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# THE SELECTIVE PRECIPITATION OF THORIUM IODATE FROM A TARTARIC ACID-HYDROGEN PEROXIDE MEDIUM*

## Application to the rapid spectrophotometric determination of thorium in silicate rocks and in ores

By

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

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## Application to the rapid spectrophotometric determination of thorium in silicate rocks and in ores

By

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

## ABSTRACT

Although the precipitation of thorium iodate from nitric acid medium is a generally reliable and widely used method for the separation of thorium from a number of elements, especially rare earths, the separation is not specific for thorium. This paper describes a selective iodate separation using a nitric acid medium containing d-tartaric acid and hydrogen peroxide. The catalytic decomposition of hydrogen peroxide is prevented by the use of 8-hydroxyquinoline. The procedure described gives a sufficiently clean separation of one or more micrograms of thorium from at least 30 mg of such elements as rare earths, zirconium, titanium, niobium, tantalum, scandium, and iron with one iodate precipitation to allow an accurate determination of thorium with the thoron-mesotartaric acid system. The method is applied successfully to the determination of 0.001 percent or more of thorium dioxide in silicate rocks and of 0.01 percent or more in such materials as black sand, monazite, thorite, thorianite, eschynite, euxenite, and zircon.

# INTRODUCTION

The precipitation of thorium iodate from nitric acid medium (4) is a generally reliable and widely used method for the separation of thorium from a number of elements, especially the rare earths. For macro amounts of thorium, the reaction is generally carried out in 6N nitric acid solution; a lower acidity is recommended for microgram amounts (2,3). Kronstadt and Eberle (3) used mercury as a carrier for the precipitation of 20 or more micrograms of thorium iodate. Lead, mercury, tin, niobium, tantalum, tungsten, cerium (IV), uranium (IV), zirconium, titanium, silver, and to a smaller extent scandium, bismuth, and iron (III) also precipitate from these media. The rare earths tend to coprecipitate with thorium iodate but, in contrast to the other elements above, a clean separation may be obtained if the precipitation of thorium iodate is repeated one or more times. With a single precipitation less contamination from foreign ions results if the precipitation is made from homogeneous solution (6). At the same time, a dense and easily filterable precipitate is obtained. Tillu and Athavale (7) increased the specificity of the separation and were able to keep as much as 20 mg each of titanium and bismuth and 40 mg of zirconium in solution by adding oxalic acid to the precipitating medium. The procedure has not been applied to the determination of small amounts of thorium.

The present investigation concerns the separation of thorium iodate from nitric acid medium containing hydrogen peroxide, d-tartaric acid, and 8-hydroxyquinoline. Tartaric acid is used to minimize the coprecipitation of such elements as zirconium, tungsten, scandium, and bismuth. Hydrogen peroxide is used primarily to minimize the precipitation of titanium, niobium, and tantalum; 8-hydroxyquinoline serves to prevent the catalytic decomposition

of hydrogen peroxide which is especially serious in the presence of cerium. For the precipitation of microgram amounts of thorium, a mixed carrier of mercury and iron is used. Although less than 10 percent of the iron added is precipitated, the mixed carrier is more effective than mercury alone. This separation procedure combined with the recently developed (1) spectrophotometric determination of thorium with the thoron-mesotartaric acid system is applied successfully to the determination of 0.01 percent or more of thorium dioxide in such materials as black sand, monazite, thorite, thorianite, eschynite, polycrase euxenite, and zircon. The method is also applied to the determination of 0.001 percent or more of thorium dioxide in silicate rocks.

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

## EXPERIMENTAL DATA

The initial objective was to separate, with one precipitation of the iodate, a few micrograms or more of thorium dioxide from as much as 30 mg each of rare earths, titanium, tantalum, niobium, zirconium, iron, and scandium. From a practical standpoint, the separation from foreign ions need not be perfect as long as the amounts occluded do not interfere subsequently in the spectrophotometric determination of thorium. The following conditions fulfilled our requirements and were adopted for the iodate separation:

A total volume of solution of 50 ml contains 3 ml nitric acid, 3 g d-tartaric acid, 0.3 ml of 30 percent hydrogen peroxide, 2 mg ferric oxide added as the nitrate, 5 mg mercuric oxide added as the nitrate, 5 mg

8-hydroxyquinoline, and 0.6 g of potassium iodate. The iron carrier may be omitted in the analysis of samples already containing iron. These conditions permit the presence of at least 500 mg of potassium pyrosulfate without loss of thorium through formation of sulfate complexes.

A peculiar reaction of iron was noted. In the presence of tartaric acid, iron in dilute nitric acid solution is reduced by hydrogen peroxide. On the addition of potassium iodate, the ferrous iron is re-oxidized with the liberation of iodine and formation of small amounts of hydrogen iodide. Although small, the amount of iodide formed is sufficient to prevent the precipitation of mercury iodate. This sequence of events is prevented if a few drops of 6 percent potassium iodate solution is added before the tartaric acid.

A brief summary of the effect of the different variables follows:

Iodate and nitric acid concentration.--The solubility of thorium iodate increases with either an increase in acidity or a decrease in iodate concentration. Thus, it is possible to obtain several points of balance between iodate and acid concentration where small amounts of thorium are completely precipitated. The ideal balance should allow complete precipitation of thorium and yet minimize the coprecipitation of foreign ions. The recommended combination of acidity and iodate concentration is one of many fulfilling these objectives. The sensitivity of the recommended system to changes is best illustrated by the fact that if more than the recommended amount of nitric acid is present, 2 ml of excess iodate solution is required for each ml of excess nitric acid to precipitate the thorium completely. At the 500-microgram level of thorium dioxide, an increase of either 1 ml of nitric acid or a decrease of 2 ml of 6 percent potassium iodate results in a 7 percent loss of thorium.

Mercury carrier.--It is advantageous to keep the amount of mercury to a minimum. The use of greater amounts than recommended results only in increased coprecipitation of foreign ions; stoichiometric amounts of halides to form $HgCl_2$ completely prevent the precipitation of mercuric iodate, thus halides must be absent.

Hydrogen peroxide.--In addition to keeping niobium, tantalum, and titanium in solution as peroxy compounds, hydrogen peroxide serves to minimize the coprecipitation of cerium by reducing quadrivalent cerium to the trivalent state. Only slightly more than the stoichiometric amounts required to form the peroxy compounds of niobium, tantalum, and titanium are required. Amounts much greater than recommended cause the precipitation of a peroxy compound of zirconium, especially when 10 mg or more of zirconium is present. No more than 0.5 ml of 30 percent hydrogen peroxide should be used, preferably less.

8-hydroxyquinoline.--The concentration of 8-hydroxyquinoline is less critical than that of any of the other reagents. Although 5 mg is recommended, 0.5 to 50 mg may be used.

d-Tartaric acid.--Tartaric acid delays the precipitation of thorium iodate. However, the concentration may be increased by a factor of 50 percent over the recommended amount without affecting the recovery of thorium if the recommended 45 minutes is allowed before filtering. Although tartaric acid is primarily useful for minimizing the coprecipitation of zirconium, bismuth, tungsten, and scandium, it is somewhat effective in helping to keep niobium, titanium, and tantalum in solution.

Table 1 illustrates the results obtained on the recovery of 2.44 to 1950 micrograms of thorium dioxide in the presence of 30 mg each of the oxides of zirconium, cerium (III), titanium, niobium, tantalum, iron (III),

Table 1.--Recoveries of thorium in the presence of various elements.

| Elements tested mg (as oxides) | Micrograms of $ThO_2$ added | | | | | |
|---|---|---|---|---|---|---|
| | 2.44 | 6.10 | 24.38 | 48.75 | 390.0 | 1950 |
| | Micrograms of $ThO_2$ found | | | | | |
| Blank | 2.18 | 5.91 | 24.4 | 47.5 | 386 | 1950 |
| 30 $ZrO_2$ | 2.50 | 6.02 | 24.3 | 47.9 | 393 | 1940 |
| 30 $Ce_2O_3$ | 2.25 | 5.85 | 24.5 | 48.2 | 396 | 1920 |
| 30 $TiO_2$ | 2.48 | 6.35 | 23.9 | 47.8 | 389 | 1940 |
| 30 $Nb_2O_5$ | 2.37 | 5.95 | 25.2 | 47.6 | 394 | 1960 |
| 30 $Ta_2O_5$ | 2.13 | 6.37 | 23.7 | 46,5 | 387 | 1920 |
| 15 $Ta_2O_5$ | 2.30 | 6.05 | 23.6 | 47.2 | -- | -- |
| 50 $Fe_2O_3$ | 2.36 | 6.62 | 24.8 | 49.4 | 394 | 1960 |
| 30 $Fe_2O_3$ | 2.60 | 6.08 | 24.3 | 48.9 | 389 | 1940 |
| 30 $Sc_2O_3$ | 2.80 | 6.20 | 23.9 | 48.1 | 388 | 1920 |
| Mixture of 5 mg each of oxides of Zr, Ce, Ti, Nb, Ta, Fe, Sc | 2.66 | 6.13 | 25.3 | 48.6 | 397 | 1950 |

or scandium; 50 mg of iron (III) oxide, and 15 mg tantalum oxide--each element tested separately. Also shown are the recoveries of the same amounts of thorium in the presence of a mixture of 5 mg each of the oxides of zirconium, cerium, titanium, niobium, tantalum, iron (III), and scandium. As no more than a 50 mg sample of thorium ores containing these constituents is used for analysis, the experiments should provide a good test of the applicability of the separation procedure to the determination of thorium in such ores. The recoveries shown are quite satisfactory. The solutions of titanium and niobium were made by fusing 0.2 g of the respective oxides with 2 g of potassium carbonate and dissolving the melt in 100 ml of solution containing 11.85 ml of nitric acid and 1 ml of 30 percent hydrogen peroxide. The tantalum solution was prepared by a similar fusion but the melt was dissolved in 100 ml of water containing 1 ml of 30 percent hydrogen peroxide. Fresh solutions were prepared daily. The zirconium was added as a (1+1) nitric acid solution of zirconyl nitrate, the remaining elements as (1+99) nitric acid solution of the nitrates. Rare earths other than cerium were not tested because, of the rare earths, cerium is most apt to coprecipitate; the yttrium earth iodates are appreciably more soluble than the cerium earth iodates and substantial amounts of yttrium earths may be present without interference in the spectrophotometric determination of thorium. Other ions which form insoluble iodates were not tested for several reasons. Some (lead, bismuth, and mercury) can be tolerated in large amounts in the spectrophotometric determination; others (tungsten and bismuth) are soluble in the proposed tartaric acid medium; still others are separated during the preparation of the sample solution. For example, tungsten and tin are separated as the soluble tungstate and stannate in the sodium hydroxide precipitation. The remaining tin is removed as insoluble metastannic acid by fuming with

perchloric acid in the last stages of the analysis.

The excellent recoveries shown in table 1 should not be interpreted as proof that thorium was completely separated from the elements tested. The determination of thorium was made spectrophotometrically as directed in the detailed procedure. This method tolerates the presence of several milligrams of zirconium and iron (II), and 20 to several hundred micrograms of the other elements without interference. Occlusion tests showed that the amount of zirconium occluded varied from 0.2 mg to 2 mg of zirconium dioxide, depending on the size of the thorium iodate precipitate and the amounts of zirconium tested (for thorium the range tested was 2 micrograms to 2 mg $ThO_2$, for zirconium 2 mg to 30 mg $ZrO_2$). Occlusion was highest for highest thorium. Similarly, the amounts of iron occluded varied from 200 micrograms to 1.6 mg $Fe_2O_3$. For microgram amounts of thorium, less than 200 micrograms of $Ce_2O_3$ was occluded when 30 mg was added and less than 20 micrograms of titanium dioxide from 30 mg of titanium oxide tested. The amounts of niobium and tantalum occluded were estimated to be less than 200 micrograms of each. Further separation of these elements is accomplished when the sample is fumed in the perchloric acid step of the procedure. No tests were made on the extent of scandium occlusion.

## Reagents and apparatus

All chemicals used are reagent grade.

Ferric nitrate (carrier solution), 1 ml is equivalent to 2 mg of $Fe_2O_3$: Dissolve 0.875 g ferric nitrate hexahydrate in 100 ml of (1+99) nitric acid.

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 50 percent potassium hydroxide solution to 500 ml with water.

Ammonium nitrate (wash solution): Dissolve 5 g of ammonium nitrate in 500 ml of water.

8-hydroxyquinoline solution: Dissolve 0.5 g of reagent in 100 ml of (1+99) nitric acid.

Hydrogen peroxide solution, 3 percent: Dilute 10 ml of 30 percent hydrogen peroxide to 100 ml with water.

d-tartaric acid solution: Dissolve 600 g of tartaric acid in sufficient water to make a liter of solution. Filter through a dry paper and do not wash.

Potassium iodate solution, 6 percent: Dissolve 60 g in water to make a liter of solution. Filter through a dry paper and do not wash.

Mercuric nitrate (carrier solution), 1 ml is equivalent to 1 mg HgO: Dissolve 1.58 g mercuric nitrate monohydrate in 10 ml of (1+1) nitric acid and dilute with water to a liter.

Iodate wash solution: Mix 60 ml of nitric acid, 6 ml of 30 percent hydrogen peroxide, and 200 ml of 6 percent potassium iodate solution with enough water to make a liter of solution.

Cupric chloride (catalyst solution), 1 ml is equivalent to 0.2 mg CuO: Dissolve 0.107 g cupric chloride dihydrate in 250 ml of water.

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

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

Mesotartaric acid, 10 percent: Dissolve 100 g of mesotartaric acid in 400 to 600 ml of hot water. Add paper pulp and filter under suction. Cool and add water to a liter. The reagent is available from the Jasonols Chemical Corp., Delta Chemical Co., and Bios Chemical Co.

Sand bath: The one used was made from aluminum sheet metal. The dimensions were 12 x 12 x 4 inches and contained a 3/4-inch layer of sand. Tubes made 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. The tubes accommodate 100-ml beakers and act as radiators for the evaporation of perchloric acid. The bath was heated by an electric hot plate which maintained the temperature of the sand (just below the surface) at about 170° to 190° C.

Spectrophotometer: A Beckman DU spectrophotometer with 5-cm cells was used. The cell compartment is preferably cooled by circulating water thermostatically controlled at room temperature.

## Detailed procedure

The preparation of the solution for analysis should present no problems except possibly for an occasional niobium and tantalum ore. Although the medium for the precipitation of thorium will keep niobium and tantalum in solution, there may be a problem in preparing the solution of the sample in this medium without prior hydrolysis of niobium and tantalum. Two alternative procedures will be given for ores. The first procedure is the simplest and is preferred. However, it may fail on high-grade tantalates containing very little titanium. The precipitate obtained with potassium hydroxide from pure tantalum solutions does not dissolve in nitric acid containing hydrogen peroxide. When titanium is present and the weight

ratio of tantalum pentoxide to titanium dioxide is 4 to 1, or less, tantalum acts like titanium and is readily dissolved. One can overcome the difficulty by adding a small amount (5 mg) of pure titanium dioxide powder to high-grade tantalum ores before the peroxide sinter. However, it is preferable to avoid this addition because titanium is a serious interference in the spectrophotometric determination of thorium. For this reason procedure 2, which is of general applicability, is recommended for ores of this type. Procedure 3 is designed for the determination of thorium in silicate rocks.

Procedure 1 (ores).--1. Mix 0.0500 g of a finely ground representative sample of the ore with 2 g of sodium peroxide in a platinum crucible.

2. Sinter the mixture (covered) in a small furnace at $460^{\circ} \pm 20^{\circ}$ C for one 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 peroxide melts and incomplete decomposition of the sample results. The platinum crucible may also be attacked.

3. Place the crucible and melt in a 150-ml beaker containing about 30 ml of water. Cover the beaker immediately with a watch glass; the dissolution reaction may be vigorous.

4. Digest the solution on a steam bath for 15 minutes. Acidify with (1+1) nitric acid, adding about 2 ml in excess. Observe whether the sample is completely decomposed. The results of this observation determine whether step 6 is required.

5. Add 1 ml of ferric nitrate carrier solution. Add one or two drops of 30 percent hydrogen peroxide and then 50 percent potassium hydroxide solution to neutrality. Add 5 ml excess for each 50 ml of solution. Digest on the steam bath for about 15 minutes. Filter on a fast 7-cm filter paper

and wash the precipitate several times with potassium hydroxide wash solution. Drain the precipitate thoroughly by placing the palm of the hand over the funnel and pressing down. If complete decomposition of the sample was indicated in step 4, proceed to step 7. If incomplete decomposition was indicated, proceed to step 6.

6. Wash the precipitate several times with ammonium nitrate wash solution. Disregard any cloudiness that may form in the filtrate. This cloudiness may be either aluminum or magnesium hydroxide. Aluminum hydroxide and silica are salted out by ammonium salts and magnesium is dissolved from the precipitate by the ammonium nitrate wash solution and may reprecipitate in the filtrate. Reject filtrate. Ignite the precipitate in a small platinum or porcelain crucible and fuse with a small amount of potassium pyrosulfate. Leach the melt with 30 ml of (3+97) nitric acid solution. Add several drops of 30 percent hydrogen peroxide and then neutralize with 50 percent potassium hydroxide solution adding 5 ml excess for each 50 ml of solution. Digest the precipitate on the steam bath for 15 minutes. Filter on a fast 7-cm filter paper and wash with potassium hydroxide wash solution. Drain the funnel as in step 5. Reject filtrate.

7. Place a 100-ml beaker under the funnel. Pipet 5 ml of water and 1 ml of 8-hydroxyquinoline into the beaker. Dissolve the hydroxide precipitate as follows: add 1 ml of 3 percent hydrogen peroxide over the precipitate, being careful to make the peroxide come in contact with all portions of the precipitate. When the hydrogen peroxide has drained add 2 ml of hot (1+1) nitric acid slowly and dropwise to allow the acid to dissolve as much precipitate as possible. After the acid drains, add 5 ml of hot water, playing the water over all surfaces of the filter paper. Repeat the sequence of peroxide, acid, and water twice more. Drain the

funnel. All reagents and water are added with pipets to insure proper concentration for the subsequent iodate separation.

8. Add 0.1 ml of potassium iodate solution and 5 ml of d-tartaric acid solution. The solution is now ready for the iodate separation.

Procedure 2 (ores).--1. Follow procedure 1 through step 5. After washing with potassium hydroxide, wash the precipitate several times with ammonium nitrate wash solution.

2. Ignite the precipitate in a small porcelain or platinum crucible and fuse with no more than 0.5 g of potassium pyrosulfate until a clear melt is obtained. If sulfur trioxide is lost completely before complete solution of the sample is obtained, cool the melt and add one drop of sulfuric acid to convert the sulfate to bisulfate. Heat gently and increase heat until a clear melt is obtained. Cool.

3. Transfer the crucible to a 100-ml beaker containing 15 ml of water, 6 ml of (1+1) nitric acid, 5 ml of d-tartaric acid solution, 1 ml of 8-hydroxyquinoline, 0.1 ml of potassium iodate solution, and 3 ml of 3 percent hydrogen peroxide solution all added with pipets. Allow the melt to dissolve in the cold by stirring the solution.

4. Remove crucible and rinse inside and outside with exactly 5 ml of water from a pipet, adding the rinses to the beaker. The solution is now ready for the iodate separation.

Procedure 3 (silicate rocks).--1. Fuse 0.3000 g sample with 3.5 g of potassium carbonate in a platinum crucible.

2. Transfer the crucible to a 150-ml beaker and leach with about 50 to 75 ml of water. Digest. Remove crucible and rinse.

3. Add 5 ml of 50 percent potassium hydroxide solution for every 50 ml of solution. Digest on the steam bath for 15 to 30 minutes. The high

alkalinity serves to keep silica in solution and to break up any carbonate complex of thorium.

4. Filter on a fast 7-cm filter paper and wash with potassium hydroxide wash solution. Drain the funnel.

5. Follow steps 7 and 8 of procedure 1. If a residue remains on the paper after step 7, the sample has not been decomposed completely. In such instances, a sodium peroxide sinter should be substituted for the potassium carbonate fusion at step 1.

Iodate separation

1. Add slowly 10 ml of potassium iodate from a pipet, stirring the solution during the addition.

2. Add slowly 5 ml of the mercury carrier solution from a pipet, again stirring the solution during the addition.

3. Place the beaker in an ice bath and allow to stand for 45 minutes.

4. Stir in a small amount of paper pulp and filter on a slow (No. 42 Whatman or equivalent) 7-cm filter paper.

5. Wash the precipitate thoroughly 6 to 8 times with ice-cold iodate wash solution (25 to 35 ml). Wash further if the sample is known to contain large amounts of titanium, niobium, or tantalum. Disregard any cloudiness or small precipitate which sometimes forms in the filtrate. This is due to post-precipitation of mercury.

6. Drain the precipitate and stem of funnel by pressing funnel with hand. Also drain the last drop from the beaker in which the precipitation was made.

7. Remove beaker containing the filtrate and substitute the beaker in which the iodate precipitation was made. Dissolve the precipitate from the

filter with alternate additions of 5 ml each of hot (1+1) hydrochloric acid and 5 ml of hot water. Repeat the cycle twice more. Drain the paper and funnel stem.

8. Add 1 ml of perchloric acid to the solution and evaporate the solution on a steam bath until the solution is colorless and fumes of perchloric acid appear. Place the beaker in a radiator on a sand bath until the perchloric acid is completely evaporated (about 30 minutes). Cool. Careful heating at sand-bath temperature is necessary at this point. Heating on a hot plate sometimes converts any zirconium which might be present to an insoluble form which may occlude thorium.

9. Add 2 ml of (1+1) hydrochloric acid and evaporate the solution on the steam bath until dry. Cool.

10. Add from pipet 1 ml (1+1) hydrochloric acid. Let stand 1 to 2 minutes, then add 4 ml of water. Work the solution up the sides of the beaker. Cover with a watch glass and heat on the steam bath for 5 minutes.

11. Add 1 ml of copper chloride catalyst solution and 1 ml of hydroxylamine hydrochloride. Cover and heat on the steam bath for 5 minutes. Without the catalyst, iron is incompletely reduced at this acidity.

12. Cool the solution. It is now ready for the spectrophotometric determination of thorium.

Note:--Ordinarily, 2 to 60 micrograms of thorium dioxide is determined in the spectrophotometric procedure. If more than these amounts of thorium are present, an aliquot of the solution obtained at step 12 immediately above should be taken. The proper size of aliquot is estimated by observing the size of the iodate precipitate obtained at step 1 of the iodate separation prior to the addition of the mercury carrier. Estimates are made by comparing the sample with a standard amount of thorium precipitated under

The absorbance is corrected for a blank and for cell differences if necessary. Both the reference and sample solutions should be at the same temperature as a difference of about 0.8° C between the two may cause an error in absorbance of 0.002 unit. It is preferable to keep the cell housing at constant temperature by circulating water whose temperature is thermostatically controlled at near room temperature. If this is not feasible, remove the cell carriage from the instrument between readings to prevent overheating of the reference solution.

5. Determine the amount of thorium by reference to a standard curve plotted from the absorbance obtained from known amounts of thorium chloride.

Note:--The blank correction is obtained by carrying about 5 water samples through the iodate separation and spectrophotometric determination and averaging the results. Once the blank correction is found, no further blank determinations are required as long as no new reagent solutions are made. Ordinarily, the blank correction amounts to an absorbance of about 0.005.

## TEST OF PROCEDURES

Several representative ores were analyzed according to the procedures outlined. The results are compared in table 2 with those obtained by careful gravimetric analysis using standard methods. The zircon samples were analyzed according to a spectrophotometric procedure of F. Cuttitta, U. S. Geological Survey (personal communication). The method for silicate rocks was tested on spiked samples because no analyzed samples were available. A standard diabase W-1 (6) containing about 0.0003 percent thorium dioxide was used as the base material to which known amounts of thorium were added in the following manner. Different amounts of standard thorium

Table 2.--Test of procedure, ores.

| Sample | Percent $ThO_2$ | |
|---|---|---|
| | Other method | New method |
| Black sand 1 | 4.00 | 4.05 |
| Black sand 2 | 2.13 | 2.16 |
| Monazite 1 a/ | 9.65 b/ | 9.84 |
| Monazite 2 | 4.24 | 4.26 |
| Zircon 1 | 0.065 | 0.065 |
| Zircon 2 | 0.15 | 0.15 |
| Polycrase euxenite | 5.47 | 5.44 |
| Eschynite | 6.28 | 6.27, 6.22 |
| Thorite | 1.94 | 2.16 |
| Thorianite | 1.72 | 1.77 |

a/ New Brunswick AEC standard monazite.
b/ Certificate value.

nitrate were transferred to platinum crucibles and the solutions evaporated. Five ml of 2 percent potassium carbonate solution was added and evaporated. This was repeated with 5 ml more. These steps insured that any thorium nitrate was washed down from the sides of the crucible and collected in a carbonate matrix. After drying, 0.3 g of sample W-1 and 3.5 g of potassium carbonate were added and the mixtures were fused. The samples were then analyzed following procedure 3 for silicate rocks. Two unspiked samples were included and the average absorbance obtained for these blanks was subtracted from the absorbances given by the spiked samples.

The results obtained are given in table 3 in terms of the percent thorium dioxide that would be present if only the spike is considered.

The silicate rock procedure also was tested on three counting standards obtained from the AEC New Brunswick laboratory. The standards were supplied as mixtures of a standard monazite in a dunite base. A sodium peroxide sinter was used to decompose the samples. The results are given in table 4.

Table 3.--Test of procedure, silicate rock.

| Percent $ThO_2$ | |
|---|---|
| Added | Found |
| 0.00081 | 0.00095 |
| 0.0020 | 0.0021 |
| 0.0049 | 0.0048 |
| 0.0081 | 0.0079 |
| 0.0097 | 0.0097 |
| 0.019 | 0.019 |

Table 4.--Test of silicate rock procedure on monazite-dunite mixtures.

| Percent $ThO_2$ | |
|---|---|
| Present | Found |
| 0.0011 | 0.0014 |
| 0.011 | 0.012 |
| 0.023 | 0.022 |
| 0.057 | 0.055 |
| 0.11 | 0.11 |
| 1.14 | 1.10 |

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