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APPLICATION OF MESITYL OXIDE TO THE DETERMINATION OF THORIUM

by

Harry Levine and F. S. Grimaldi

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ABSTRACT

Thorium nitrate is quantitatively extracted by mesityl oxide from solutions saturated with aluminum nitrate even in the presence of relatively large amounts of phosphate. Uranium is the only other nitrate extracted quantitatively by a single extraction. Zirconium is largely extracted while yttrium and vanadium are extracted to a small extent. Cerium in both valence states is extracted only to a very slight degree, ceric cerium being reduced probably by the olefinic bond in the solvent. Mesityl oxide thus is useful not only for the concentration of uranium and thorium but also for the separation of thorium from the rare earths, the separation taking about 10 minutes per sample.

The mesityl oxide procedure for the determination of thorium has been applied to a wide variety of thorium ores such as monazite, black sands, thorianite, thorite, euxenite, and eschynite.

INTRODUCTION

Solvent extraction methods for the concentration and purification of thorium are important because of their

analytical and commercial applications. Extraction from nitric acid solutions is of special interest in that not only thorium but also uranium may be concentrated. That thorium nitrate is soluble in organic solvents has been known for some time. The earliest papers on this subject were by Misciattelli (1) and Wells (2) and gave data on the solubility of thorium nitrate in ether. In a very recent paper, Rothschild, et al (3) give data on the distribution of thorium nitrate to various ketones and alcohols.

Much work on the commercial aspects of the solvent extraction of thorium nitrate has been published in the project literature. Workers in this field include Spedding, et al (4), Newton, et al (5), Tucker and Wilhelm (6), and Hyde and Tolmach (7). In this work many solvents as well as their use in conjunction with various salting agents are described.

As far as we know practically no work has been done on the application of the thorium nitrate extraction process to the chemical analysis of thorium. This paper describes the use of a new solvent, mesityl oxide, together with aluminum nitrate as the salting agent, in the analysis of thorium ores.

EXTRACTION OF THORIUM NITRATE BY SOME ORGANIC SOLVENTS

Preliminary studies were made on some organic solvents to determine which were most efficient in extracting thorium nitrate. This data is included in this paper because it is thought to be of more than passing interest and may prevent needless duplication of work by other investigators.

In these experiments a standard solution of thorium nitrate (1 ml = 0.0010 g ThO_2) was first made by dissolving the pure salt of known composition in nitric acid (15 + 85). To 5 ml of this solution 9.5 g of $Al(NO_3)_3.9H_2O$ crystals were added and the mixture was warmed to dissolve the aluminum nitrate. The solution was then cooled to room temperature. This amount of aluminum nitrate was found to nearly saturate 5 ml of solution (15% by volume in nitric acid) at room temperature. After the aluminum nitrate is dissolved the volume of the solution increases to about 10 ml or to just about double the original volume. The solution was then poured into a 60-ml separatory funnel. Ten ml of the organic solvent under test was then pipetted into the beaker that contained the original solution and the solvent was agitated. The solvent was then poured into the separatory funnel containing the thorium solution to be extracted. The separatory funnel was shaken vigorously for 15 seconds and the liquid layers were allowed to separate. The water layer was then drawn off and rejected. The solvent layer was then washed once with 10 ml of aluminum nitrate wash solution (2.5M in aluminum nitrate and 1.2N in HNO_3), the wash solution later being rejected. The washed solvent layer was withdrawn and evaporated to dryness. The residue obtained was gently ignited to remove carbon. The residue was then treated with HF to remove aluminum and the ThF_4 was collected, washed, and ignited. This was brought into solution by fusing with $K_2S_2O_7$. The melt was cooled, a little dilute nitric acid was added, and the mixture was then warmed to dissolve the cake. The thorium

was then precipitated with an excess of freshly distilled ammonium hydroxide and finally the thorium hydroxide was ignited to ThO_2 and weighed as such.

Table 1 shows the results obtained with the organic solvents tested. This shows that butyl lactate, cyclopropyl methyl ketone, and mesityl oxide gave the best recoveries of thorium. Cyclopropyl methyl ketone is expensive and largely unavailable and was not considered further. Both butyl lactate and mesityl oxide extracted about the same amount of zirconium. Butyl lactate, however, extracted much more aluminum nitrate than did mesityl oxide and for this reason was not studied further.

EXTRACTION OF THORIUM NITRATE BY MESITYL OXIDE

In these experiments thorium nitrate representing respectively 0.4 mg, 1.0 mg, 5.0 mg, 15.0 mg, 50.0 mg and 100.0 mg of ThO_2 were added to 10 ml portions of nitric acid (15 + 85). Nineteen grams of $Al(NO_3)_3.9H_2O$ crystals were added and dissolved and the solutions obtained were each extracted once with 20 ml of mesityl oxide by shaking for 15 seconds. The mesityl oxide extract was then analyzed for thorium after eliminating any aluminum with HF. The results are shown in table 2 and show that for all portions quantitative recovery was obtained.

Table 1.—Extraction of thorium nitrate by an equal volume of various organic solvents

(Thorium solution 2.5M in aluminum nitrate and 1.2N in HNO_3)

Solvent	% Th extracted
Amyl acetate	40
Benzyl acetate	30
n-Butyl n-butyrate	< 1
iso-Butyl crotonate	< 1
n-Butyl lactate	>99.9
iso-Butyl propionate	< 1
Cyclohexyl acetate	32
B'Ethoxy ethyl acetate	80
Ethyl acetate	45
Ethyl butyrate	35
Methyl benzoate	< 1
Methyl propionate	45
Amylene dichloride	< 1
Anisole	< 1
n-Butyl ether	35
2,5 dimethyl furan	< 1
Ether	35
Cyclohexanone	92
Cyclopropyl methyl ketone	>99.9
Methyl n-amyl ketone	90
Methyl cyclohexanone	96
Mesityl oxide	>99.9

Table 2.--Extraction of thorium nitrate by an equal volume of mesityl oxide

(Thorium solutions 2.5M in aluminum nitrate and 1.2N in HNO_3)

ThO_2 taken (mg)	ThO_2 extracted (mg)
0.4	0.4
1.0	1.0
5.0	5.0
15.0	15.1
50.0	50.0
100.0	100.1

METAL NITRATES EXTRACTED BY MESITYL OXIDE

In these experiments a salt (generally the nitrate) of the element under test was dissolved in 10 ml of HNO_3 (15 + 85). Nineteen g of $Al(NO_3)_3.9H_2O$ crystals were then added and dissolved. The solution obtained was then extracted once by shaking with a 20-ml portion of mesityl oxide for 15 seconds. The mesityl oxide extract was washed once with 20 ml of aluminum nitrate wash solution and was then evaporated to dryness on the steam bath after the addition of a slight excess of NH_4OH (it was found necessary to add NH_4OH to prevent violent bumping during the evaporation of mesityl oxide). The residue was ignited, dissolved, and tested quantitatively for the element under study. The results are shown in table 3.

EFFECT OF PHOSPHATE, ARSENATE, SULFATE, AND BORATE IN THE EXTRACTION OF THORIUM NITRATE BY MESITYL OXIDE

Combinations of 1 g $Na_2HAsO_4.12H_2O$ plus 5 mg ThO_2, 1 g $Na_2B_4O_7.10H_2O$ plus 5 mg ThO_2, and 1 g Na_2SO_4 plus 5 mg ThO_2 were separately extracted (see preceding). The results obtained showed that mesityl oxide quantitatively extracts thorium from these combinations. The effect of phosphate was studied in more detail. Table 4 shows that quantitative results are obtained in the presence of relatively large amounts of phosphate.

Table 3.--Extraction of different elements by an equal volume of mesityl oxide

(Solution 2.5M in aluminum nitrate and 1.2N in HNO_3)

Salt taken	Wt. of element taken (g)	Amount extracted (g)	Method of test
Calcium nitrate	0.1g Ca	none	Oxalate
Beryllium nitrate	0.1g Be	0.00008 BeO	Fluorimetric-quinizarin
Magnesium nitrate	0.1	none	NaOH ppt.
Zirconyl nitrate	0.1	0.074 Zr	Evaporation of solvent and ignition of residue
Aluminum nitrate	1.36	0.004 Al_2O_3	Do.
Neodymium ammonium nitrate	0.05	none	No precipitate with HF
Cerous ammonium nitrate	0.05	0.0008 CeO_2	NaOH-H_2O_2
Ceric sulfate	0.05	0.0008 CeO_2	NaOH-H_2O_2
Lanthanum nitrate	0.05	none	No precipitate with HF
Yttrium nitrate	0.025	0.0024 Y_2O_3	HF; NaOH-H_2O_2 followed by NH_4OH; also spectrographic
Titanium nitrate	0.05	0.00016 TiO_2	H_2O_2
Manganous nitrate	0.05	0.0002 MnO	KIO_4
Ammonium meta-vanadate	0.05	0.008 V_2O_5	H_2O_2
Cobaltous nitrate	0.05	0.00004 Co	NH_4CNS - Acetone
Ferric nitrate	0.05	0.002 Fe	KCNS
Uranyl nitrate	0.0500	0.0500 U	Zinc reduction and $KMnO_4$ titration
Cupric nitrate	0.05	0.0004 CuO	Ammonia blue color
Zinc nitrate	0.05	0.0002 ZnO	Spectrographic
Nickelous nitrate	0.05	none	Dimethylglyoxime
Sodium molybdate	0.05	none	$SnCl_2$ - KCNS
Stannous chloride	0.025	0.0004 SnO_2	Spectrographic
Barium nitrate	0.05	none	No $BaSO_4$ ppt.
Lead nitrate	0.05	none	No PbS ppt.
Indium nitrate	0.05	0.002 In	Spectrographic
Chloroplatinic acid	0.05	0.004 Pt	Reduction with formic acid

Table 4.—Effect of phosphate in the extraction of thorium by mesityl oxide

(Thorium solutions 2.5M in $Al(NO_3)_3$ and 1.2N in HNO_3)

$(NH_4)_2HPO_4$ added (g)	ThO_2 added (g)	ThO_2 extracted (g)	Mol ratio P_2O_5 to ThO_2 (a)
0.0044	0.0200	0.0201	2:9
0.0088	0.0200	0.0200	4:9
0.0133	0.0200	0.0200	2:3
0.0400	0.0200	0.0200	2:1
0.1200	0.0200	0.0199	6:1
0.2000	0.0200	0.0198	10:1
0.8000	0.0200	0.0198	40:1

(a) The most likely mol ratio of P_2O_5 to ThO_2 for monazite lies between 2:1 and 6:1

The conclusions to be drawn from an analysis of the results in tables 2, 3, and 4 are as follows:

1. The extraction of thorium nitrate by mesityl oxide when aluminum nitrate is used as the salting agent is quantitative in a single extraction. Equilibrium is attained rapidly and the same percentage extraction is obtained for both small and large amounts of thorium.
2. Uranium is also extracted quantitatively. Zirconium extracts about 70% and vanadium about 9% in the concentrations selected.
3. Yttrium and cerium are very incompletely extracted. It is expected that erbium will extract in about the same order of magnitude as yttrium. The other rare earths extract to an even smaller extent.
4. The mesityl oxide extraction process may be used for the separation of thorium from the rare earths. This separation should be especially efficient when thorium is in large excess over the rare earths and/or the amount of rare earths is small.

ANALYSIS OF THORIUM ORES

Outline of Procedure

1. Decomposition of sample by fusion with a mixture of $NaF-K_2S_2O_7$.

2. Precipitation of thorium oxalate (separation from U, Cb, Ti, etc.)
3. Separation of rare earths by mesityl oxide extraction, the rare earths accompanying thorium being stripped from the solvent by several washings with aluminum nitrate solution.
4. Precipitation of thorium oxalate and ignition to ThO_2.

Discussion of Procedure

A 0.5-gram sample is decomposed in a platinum crucible by fusing with 3 g of flux (2 parts by weight NaF, 3 parts by weight $K_2S_2O_7$). This flux is similar to $NaHF_2$ and will decompose essentially all the refractory minerals associated with thorium. After the fusion the melt is allowed to cool. Two ml of H_2SO_4 are added (this amount is a little in excess of that required to convert all the NaF to $NaHSO_4$) and the crucible gently heated until all the HF is removed and a clear bisulfate melt is obtained. This process may take as long as 20 minutes. It is most important to remove all the HF (in the last stages of heating copious fumes of SO_3 are evolved) as otherwise some thorium would be lost as ThF_4 in the later steps of the procedure. The crucible containing the cool melt is then immersed in a hot solution of oxalic acid and the thorium oxalate is allowed to digest on the steam bath for about two hours.

The thorium oxalate is filtered off on sintered glass and dissolved with hot (1 + 1) nitric acid. The residue left on

the filter will usually consist of quartz and, surprisingly, hydrolytic precipitates of titanium and zirconium.

In our experience the residue was always found to be free from thorium. The nitric acid solution of thorium oxalate is evaporated to dryness and the residue treated with a little fuming nitric acid to insure the destruction of the oxalate. Aluminum nitrate is added and thorium nitrate is extracted with two portions of mesityl oxide. The small amounts of rare earths accompanying thorium are stripped from the organic solvent by three washings with aluminum nitrate solution. The acid concentration of the solution before extraction is not too critical and may be as high as 25% by volume. Low results were obtained when the concentration of nitric acid was high as 40% by volume due probably to oxidation of the solvent. A final thorium oxalate precipitation is made to free thorium from the last traces of impurities and the thorium oxalate is ignited and weighed as ThO_2.

Procedure

1. Weigh a 0.5-g sample of finely ground ore sample and transfer it to a platinum crucible.
2. Add 3 g of flux (2 parts by weight NaF and 3 parts by weight of $K_2S_2O_7$). Mix and fuse the sample over a burner for about 2 minutes. Cool.
3. Add 2 ml H_2SO_4 and heat gently over a burner until all the HF is removed and a clear bisulfate melt is

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obtained (in the latter part of the heating copious fumes of SO_3 should be evolved). Cool.

4. Immerse the crucible and contents in 80 cc of warm oxalic acid solution (5 g oxalic acid to 100 ml of water). After the melt has disintegrated the crucible is removed, rubbed, and rinsed and the washings added to the main solutions. Bring the solution to a gentle boil and boil for 1 minute, stirring the solution continuously.

5. Digest the oxalate (beaker covered) on the steam bath for at least two hours. There is sometimes a period of induction before the thorium oxalate precipitate appears and thus if no oxalate precipitate is obtained after two hours the solution should be digested preferably overnight.

6. Filter (suction) the thorium oxalate on a glass-fritted medium filter tube and wash with 2% oxalic acid. Reject filtrate.

7. Place a 100-ml beaker under the funnel and dissolve the thorium oxalate with three 10-ml portions of hot (1 + 1) HNO_3, alternating each portion with a limited amount of hot water. Reject residue left on the filter.

8. Evaporate the solution to dryness. Add 3 to 4 ml of fuming nitric acid, cover the beaker, and digest the solution for several minutes on the steam bath. Remove the cover and evaporate the solution to dryness.

9. Take up the residue in 10 ml of nitric acid (15 + 85) warming the solution to dissolve the residue. Sometimes a cloud remains. This will disappear after the addition of the aluminum nitrate.
10. Add 19 g $Al(NO_3)_3.9H_2O$ and warm the mixture to dissolve the crystals. Cool. Pour the solution into a 60-ml separatory funnel.
11. Add 20 ml of mesityl oxide to the beaker containing the original solution. Agitate the solution gently and pour the solvent into the separatory funnel containing the nitric acid solution of the sample.
12. Shake the funnel vigorously for about 20 seconds and then allow the layers to separate. Draw off the aqueous layer into a 60-ml separatory funnel. Reserve the organic solvent layer.
13. Repeat the extraction of the aluminum nitrate solution with 10 ml of mesityl oxide and combine the mesityl oxide layers, rejecting the aqueous layer.
14. Strip the rare earths from the organic solvent by shaking for 20 seconds with three separate 20-ml portions of aluminum nitrate wash solution (9.5 g $Al(NO_3)_3.9H_2O$ to 5 ml of (15 + 85) HNO_3), rejecting each wash solution.
15. Strip the thorium from the organic solvent with two 20-ml portions of water and transfer the aqueous layers to a 150-ml beaker.

16. Add 1 ml of H_2SO_4 and adjust the volume of the solution to about 80 ml. Bring the solution to a gentle boil, add 4 g of oxalic acid, and boil gently for one minute, stirring continuously. Digest the thorium oxalate for at least 3 hours, preferably overnight.
17. Filter the thorium oxalate on No. 40 Whatman filter paper and wash with 2% oxalic acid solution.
18. Ignite to ThO_2 (final temperature about 900°C) and weigh.

RESULTS OF ANALYSES

The mesityl oxide procedure was tried on 12 samples from the Massachusetts Institute of Technology Mineral Engineering Laboratory and two Geological Survey samples which had been analyzed carefully by other methods. The M.I.T. samples had been analyzed in the Institute's Mineral Engineering Laboratory by the oxalate method. The results and comparisons are shown in table 5. In general there is good agreement among the results of the several methods although the discrepancy for sample No. 3927 cannot be explained.

Mr. James H. Pannell of M.I.T., who kindly furnished us the samples and consented to the use of the M.I.T. analytical figures, wishes to stress the fact that the M.I.T. results should be regarded as good estimations only.

Table 5.—Analysis of thorium ores

Sample No.	Description	% ThO_2 M.I.T.	% ThO_2 Method A (8)	% ThO_2 Mesityl oxide method
A-5	Black sand	0.5	---	0.48
A-21	Do	0.2	---	0.24
A-23	Do	2.6	---	2.68
A-25	Do	0.3	---	0.32
A-26	Do	2.0	---	1.82
3063	Thorianite	1.9	---	1.90, 1.80
3181	Do	3.3	---	3.40
3905	Thorite	2.0	---	2.12
3923	Monazite	4.5	---	4.30
3924	Polycrase-euxenite	5.0	---	5.02, 4.90, 5.12
3926	Aschynite	6.9	---	6.60, 6.30
3927	Euxenite	4.3	---	2.20, 2.40, 2.38
HL1	Monazite	---	4.27, 4.32	4.1, 4.2, 4.28, 4.15
HL2	Monazite	---	4.25, 4.27	4.2, 4.3, 4.15

(8) See reference 8.

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