THE DETERMINATION OF THORIUM IN HIGH GRADE AND LOW GRADE ORES

By F. S. Grimaldi and Charlotte A. Marsh

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Contents

Abstract

A procedure is described for the determination of thorium in monazite ores, which is applicable to other ores of a wide range of composition. It is successful for both high and low (down to 0.01% ThO_2) grade ores.

Thorium is separated from calcium, magnesium, and the bulk of the rare earths by double precipitation with ammonia, then from such elements as zirconium, titanium and columbium by precipitation as fluoride, and separated from the remaining rare earths by peroxynitrate precipitation.

Zirconium and sulfate interfere with the peroxynitrate precipitation. Conditions have been found that successfully overcome these interferences.

Introduction

This report revises and supersedes the tentative procedure for the determination of thorium in monazite by the Geological Survey "Peroxide Method" outlined by the writers in Report A-2946.[1] The sources of difficulties mentioned in that report have been further investigated and eliminated, and at the same time the procedure has been adapted to the determination of thorium in low grade ores.

The new procedure is designed to handle ores containing about 0.04% ThO_2 and up. It is reasonably rapid, enabling a chemist to start a sample one day and obtain the results the next day.

Acknowledgment

We thank C. J. Rodden of the National Bureau of Standards for the use of laboratory space at the Bureau, and also for permission to quote Maczkowske's thorium analyses.

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[1] Grimaldi, F. S., and Marsh, C. A., U.S.G.S., Rept. A-2946, June 1947; also in Rodden, C. J., "Thorium Standard Samples", N.B.S., A-2945, June 1947, p. 11.

Outline of procedure

The essential features of the method are:

(1) Decomposition of the sample by fusion with sodium peroxide.

(2) Solution in HNO_3 and precipitation with $NaOH - H_2O_2$ (separation from most of the phosphorus, aluminum, and silica).

(3) Double precipitation with ammonia at the methyl red end point (separation from calcium, magnesium, manganese, and the bulk of the rare earths).

(4) Precipitation as fluoride (separation from zirconium, titanium, columbium, iron, etc.).

(5) Solution of the fluoride by fusion with $K_2S_2O_7$ and removal of sulfate by two $NaOH - H_2O_2$ precipitations.

(6) Repetition of Nos. 3, 4, and 5.

(7) Precipitation as peroxynitrate (separation from remaining rare earths) and ignition to oxide.

Discussion of procedure

A. Solution of the sample. The sample taken for analysis should be two grams or less. In general, a 0.5 gram sample suffices. If a 2 gram sample contains less than 0.5 mg ThO_2, the trace procedure given in report A-2507 2/ is more suitable.

2/ Grimaldi, F. S. and Fairchild, J.G., "Preliminary Report on methods of analysis for very small percentages of thorium, U.S.G.S., A-2507, June, 1945.

The finely powdered sample is decomposed by fusion with sodium peroxide, and the melt leached with water. The hydroxide precipitates that form tend to go through the filter, if filtered off at this point. Acid is therefore added to dissolve the precipitate, and then a NaOH-H_2O_2 precipitation is made. This precipitation separates thorium from the bulk of the silica, phosphorus, and aluminum. Magnesium and a large part of the calcium accompany thorium and are separated later.

B. Major Separations.

1. Separation of thorium from rare earths, calcium, magnesium, and manganese, by ammonium hydroxide.

Thorium is separated from calcium, magnesium, manganese and the bulk of the rare earths by ammonium hydroxide precipitations at controlled acidity.

The precipitation of thorium with ammonia is quantitative at a pH corresponding to the neutral color of methyl red, and at this acidity trivalent cerium and the other rare earths remain largely in solution. Either nitrate or chloride solutions of thorium may be used, but sulfate must be absent. If sulfate is present, considerable losses of thorium result at the methyl red end point, although precipitation of thorium is complete when excess ammonia is used. It is absolutely necessary, therefore, to remove sulfate before making ammonia precipitations at the neutral point of methyl red.

2. Separation of thorium from iron, aluminum, zirconium, titanium, columbium, and the like, by hydrofluoric acid.

Thorium is separated from the members of the R_2O_3 and acid-insoluble groups with hydrofluoric acid. It has been our experience that hydrofluoric acid is faster and more reliable than oxalic acid for this separation especially when small amounts of thorium are involved. Hydrofluoric acid has the added advantage of dissolving any hydrolytic precipitate of the above elements. As an example, if titanium or columbium were to hydrolyse out of solution, oxalic acid solution would not dissolve the precipitate unless the precipitate were filtered off, fused with pyrosulfate, and the melt leached with oxalic acid. Hydrofluoric acid takes these hydrolytic precipitates directly into solution.

3. Separation of thorium from rare earths by peroxynitrate precipitation.

The small amounts of rare earths left with the thorium after ammonia precipitation are removed by precipitation of thorium peroxynitrate in 0.03 N HNO_3. Fenner 3/ says, "The precipitation of thorium with hydrogen peroxide is apparently sensitive to changes of conditions, and the method has been thought by some workers to be unreliable. There seems to be some basis for this view, as I have found that unless certain requirements are fulfilled, hydrogen peroxide will fail to precipitate some or even a large part of the thorium..." We agree with Fenner, except perhaps that he may be

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3/ Fenner, C. N., Am. J. Sci., vol. 16, 369-381 (1928).

understating the case. The peroxynitrate precipitation is influenced by the acidity of the solution, by the concentration of hydrogen peroxide, by various anions and cations, as well as by the order of addition of reagents. For best separation from the rare earths, the acidity should be as high as possible, because at lower acidities cerium tends to be oxidized by the peroxide and to strongly contaminate the thorium. We believe that the highest acidity at which no thorium is lost is very close to a pH of 1.5. Precipitation at this acidity is strongly influenced by the presence of zirconium. When zirconium is present, both thorium and zirconium "lose their identity." Certain combinations of zirconium and thorium will actually fail to yield any peroxynitrate precipitate, but in general both thorium and zirconium are incompletely precipitated.

For many combinations of zirconium and thorium, it was found that the interference of zirconium could be decreased if the excess acid used in adjusting the acidity is added after the hydroxide precipitate of thorium is aged at the neutral point. This is a valuable addition to the procedure, but one combination (5 mg ThO_2+10 Mg ZrO_2) failed to give quantitative precipitation of thorium in spite of considerable variation in conditions and technique (see Experiments I below). For this reason the peroxynitrate precipitation cannot be used unless provision is made first to remove zirconium completely. The procedure here given is designed to do a very thorough job of eliminating this element. The separation obtainable when zirconium is absent is illustrated under Experiments II, below.

The effect of titanium on the peroxynitrate precipitation of thorium was not studied thoroughly, but it is of interest to note that in one experiment (5 mg ThO_2 + 10 Mg TiO_2) it was found that this element did not behave like zirconium, as complete precipitation of thorium was obtained.

Sulfate also interferes in the peroxynitrate precipitation of thorium in 0.03 N nitric acid, causing low recoveries. The losses are of the order of about a mg or less. Sulfate is eliminated by $NaOH$-H_2O_2 precipitation of thorium before the peroxynitrate step.

The amount of ammonium nitrate used does not seem to be an important factor in the peroxynitrate precipitation, but some should be present. The amount of hydrogen peroxide had best be more than 2 ml. 30% H_2O_2 per 100 ml. of solution, since with higher concentrations of peroxide there are less interferences.

Procedure

1. Fuse 0.5 g. of finely powdered sample with about 3 g. Na_2O_2 in a porcelain crucible.

2. Disintegrate the melt with 180 ml. warm water. Neutralize with HNO_3 (1 + 1) and add a few ml. excess. Remove and rinse crucible, adding rinses to the solution. Cool the solution to about 50° C.

3. Add 1 ml. of 30% H_2O_2 and precipitate with 50% NaOH solutions adding 10 ml. in excess. Digest on the steam bath a few minutes. Cool. Filter and wash thoroughly with warm 0.1% $NaNO_3$.

4. Transfer the precipitate from the filter to the original beaker and dissolve what remains on the filter with 15 ml. warm HNO_3 (1 + 1). Wash the paper with water. Reserve the paper. Boil the solution gently for about 5 minutes to destroy most of the peroxide. Dilute to 190 ml. with water. Cool. Add NH_4OH until a precipitate forms which clots, avoiding too great an excess of ammonia (one or two drops excess is just about right). Now add 3 drops 0.1% methyl red in alcohol and neutralize very carefully with HNO_3 (1 + 50) until the methyl red color is just yellow or just under salmon pink. Heat the solution until it just starts to boil. Remove the heater and after the precipitate settles, check the acidity as indicated by methyl red color and adjust if necessary. Filter the solution and wash with 0.1% NH_4NO_3.

5. Dissolve the precipitate off the filter with 15 ml. of warm HNO_3 (1 + 1) and wash the filter paper thoroughly with water. Reserve the paper. Repeat the ammonia precipitation as in step. 4.

6. Unfold the paper and with a little water transfer the hydroxide precipitate to a Pt dish. Combine the filter paper with those reserved in steps 4 and 5, ash them, and add the ash to the dish containing the major precipitate. The volume of the solution at this point should be about 15-25 ml.

7. Add 10-15 ml. of HF, cover the dish with a Pt cover, and digest the solution on the steam bath for at least one hour, stirring occasionally. Allow the sample to stand 1/2 hr. at room temperature.

8. Filter on No. 40 Whatman paper through a hard rubber funnel and wash once with dilute HF and twice with water. Transfer the precipitate to a Pt crucible, cover the crucible loosely with a Pt cover to allow access of air, and burn the precipitate carefully at low heat.

9. Add as little $K_2S_2O_7$ as will dissolve all of the precipitate (1 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 lest the reaction be vigorous and thorium be lost by spattering. Cool. Leach the melt with 300 ml. of water containing 10 ml. HNO_3 (1 + 1).

10. Warm the solution to about 50°C. Add 1/2 ml. 30% H_2O_2 and precipitate with 50% NaOH solution, adding about 4 ml. excess. Digest the sample a few minutes on steam bath. Cool. Filter through a fast paper and wah the precipitate thoroughly with warm 0.1% $NaNO_3$. This precipitation as well as the precipitation in step 11 is made to free the sample from sulfate.

11. Dissolve the precipitate off the paper with 10-15 ml. of warm HNO_3 (1 + 1) and wash the paper with water. Reserve the filter paper. Reprecipitate with $NaOH-H_2O_2$ as in step 10. Filter and wash the precipitate with 0.1% $NaNO_3$.

12. Dissolve the precipitate off the paper with 10-15 ml. of warm nitric acid (1 + 1) and wash the paper with water. Reserve the filter paper. Bring the solution to a boil and simmer gently for about 5 minutes to destroy the peroxide. Adjust the volume of solution to about 150 ml. Cool. Add NH_4OH in very slight excess until a precipitate forms which clots. Add a few drops of methyl red and very carefully neutralize to just yellow or just under the salmon pink color of methyl red. Heat the solution until it just starts to boil. Remove the heater and allow the precipitate to settle. Check the acidity and adjust if necessary. Filter through a fast paper and wash with 0.1% NH_4NO_3 solution.

13. Dissolve the precipitate off the filter with 10-15 ml. HNO_3 (1 + 1) and wash the paper with water. Reserve the filter paper. Reprecipitate with NH_4OH in the same manner. Filter and wash with 0.1% NH_4NO_3. Transfer the paper with precipitate to a Pt crucible and add the filter papers reserved in 11, 12 and 13. Ash at a low heat, keeping the crucible loosely covered.

14. Fill the crucible 2/3 full with HF (about 10 ml.), cover and digest on the steam bath 1/2 to 1 hour, depending on the size of the precipitate. Transfer to a Pt dish with a stream of water, scrubbing the crucible thoroughly. Adjust the volume of the solution to 25-30 ml. with water. Allow to settle a few minutes and filter. Wash with dilute HF and then twice with water. Burn the precipitate carefully in a covered crucible.

15. Dissolve the fluoride precipitate with potassium pyrosulfate as before. Make two NaOH-H_2O_2 precipitations as before.

16. Dissolve the final NaOH-H_2O_2 precipitate with 10 ml. of HNO_3 (1 + 1). Boil the solution 5 minutes to destroy most of the peroxide and to reduce the cerium. Cool. Add NH_4OH in very slight excess so that a precipitate forms and clots. Add 2 drops of methyl red and neutralize with dilute HNO_3 until the color is just red. Heat the solution until it starts to boil and remove the heater. Add 5 ml. of 30% H_2O_2, stir once, and immediately add exactly 1 ml. of HNO_3 (1 + 4). The total volume of solution should be 100 ml. Digest on the steam bath 5 minutes, add filter paper pulp, filter, and wash thoroughly with NH_4NO_3 wash solution. Burn the precipitate very carefully in a loosely covered Pt crucible at low heat and weigh the thorium oxide. The peroxynitrate precipitate of thorium tends to spatter and may be lost mechanically if the heating is hurried and the crucible not covered.

It is seldom that another peroxynitrate precipitation is necessary, but if the precipitate is off-color instead of white, the peroxynitrate precipitate is dissolved in 10 ml. of hot (1 + 1) nitric acid, the solution is boiled to remove peroxide and reduce cerium, and the thorium is reprecipitated with peroxide before igniting and weighing.

Comparison with results by the phosphate - iodate method

Half gram samples were taken for analysis. The samples were analyzed by the above procedure and also by the phosphate-iodate procedure described in Report A-2507. Table I gives the results obtained.

Table I

Comparison with results by the phosphate-iodate method

Sample No.	% ThO_2 Procedure in Text	% ThO_2 Phosphate-iodate Procedure	Remarks
NBS No. 2601	9.60	9.65	This is a standard monazite sand. The average result of five cooperating laboratories was 9.65% ThO_2.
NBS-CP 75-10	4.16	4.30	Maczkowske at NBS reports 4.34, 4.20.
SFRX-11	3.65	3.65	Monazite sand.
NBS No. 2601, diluted	1.14	1.13	Maczkowske at NBS reports 1.13.
Euxenite	1.01	1.00	
NBS-CP 75-4	.68	.66	
NBS-CP 75-6	.44	.41	

Experiments

I. Failure of the Peroxynitrate Precipitation of Thorium in the Presence of Zirconium.

In all these experiments the combination 5 mg of ThO_2 and 10 mg ZrO_2 (added as the nitrates) was used. Analyses of solutions containing this combination failed to give quantitative recoveries of thorium no matter what conditions or techniques were used. The losses generally amounted to about a mg of ThO_2 or less.

The procedure used except for test No. 1 was as follows: The thorium and zirconium nitrates were added to a 150 ml beaker. The solution was diluted to 90 ml with water. A prescribed amount of solid NH_4NO_3 was added and dissolved. Dilute NH_4OH was next added to the yellow color of methyl red. Dilute nitric acid was added until the color turned to just red. The solution was heated just to boiling and the source of heat was removed. A prescribed amount of 30% H_2O_2 was added, the solution stirred once, and immediately a prescribed amount of nitric acid was added. The volume of the solution was made to 100 ml with water and the sample then digested on the steam bath for a prescribed length of time. The precipitate was filtered and washed with ammonium nitrate solution. Quantitative analyses for thorium were made on some of the precipitates; in other tests, the filtrates were tested qualitatively for thorium.

In Test No. 1 the solution of zirconium and thorium was made neutral to methyl red and a prescribed excess of dilute HNO_3 was added. The peroxide was next added and the solution digested before filtering.

In Test No. 20 the precipitation was made in a glass-stoppered Erlenmeyer flask and the solution heated on the steam bath under its own pressure 10 minutes before filtering off the peroxynitrate precipitate.

Table II shows that in no case was precipitation of thorium complete.

Table II

Incomplete precipitation of thorium peroxynitrate in presence of zirconium

5 Mg ThO_2 + 10 mg ZrO_2 used for each experiment. Total volume 100 ml.

Test No.	Amount NH_4NO_3 gram	Amount of excess (1+4) HNO_3 ml	Amount of 30% H_2O_2 ml	Time (minutes) of digestion of peroxynitrate precipitate before filtration	Thorium recovere Mg ThO_2
1	7	1.00	2	5	None
2	2	1.00	2	5	3.9
3	10	1.00	2	5	4.2
4	20	1.00	2	5	4.2
5	7	1.00	5	5	4.3
6	7	1.00	10	5	4.4
7	7	1.00	20	5	4.5
8	7	1.00	5	30	Incomplete
9	7	1.00	15	60	Incomplete
10	5	0.50	2	5	Incomplete
11	20	0.50	2	5	Incomplete
12	7	0.50	5	5	Incomplete
13	7	0.50	20	5	4.5
14	7	0.50	5	10	4.4
15	7	0.50	5	60	Incomplete
16	7	0.50	20	20	4.6
17	20	0.50	10	5	Incomplete
18	20	0.50	10	20	Incomplete
19	20	0.50	20	20	Incomplete
20	7	1.00	10	10 (under pressure)	Incomplete

II. Separation of thorium from rare earths by the peroxynitrate method.

The procedure described in the text was used, and Table III illustrates separations obtainable by peroxynitrate when zirconium is absent.

Cerium was added as cerous ammonium nitrate, thorium as nitrate and the yttrium group as nitrates.

Table III

Separation of thorium from rare earths by the peroxynitrate method

Taken	No. Peroxynitrate precipitations made	ThO_2 found (grams)
0.0564 g ThO_2 + 0.36 g CeO_2	2	0.0568
0.0564 g ThO_2 + 0.20 g Y_2O_3 group	2	0.0567
0.2256 g ThO_2 + 0.006 g CeO_2	1	0.2256
0.2256 g ThO_2 + 0.006 g Y_2O_3 group	1	0.2255
0.0023 g ThO_2 + 0.36 g CeO_2	2	0.0023
0.0023 g ThO_2 + 0.20 g Y_2O_3 group	1	0.0026
0.0023 g ThO_2 + 0.006 g CeO_2	1	0.0023
0.0023 g ThO_2 + 0.006 g Y_2O_3 group	1	0.0023