, add 5 ml concentrated HNO_3 , and then continue the evaporation to dryness. Add 30 ml 1:4 HNO_3 to the residue remaining in the beaker, cover with watch glass, and heat gently until solution has been completed.

Oxalate precipitation and preparation of solution.--Add 3 ml of $\text{Ca}(\text{NO}_3)_2$ solution (15 mg Ca) and 4 g of oxalic acid, and boil gently for one minute, stirring continuously. Add a few drops of bromphenol blue and heat to boiling. Carbonate-free NH_4OH solution is then added dropwise until the color changes to pure green (pH 3 to 4). The mixture is digested at 100°C for 2 hours, or at room temperature for at least 4 hours, preferably overnight. Filter the oxalates on a no. 40 Whatman paper and wash with a 2 percent oxalic acid solution whose pH has been

adjusted to the neutral color of bromphenol blue with carbonate-free NH_4OH . Transfer the paper and oxalate precipitate to a 30-ml beaker, add 5 ml of fuming nitric acid and 0.5 ml of HClO_4 , cover the beaker, and digest on the steam bath until the solution is clear (about 10 to 15 minutes). Remove the cover and evaporate the solution to dryness on a hot plate. Take up residue in 0.5 ml HClO_4 and 5 ml water, warming the solution to dissolve the residue. Transfer the solution to a 25-ml volumetric flask with a minimum amount of water.

Fluoride precipitation and preparation of solution (alternate method in place of oxalate precipitation).--The water strippings of thorium from the mesityl oxide are evaporated to a volume of about 5 to 10 ml in platinum ware. Add 2 mg lanthanum, 10 ml HF, cover, and digest on the steam bath for 1/2 to 1 hour. Allow to settle and filter. Wash with dilute HF and then twice with water. Burn the precipitate carefully in a covered crucible. Add as little $\text{K}_2\text{S}_2\text{O}_7$ as will dissolve all the precipitate (1.0 g or less depending on the size of the fluoride precipitate) and fuse carefully until a clear melt is obtained. Care should be taken during the fusion to prevent loss of thorium by spattering. Cool and then leach the melt with 100 ml of water containing 2 ml HNO_3 (1:1). Add a few drops of methyl red and then NH_4OH (1:1) until indicator turns yellow. Add 1 ml NH_4OH in excess and heat the solution until it starts to boil. Remove the heat and allow the precipitate to settle. Filter through a fast paper and wash with a 1 percent NH_4NO_3 solution. Transfer the paper and hydroxide precipitate to a 30-ml beaker, add 5 ml fuming HNO_3 and 0.5 ml HClO_4 , cover the beaker, and digest on the steam bath until solution is clear (about 10 to 15 minutes). Remove the cover and evaporate the solution to dryness on a hot plate.

Take up residue in 0.5 ml HClO_4 and 5 ml water, warming the solution to dissolve the residue. Transfer the solution to a 25-ml flask with a minimum amount of water.

Spectrophotometric determination of thorium.--The optimum sample size is one which will yield 30 to 45 micrograms of ThO_2 . This amount will give an absorbance near 0.45 which is the point of greatest accuracy (Ayres, 1949). Add 5 ml of 0.02 percent thoron to the 25-ml flask and dilute the solution to volume with water. Mix thoroughly and allow the solution to stand for 30 minutes to permit complete color development. Solutions should be read within 24 hours after being prepared.

The absorbance is measured on a Beckman DU spectrophotometer at a wavelength of 545 $m\mu$ using a 5-cm corex cell and a slit width of 0.04 mm. The instrument is adjusted to zero absorbance with a reagent blank containing the same concentration of acid, calcium, or lanthanum, and thoron as the sample. Prepare an absorbancy-concentration curve (figs. 1 and 2) by plotting absorbancy measurements of the color developed with known quantities of thoria. This system conforms to Beer's Law at least up to a concentration of 50 micrograms of thoria per 25 ml. The amount of ThO_2 in the sample is read from this curve and the percent ThO_2 in the sample is calculated.

Note. When larger quantities of thorium are present (from 50 to 100 micrograms thoria), the sample should be diluted to 50 ml, more reagent added, and the pH adjusted with a pH meter to 0.9 ± 0.1 using perchloric acid before measuring its absorbance. However, when the range of thoria is from 100 to 250 micrograms ThO_2 , the 25-ml volume

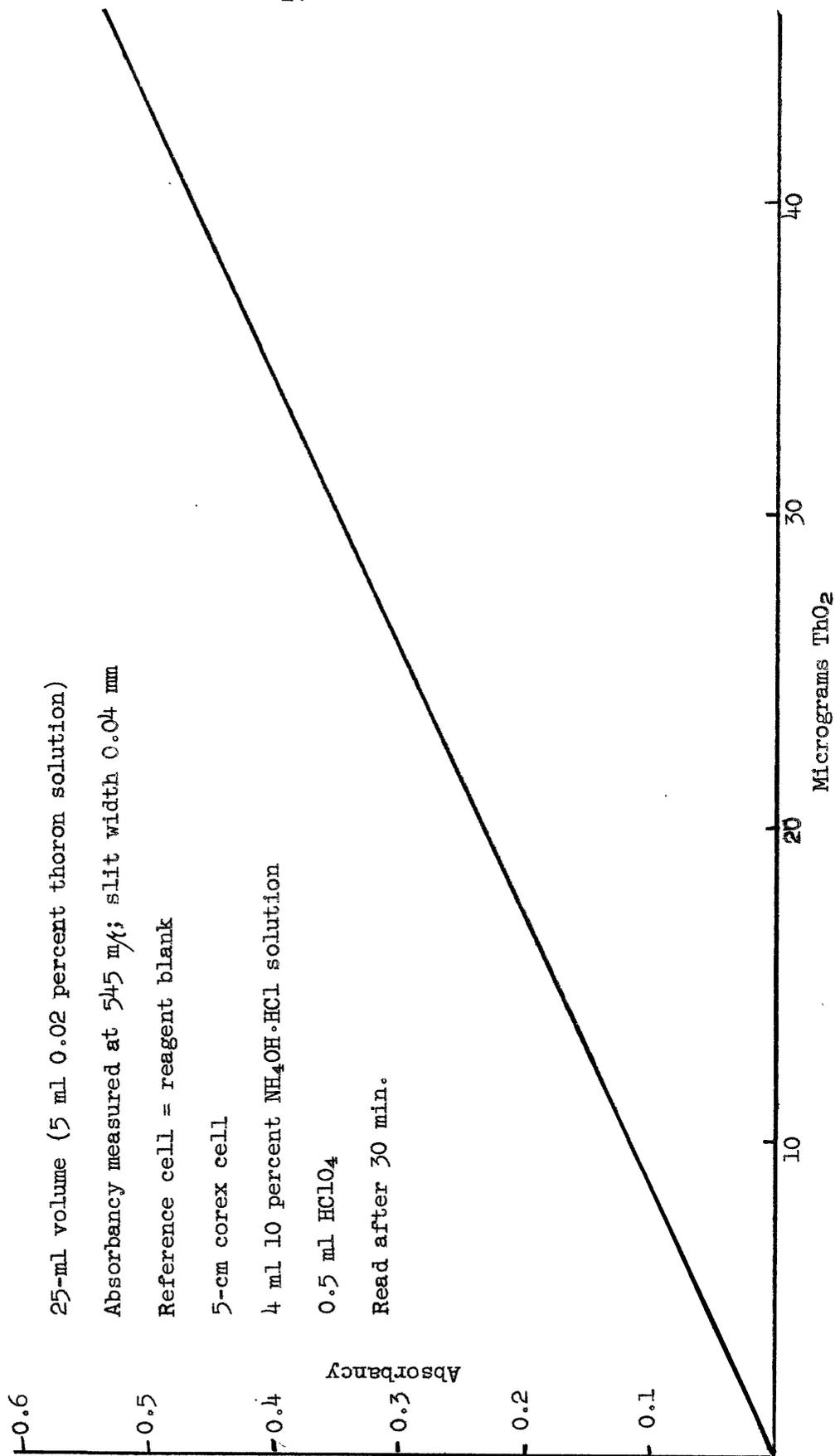


Figure 1.--Sensitivity and conformity of thorium-thoron system to Beer's Law (5-cm light path).

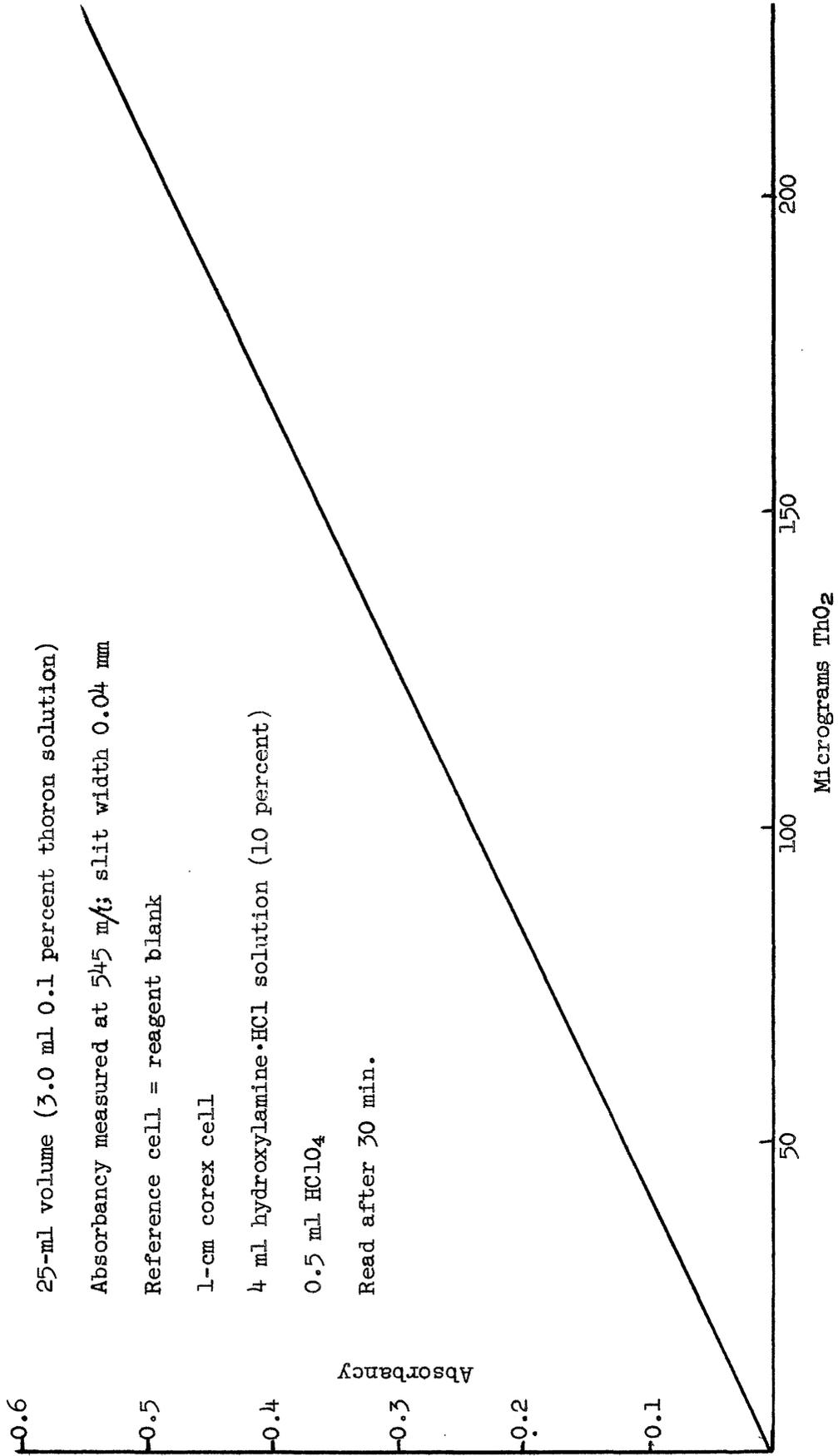


Figure 2.--Sensitivity and conformity of thorium-thoron system to Beer's Law (1-cm light path).

is maintained. In this instance, add 3 ml of a 0.1 percent solution of thoron instead of the 0.02 percent thoron solution and the absorbancy measurements are made in a 1.00-cm corex cell. Here again, the analyst must construct a standard curve by preparing a series of solutions containing known concentrations of ThO_2 and plotting the concentrations against absorbance.

FACTORS AFFECTING THE THORIUM-THORON COLOR SYSTEM

When thoron is added to an acid solution of thorium a crimson-pink color is obtained. Thomason et al. (1949) studied various factors affecting the color system in order to establish optimum working conditions and these findings have been substantiated in this laboratory. Thomason's conditions were used and are as follows: Absorbancies are measured at 545 m μ against a reagent blank solution in the reference cell so that the true absorption of the thorium complex can be obtained. The effects of pH change are very small over the range from 0.29 to 1.21. The maximum error due to variation in pH over this range is about 2 percent. However, above pH 1.5 the absorbancy decreased rapidly and approached zero at pH 7. For subsequent work, a pH of 1 was used.

It was found that 3 ml of 0.1 percent solution of thoron is sufficient to complex at least 230 micrograms ThO_2 . Hydroxylamine hydrochloride was used as the reducing agent in all work on interfering ions. Results show that as much as 5 ml of the 10 percent NH_2OH solution has no effect on the absorbancy. For further work, it was decided to use 3 ml of the 10 percent NH_2OH solution at a pH of 3 to 4. After reduction the pH was adjusted to 1. Data for the working curve are given in

figures 1 and 2. These data were obtained using the optimum conditions previously established. A straight-line relationship between absorbancy and micrograms of thorium up to 230 micrograms ThO_2 indicates close conformance to the Beer-Lambert-Bouguer law. The spectrophotometric sensitivity of the thorium-thoron color reaction is 0.016 micrograms ThO_2 per cm (Ayres, 1949). The solutions containing as much as 287.5 micrograms ThO_2 , were allowed to stand for 24 hours, after which time the absorbancies were redetermined. The maximum change in absorbancy was found to be 0.002. Reproducibility tests of the thorium-thoron system in the low thoria range up to 6 micrograms ThO_2 show an average deviation in the absorbancy readings of ± 0.001 (using a 5-cm light path) which is equivalent to 0.012 micrograms ThO_2 .

A carrier is necessary to recover or concentrate microgram amounts of thorium. Taylor and Dillon (1952) and Waring and Mela (1953) have proved that calcium can be a suitable carrier for thorium oxalate. Two milligrams of lanthanum has also proven to be an excellent carrier for thorium fluoride.

REACTIONS OF THORON WITH OTHER ELEMENTS

Most of the elements tested are associated with thorium and some data were necessary to determine their behavior with thoron under the conditions used for the thorium-thoron reaction. Each element was tested in the absence of thorium and at two levels of thorium (57.5 micrograms and 115 micrograms ThO_2) in a total volume of 25 ml. The absorption given by colored ions in HCl or HClO_4 was also studied. An absorbancy difference of 0.003 unit (equivalent to 1.25 micrograms ThO_2) was taken as the cut-off for reporting interference.

Following are the maximum amounts of ions that do not interfere in the determination of thorium:

0.5 g	Na ⁺ , K ⁺ , NH ₄ ⁺ , NO ₃ ⁻ , NO ₂ ⁻ , Cl ⁻ , Br ⁻ , and C ₂ H ₃ O ₂ ⁻
0.1 g	Mg, Mn ⁺⁺
0.02 g	Hg ⁺⁺
0.005 g	Zn
0.0025 g	Be, Co ⁺⁺ , Cu ⁺⁺ , Ni ⁺⁺ , Pb ⁺⁺
0.0010 g	As, Sb, V

Table 1 shows the maximum amount of each element that can be tolerated, the nature of the interference, and the absorbancy per milligram of ion. Serious interference is given by the following ions: ceric, dichromate, fluoride, oxalate, titanium, and uranium (IV). Some additional observations are to be noted. Above 10 mg Ba, an orange precipitate is formed, and the light-yellow supernate absorbs only a small amount of light. Cerium (IV) in amounts of more than 0.5 mg will decolorize the thorium complex formed with 115 micrograms ThO₂. A fine orange-red precipitate was formed. Ceric ion interference can be minimized by reduction to the cerous state with NH₂OH. Chromium (VI) bleaches the thorium reagent and must not be present even in microgram quantities. The presence of fluoride diminishes the color of the thorium complex and cannot be tolerated even in the microgram range. This effect was used by Horton et al. (1952) as a colorimetric method for the determination of microgram amounts of fluoride in the range up to 50 micrograms with an overall accuracy of ± 4 percent. Ti (III) bleaches the reagent and thereby introduces a serious negative error. 1000 micrograms Ti (III) will completely bleach the colored

Table 1.--Reactions of thoron with other elements.

Ion	Maximum amount in mg at level of 57.5 γ ThO ₂	Maximum amount in mg at level of 11.5 γ ThO ₂	Absorbancy per mg	Nature of interference
Al	37.5	37.5	0.00008	Positive.
Ba	6.0	6.0	0.0005	Negative. Orange precipitate with 10 mg.
Cd	2.0	1.5	0.00020	Positive.
Ca	15.0	15.0	0.00021	Positive.
Ce (III)	0.24	0.24	0.01204	Positive.
Ce (IV)	0.003	0.005		Negative. Decolorized with >0.5 mg
Cr (III)	0.04	0.04	0.075	
Cr (VI)				50 micrograms bleached the color completely.
F	0.001	0.002		Negative. >0.003 mg decrease in absorbancy was proportional to F concentration up to 50 micrograms.
Fe (II)	5.0	5.0	0.00080	Positive.
Fe (III)	0.010	0.010	0.15200	Positive. Colored ion.
La	1.2	0.8	0.00390	Positive.
Pb	2.5	2.5	0.00122	Positive.
Molybdate	0.5	0.5	0.00500	Positive.
Nb	0.027			
Nd	0.39	0.5	0.00770	Positive.
Oxalate	0.002	0.005		Negative.
Phosphate		0.45		Negative. 1000 micrograms P ₂ O ₅ caused a 0.007 decrease in absorbancy.
Pr	0.40	0.25	0.0125	Positive.
Sm	0.375		0.008	
Sr	15.8	17.6	0.00019	Positive.
Sulfate		2.2	0.003	Negative.
Tl (IV)	0.015	0.013		Negative.
Y	2.0	2.0	0.00310	Positive.
U (IV)	0.004	0.004	0.844	Positive.
U (VI)	0.15	0.15	0.021	Positive. Yellow colored solution.
Zr	0.003	0.003	0.775	Positive.

complex developed by 57.5 micrograms ThO_2 . Ti (IV) when present in concentrations up to 7 micrograms has a bleaching effect equivalent to 1.25 micrograms ThO_2 . In the presence of 230 micrograms ThO_2 , 250 micrograms Ti (IV) reduces the solution absorbancy from 0.548 to 0.478. Uranium (IV) forms a complex with thoron but much greater amounts are required than in the case of thorium; 250 micrograms uranium (IV) has an optical density of 0.211 which is equivalent to 87 micrograms ThO_2 . Interference from U (IV) can be minimized or eliminated by the oxidation of U (IV) with $\text{HNO}_3 \cdot \text{HClO}_4$ to the sexivalent state. Zirconium is a serious interference and measurements indicate that 3 micrograms Zr is equivalent to 1 microgram ThO_2 . An extensive and complete study on the use of thoron as a spectrophotometric reagent for zirconium has been published by Horton (1953). Interference from zirconium has been eliminated in the general procedure by the extraction of $\text{Th}(\text{NO}_3)_4$ with mesityl oxide using Na_2HPO_4 as a retainer for zirconium. Data shown in tables 2 and 3 indicate that the recovery of thorium and its separation from zirconium is quantitative. As little as 57.5 micrograms ThO_2 were quantitatively separated from 50 milligrams Zr. It was also found that the order of addition of Na_2HPO_4 is important. Low recoveries of thorium resulted when the phosphate was added before the saturation of the sample solution with $\text{Al}(\text{NO}_3)_3$.

REPRODUCIBILITY OF RESULTS

A series of synthetic samples was prepared to test the procedure. The results of these determinations are shown in table 4. Samples of zircon were also analyzed to test the reliability of the thorium determination in the presence of macro amounts of zirconium (table 5). In

Table 2.--Separation of thorium in presence of 50 mg Zr $[\overline{\text{Na}_2\text{HPO}_4}$ added after saturation with aluminum nitrate and before extraction with mesityl oxide].

ThO ₂ (γ)	Absorbancy	ThO ₂ recovered (γ)	Percent recovery
57.5 standard	0.143		
57.5	.145	58.5	101.7
57.5	.148	60.0	104.3
57.5	.139	56.5	98.2
57.5	.137	56.0	97.5
115 standard	0.280		
115	.282	116.0	100.9
115	.278	114.5	99.6
115	.288	118.0	102.6
115	.273	112.5	98.0
172.5 standard	0.418		
172.5	.415	172.0	99.8
172.5	.410	169.5	98.3
172.5	.425	175.5	101.7
172.5	.430	177.5	102.8

Table 3.--Separation of thorium in presence of 50 mg Zr $[\overline{\text{Na}_2\text{HPO}_4}$ added before saturation of solution with $\text{Al}(\text{NO}_3)_3$].

ThO ₂ (γ)	Absorbancy	ThO ₂ recovered (γ)	Percent recovery
172.5 standard	0.418		
172.5	.306	127.5	73.8
172.5	.352	146.0	84.6
172.5	.420	173.0	100.3
172.5	.342	142.0	82.3

Table 4.--Analysis of synthetic samples.

Composition (mg)	Thoria (γ)	
	Taken	Found
Ca 100, Zr 10, Mg 10, La 10, Si 10	46	46.4 45.8
Ca 100, Zr 20, Mg 20, La 20, Si 20	92	91.0 92.5
Zr 50, Si 50	57.5	58.5 60.0 56.5 56
Zr 50, Si 50	115	116.0 114.5 118.0 112.5
Zr 50, Si 50	172.5	172.0 169.5 175.5 177.5

Table 5.--Analyses of zircon.

Sample no.	Thoria (percent)	
	Colorimetric	Radiometric
R-1932	0.045 0.045 0.048 0.049	0.047 <u>1/</u>
Z-39	0.026 0.024	0.024
Z-61	0.092 0.094	0.098 <u>1/</u>
Z-63	0.757 0.748	0.77 0.74 <u>1/</u>

1/ Analyst: Dr. P. M. Hurley, Massachusetts Institute of Technology.

addition, the method was extended to include the analysis of bostonite (table 6).

Table 6.--Analyses of bostonite samples.

Sample no.	Thoria (percent)	
	Nephelometric <u>1/</u>	Colorimetric <u>2/</u>
118	0.005	0.005
465	0.018	0.019
506	0.004	0.006
548	0.005	0.005
559	0.004	0.003
597	0.005	0.004
629	0.005	0.004
633	0.005	0.007
640	0.004	0.005

1/ Analyses by Harry Levine (Grimaldi and Fairchild, 1954, p. 141).
2/ Analyses by Alexander Sherwood and Frank Cuttitta.

It can be seen from table 4 that the maximum absolute difference between 4 determinations on the same sample (containing 172.5 micrograms thoria) is 8.0 micrograms ThO_2 or about 4.6 percent of the total thorium content. Accurate results were also obtained with a variety of other samples, including synthetic samples, zircon, and bostonite.

SUMMARY

A spectrophotometric study confirms that 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid is an excellent reagent for the determination of thorium in zircon and other silicates. It has been established that the procedure can be applied to bostonite, and with modifications, the method can be extended to include analysis of other mineral

associates of igneous rocks. The interferences present may be reduced to noninterfering valence states or be removed by the extraction of thorium nitrate with mesityl oxide using Na_2HPO_4 as a retainer for zirconium. Thoron can also be used routinely for the determination of thorium in solutions containing relatively large amounts of Al, Ca, Sr, Mg, Mn, and Hg.

The method is very sensitive and covers the range up to 230 micrograms ThO_2 per 25-ml volume when using a 1.00-cm light path, and up to 50 micrograms ThO_2 per 25-ml volume when using a 5.00-cm light path. The color reaction conforms to Beer's Law over the entire range of concentrations studied, and pH has no significant effect on the intensity of the color over the applicable range, 0.5 to 1.2. In order that the ThO_2 concentration does not exceed the complexing capacity of the reagent, at least 3 ml of an aqueous 0.1 percent solution of thoron is required to produce the maximum color with 230 micrograms thoria in a 25-ml volume.

REFERENCES

- Ampt, G. A., 1935, Determination of zirconium: Australian Chem. Inst. Jour. Proc., v. 7, p. 321-334.
- Ayres, G. H., 1949, Evaluation of accuracy in photometric analysis: Anal. Chemistry, v. 21, p. 652-657.
- Banks, C. V., and Byrd, C. H., 1953, Spectrophotometric determination of thorium in monazite sands: Anal. Chemistry, v. 25, p. 416-419.
- Banks, C. V., Klingman, D. W., and Byrd, C. H., 1953, Spectrophotometric determination of thorium in black sands: Anal. Chemistry, v. 25, p. 992-993.
- Grimaldi, F. S., and Fairchild, J. G., 1954, The Geological Survey phosphate-fluoride-iodate method for the determination of very small amounts of thorium in naturally occurring materials: U. S. Geol. Survey Bull. 1006, p. 133-167.

- Horton, A. D., 1953, Spectrophotometric determination of zirconium: Anal. Chemistry, v. 25, p. 1331-1333.
- Horton, A. D., Thomason, P. F., and Miller, F. J., 1952, Spectrophotometric determination of inorganic fluoride: Anal. Chemistry, v. 24, p. 548-550.
- Kuznetsov, V. I., 1944, Color reaction of thorium, I: Jour. Gen. Chem. (U.S.S.R.), v. 14, p. 914-919.
- Larsen, E. S., Jr., Keevil, N. B., and Harrison, H. C., 1952, Method for determining the age of igneous rocks using the accessory minerals: Geol. Soc. America Bull., v. 63, p. 1045-1062.
- Levine, H., and Grimaldi, F. S., 1954, Mesityl oxide extraction method for thorium analysis: U. S. Geol. Survey Bull. 1006, p. 177-184.
- Margerum, D. W., Byrd, C. H., Reed, S. A., and Banks, C. V., 1953, Preparation and properties of thoron: Anal. Chemistry, v. 25, p. 1219-1221.
- Taylor, A. E., and Dillon, R. T., 1952, Determination of microgram amounts of thorium in water: Anal. Chemistry, v. 24, p. 1624-1625.
- Thomason, P. F., Perry, M. A., and Byerly, W. M., 1949, Determination of microgram amounts of thorium: Anal. Chemistry, v. 21, p. 1239-1241.
- Waring, C., and Mela, H., 1953, Method for determination of small amounts of rare earths and thorium in phosphate rocks: Anal. Chemistry, v. 25, p. 432-435.
- Waring, C., and Worthing, H., 1953, A spectrographic method for determining trace amounts of lead in zircon and other minerals: Am. Mineralogist, v. 38, p. 827-833.