

THE CHEMICAL DETERMINATION OF THORIUM IN ITS ORES

Dep. Mines & Resources
BUREAU OF MINES
APR 4 1951
LIBRARY
OTTAWA, CANADA

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

MINES BRANCH

OTTAWA

Introduction 1

Details of experiments 2

Colorimetric determination of thorium
Synthesis 2
Interferences 3

Colorimetric determination of thorium by
John C. Ingles 7
Decomposition of ores 8
Radioactivity Division
Separation of thorium ions 9
The fluoride separation 9
The oxalate separation 11

Separation of thorium from zirconium 14
The mandelic acid separation 14
Separation of thorium from the rare earths 15
The ammonium benzoate separation 15
The hexamine separation 17
The urea-formate separation 18
The mesityl oxide separation 19

Recommended procedure for the determination of thorium
Memorandum Series No. 110
February, 1951. 21
Oxalate separation 22
Mesityl oxide separation 22
Results 24

References 25

Appendix 26
Reporting of uranium or thorium determinations 26

This document was produced by scanning the original publication.
Ce document est le produit d'une numérisation par balayage de la publication originale.

THE CHEMICAL DETERMINATION OF THORIUM IN ITS ORES

by

John C. Ingles

Radioactivity Division

CONTENTS

	<u>Page</u>
Introduction	1
Details of experiments	2
Colorimetric determination of thorium	2
Synthesis of reagent	3
Interferences	4
Colorimetric determination of cerium	7
Decomposition of ores	8
Separation of thorium from the common interfering ions	9
The fluoride separation	9
The oxalate separation	11
Separation of thorium from zirconium	14
The mandelic acid separation	14
Separation of thorium from the rare earths	15
The ammonium benzoate separation	15
The hexamine separation	17
The urea-formate separation	18
The mesityl oxide separation	19
Recommended procedure for the determination of thorium in ores	21
Oxalate separation	22
Mesityl oxide separation	22
Results	24
References	25
Appendix	26
Reporting of uranium or thorium determinations	26

TABLES

	<u>Page</u>
TABLE No. 1 - Effect of various cations on the absorption of 1-(o-arsonophenylazo)-2 naphthol 3-6 disulphonic acid	5
Table No. 2 - Spectrographic analyses showing separations achieved by hydrofluoric acid treatment ..	11
Table No. 3 - The separation of thorium from cerium by methyl oxalate precipitation	13
Table No. 4 - The separation of zirconium from thorium by mandelic acid precipitation	15
Table No. 5 - The separation of thorium from cerium and zirconium by ammonium benzoate precipitation	17
Table No. 6 - The separation of thorium from cerium and aluminum by hexamine precipitation	18
Table No. 7 - The separation of thorium from cerium by urea-formate precipitation	19
Table No. 8 - The separation of thorium from cerium by extraction with mesityl oxide	20

ILLUSTRATIONS

The spectrophotometric absorption of 1-(o-arsonophenylazo)-2 naphthol 3-6 disulphonic acid	6
--	---

THE CHEMICAL DETERMINATION OF THORIUM IN ITS ORES

by

John C. Ingles

Radioactivity Division

INTRODUCTION

Thorium, as it occurs in nature, is invariably associated with elements such as the rare earths which resemble it closely in chemical properties, and with others, such as niobium and tantalum, that do not respond readily to conventional analytical procedures. Like uranium, it is frequently present in considerable amounts in refractory minerals not ordinarily considered to be radioactive, such as biotite and zircon. The steps required to decompose the sample must, therefore, be severe. To date no simple procedure for the solution and subsequent separation of thorium from the other constituents of an ore has proved entirely satisfactory.

Thorium does not cause interference in the chemical and fluorimetric procedures used in the Division's laboratories for the determination of uranium. It does cause interference however, in routine radiometric determinations but its presence is detected readily and the amount present may be estimated roughly by a simple calculation. The direct radiometric determination of thorium can be carried out with good precision provided the uranium-thorium ratio is not too high, and the sample is in a state of radioactive equilibrium. Since this determination requires much less time than any chemical procedure presently available, it is preferred where applicable. However, a chemical determination is

necessary as a check on radiometric methods and for altered ores or other materials in which the radioactive decay products are not in equilibrium.

The Division undertook the present investigation to evaluate a number of procedures for the separation and determination of thorium, and to combine those separations which appeared most reliable into an integrated procedure. With a view to lowering the limits of determination, the possibility of employing certain elements as carriers for thorium precipitates was also investigated. However, it was found that the introduction of the elements used reduced the specificity of the separations to a marked degree and the use of carriers is not, therefore, included in the recommended procedure described in this report.

This procedure requires from three to six days to complete, depending upon the complexity of the samples. With proper facilities, from six to ten samples can be handled by one analyst, allowance for overnight evaporation of solutions and the digestion of precipitates being particularly desirable.

DETAILS OF EXPERIMENTS

The Colorimetric Determination of Thorium

A rapid method for the detection and the determination of small amounts of thorium in the samples is essential in the investigation of procedures for separating thorium from the various elements commonly associated with it.

A colorimetric reagent which meets the above requirements, 1-(o-arsonophenylazo)-2 naphthol 3-6 disulphonic acid, is described in a recent publication by Thomason, Perry, and Byerly (1). Although this reagent is subject to many interferences, it has outstanding advantages. It will detect 10 micrograms of thorium in a 10 ml. volume of solution. Since the sensitivity of the reagent to the interfering ions, except zirconium, is much less than to thorium, the purity of thorium precipitates can be checked by weighing them, then ~~the~~ dissolving and estimating the thorium content colorimetrically. If the weight of the precipitate is much in excess of that calculated from the colorimetric result, the precipitate is almost certainly contaminated. The amount of sample consumed by this check is insignificant in relation to the usual weight of thorium precipitated so that the balance can be re-treated, and again weighed without affecting the over-all accuracy. In a qualitative way, this sometimes serves to identify such contaminants as cerium IV which decolorizes the reagent, and zirconium which gives a distinctive red turbidity.

Synthesis of 1-(o-arsonophenylazo)-2 naphthol 3-6 disulphonic acid

This reagent is not available commercially so it was necessary to produce it synthetically. The starting material was o-nitroaniline which was converted to o-nitrophenylarsonic acid in good yield by the method developed by Kashima (2). The next step, reduction of the o-nitro acid to the o-amino acid, presented considerable difficulty but was finally accomplished by a procedure devised by Jacobs, Heidelberger and Rolfe (3). Kalb's method (4) was tried but without success. The conversion of the o-aminophenylarsonic acid to the corresponding diazo-

compound and its subsequent coupling with R-salt (sodium salt of 2,3,6 naphthol-sulphonic acid) to form the colorimetric reagent was carried out as described by Thomason and others (1).

Approximately 3 grams of the reagent were prepared. It was not analysed for arsenic content to verify its purity, but the absorption spectrum (page 6) coincided with that given by Thomason. Since only 1 ml. of 0.1 per cent aqueous solution is used per determination, the above amount has proved more than sufficient for all the investigational work done to date. The reagent is adequately stable. The properties of a solution exposed in a clear glass bottle in a well-lighted room with northern exposure for several months remained unchanged.

Interferences

Table No. 1 illustrates the effect of various cations on the absorption of the reagent as determined by the same procedure used with thorium solutions.

EFFECT OF VARIOUS CATIONS ON THE ABSORPTION OF
1-(O-ARSONOPHENYLAZO)-2 NAPHTHOL 3-6 DISULPHONIC ACID

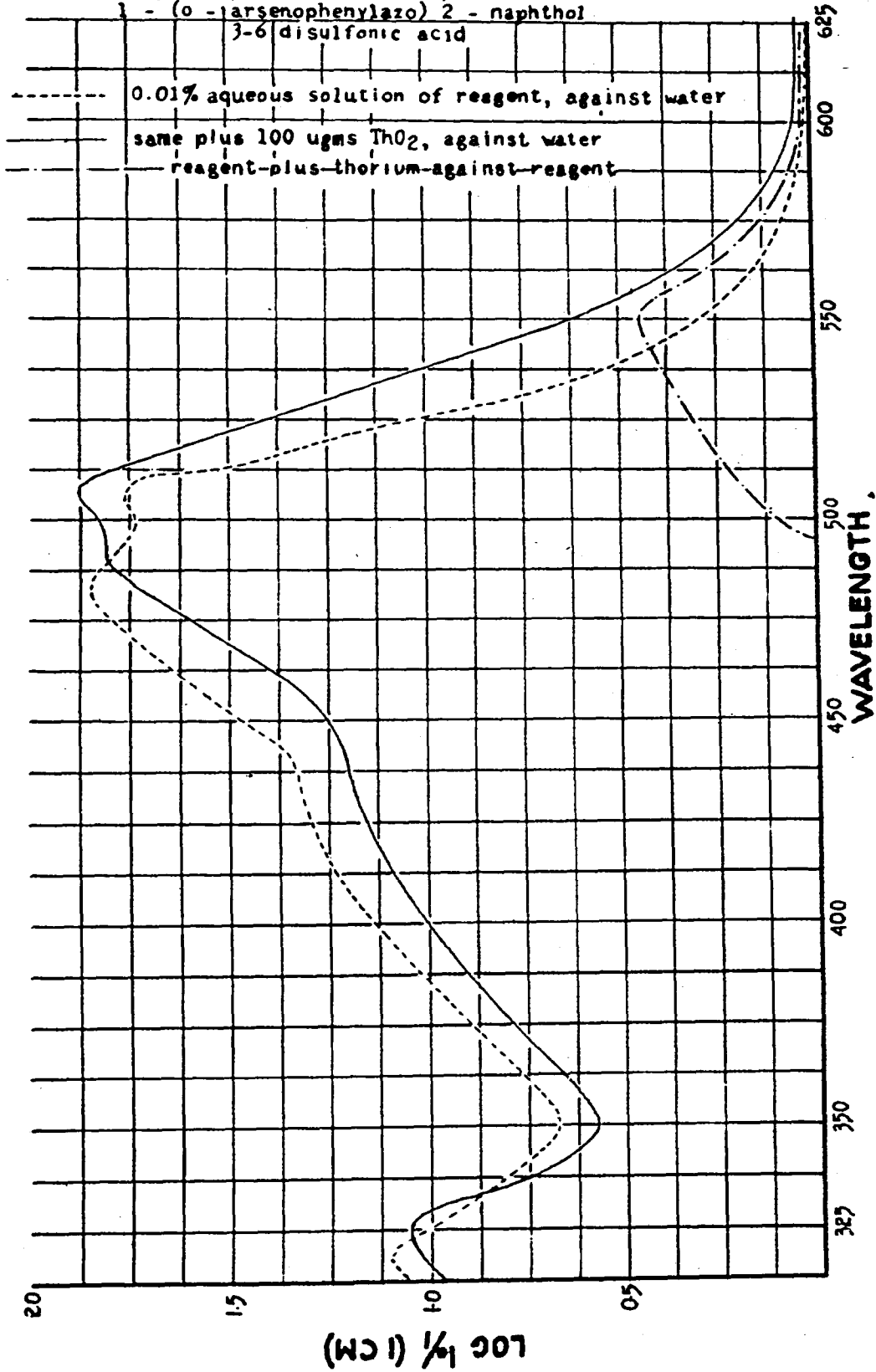
TABLE NO. 1

Cation	Amount in 10 ml. vol. micrograms	Optical Density	Thorium equiv. as ThO ₂
ThO ₂	20	0.103	
	40	0.206	
	80	0.412	
U ⁺⁴	20	0.030	5
	40	0.075	14
	100	0.205	40
Zr	50	0.320	62
	100 (1)	0.365	72
Ge ⁺³	10,000 -	0.115	22
Y	2,000	0.085	16
	4,000	0.157	30
	8,000 (2)	0.192	37
Nd	2,000	0.000	nil
	6,000	0.000	nil
Al	10,000 alone	0.023	4
	in pres. of 12 $\frac{y}{h}$ ThO ₂	0.033	6
	in pres. of 24 $\frac{y}{h}$ ThO ₂	0.040	7

(1) began to precipitate

(2) insufficient reagent to complex all the yttrium

Spectrophotometric Absorption of
1 - (o - arsenophenylazo) 2 - naphthol
3-6 disulfonic acid



Colorimetric Determination of Cerium

A preliminary survey of the problems involved in the determination of thorium in ores showed that the elimination of the rare earths constitutes one of the major difficulties from the standpoint of quantity involved, frequency of occurrence, and difficulty of chemical separation.

A rapid, sensitive method was therefore required for the determination of these compounds in the initial work on separations of synthetic mixtures. Since the determination of most of the rare earths is a difficult, time-consuming operation, it was decided for a number of reasons to use cerium as a typical rare earth. It is one of the commonest of these earths; in its III oxidation state its chemical properties are practically identical with many of the rare earths commonly associated with thorium; and it is a common constituent of thorium ores. It is the most readily available in a state of high purity and by virtue of its IV oxidation state, is readily determined chemically.

Although small amounts of cerium may be determined by a micro-volumetric procedure, it was believed that a colorimetric method would prove more rapid. Some preliminary work was done on a method based on the use of hydrogen peroxide in alkaline solution. This method has been recommended by many writers, all of whom used visual standards for quantitative determinations. It was found that the percerate compound, though highly coloured, is not soluble in the solution from which it is prepared and hence, cannot be used for optical measurements in a spectrophotometer.

It was decided therefore, to use the colour of cerium IV in sulphuric acid solution which, although somewhat less sensitive, is

amenable to objective measurement and is adequately sensitive for the purpose. Furthermore, if the amount of cerium is too great for colorimetric observation it can be determined volumetrically without further treatment.

The method described below is based on one suggested by Sandell (5). A practically identical procedure has since been published by Freedman and Hume (6).

Transfer a 10 ml. aliquot of the sample solution which should be 2N in sulphuric acid, to a 15 ml. beaker with a mark corresponding to a 10 ml. volume. Add 1 drop N/10 AgNO_3 and exactly 0.2 grams ammonium persulphate. Boil exactly 5 minutes, keeping the volume at 10 ml. throughout. Cool quickly in a water bath and adjust to exactly 10 ml. in a volumetric flask using 2N sulphuric acid which has been boiled with ammonium persulphate and silver nitrate. Mix well and read immediately on a Beckman spectrophotometer in a 1 cm. cell at 320 m μ , slit width 0.4 mm. A blank determination should be carried through the whole procedure with the samples. The procedure of bleaching ceric sulphate with a reducing agent and using the bleached solution as a blank introduces serious errors and is not recommended. The observed optical density corrected for the blank is converted to concentration of ceric sulphate by means of an analytical calibration curve.

Decomposition of Ores

It was desired to utilize some of the methods used in the Division for the decomposition of ores for uranium determination as many of the minerals encountered are similar. These methods include treatment with three acids, nitric, hydrochloric and sulphuric, and fusion with potassium

bisulphate, and sodium peroxide sinter. While they have proved entirely satisfactory over a period of years as a first step in uranium determinations, they are not as well adapted to the preliminary treatment of thorium-bearing ores as they introduce large quantities of salts, and necessitate the separation, and the separate treatment of silica, tantalum, niobium, and titanium.

An initial attack with hydrofluoric acid avoids both these difficulties and thus reduces the time required for a determination. Platinum equipment must be used, however, and since these ores sometimes contain constituents such as sulphides, and compounds of arsenic and antimony, the weighed sample must first be roasted in a porcelain or refractory dish. This initial roasting also serves to "open up" the ore to the action of the acid.

Some minerals, for example, zircon and cassiterite, are resistant to the action of hydrofluoric acid. Small amounts can be treated separately after the main part of the ore has been brought into solution, but, if the bulk of the sample consists of such minerals, one of the other methods of attack must be used, the sodium peroxide sinter being most valuable in these cases. It is essential that the entire sample be brought into solution as any undissolved residue may contain thorium.

Separation of Thorium from the Common Interfering Ions

The Fluoride Separation

The initial treatment with hydrofluoric acid removes a large number of interfering elements. Thus, phosphate, niobate, tantalate, titanate, silicate, zirconium, aluminum, and wolfram (tungsten) are largely removed, and some uranium is also separated. Many of these are elements which cause

losses of thorium by occlusion in hydrolytic precipitates and the use of this separation as a preliminary step in the method greatly simplifies the subsequent operations of the procedure.

Using the recommended procedure outlined below, the results of a check of the separation by qualitative spectrographic examination of the residue and filtrates from a typical ore sample confirmed the efficiency of the method.

Method

A one-gram sample of a typical thorium mineral, euxenite - a rare earth colombo-titanate, was roasted in a porcelain dish at 1000° C. and the cooled material was transferred to a platinum dish. A 50 ml. portion of 48 per cent hydrofluoric acid was added and the solution was taken to dryness. A second portion of hydrofluoric acid (20 ml.) was added and taken down to a volume of 10 ml. This was made to a volume of 50 ml. with water and filtered on a # 41 H filter paper in a hard rubber funnel. The residue was washed twice with 20 ml. portions of water. The paper was transferred to the original dish, dried, and ignited. This procedure was repeated twice.

The individual filtrates were taken to dryness and together with the residue insoluble in hydrofluoric acid, were submitted for qualitative analysis. The procedure employed, D.C. arc excitation with graphite electrodes, prevents the detection of some of the rare earths but most of the elements of interest in this separation can be detected with adequate sensitivity.

The results are given in Table No. 2 below.

SPECTROGRAPHIC ANALYSES SHOWING SEPARATIONS ACHIEVED

BY HYDROFLUORIC ACID TREATMENT

TABLE NO. 2

Ore: Euxonite				
Weight taken: 1.00 grams				
Sample	Wt. gms.	Major Constituents	Minor Constituents	Strong Trace
Residue insol. in hydrofluoric acid	0.2440	Y, Yb (1)	Ca, Pb	Fe, Si, Mg
1st filtrate	0.6212	Ti	Nb, Fe	Si, Mg, Y, Yb
2nd filtrate	0.0690	(2)	Y, Yb	Fe, Si, Mg
3rd filtrate	0.0180	(2)	Y, Yb	Fe, Si, Mg
<p>(1) The presence of thorium is not indicated since the amount present was below the limit of detection in the method used.</p> <p>(2) Major constituent not definitely assigned.</p>				

The Oxalate Separation

A survey of the literature indicated that oxalate compounds provide one of the best general separations of thorium from the common ions. The conventional oxalate precipitation is time-consuming since the thorium precipitate requires a long digestion period before obtaining a granular form which can be successfully filtered and washed. The

elapsed time can be considerably shortened by an operation, "Precipitation from Homogeneous Solution", devised by Willard and Gordon (7). In the experiment described below, methyl oxalate was used as the precipitant in place of oxalic acid and gave satisfactory recoveries of small amounts of thorium. It is noted that a considerable amount of cerium was separated from the thorium which of course increases the value of the reagent.

Method

Synthetic solutions containing 11.8 mg. of thorium oxide and 20.8 mg. of cerium were precipitated and washed according to the directions of Willard and Gordon (7). The filtrates were analysed colorimetrically for cerium and thorium. The precipitates were redissolved and the thorium was precipitated again. The second filtrate was similarly examined. Finally, the precipitate was dissolved and tested colorimetrically for cerium and thorium. In all cases, the apparent thorium content was corrected for the known cerium content of the solution.

The results are given in Table No. 3 below.

THE SEPARATION OF THORIUM FROM CERIUM

BY METHYL OXALATE PRECIPITATION

TABLE NO. 3

Thorium taken: 11.8 mg. ThO ₂			
Cerium taken: 20.8 mg. Ce			
Sample	Test	ThO ₂ found (mg.)	Ce found (mg.)
Filtrate from 1st Precipitation	1	0.09	2.3
	2	0.14	4.6
	3	0.07	4.0
	4	0.10	3.9
Filtrate from 2nd Precipitation	1	0.04	5.9
	2	0.09	4.6
	3	0.02	4.3
	4	0.12	6.0
Precipitate	1	11.3	12.1
	2	11.4	10.2
	3	11.5	12.3
	4	11.6	11.1

Separation of Thorium from Zirconium

The Mandelic Acid Separation

The general excellence of the mandelic acid precipitation of zirconium (8) was verified in the Division's laboratories in the estimation of zirconium in ores. Since zirconium is the most serious source of interference with the colorimetric method for thorium, a number of tests were carried out to determine whether or not this reagent can be used to separate these two elements quantitatively. Thorium was determined colorimetrically in the filtrate after destruction of the excess mandelic acid with nitric and perchloric acids.

The results confirmed the cleanness of this separation, and indicated that it would be useful in the determination of thorium in a high-grade zirconium ore. However, the extreme difficulty of destroying the large amount of mandelic acid present in the filtrate rules this method out as a practical thorium separation for routine use. Nevertheless, it is possible that a rapid method of removing the excess mandelic acid will be found, in which case this separation could be extremely valuable.

The results obtained are given in Table No. 4 below.

THE SEPARATION OF ZIRCONIUM FROM THORIUM
BY MANDELIC ACID PRECIPITATION

TABLE NO. 4

Wt. ThO ₂ taken	Wt. Zr taken ng.	Wt. ThO ₂ found in filtrate
11.8 ng.	100.0	11.6 ng.
11.8 ng.	100.0	11.4 ng.
23.6 ng.	100.0	23.4 ng.
23.6 ng.	100.0	23.3 ng.
51 μgm.	10.0	43 μgm.
51 μgm.	10.0	48 μgm.

Separation of Thorium from the Rare Earths

Most thorium minerals contain a high proportion of the rare earth elements. A number of the methods most recently recommended for this separation were therefore, studied using simple mixtures of synthetic solutions. The composition of these mixtures and the results of the separation are shown below in tabular form for each method investigated. The cerium and thorium contents of the precipitates and filtrates were determined colorimetrically in each case.

The Ammonium Benzoate Separation

In an investigation into the applications of ammonium benzoate to analytical separations, Jewsbury and Osborne (9) reported that thorium

can be separated from the rare earths, yttrium, scandium, and iron by precipitation with this reagent at pH 2.0. A number of tests were, therefore, made to determine the effectiveness of the thorium-cerium separation. Since zirconium is a common constituent of thorium ores and is also precipitated by ammonium benzoate, it was included in some of the synthetic solutions to ascertain the effect its presence might have on the separation of cerium.

The possibility of employing zirconium as carrier for trace amounts of thorium and subsequently using mandelic acid to remove the zirconium, was also entertained at this time. For this reason, zirconium was added to some of these solutions to determine its effect on the separation. However, as is seen in Table No. 5, cerium III can not be satisfactorily separated from thorium and zirconium when both are present, although satisfactory separations can be achieved from either one separately. The double precipitation required makes the operation lengthy and filtration is slow due to the limited solubility of the ammonium benzoate at the low pH used.

Method

The method outlined by Jewsbury and Osborne (9) was employed with the exception of an adjustment of the final pH of the solution containing the ammonium benzoate to a pH of 3.5 to ensure complete precipitation,

The results are given in Table No. 5 below.

THE SEPARATION OF THORIUM FROM CERIUM AND ZIRCONIUM
BY AMMONIUM BENZOATE PRECIPITATION

TABLE NO. 5

Wt. ThO ₂ taken, mg.	Wt. Ce III taken, mg.	Wt. Zr taken, mg.	Ce in ppt. mg.	Wt. ThO ₂ in ppt. mg.
11.8	20.1	none	<0.1	11.6
11.8	20.1	none	0.3	11.8
11.8	20.1	10.0	7.9	-
11.8	20.1	10.0	4.0	-
11.8	20.1	10.0	6.1	-
11.8	20.1	10.0	7.4	-
none	20.1	10.0	<0.1	-
none	20.1	10.0	<0.1	-

The Hexamine Separation

The use of hexamethylene tetramine for the separation of cerium and thorium was investigated thoroughly by Ismail and Harwood (10). Two precipitations are required as with the previous method. The precipitate is not bulky, and the possibility of using aluminum as a carrier for trace amounts of thorium was investigated. Although this method gives fairly satisfactory results, it does not appear to offer any advantages over the other methods tested. The use of aluminum as a carrier for thorium in the procedure is inadvisable since it leads to

increased contamination of the precipitated thorium.

The results are given in Table No. 6 below.

THE SEPARATION OF THORIUM FROM CERIUM AND ALUMINUM

BY HEXAMINE PRECIPITATION

TABLE NO. 6

Wt. ThO ₂ taken, mg.	Wt. Ce taken, mg.	Wt. Al taken, mg.	Ce in ppt., mg.	ThO ₂ in ppt., mg.
-	100	50	5.4	-
-	100	50	6.4	-
11.8	100	50	7.0	11.5
11.8	100	50	5.5	10.0
11.8	100	-	0.1	11.5
11.8	100	-	0.1	11.3
11.8	-	50	-	10.0
11.8	-	50	-	9.1

The Urea-Formate Separation

This method was recommended recently by Willard and Gordon (7) as a step in their method for the analysis of monazite sand. Hydrolysis of urea slowly raises the pH of the boiling solution, and the presence of formic acid improves the density of the precipitate. The separation of cerium and thorium was investigated as described. The results

showed that an adequate separation is possible but like all the foregoing methods, it is laborious and time-consuming.

THE SEPARATION OF THORIUM FROM CERIUM
BY UREA-FORMATE PRECIPITATION

TABLE NO. 7

Wt. ThO ₂ taken, mg.	Wt. Co taken, mg.	Wt. ThO ₂ in ppt., mg.
11.8	20.8	11.4
11.8	20.8	11.3
11.8	20.8	11.5
11.8	20.8	11.6

The Mesityl Oxide Separation

The use of mesityl oxide, an organic solvent, for the extraction of thorium nitrate from mixtures of other nitrates has been proposed by Lovino and Grimaldi (11). The advantages afforded by this separation are:

- (1) There is no interference from complexing agents such as phosphate and sulphate ions.
- (2) Thorium is separated from cerium (in both valence states) and from other rare earths as well as from most common cations.
- (3) The operation takes only 10 minutes.

There are, however, drawbacks to the method. Uranium, zirconium,

and vanadium are not separated from thorium, and the extract is contaminated with aluminum (aluminum nitrate is used as a salting-out agent) which must be removed prior to the determination of the thorium either gravimetrically or colorimetrically.

Method

A series of tests was carried out similar to those for the separations previously described. Typical results are given in Table No. 8, and show that the recovery of thorium is quite satisfactory. Because of the speed and the simplicity of the apparatus required, this separation has been incorporated into the recommended procedure. As sulphate and phosphate will be removed during the initial steps of the recommended procedure the effect of these ions on the mesityl oxide extraction was not investigated.

THE SEPARATION OF THORIUM FROM CERIUM

BY EXTRACTION WITH MESITYL OXIDE

TABLE NO. 8

Wt. ThO ₂ taken, mg.	Wt. Ce taken, mg.	Wt. Ce found in extract, mg.	Wt. ThO ₂ found in extract mg.
11.8	20.8	<0.1	11.65
11.8	20.8	<0.1	11.60

RECOMMENDED PROCEDURE FOR THE DETERMINATION OF THORIUM IN ORES

On the basis of the experimental work described, a series of separations was integrated into the following procedure which has been used successfully by the Division for the determination of thorium in several of the common minerals in which it is found.

Weigh accurately a sample sufficient to give 50-100 mg. of thorium oxide. Roast in a porcelain dish for one hour at 1000°C. Transfer to a 60 ml. platinum dish. Add 10 ml. water, moistening the sample thoroughly. Cautiously pour in 30 ml. of 48 per cent hydrofluoric acid. Evaporate to dryness, taking care not to bake the residue. Moisten with hydrofluoric acid and again take to dryness. Add 5 ml. of hydrofluoric acid and 40 ml. of water, and warm. Stir with a plastic rod. Cool, filter on a Whatman # 41 filter paper in a hard rubber funnel. Wash twice with 5 per cent hydrofluoric acid which may be made conveniently by diluting the concentrated acid in the platinum dish and wash twice with water. Transfer the residue and paper to a porcelain crucible. Moisten the paper with concentrated nitric acid, dry thoroughly, and burn off the filter paper at a low temperature (400° C). Wash the residue into a 600 ml. beaker, add 5 ml. concentrated sulphuric acid, 10 ml. concentrated hydrochloric acid, and a few drops of Superoxol. Take to fumes, and repeat the treatment several times to remove the last trace of hydrofluoric acid. Make the solution to 100 ml. and filter off any residue. Fuse the residue with an equal weight of sodium peroxide at 800° F for $\frac{1}{2}$ hour, take up in water, neutralize with sulphuric acid,

and combine with the original solution, keeping total volume below 150 ml.

Oxalate Separation

To the solution in the beaker add concentrated ammonium hydroxide dropwise with vigorous stirring until a slight permanent turbidity remains. If the solution is already slightly turbid at this point, adjust the pH to 2.5. Add 10 ml. concentrated hydrochloric acid and let stand 5 minutes with occasional stirring. Add 6.0 grams of methyl oxalate. Warm the solution to about 75° C and stir slowly with a mechanical stirrer for 30 minutes. Then add a hot solution of 8 grams of oxalic acid in 300 ml. water and stir for an additional 30 minutes, keeping the solution warm. Cool the solution and filter through a Whatman #40 paper. Wash 10 times with a 2 per cent oxalic acid solution adjusted to pH 2.0 with hydrochloric acid. Transfer the paper and precipitate to a porcelain dish, moisten with concentrated nitric acid, and dry thoroughly. Burn off the paper at a low temperature (400° C) and dissolve the residue in concentrated nitric acid. Transfer to a 100 ml. beaker and evaporate to dryness on the steam bath.

Mesityl Oxide Separation (11)

Take up the residue in 10 ml. of nitric acid (15 + 85) warming ~~the solution to dissolve the residue.~~ Add 19 grams $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and warm to dissolve the crystals. Cool. Pour into a 60 ml. separatory funnel. Add 20 ml. of mesityl oxide to the beaker containing the original solution. Agitate gently and pour the solvent into the

separatory funnel. Shake the funnel vigorously and allow the layers to separate. Draw off the aqueous layer into a second 60 ml. separatory funnel. Reserve the organic solvent layer. Repeat the extraction of the aluminium nitrate solution with 10 ml. of mesityl oxide. Combine the mesityl oxide extracts and discard the aqueous layer. Backwash the organic solvent with 3 separate 10 ml. portions of aluminium nitrate solution (9.5 gms. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 5 ml. of (15 + 85) HNO_3) and reject the washings. Strip the thorium from the organic solvent with 3 - 20 ml. portions of water and transfer the aqueous layers to a 600 ml. beaker.

Make to 300 ml. with water and add concentrated ammonium hydroxide dropwise with vigorous stirring until a slight permanent turbidity remains. Add 10 ml. concentrated hydrochloric acid and stir. Let stand 5 minutes. Add 6 grams methyl oxalate. Warm the solution to 75°C and stir slowly for 30 minutes. Add a hot solution of 8 grams of oxalic acid in 300 ml. of water and stir for an additional 30 minutes keeping the solution warm. Cool the solution and filter through a Whatman #40 filter paper. Wash 10 times with 2 per cent oxalic acid solution adjusted to pH 2.0 with hydrochloric acid. Transfer the paper and precipitate to a tared porcelain dish, moisten with concentrated nitric acid, and dry thoroughly. Burn off the paper at a low temperature ($400 - 500^\circ \text{C}$), cool, and weigh as ThO_2 . Dissolve the residue in the crucible in concentrated hydrochloric acid, using a few drops of "Superoxol" and taking care to avoid losses due to effervescence. Transfer to a 50 ml. beaker. Take to dryness several times with hydrochloric acid. Transfer to a volumetric flask of suitable size, so that the diluted

solution will contain 20-80 ugms. ThO_2 per ml. A 500 ml. volumetric flask is required for the sample size recommended. Make to the mark with dilute (1:20) hydrochloric acid. Pipette 1.0 ml. of this solution into a 50 ml. beaker and take to dryness. Add 5 ml. of 1:20 hydrochloric acid, 10 ml. water, 1 ml. of 10 per cent hydroxylamine hydrochloride and boil down to a 5 ml. volume. Transfer to a 10 ml. volumetric flask, add 1 ml. of a 0.1 per cent aqueous solution of 1 - (o-arsenophenylazo) 2 - naphthol 3-6 disulphonic acid and make to the mark. Prepare a blank at the same time, using identical quantities of reagents. Read the developed colour against the blank using the Beckman Spectrophotometer, set at 545 m μ , slit 0.03 mm. in 1.0 cm. cells.

Determine the thorium concentration from an analytical calibration graph.

If there is any serious discrepancy between the colorimetric and gravimetric results, the thorium sample solution should be subjected to a second methyl oxalate precipitation and again determined by the two methods.

Results

The following results were obtained on typical thorium ores. The only analyzed samples available were all monazites.

	ThO_2 per cent	Found
Monazite A 210	7.17	7.3; 7.5
Euxenite W 126		0.78, 0.79
Fergusonite RD 3		0.70, 0.85, 0.70 0.70, 0.90

REFERENCES

1. Thomason, P. F., Perry, M. A., and Byerly, W. M., Anal. Chem. 21, 1239-41 (1949)
2. Káshima, K., J. Am. Chem. Soc., 47, 2207 (1925)
3. Jacobs, Heidelberger, and Rolfo, J. Am. Chem. Soc., 40, 1582 (1918)
4. Kalb, L., Ann., 423, 43, 56 (1921)
5. Sandell, E. B. "Colorimetric Determination of Traces of Metals" Interscience, 1944, p. 185.
6. Froedman, A. J. and Hume, D. N., Anal. Chem. 22, 932 (1950)
7. Willard, H. H. and Gordon, L. Anal. Chem. 20, 165-9 (1948)
8. Kumins, C. A., Anal. Chem. 19, 376-7 (1947)
9. Jewsbury, A. and Osborne, G., Anal. Chin. Acta, 3, 642-55 (1949)
10. Ismail, A.S. and Harwood, H. F., Analyst, 62, 185 (1937)
11. Levine, H., and Grimaldi, F. S., U. S. Geol. Survey; Trace Elements Lab. Invest. 7 Feb. 1950.

APPENDIX

Reporting of Uranium or Thorium Determinations

Under the Atomic Energy Regulations of Canada, the results of an assay or analysis of a mineral that indicates a content of more than 0.05 per cent by weight of uranium or thorium are to be reported forthwith to the Director of the Geological Survey, Department of Mines and Technical Surveys, Ottawa, for the Atomic Energy Control Board, together with full particulars relating to the material assayed or analysed, including the name and address of the person from whom such material was received, the purpose of the assay or analysis, and the origin of the material so far as known to the person making the report. This requirement does not apply to assays or analyses made for persons operating under orders of the Board which provide for periodical reports.

Copies of the Regulations may be obtained on application to the Secretary, Atomic Energy Control Board, Ottawa.