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UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D.C.

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June 13, 1956

Mr. Robert D. Nininger
Assistant Director for Exploration
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Bob:

Transmitted herewith are three copies of TEI-350, "The thoron-mesotartaric acid system for the determination of thorium," by Mary H. Fletcher, F. S. Grimaldi, and Lillie B. Jenkins, April 1956.

We are asking Mr. Hosted to approve our plan to submit this report for publication in Analytical Chemistry.

Sincerely yours,

George N. Pipiringos
for W. H. Bradley
Chief Geologist

Chemistry

This document consists of 24 pages
Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

THE THORON-MESOTARTARIC ACID SYSTEM FOR THE DETERMINATION OF THORIUM*

By

Mary H. Fletcher, F. S. Grimaldi, and Lillie B. Jenkins

April 1956

Trace Elements Investigations Report 350

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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THE THORON-MESOTARTARIC ACID SYSTEM FOR THE DETERMINATION OF THORIUM

By

Mary H. Fletcher, F. S. Grimaldi, and Lillie B. Jenkins

ABSTRACT

In the spectrophotometric determination of thorium with thoron, mesotartaric acid is used as a masking reagent for zirconium. The effects of different experimental variables such as the concentrations of the reagents, time and temperature, and the behavior of 35 ions which might be present in thorium ores are discussed in detail. A procedure is given for the direct determination of thorium in zircon ($ZrSiO_4$) that is also generally applicable to other materials.

INTRODUCTION

An earlier paper (2) stated that mesotartaric acid should be superior to d-tartaric acid as a masking reagent for zirconium in the determination of thorium with thoron. The present work confirms this statement and shows that with mesotartaric acid the equivalent of as much as 8 mg of zirconium dioxide per 25 ml of solution can be present with all concentrations of thorium normally determined. This limit is in sharp contrast to the 0.36 to 0.13 mg which can be present with 50 micrograms and less of thorium dioxide if d-tartaric acid is used (2). This is the only major change resulting from the substitution of mesotartaric acid for d-tartaric acid.

The new system is applicable to the direct determination of 0.10 percent or more of thorium dioxide in zircon. The direct method for zircon is applicable also in the range below 0.1 percent thorium dioxide, but here the results are good to only one significant figure. The thoron-mesotartaric acid spectrophotometric method used in conjunction with the recently developed separation for thorium (3) has been successfully applied to the determination of 0.01 percent or more thorium dioxide in a variety of complex minerals and ores and to the determination of 0.001 percent or more of thorium dioxide in silicate rocks (3).

This work is part of a program conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

GENERAL CONSIDERATIONS

At least five competing reactions, thorium-thoron, thorium-tartaric acid, thoron-tartaric acid, zirconium-thoron, and zirconium-tartaric acid (2) are involved when thoron-tartaric acid systems are used for the determination of thorium in the presence of zirconium. In the development of thoron-tartaric acid systems for the spectrophotometric determination of thorium, the primary aim was to find conditions which give least interference from zirconium and minimum loss in the sensitivity of the thorium-thoron reaction. Various combinations of acidity and concentrations of thoron and tartaric acid will fulfill these requirements. Interference from ions other than zirconium will be different with different combinations of reagents and should be considered in selecting the final system. The interference from other ions is related primarily to the concentration of dye and to the pH of the solution and not to the concentration or structure of the tartaric acid. The sensitivity of the thorium-thoron reaction, although related to both the concentrations of dye and tartaric acid and to the pH of the solution, is not related to the structure of the tartaric acid. As a consequence, the data obtained with d-tartaric acid were helpful in considerations regarding the sensitivity of the thorium-thoron reaction and the extent of interference from other ions. From these data it was decided to develop a thoron-mesotartaric acid system based on 3 mg of thoron and 1 ml of (1+1) hydrochloric acid per 25 ml of solution. Three milligrams of thoron is a sufficient excess to permit the determination of as much as 150 micrograms of thorium dioxide; with 3 mg of thoron, the amounts of rare earths and negative ions that can be tolerated are somewhere between that of the two systems which use d-tartaric acid (2). One milliliter of (1+1) hydrochloric acid seemed best in relation to interference from other ions and to sensitivity and linearity of the standard absorbance-concentration curve for thorium.

EXPERIMENTAL DATA

All solutions for work in this study were prepared in 25-ml volumetric flasks. Unless stated otherwise, all solutions were at pH of 0.65 and had a total acid content, including that supplied by solutions of the metal ions, of 1 ml of (1+1) hydrochloric acid; in addition, all solutions contained 1 ml of 10 percent hydroxylamine hydrochloride and 3 mg of thoron. The order of addition of the reagents was always the same: acid first followed by hydroxylamine hydrochloride, the metal ions, mesotartaric acid, and thoron. All absorbances were measured at 545 mμ with a Beckman DU spectrophotometer using 5-cm cells for the solutions.

Establishment of operating conditions

The effect of the concentration of mesotartaric acid in the thoron-mesotartaric acid system is shown in figure 1. In this figure the difference in the absorbances due to mesotartaric acid of solutions containing thoron alone (3 mg), thoron with 20.12 and 60.36 micrograms of thorium dioxide, and thoron with 1 and 5 mg of zirconium dioxide are plotted as functions of the concentration of mesotartaric acid. The absorbances were measured against a reference solution containing 3 mg of thoron but no mesotartaric acid. In figure 1, curve D for 1 mg of zirconium dioxide almost coincides with the thoron curve (E) when more than 20 mg of mesotartaric acid are present; curve C for 5 mg of zirconium dioxide intersects the thoron curve when 300 to 400 mg of mesotartaric acid are present. Hence, the data in figure 1 indicate that 300 to 400 mg of mesotartaric acid will mask the effect of 5 mg of zirconium dioxide.

Although zirconium may be effectively masked, there are certain complications attending the use of mesotartaric acid for this purpose. In the experiments with 5 mg of zirconium dioxide, a precipitate of zirconium-mesotartrate formed with time. This precipitation phenomena was in sharp contrast to the high solubility of zirconium-d-tartrate. The effect of the concentration of mesotartaric acid was, therefore, examined further. Absorbance measurements were made periodically on three solutions all of which contained 5 mg of zirconium dioxide and 3 mg of thoron and all of which were identical except for their mesotartaric acid contents which were 200, 400, and 500 mg. The absorbances of these solutions were measured against corresponding reference solutions containing the same amount of mesotartaric acid and other reagents but no zirconium. The data for this test are presented in figure 2

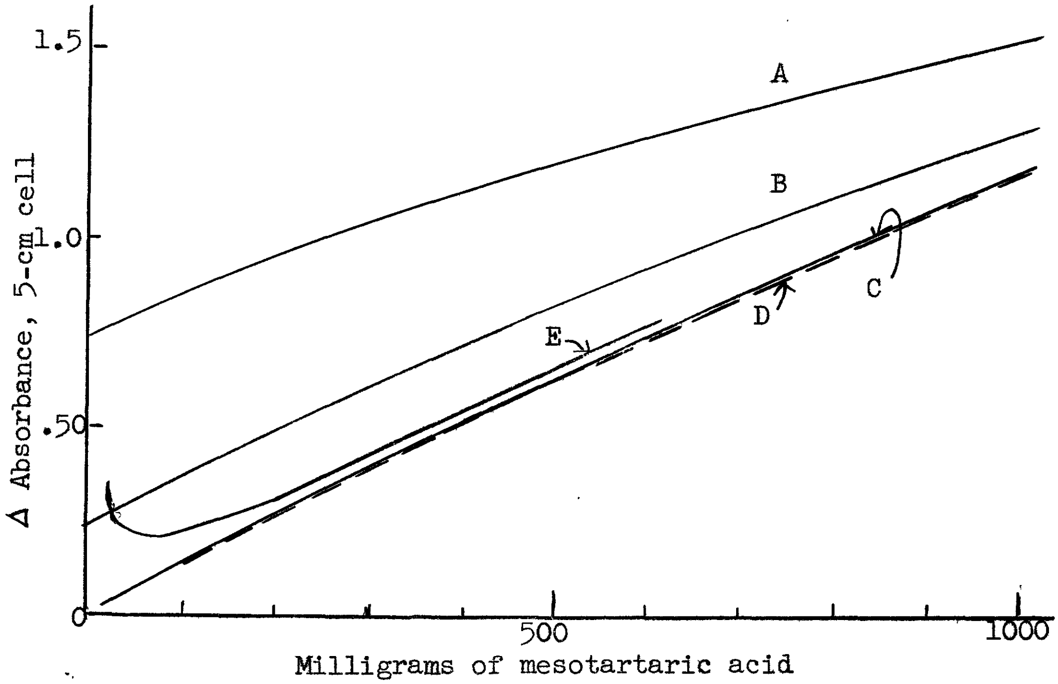

Figure 1.--Effect of mesotartaric acid

Curve A - 60.36 micrograms of ThO_2 + 3 mg thoron

B - 20.12 micrograms of ThO_2 + 3 mg thoron

C - 5 mg of ZrO_2 + 3 mg thoron

D - 1 mg of ZrO_2 + 3 mg thoron

E - 3 mg of thoron

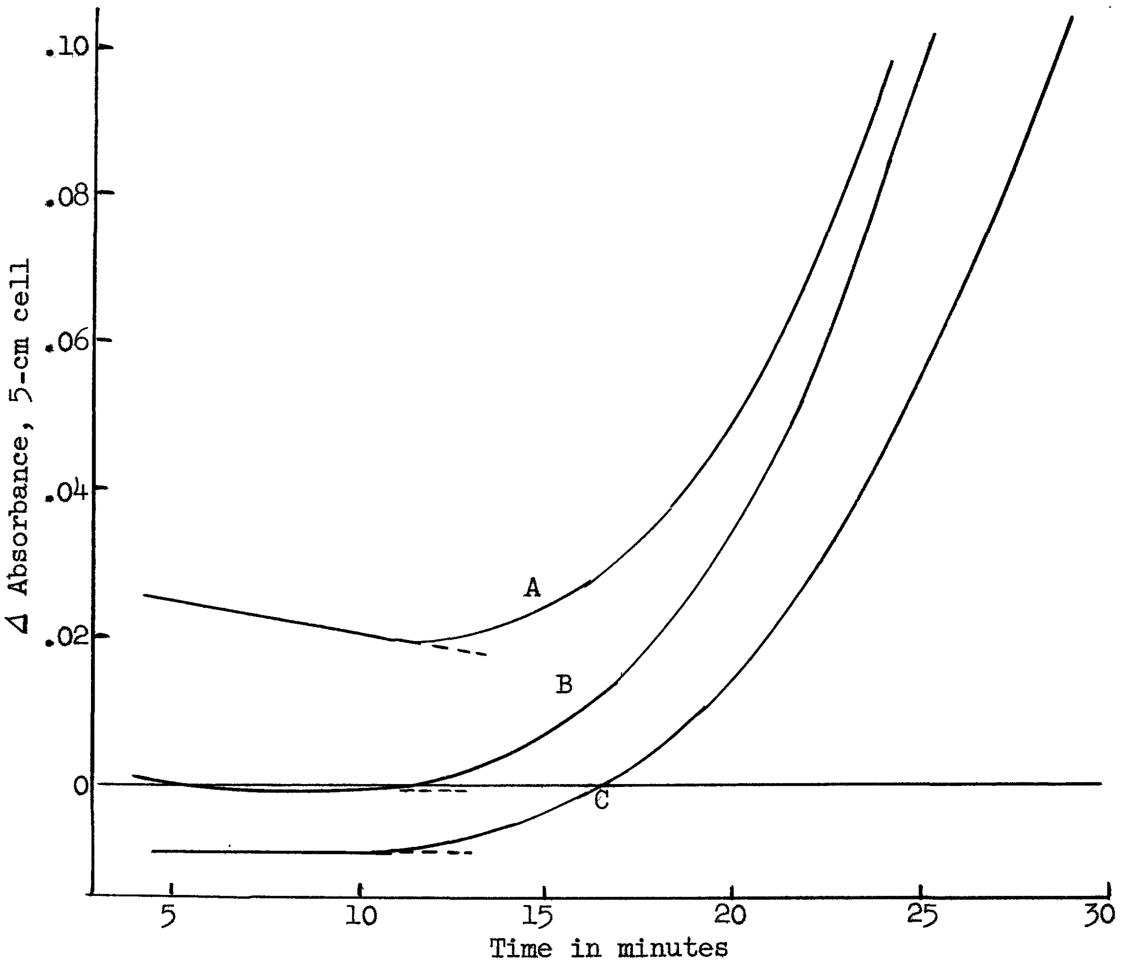

Figure 2.--Effect of concentration of mesotartaric acid on the reaction of 5 mg of zirconium dioxide.

Curve A - 200 mg mesotartaric acid

B - 400 mg mesotartaric acid

C - 500 mg mesotartaric acid

where the absorbance differences due to zirconium are plotted as a function of the period of time between the addition of mesotartaric acid and measurement of absorbance. The data in figure 2 show that practically no changes in the absorbances of the solutions occur during the first of 5 to 11 minutes following the addition of mesotartaric acid. In this region of the curve, it can be seen that 400 mg of mesotartaric acid is effective in preventing the formation of enough zirconium-thoron complex to interfere. The break at the end of the regions of almost constant absorbance in each of the curves in figure 2 corresponds to the time required for precipitation of zirconium-mesotartrate to begin. After the start of precipitation, the absorbances increase rapidly as more and more precipitate forms. As the break in each of the various curves occurs after the same period of time, the precipitation time is essentially independent of the concentration of mesotartaric acid at these concentration levels. This is probably because mesotartaric acid is used in large excess of the stoichiometric amount.

The precipitation was also followed by observation of the Tyndal effect which is evident at the start of the precipitation. The same period of time was required for the appearance of a Tyndal beam in solutions containing 5 mg of zirconium dioxide and 400 mg of mesotartaric acid with and without thoron. The precipitation time for zirconium-mesotartrate is thus practically independent of the thoron concentration. However, the precipitation time for zirconium-mesotartrate is affected by the acidity of the solution. A change of ± 0.5 ml from the standard amount of 1 ml of (1+1) hydrochloric acid resulted in a change of ± 5 minutes in the precipitation time of 5 mg of zirconium dioxide. A gain of only 5 minutes did not seem to justify increasing the acid content of the system because a shorter linear relationship between absorbance and concentration for thorium would then obtain.

On the basis of previous considerations and the foregoing tests, the concentrations of the reagents selected for the final system are as follow: 3 mg of thoron, 400 mg of mesotartaric acid, 1 ml of (1+1) hydrochloric acid, and 1 ml of hydroxylamine hydrochloride per 25 ml of solution. The hydroxylamine hydrochloride is used to minimize the interference of iron in the analysis of samples. This final system was used to establish the standard absorbance-concentration curve for thorium and to determine the behavior of zirconium and other ions.

Tests under the operating conditions

Behavior of thorium

The thorium-thoron complex forms immediately and absorbance readings may be made at any time within several hours after the solutions are prepared. The relationship between absorbance and concentration of thorium is linear from 3 to 150 micrograms of thorium dioxide per 25 ml of solution. In this range of concentration an absorbance difference of 0.010 is equivalent to 1 microgram of thorium dioxide. Below this range the standard curve has a slight heel.

For greatest accuracy, which is especially desired when measuring low absorbances, the sources of possible error should be recognized and precautions taken to minimize the errors. The reference blank used in this study has an absorbance of 1.33 with respect to water. If an absorbance difference of 0.002 is to be meaningful, great care must be exercised in preparing both the reference and sample solutions. An absorbance difference of 0.002 which results from 0.2 microgram of thorium dioxide is only 0.15 percent of the absorbance due to the reagents. Hiskey and coworkers (4,5) have shown that differential measurements can be made with an accuracy better than 1 part per 1,000; instrumental errors are not therefore the limiting factor. The absorbance of the reagents depends on both the thoron and mesotartaric acid concentrations. For maximum accuracy the volume of thoron added to the reference and sample solutions must be reproduced to 1.5 parts per 1,000; the volume of mesotartaric acid added to 2.5 parts per 1,000; and the final volume of the solution to 1.5 parts per 1,000. The precision in the reproduction of the measurements of these volumes for the reference and sample solutions is the significant factor and not the absolute volumes added. Therefore, the same pipet should be used to add a given reagent to both sample and reference solutions. The ground-glass portion of the neck of the flask must be washed after the addition of the dye in order that all of the reagents get into the sample solution, and time must be allowed for the neck of the flask to drain completely in order to have the final volume as accurate as possible (± 0.038 ml of water is equal to 1.5 parts per 1,000 of the final 25-ml volume).

In addition to the effects of variable concentrations, the absorbance of the thoron-mesotartaric acid complex is affected by temperature. If the reference solution is hotter than the sample solution, the sample solution will read too high; if the temperature of the reference solution is less than the sample solution, the sample solution will read too low. The relationship between the difference in temperature of the two solutions and the difference in their absorbances is linear. A difference of ± 0.8°C between the two solutions results in an absorbance difference of ± 0.002.

For this reason, it is desirable to cool the lamp housing of the instrument with water thermostatically controlled at room temperature. If this is not feasible, the sample carriage should be removed from the instrument between readings to prevent heating of the reference solution.

Behavior of zirconium

The behavior of zirconium under the standard conditions was determined by periodic absorbance measurements of a series of solutions which contained amounts of zirconyl chloride ranging from 1 to 8 micrograms of equivalent zirconium dioxide. The data from this test are summarized in figure 3 where the difference in absorbance between the reference solutions and the solutions containing zirconium are plotted as a function of time between the addition of mesotartaric acid and measurement of the absorbance. The shape of these curves is similar to the shape of those in figure 2. The small variations between the absorbances in the horizontal portions of the different curves are probably not significant. Insufficient time was allowed for proper drainage in the necks of the flasks in order to start measuring the absorbances as quickly as possible. The changes which occur in the individual curves were of primary interest in this test.

In figure 4, curve A, the time after the addition of mesotartaric acid at which the break occurs in each of the curves in figure 3 is plotted as a function of the amount of zirconium present. Thus, in figure 4 the area under curve A represents the region of safety for the measurement of the absorbance of solutions containing different amounts of zirconium. It is safe to measure the absorbance of a solution containing a given amount of zirconium at any time along that portion of its ordinate that lies below

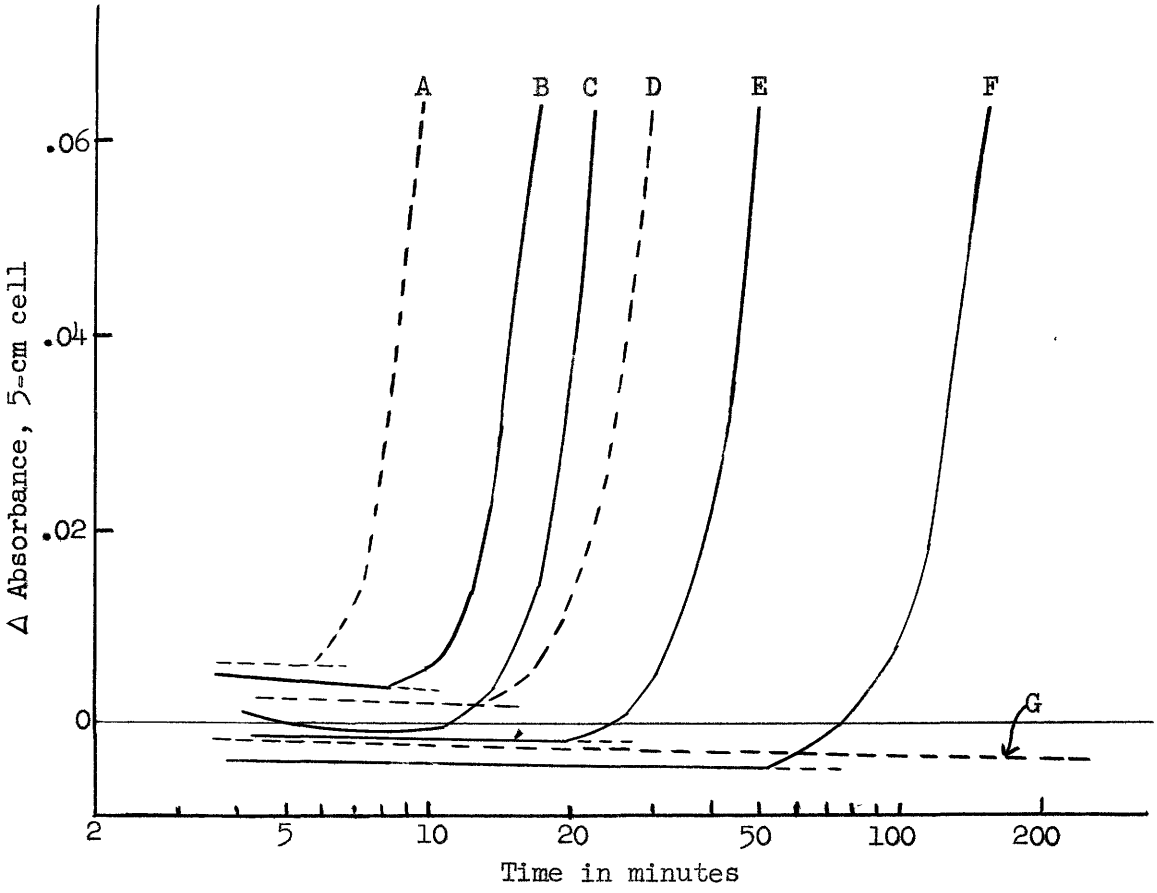

Figure 3.--Effect of time on the interference from different amounts of zirconium dioxide.

Curve A - 8 mg ZrO_2

B - 6 mg ZrO_2

C - 5 mg ZrO_2

D - 4 mg ZrO_2

E - 3 mg ZrO_2

F - 2 mg ZrO_2

G - 1 mg ZrO_2

curve A in figure 4. Curve B, figure 4, represents the total time required for an absorbance change 0.010 greater than the absorbance of the horizontal portion of the curves.

As the precipitation of the zirconium-mesotartrate is related primarily to the amount of zirconium present and to the time and as it is independent of the thoron concentration, the data presented in figures 3 and 4 would be the same if thorium were also present in the solutions.

It must be stressed that the relationship between time and the beginning of precipitation of zirconium-mesotartrate shown by the curves in figures 3 and 4 hold only if the zirconium used is present as a simple ionic species. The standard zirconium solutions used in these studies were prepared by boiling zirconyl chloride in (1+1) hydrochloric acid and by maintaining this high acidity whenever weaker zirconium solutions were made by dilution. In more dilute acid solutions of zirconium, unless freshly diluted from strong acid solutions, zirconium is often present in polymerized form. As little as 1.5 mg of zirconium in this form gives a precipitate almost immediately with mesotartaric acid. Provision is made in the detailed procedure to guard against polymerization of zirconium. Using this procedure 5 to 8 mg of zirconium dioxide may be present in the spectrophotometric determination of thorium if absorbance measurements are made within the time shown to be safe by curve A, figure 4.

Behavior of other ions

The behavior of other ions when 0, 50.3, and 150.9 micrograms of thorium dioxide are also present is summarized in table 1. This table shows the amount of the element calculated to the equivalent amount oxide, which causes a change in the absorbance of 0.010 at three concentration levels

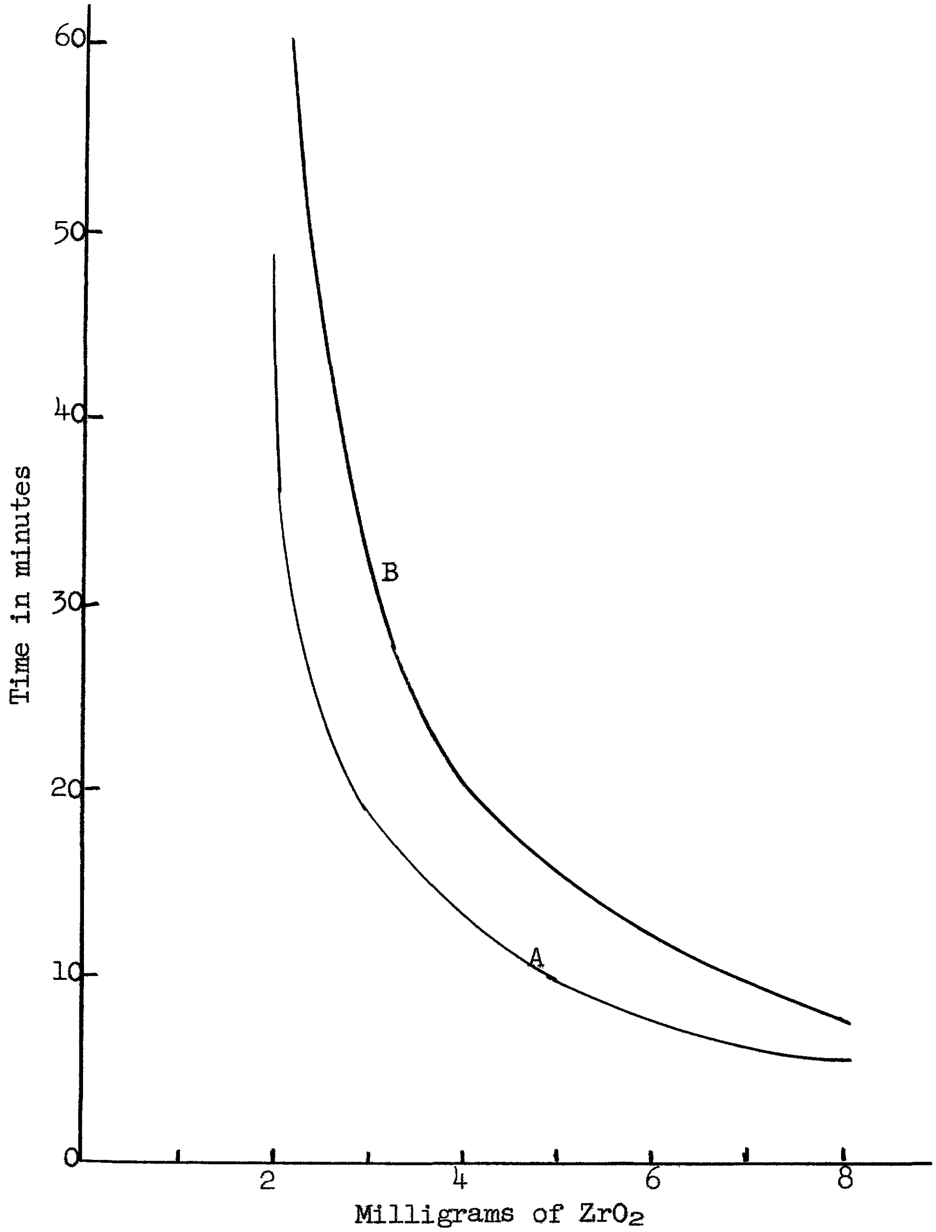

Figure 4.--Time-zirconium areas for noninterference of zircon.

Curve A - time for start of precipitation

B - time for an increase of 0.010 in absorbance

Table 1.--Milligrams of various elements (as oxides) equivalent to an absorbance difference of 0.010

Element tested	Mg equivalent to an absorbance difference of 0.010		
	0 ThO_2	50.3 γ ThO_2	150.9 γ ThO_2
Sc_2O_3	> 2.0	0.11	0.120
Y_2O_3	2.6	2.6	6.56
La_2O_3	.45	.70	> 10.0
Ce_2O_3	.37	.49	1.12
Pr_2O_3	.43	.83	1.3
Nd_2O_3	.68	.76	1.0
Sm_2O_3	.60	.56	3.6
Eu_2O_3	1.25	1.25	4.5
Gd_2O_3	1.45	1.85	7.4
Ho_2O_3	2.2	--	--
Yb_2O_3	3.8	8.5	> 10.
TiO_2	1.2	.019	.009
ZrO_2 1/	8.	8.	8.
Nb_2O_5	.22	.20	.075
Ta_2O_5	> 1.0	.045	.035
WO_3	> 10.	2.0	1.2
UO_3	.36	.42	.55
Fe_2O_3	.47	.10	.056
Fe_2O_3 2/	> 10.	> 10.	> 10.
Au_2O_3	> 5.0	> 5.0	> 5.0
HgO	> 30.	> 30.	> 30.
Al_2O_3	5.7	21.	25.2
SnO_2	.062	.055	.035
PbO	7.0	11.0	20.0
Bi_2O_3	11.5	12.0	12.5
P_2O_5	> 10.	.42	.12
SO_3	> 10.	1.25	.65
F	4.1	.003	.001
ZnO	> 30.0	> 30.0	> 30.0
Pt	5.9	6.8	8.5
Na_2O	40.	88.	42.
K_2O	>500.	68.	29.
MgO	23.	>100.	30.
CaO	10.	39.	13.
MnO	> 40.	--	10.
CuO	> 5.0	4.0	> 5.

1/ Time dependent

2/ Reduced to Fe^{++} using cupric chloride catalyst of thorium.

The cations used in this test were introduced into the solutions as chlorides and the anions as sodium or potassium salts. The niobium and tantalum solutions were prepared by fusing each pentoxide (purity > 99.9 percent) with potassium carbonate and leaching the melts with water to yield very dilute solutions. (The acidity of the test solutions was adjusted to compensate for the alkalinity of these solutions when necessary.) The titanium solutions were prepared by fusion of the dioxide with potassium carbonate and solution of the melt in (1+1) hydrochloric acid. The rare earths used were spectrograhically pure and determined to be free from thorium and zirconium by chemical tests.

Fluorine, titanium, tantalum, tin, and niobium are serious interferences. Iron is not included in this group of seriously interfering elements because it is readily reduced by hydroxylamine hydrochloride in the presence of cupric chloride which serves as a catalyst for the reduction (3). When reduced to the ferrous state, as much as 10 mg of equivalent ferric oxide may be present.

A direct spectrophotometric procedure can be used when the sample contains enough thorium to permit using aliquots of the sample solution small enough to reduce the concentrations of other ions below their interference threshold. However, it is advantageous to make a simple potassium hydroxide separation which reduces the amount of several undesirable ions such as tin and fluorine.

The determination of thorium in mineral separates such as zircon is important in Geological Survey programs on geochronology. The procedure which follows was designed primarily for zircon samples containing 0.1 or more percent thorium dioxide, but it is generally applicable.

SPECTROPHOTOMETRIC DETERMINATION OF THORIUM IN ZIRCON

Apparatus and reagents

Spectrophotometer.--A Beckman DU spectrophotometer with a sample housing for 5-cm cells and with the lamp housing cooled by circulating water thermostatically controlled at room temperature was used.

Sand bath.--The one used was made from aluminum sheet metal. Its dimensions were: 12 x 12 x 4 inches, and it contained a three-quarter-inch layer of sand. Tubes of copper metal, 2 inches inside diameter, 3 inches long and slightly less than 1 mm thick, were inserted through the sand to the bottom of the bath. These tubes accommodate 100-ml beakers and act as radiators for evaporations of perchloric acid. The sand bath was heated by a hot plate which maintained the temperature of the sand (just below the surface) at 170-190° C.

All chemicals used were reagent grade.

Potassium hydroxide (precipitating solution) 50 percent: Dissolve 500 g of potassium hydroxide in 500 ml of water.

Potassium hydroxide (wash solution): Dilute 2 ml of the 50 percent solution to 500 ml with water.

Hydroxylamine hydrochloride 10 percent solution: Dissolve 100 g of the reagent in water to make a liter.

Cupric dhloride (catalyst solution): 1 ml equivalent to 1 mg of CuO: Dissolve 0.538 g of cupric chloride-dihydrate in 250 ml of water.

Thoron (the disodium salt of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzene arsonic acid) 0.1 percent: 1 ml equivalent to 1 mg of thoron: Dissolve 1 g of thoron in 500 ml of hot water. Cool and add water to 1 liter.

Mesotartaric acid 10 percent solution: Dissolve 100 g of mesotartaric acid in 400-600 ml of hot water. Add paper pulp and filter under suction, wash the paper well. Cool the filtrate and make up to 1 liter with water. The reagent is available from several suppliers such as The Jasonols Chemical Corp., Delta Chemical Co., and Bios Chemical Co.

Detailed procedure for the direct determination of thorium in zircon

1. Mix 50 mg of a representative finely ground sample with 4-5 g of fresh sodium peroxide in a small crucible and cover the crucible.

2. Sinter the mixture in a small furnace at 460 ± 20°C for 1 hour. A true sinter with no attack on the platinum will be obtained if the sodium peroxide is fresh and dry. If the sodium peroxide is old and contains moisture, the mixture melts and incomplete decomposition of sample results. The platinum crucible may also be attacked.

3. Remove the crucible from the furnace and allow the sinter to cool. Leach the sinter by placing the crucible and sinter in a 150-ml beaker containing 30 to 50 ml of water. Cover the beaker immediately because the dissolution may be vigorous.

4. Place the covered beaker on a steam bath and digest the solution for about 30 minutes to remove hydrogen peroxide.

5. Acidify the solution with (1+1) hydrochloric acid and add about 2 ml excess. Remove the crucible and lid, police, and rinse them with water. Usually the sample is now decomposed and ready to be treated according to the directions in step 7.

6. If the sample is not completely decomposed after step 5, add a little paper pulp to the solution, filter off the residue through a slow 7-cm filter paper and wash well with water. Reserve the filtrate. Ignite the residue, add sodium peroxide and repeat steps 2 through 5. Add the solution from the sinter to the filtrate reserved in step 5.

7. Neutralize the combined solutions with 50 percent potassium hydroxide and add 5 ml excess for each 50 ml of solution. Digest the solution on a steam bath for 15-20 minutes, then filter it through a fast 7-cm filter paper, and wash with dilute potassium hydroxide wash solution. Drain the precipitate and funnel stem by placing the palm of the hand over the funnel and pressing down.

8. Dissolve the precipitate from the paper with hot (1+1) hydrochloric acid (total volume about 20 ml).

9. Heat the solution on a steam bath for several minutes to insure complete solution.

10. Cool the solution, transfer it to a 25-ml volumetric flask and make to volume with (1+1) hydrochloric acid. One milliliter of this solution is equivalent to 2 mg of the sample.

11.. Transfer a 3-5 ml aliquot of this sample solution to a 100-ml beaker and add 1 ml of perchloric acid.

12. Evaporate the solution on a steam bath until all of the hydrochloric acid has been removed and fumes of perchloric acid appear. Transfer the beaker to a radiator on a sand bath and evaporate until all of the perchloric acid has been removed. Careful heating at sand bath temperatures is necessary here. Heating on a hot plate or fuming over a burner often converts zirconium to an insoluble form which occludes thorium.

13. Cool the beaker and add 1 ml of (1+1) hydrochloric acid. Rotate and tip the beaker so that the acid comes in contact with all portions of the residue. Allow to stand 1-2 minutes then add 4 ml of water. Cover the beaker and place on a steam bath for 5 minutes.

14. Add 1 ml of hydroxylamine hydrochloride solution and 0.2 ml of cupric chloride catalyst solution.

15. Re-cover the beaker and heat on a steam bath for 5 more minutes. Cool to room temperature.

16. If the solution is clear and there is no residue, transfer the solution directly to a 25-ml volumetric flask. If there is any cloudiness or small residue, add a little paper pulp and filter the solution into the flask through a very small slow filter paper and wash. Rinse the neck of the flask with a little water.

17. Add 4 ml of mesotartaric acid and mix.

18. Add 3 ml of thoron solution, rinse the ground glass portion of the neck of the flask, and add water almost to volume.

19. Allow 1 to 2 minutes for drainage in the neck of the flask, then make the solution to volume adding the water from a dropping pipet that has a very fine curved tip which has been wiped dry on the outside. Stopper the flask and mix the solution.

20. Measure the absorbance of the solution at 545 m against a reference blank which contains 1 ml of (1+1) hydrochloric acid, 1 ml of hydroxylamine hydrochloride, 4 ml of mesotartaric acid, and 3 ml of thoron per 25 ml of solution. Make the measurement within 5-10 minutes after adding the mesotartaric acid if a 10-mg sample aliquot was used. Use 5-cm matched or calibrated cells for the solutions. If the measurements are made with a Beckman

spectrophotometer, use a slit width of 0.15 mm.

22. Determine the amount of thorium present in the aliquot by reference to a standard curve or by calculation. Data for a standard curve are obtained from measurements of solutions containing known amounts of thorium chloride.

Test of the procedure

The procedure was used to determine thorium in several zircon samples that had been analyzed carefully by other methods. The percent thorium dioxide determined by independent means and by the new method are shown in table 2. The size of the sample aliquot used for each determination by the new method is also included.

Table 2.--Test of the new procedure for the determination of thorium in zircon

Sample	Thorium dioxide found		Sample in final aliquot (mg)
	By other methods (percent)	By new method (percent)	
Zircon 2	0.15 1/	0.15	4
Zircon 1	0.065 1/	0.07	8
		0.07	8
Zircon 3	0.059 2/	0.06	8
		0.07	8
		0.06	10

1/ Analyst: A. M. Sherwood, U. S. Geological Survey. Method of Cuttitta (1).

2/ Method described by Grimaldi and others (3).

LITERATURE CITED

1. Cuttitta, Frank, 1955, Determination of thorium in zircon: U. S. Geol. Survey Trace Elements Inv. Rept. 498.

2. Grimaldi, F. S. and Fletcher, Mary H., 1956, Thoron-tartaric acid systems for spectrophotometric determination of thorium: Anal. Chemistry, v. 28, p. 812-816.

3. Grimaldi, F. S., Jenkins, Lillie and Fletcher, Mary H., 1956, The selective precipitation of thorium iodate from a tartaric acid-hydrogen peroxide medium. Applications to the rapid spectrophotometric determination of thorium in silicate rock and ores: U. S. Geol. Survey Trace Elements Inv. Rept. 489.

4. Hiskey, C. F., 1949, Principles of precision colorimetry: Anal. Chemistry, v. 21, p. 1440-1446.

5. Hiskey, C. F., Rabinowitz, Jacob, and Young, I. G., 1950, Principles of precision colorimetry. Measuring maximum precision attainable with commercial instruments: Anal. Chemistry, v. 22, p. 1464-1470.