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CHEMICAL PROCEDURES FOR THE
DETERMINATION OF THORIUM
IN MINERALS AND ORES

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CHEMICAL PROCEDURES FOR THE DETERMINATION OF THORIUM IN MINERALS AND ORES

By A. F. Williams

INTRODUCTION

This report describes the principal chemical methods which are in use at the Chemical Research Laboratory for the determination of thorium in a wide variety of minerals and ores. This report represents a revision of some of the procedures recorded in an earlier report* in the light of experience gained during the past four years.

The method for decomposition of the ore has been standardized for most ores, including very refractory types. A procedure based on the use of m-nitrobenzoic acid is included for the precipitation and separation of thorium. This procedure has been extensively used and, under the conditions described, gives accurate results.

The methods are suitable for the determination of thorium from a concentration of about 0.1 per cent ThO_2 in the original ore up to practically pure thorium oxide (thorianite).

SCHEME OF ANALYSIS

*F. H. Burstall and W. Ryan, CRL/AE-2, Chemical Methods for the Estimation of Thorium in Mineral Products.

INTRODUCTORY NOTES ON ANALYTICAL PROCEDURES

Decomposition of Ore

The method given under Procedures is a standard procedure universally applicable to the decomposition of ores containing thorium and is based on decomposition of the ore by fusion with an excess of potassium hydroxide. Details are given in Procedures, Sec. 1, steps 1 and 2. Steps 3 and 4 deal with the extraction of the cold potassium hydroxide melt by hydrochloric acid solution. The addition of a few drops of dilute hydrofluoric acid solution* exerts a catalytic effect in promoting solution of the fusion product in the acid. This technique has been found particularly valuable for ores which contain zirconium. Even so, a clear acid solution is not always obtained since silica, tin, and titanium, for example, sometime separate as insoluble oxides due to hydrolysis. Experience has shown that any precipitate obtained must not be filtered off at this stage.

Precipitation of Thorium and Rare-earth Oxalates

The acid solution of the potassium hydroxide melt is treated with oxalic acid in order to precipitate thorium and rare earths as oxalates. It has been found that during this procedure much of the hydrolysis precipitate, which sometime separates at step 4, dissolves in excess oxalic acid. This solubility is a reason for not removing the insoluble material before oxalic acid treatment because such material may contain appreciable amounts of adsorbed thorium. Treatment of the oxalates and filter paper with fuming or concentrated nitric acid is employed to destroy oxalic acid and convert thorium and rare earths to soluble nitrates. By evaporating the solution just to the point where solids begin to separate, most of the silica carried down with the precipitated oxalates is rendered insoluble on dilution with water (see Sec. 1, step 10).

The second oxalic acid precipitation described in step 12 is a further stage in the purification of the thorium and rare earths and is only necessary when the original ore contains gross amounts of silica, tin, titanium, etc. In the case of a pure monazite, it is possible to proceed directly to the iodate separation (Sec. 2) or m-nitrobenzoic acid separation (Sec. 5). When a potassium hydroxide fusion is employed for decomposition of the ore, a preliminary oxalate or hydroxide separation is made in order to remove the bulk of the potassium salts derived from the fusion.

Precipitation of Thorium Iodate

The precipitations with potassium iodate separate thorium from the rare earths. Only minor modifications have been introduced to the procedure as described in CRL/AE-2. The thorium is precipitated finally as oxalate (see Sec. 3) or as meta-nitrobenzoate (see Sec. 4).

*R. A. Wells, unpublished work.

Procedure Employing m-Nitrobenzoic Acid for Separation of Thorium from Rare Earths

A useful method for separation of thorium from rare earths involves precipitation with m-nitrobenzoic acid.* Under the conditions given in Secs. 4 and 5, thorium forms an insoluble m-nitrobenzoate, but those of the rare earths are soluble. The procedure is employed directly after the oxalate precipitations. If the amount of rare earths present are appreciable, a double precipitation is used. The method is considerably quicker than the iodate procedure and possesses the advantage that the precipitate filters rapidly and is ignited directly to ThO_2 . Control of pH of the solution before addition of m-nitrobenzoic acid is important, and the technique employed by Neish, namely, adjustment to methyl orange indicator, is not well suited to routine work. The use of acetic acid (see Sec. 4 and 5) for adjustment of the pH of the alkaline solution containing thorium and rare earths allows considerable latitude, and the modified procedure has been shown to give reliable results. The m-nitrobenzoic acid method can be used in the presence of ceric salts; whereas if the iodate separation is employed, the cerium must be in the reduced form. Sulfates must not be present in solution when thorium is to be precipitated by m-nitrobenzoic acid since such material inhibits precipitation of thorium.

PROCEDURES

Sec. 1. Decomposition of Ore and Separation of Thorium and Rare Earths

1. Heat 8 to 10 g of KOH (use analar KOH pellets) to red heat in a nickel crucible (5 in. diameter and $4\frac{1}{2}$ in. deep), maintain at this temperature for about 5 min (in order to remove water), and then allow to cool.

2. Weigh accurately about 1 g of sample and gently transfer to the surface of the cold KOH melt. Replace the crucible lid, slowly raise the temperature of the crucible, and maintain at red heat for about 45 min (A pure monazite may be decomposed in a shorter period of time. The amount of sample taken should be adjusted to give not more than about 0.25 g of ThO_2).

3. Place 100 ml of water and 50 ml of HCl (conc.) in a 600-ml beaker. Quickly leach the cold Ni crucible and lid and remove them with the aid of a pair of tongs, washing well with distilled water.

4. Bring the contents of the beaker to boiling point and add one or two drops of dilute HF solution (1 volume of HF (40% w/v) and 20 volumes of water), continue boiling for about 15 min and allow to cool (See section on decomposition of ore under Introductory Notes).

5. Add ammonia solution (sp gr 0.880) to the beaker with stirring and then make just acid by addition of HCl (conc.) and adjust the volume to 400 ml.

6. Bring the solution again to boiling point, add slowly a hot solution of 12 g of oxalic acid in 10 to 20 ml of water, and stir well. Continue boiling while adding 10 to 12 ml of HCl (conc.) and then set the beaker on one side for about 6 hr or allow to stand overnight.

*First described by Neish, J. Am. Chem. Soc., 26: 780 (1904).

7. Filter the oxalate precipitate using a No. 42 Whatman paper and wash the oxalates with cold oxalic acid solution (Dissolve 2 g of oxalic acid in 100 ml of water acidified with a few drops of conc. HCl).

8. Place the filter paper and oxalate precipitate in the original beaker, add 20 to 30 ml of HNO_3 (conc.) and 5 to 10 ml of perchloric acid (60% w/v), and cover with a clock glass.

9. With the beaker covered, evaporate the solution on a hot plate in a fume cupboard to about 3 ml, add 20 ml of HNO_3 (conc.), and re-evaporate almost to dryness so that the residue has the appearance of being just moist.

10. Add 1 ml of HNO_3 (conc.) and 25 ml of water. Boil the solution and filter through a No. 541 paper containing a little paper pulp. (Suspend a few grams of Whatman paper clippings (No. 42) in water in a stoppered conical flask and shake vigorously.) Wash with hot water. (Acidify with a few drops of HCl (conc.).

11. Dilute the filtrate to a volume of 250 ml, make just alkaline with ammonia (litmus) (sp gr 0.880), and then make just acid with HCl.

12. Repeat step 6; but since the volume of solution is now only 250 ml, use 8 to 10 g of oxalic acid and 8 to 10 ml of conc. HCl. Repeat steps 7, 8, 9, and 10.

13. To the solution, the volume of which should be 100 ml, add 50 ml of HNO_3 (conc.). Add a few drops of H_2O_2 (20 vol) with stirring and heat to reduce ceric ions to cerous. Do not add more than 1 drop excess of H_2O_2 , or iodine will be liberated at step 7, Sec. 2.

Sec. 2. Iodate Separation of Thorium and Rare Earths

1. Slowly add 16 g of KIO_3 dissolved in a mixture of 50 ml of HNO_3 (conc.) and 30 ml of water. Stir continuously. Cool to room temperature, on ice if necessary.

2. Filter through a No. 541 filter paper and wash the iodate as completely as possible on to the paper with iodate wash solution (8 g of KIO_3 and 50 ml of HNO_3 (conc.) diluted to 1 liter, with distilled water), using about 100 ml of wash liquor. Small volumes of wash liquor with frequent drainings should be employed.

3. Remove the filter funnel and carefully wash out the precipitate with distilled water (50 to 100 ml) into a 400-ml beaker. Raise the suspension nearly to the boiling point and add 30 ml of nitric acid (conc.) in small amounts. Complete solution should be obtained. Reserve the filter paper and use again in step 5. Stand the funnel over a beaker.

4. Dissolve 4 g of KIO_3 (sufficient to precipitate 0.25 g of ThO_2) in 15 ml of boiling water and add this to the hot thorium solution from step 3. Stir well and then cool to room temperature, on ice if necessary.

5. Filter the thorium iodate suspension using the original filter paper reserved from step 3. Wash the precipitate with about 100 ml of iodate wash solution (see step 2).

6. Wash off the precipitate (as described in step 3) into the original beaker, using 50 to 100 ml of distilled water. Stand the funnel over a beaker.

7. Add 20 ml of HCl (conc.) to the thorium iodate suspension, warm and pass SO_2 gas until a clear solution is obtained, and then pass sufficient SO_2 gas to give a slight excess.

8. Filter the solution through the original paper (see step 6) and pour the filtrate again through the paper in order to remove all traces of iodate. If iodine is liberated in the solution, insufficient SO_2 has been passed through the solution at step 7. Wash the paper thoroughly with hot distilled water.

9. Boil the filtrate to remove dissolved SO_2 gas. Make the solution just ammoniacal with ammonia (sp gr 0.880). Filter the hydroxide precipitate and wash with dilute ammonia solution (Add 5 g of NH_4Cl and a few drops of NH_4OH (0.880) to 500 ml of distilled water).

Sec. 3. Oxalate Procedure for Final Determination of Thorium

1. Mix 10 ml of HCl (conc.) and 40 to 50 ml of water, heat to the boiling point, and then pour through the filter paper to dissolve the precipitated hydroxides from Sec. 2, step 9. Heat the filtrate and pour this through the same paper. Thoroughly wash the paper with hot distilled water. The filtrate and washings must have a final volume of about 250 ml. Make the solution just alkaline with ammonia and then just acid with HCl.

2. Heat the solution to the boiling point, add a hot solution of 10 g of oxalic acid in 20 ml of water, and stir vigorously. Add 8 to 10 ml of HCl (conc.) while the solution is still boiling and set aside to cool and stand, preferably overnight.

3. Filter the oxalate precipitate on a No. 42 Whatman filter paper, wash with oxalic acid wash solution (see Sec. 1, step 7), and then ignite the paper and precipitate in a tared platinum crucible. (Finally, ignite strongly at about 850°C).

4. Weigh the ThO_2 and express the result as % ThO_2 in the original ore.

Sec. 4. Meta-nitrobenzoic Acid Procedure for Final Determination of Thorium

1. Dissolve the hydroxide precipitate from Sec. 2, step 9, in hydrochloric acid by pouring hot dilute HCl solution through the paper containing the hydroxides of thorium and rare earths; collect in a 400-ml beaker.

2. Evaporate the HCl solution to a volume of about 2 ml. Dilute to 20 to 25 ml with water, add a few drops of bromphenol blue indicator and strong ammonia (sp gr 0.880) solution (contained in a dropping bottle) until the solution is just blue. (A permanent precipitate forms.)

3. Add glacial acetic acid from a dropping bottle until the precipitate just dissolves and the blue color of the indicator turns greenish violet.

4. Add 15 to 20 drops excess of acetic acid and then 250 ml of a saturated solution of meta-nitrobenzoic acid (Add 4 g of meta-nitrobenzoic acid to 1 liter of distilled water. Heat to 80°C on the steam bath, cool, and filter; 250 ml is sufficient to precipitate about 0.15 g of ThO_2). Stir well and then heat to 80°C (approximately) for about 20 min.

5. Filter the hot solution through a Whatman No. 541 filter paper (The precipitate is very easily filtered and washed).

6. Wash the precipitate thoroughly with a cold wash solution of meta-nitrobenzoic acid (5 ml of the saturated m-nitrobenzoic acid solution added to 100 ml of water). Ignite the precipitate and weigh as ThO_2 .

Sec. 5. M-nitrobenzoic Acid Separation of Thorium

1. After destruction of the final oxalate precipitate (Sec. 1) with HNO_3 , add 1 ml of HNO_3 (conc.) to the moist residue and dilute the solution to 20 to 25 ml.

2. Add a few drops of bromphenol blue indicator to the solution and then add ammonia (sp gr 0.880) from a dropping bottle until the solution is just blue (with formation of a permanent precipitate). Add glacial acetic acid drop by drop until the solution becomes greenish violet and the precipitate just dissolves. Add 15 to 20 drops in excess and then 250 ml of a saturated solution of m-nitrobenzoic (see Sec. 4, step 4) acid. Stir well and heat the solution to about 80°C for 20 min.

3. Filter the hot solution through a No. 541 Whatman filter paper and wash with m-nitrobenzoic acid wash solution (See Sec. 4, step 6).

4. Dissolve the precipitate in dilute nitric acid solution by pouring a hot solution of 6 ml of HNO_3 (conc.) and 14 ml of water through the paper containing the precipitate. (Reheat the filtrate and again pour the hot solution through the No. 541 paper.) Wash the filter paper with hot water acidified with nitric acid.

5. Evaporate the solution to about 5 ml. Dilute the solution to 20 to 25 ml with water, add a few drops of bromphenol blue indicator solution, and continue as described in steps 2 and 3. Ignite the final precipitate of thorium-m-nitrobenzoate to ThO_2 and weigh.

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ABSTRACT AND
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