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**THE DETERMINATION OF THORIUM IN ORES  
BY THE COLUMN METHOD**

*7*

by

**R. J. GUEST**  
RADIOACTIVITY DIVISION

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## Abstract

The report describes a method for the determination of thorium in radioactive ores. Thorium nitrate and uranyl nitrate are extracted with ether containing nitric acid in the presence of activated alumina and activated cellulose contained in a water-jacketed glass column. Uranium and thorium are then separated by a second column extraction using different concentrations of ether-nitric solvent, or by an oxalate precipitation of thorium. The thorium is finally precipitated as the oxalate and the precipitate ignited and weighed as thorium oxide.

Microgram amounts of thorium can be determined colorimetrically with 1-(o-arsonophenylazo) -2-naphthol-3, 6-disulphonic acid. This method is used in conjunction with the column method when the amount of thorium oxide in the sample is one per cent or less. Samples containing as low as 0.001 per cent thorium oxide can be analysed successfully. By using lanthanum as a carrier, small amounts of thorium may be recovered by means of an oxalate precipitation. The method compares favourably in rapidity and accuracy with other analytical methods for the determination of thorium in ores.



## CONTENTS

	<u>Page</u>
Part I - Separation of Thorium by the Alumina Cellulose Column and Gravimetric Estimation .....	1
Introduction .....	1
Reagents and Apparatus .....	2
Special reagents .....	2
Special apparatus .....	2
Experimental .....	2
Procedure .....	4
Dissolution of sample .....	4
Preparation of sample for column .....	5
Column extraction .....	5
Oxalate precipitation .....	6
Note 1 .....	7
Note 2 .....	7
Note 3 .....	8
Note 4 .....	8
Results and Discussion .....	9
Summary .....	10
Part II - The Colorimetric Estimation of Small Amounts of Thorium .....	11
Introduction .....	11
Reagents and Apparatus .....	12
Apparatus .....	12
Reagents .....	12
Experimental .....	13
Colour development of neodymium and lanthanum with the colorimetric reagent .....	13
The oxalate precipitation of small amounts of thorium .....	14
Dissolution of the mixed oxides after their ignition .....	16
Effect of lanthanum on colorimetric values for thorium .....	17

	<u>Page</u>
Procedure .....	19
Alternative Procedure .....	20
Note 1 .....	20
Note 2 .....	21
Note 3 .....	21
Results and Discussion .....	21
Summary and Conclusions .....	23
References .....	24
Appendix .....	24

#### TABLES

Table 1 - Comparison of analyses .....	10
Table 2 - Use of lanthanum as a carrier .....	16
Table 3 - Colorimetric and gravimetric analyses of representative samples .....	22

#### ILLUSTRATIONS

Figure 1 - Water-jacketed Glass Column .....	3
Figure 2 - Effects of Lanthanum and Neodymium on the Colorimetric Determination of Thorium .....	15
Figure 3 - Effect of Lanthanum on the Thorium-Thoron Colour ...	18

# THE DETERMINATION OF THORIUM IN ORES BY THE COLUMN METHOD

## PART I - SEPARATION OF THORIUM BY THE ALUMINA-CELLULOSE COLUMN AND GRAVIMETRIC ESTIMATION

### INTRODUCTION

A fast, accurate method for the determination of thorium and uranium in ores was developed recently at C.R.L.\* This method utilizes selective extraction of these elements with ether-nitric solvent through a column of activated alumina and activated cellulose.<sup>(1)</sup> C.R.L. widened the scope of this method to include the analysis of micro-quantities of thorium by developing an accurate spectrographic procedure to be used in conjunction with it. The procedure described in this report is essentially the same as that used at C.R.L., except for some necessary minor modifications.

The general method used begins with fusion of the sample with potassium hydroxide in a nickel crucible, dissolution of the melt in the appropriate acids, and removal of most of the potassium salts by means of an ammonium hydroxide precipitation. The hydroxide precipitate is then dissolved in nitric acid and the sample prepared for the column by "wadding" with activated alumina. The column consists of a layer of activated alumina over a layer of activated cellulose. It is made up in 12.5 per cent ether-nitric solvent and contained in a water-jacketed glass column. The selective absorption is accomplished by means of the alumina. The cellulose serves as a base and as a purifier for the uranium and thorium. Under the conditions used, thorium and uranium are extracted in a pure state and can be easily separated from each other.

\* Chemical Research Laboratory, Teddington, Middlesex, England



If uranium is required, a second column extraction is performed with uranium being extracted by one per cent ether-nitric solvent and then, thorium by 12.5 per cent ether-nitric solvent. The uranium is determined in the usual manner while thorium is precipitated as the oxalate. In cases where the thorium content is less than one per cent, a second column extraction should be carried out thereby lessening the danger of error through contamination. When the thorium content is less than 0.1 per cent the analysis should be finished spectrographically or colorimetrically.

### REAGENTS AND APPARATUS

#### Special reagents

1. Ether, redistilled over potassium hydroxide.
2. Activated alumina (80-200 mesh, Fisher).
3. Whatman's Ashless Cellulose powder, standard grade.
4. Ether-nitric solvent A: Redistilled ether containing one per cent (v/v) nitric acid.
5. Ether-nitric solvent B: Redistilled ether containing 12.5 per cent (v/v) nitric acid.
6. Lanthanum solution: 2.673 gm. lanthanum chloride ( $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ ) dissolved in 100 ml. of 1 per cent hydrochloric acid (v/v).  
1 ml. = 10 mg. lanthanum.

#### Special apparatus

A water-jacketed glass column (internal diameter 2.7 cm., length about 45 cm.). See Figure 1.

### EXPERIMENTAL

Standard samples from C.R.L. and the National Bureau of Standards were run according to the regular C.R.L. method and results were found to be low. Recovery was especially poor on samples low in thorium content,

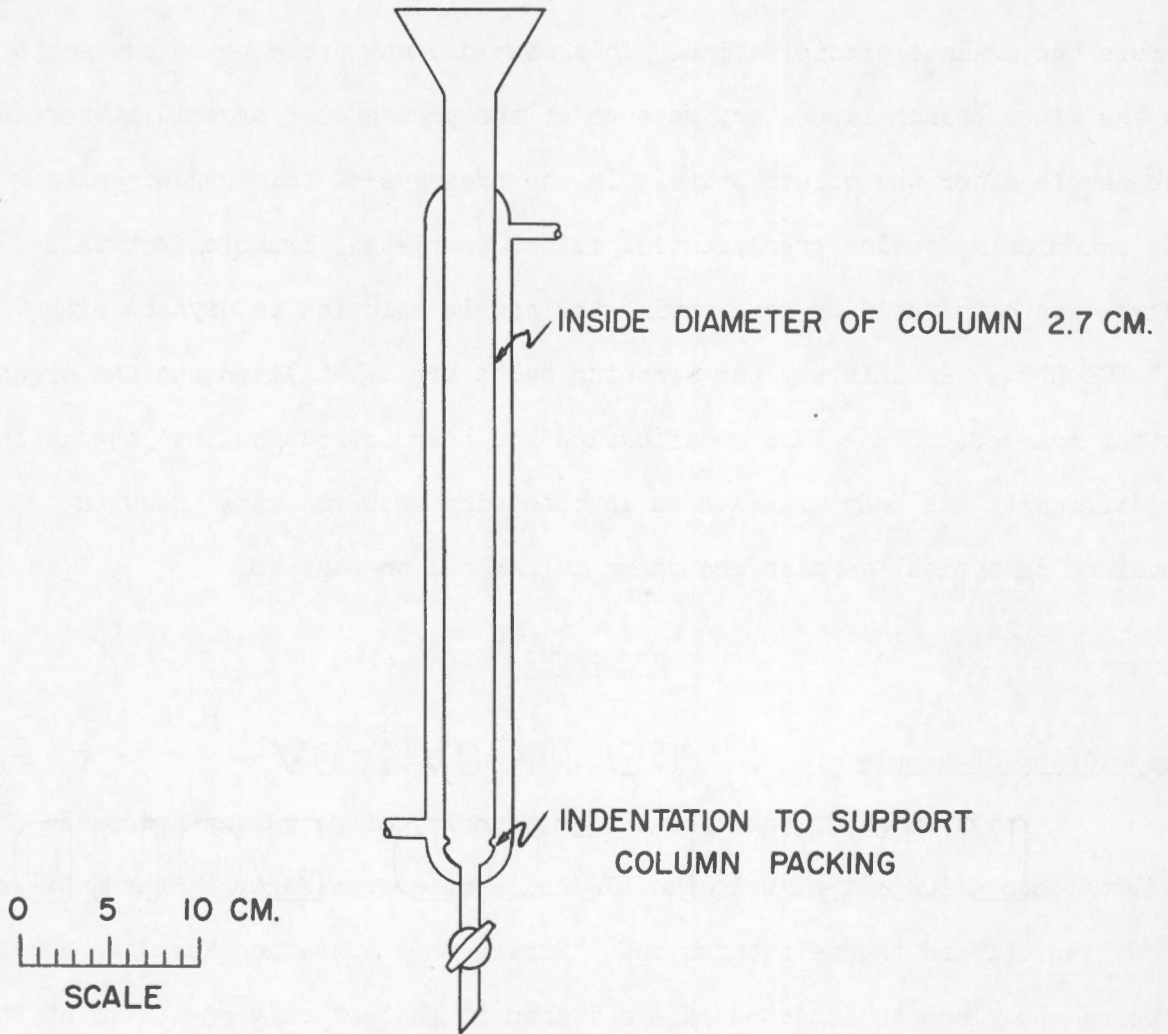


FIGURE 1

losses here running as high as 50 per cent when 4-5 mg. of thorium were being recovered. An intensive program was undertaken to discover the reason for this.

The procedure was followed through step by step with experimental conditions being varied at points where error seemed possible, the cause of the low results being finally traced to the oxalate precipitation stage. At C.R.L., after the ether has been removed from the column extract, an ammonium hydroxide precipitation is done to remove most of the neutral salts before the oxalate precipitation. This step did not prove to be advisable in the Mines Branch laboratory because of the presence of organic matter in the sample after the column stage. In the presence of this organic matter the ammonium hydroxide precipitation is not complete. Trouble from this source was eliminated by evaporating the sample solution to dryness with 1:1 HCl-HNO<sub>3</sub>. In this way the ammonium salts are volatilized and the organic matter removed. Since this modification has been introduced into the method, no difficulty has been experienced in obtaining good results. Results obtained on typical samples are shown in Table 1 on page 10.

#### PROCEDURE

##### Dissolution of sample

Weigh 10 gm. (15gm. for a 2 gm. sample) of potassium hydroxide pellets into a 100 ml. nickel crucible and heat over a Meker burner until water is driven off and the melt turns red. During this operation keep the crucible covered and place an asbestos shield around it so that only one-third of the outer crucible surface is in the direct flame. Cool the melt and place a one gm. sample in the crucible. Heat slowly to red heat as before and continue at red heat for one hour. Cool. Immerse the crucible in a 400 ml. beaker

containing about 200 ml. 25 per cent (v/v) nitric acid and wash out the crucible with water after the reaction ceases to be violent. Boil for about 20 minutes, then add 3-4 drops of 1:40 (v/v) hydrofluoric acid and boil until clear.

#### Preparation of sample for column

Carry out an ammonium hydroxide precipitation and filter on 15 cm. Whatman's 41H paper. Wash the beaker and filter paper twice each with boiling 0.5 per cent ammonium hydroxide, transfer the precipitate to the original beaker and dissolve it in nitric acid. Evaporate to a low volume on the side of the hot plate and evaporate further by means of an infra-red lamp until the contents are just moist. Add 20 ml. of 25 per cent (v/v) nitric acid, cover and heat for 5 minutes under the lamp. After cooling somewhat, add 0.5-1.0 ml. 30 per cent hydrogen peroxide and heat for 10 minutes more. Finally add in the proper order, 8 gm. ferric nitrate and then 1.4 gm. disodium hydrogen phosphate, following each addition with 5-10 minutes heating under the infra-red lamp. (In the case of pure monazite add 4.0 gm. ferric nitrate and 0.3 gm. disodium hydrogen phosphate). Cool for 30 minutes. See Note 1 on page 7 .

#### Column extraction

Add 50 gm. activated alumina to the thoroughly chilled mix and stir thoroughly until the "wad" is a dry homogeneous mass. Cool. Prepare the column with 12.5 per cent ether-nitric solvent B which has been kept cool. Place a porcelain disc covered by a disc of Whatman's 41H filter paper in the bottom of the column. Add 12.5 per cent ether-nitric solvent B to the column and add activated cellulose pulp, mixing well with a glass plunger until a cellulose layer 5 cm. thick is formed. Add activated alumina to the column until a layer of 6 cm. has formed. Mix the activated

alumina with the glass plunger to obtain a homogeneous layer. The layers of cellulose and alumina should be distinctly separate. Keep these layers covered by ether nitric solvent B at all times. Transfer the contents of the beaker to the column. Rinse the beaker several times with the solvent and pass the solvent through the column until 500 ml. of effluent have been collected (Note 3 on page 8). Add 20 ml. water and then, cautiously, 50 ml. ammonium hydroxide. Remove the ether on the steam bath. If uranium is required or if the thorium is less than one per cent, a second column extraction will be necessary. In this case see Note 2 on page 7 and continue with the procedure as outlined there.

#### Oxalate precipitation

Transfer the residual solution to a 250 ml. beaker, boil for 5 minutes and add 10 ml. hydrochloric acid. Warm cautiously until most of the activity has subsided and then take to dryness on the side of the hot plate. Dissolve the residue in a little 1:1 hydrochloric-nitric and evaporate to dryness again. Add a little more 1:1 hydrochloric-nitric, warm until the solution is clear and dilute to slightly under the volume in which the oxalate precipitation is to be made. Neutralise with ammonia and add one ml. of hydrochloric acid for every 25 ml. of solution present. Boil and add one gm. of oxalic acid for every 25 ml. of solution present. Continue boiling for 2 to 3 minutes more and allow to stand for at least 4 hours. Filter on Whatman's #42 paper, wash twice with 2 per cent oxalic acid solution containing 0.1 per cent hydrochloric acid (conc.) and ignite the precipitate at about 900°C. in a tared porcelain or platinum crucible. Weigh as thorium oxide ( $\text{ThO}_2$ ).

NOTE 1

These directions should be followed exactly. Any alteration in volume or order of addition of reagents may cause erratic results.

NOTE 2

After the ether has been removed from the first column extract, transfer the residual solution to a 250 ml. beaker and evaporate to a low volume. Take the solution just to dryness with nitric acid or until most of the ammonium salts are removed. Add a little nitric acid and evaporate the solution by means of an infra-red lamp until just moist. Add 5 ml. 25 per cent (v/v) nitric acid and heat for 5 minutes under the infra-red lamp. Then add 0.5 ml. hydrogen peroxide and heat 5 minutes more. Add 0.25 gm. ferric nitrate and heat for 5 minutes. Finally add 0.05 gm. disodium hydrogen phosphate and heat for 5 minutes more. Cool. Add 12.5 gm. activated alumina to the beaker, stir, cool and transfer to the column which has been prepared as above except that one per cent ether-nitric solvent A has been used and the column consists of 4 cm. activated cellulose and 5 cm. activated alumina. Extract with one per cent ether-nitric solvent A and collect 250 ml. This fraction can be used for the uranium determination. When the level of the one per cent solvent A has dropped to the top of the wad, add 12.5 per cent solvent B and beat up the wad with a glass plunger. Pass 12.5 per cent solvent through the column and collect 350 ml. for the thorium determination. If the thorium content is expected to be less than 0.10 per cent, the analysis should be finished spectrographically. In this case see Note 4. Add 20 ml. water and 25 ml. ammonium hydroxide. Remove the ether, transfer the residual solution to a beaker, boil 5 minutes, add hydrochloric acid and cautiously evaporate to dryness. Continue as above, finally precipitating the thorium as the oxalate.

NOTE 3

The effluent from the column should be collected dropwise over a period of at least 45 minutes.

NOTE 4

To the thorium effluent from the second column extraction add 200 ml. distilled water and remove the ether on the steam bath. (Caution. Do not use ammonia at this stage.) Transfer the residual solution to a beaker and evaporate to a low volume. Add 20 mg. lanthanum in solution form and evaporate the sample just to dryness. Take up the salts in a little dilute nitric acid, neutralize with as little ammonia as possible, and add 4ml. hydrochloric acid. Adjust the volume to about 100 ml. and boil the solution. Add 4 gm. oxalic acid and boil for 2 to 3 minutes more. Allow to stand overnight, filter on Whatman's #43 paper and wash twice with a solution containing 2 per cent oxalic acid and 0.1 per cent concentrated hydrochloric acid. Ignite the precipitate at about 900°C in a tared platinum or porcelain crucible and weigh as thorium and lanthanum oxides. Transfer the oxides to a small tube or sample bottle and determine the per cent ThO<sub>2</sub> spectrographically or colorimetrically as outlined in Part II of this report.

Suggested volumes for oxalate precipitation	ThO <sub>2</sub> present	Suggested sample weight
12.5 ml.	← 2.0 mg.	2 gm.
25 ml.	2-10 mg.	1 gm.
100 ml.	10-40 mg.	1 gm.
200 ml.	40-80 mg.	1 gm.
250 ml.	80-100 mg.	0.5 gm.

## RESULTS AND DISCUSSION

After uranium and thorium, zirconium is the most mobile element in ether-nitric solvent. By adding phosphate to the sample, zirconium is complexed and is not extracted. The presence of phosphate, however, will prevent complete extraction of uranium and thorium so ferric iron is added to complex the excess phosphate. The ferric iron is unable to complex the phosphate unless the iron is added first, so the order of addition of reagents when preparing the sample for the column is a critical factor.

Neutral salts must not be present in appreciable quantities when thorium is being precipitated as the oxalate precipitation will be incomplete. In the procedure described here, neutral ammonium salts are removed by volatilization with  $\text{HCl-HNO}_3$  before the oxalate precipitation stage.

Cerium will move during the column extraction unless it is reduced beforehand. The addition of hydrogen peroxide before the column stage prevents interference from cerium by reducing it to the cerous form which is retained in the "wad".

Iron will occasionally move in the column and be collected with the thorium extract. This contaminant can be easily removed by means of a second column extraction or by the oxalate precipitation. If care is taken with the sample "wadding" before the column stage, little trouble will be met from this source.

Most of the potassium salts are removed before the column stage by performing an ammonium hydroxide precipitation. The presence of a large amount of potassium salts will make the physical state of the sample "wad" unsatisfactory.



Table 1

Comparison of analyses

Sample	Description	Per cent ThO <sub>2</sub> original value	Per cent ThO <sub>2</sub> column method
Bureau of Standards #2601 (A)	Dunite-monazite	0.114 <sup>(1)</sup>	0.125, 0.130
Bureau of Standards #2601 (B)	Dunite-monazite	1.14 <sup>(1)</sup>	1.12, 1.14, 1.07
Sample 1	Monazite	6.48 <sup>(2)</sup>	6.41, 6.28, 6.44, 6.48, 6.50
Sample 2	_____	9.60 <sup>(2)</sup>	9.58, 9.61
Sample 3	Fergusonite	1.06 <sup>(3)</sup>	1.12
Sample 4	Euxenite	1.82 <sup>(3)</sup>	1.90
Sample 5	_____	2.41 <sup>(4)</sup>	2.49

(1) Bureau of Standards value (average value from eight different methods).

(2) C.R.L. value (column method).

(3) Method of J.C. Ingles<sup>(3)</sup>

(4) Geological Survey value.

SUMMARY

This procedure provides a fast, accurate method of analysis for thorium in ores. If desired, uranium can be determined on the same sample. Thorium as low as 0.1 per cent can be determined gravimetrically while samples of lower thorium content can be determined spectrographically or colorimetrically. A determination for thorium by the column method can be completed in 12 hours. Classical methods require at least 24 hours for a determination.

PART II - THE COLORIMETRIC ESTIMATION  
OF SMALL AMOUNTS OF THORIUM

INTRODUCTION

Gravimetric procedures for the determination of thorium leave much to be desired if the amount of thorium present is very low. In such cases weighing errors have serious effects on the final results. In the column method for the determination of thorium, the thorium is precipitated finally as the oxalate. When the quantity of thorium present is small (one mg. or less) the oxalate precipitation may not be complete and it is necessary to use a carrier such as lanthanum and determine the thorium spectrographically.

Thomason, Perry and Byerly<sup>(5)</sup> have described a colorimetric method for thorium utilizing the fact that thorium develops a colour with the compound 1-(0-arsonophenylazo)-2-naphthol-3,6-disulphonic acid (Thoron reagent). While this colorimetric reagent is not specific for thorium, small amounts of contaminants such as uranium and iron can be tolerated. The only elements present after the column separation should be uranium and thorium and these can be separated by an oxalate precipitation, sometimes using a rare earth as a thorium carrier during the precipitation. As the colour development of the rare earths with Thoron reagent is known to be considerably less than that of thorium (3,5), it was decided to attempt to apply the colorimetric method to solutions containing small amounts of thorium and preponderant amounts of rare earths. An alternative consideration was the application of the colorimetric method after a double column separation. In this case uranium will have been removed and the oxalate precipitation can be eliminated.

REAGENTS AND APPARATUS

Apparatus

Beckman spectrophotometer, model "B".

Reagents

(1) Lanthanum solution

Dissolve 11.4 gm. lanthanum chloride ( $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ ) in water slightly acidified with hydrochloric acid. Make the solution up to 500 ml. in a volumetric flask.

One ml. is equivalent to approximately 10 mg. lanthanum oxide ( $\text{La}_2\text{O}_3$ ). The strength of the solution should be checked by means of an oxalate precipitation.

(2) Thorium solution

Dissolve 10.5 gm. thorium nitrate ( $\text{Th}(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ ) in water slightly acidified with hydrochloric acid. Make the solution up to 500 ml. in a volumetric flask.

One ml. is equivalent to approximately 10 mg. thorium oxide ( $\text{ThO}_2$ ). This solution is then diluted to the desired strength. An oxalate precipitation is carried out on the solution as a check on its thorium content.

(3) 0.1 per cent Thoron reagent

Dissolve 0.1 gm. of 1-(0-arsenophenylazo)-2-naphthol-3,6-disulphonic acid in 100 ml. of water.

(4) 1:40 hydrofluoric acid solution

One ml. of 40 per cent hydrofluoric acid is added to 40 ml. of water.

### EXPERIMENTAL

Amounts of thorium oxide varying from 5 micrograms to 225 micrograms were fumed to dryness with perchloric acid, taken up with 12 drops hydrochloric acid (conc.) and made up to about 20 ml. volume. 2.5 ml. of 0.1 per cent Thoron reagent were added and the solution made up to 25 ml. in a volumetric flask. The colour intensity was read at 545 millimicrons on the Beckman spectrophotometer. Standard curves for 10 ml. and 25 ml. volumes using 10 mm. and 50 mm. cells were drawn up. The plots were linear agreeing with previous results.<sup>(5)</sup>

For the oxalate precipitation of small amounts of thorium, especially amounts under one mg., it was expected that the use of a carrier would be necessary. Accordingly, the suitabilities of neodymium and lanthanum for this purpose were tested. It had been indicated in the literature (3) that neodymium produced a negligible colour with the colorimetric reagent. Lanthanum, while giving a definite colour with the colorimetric reagent (3,5), had proven valuable as a carrier in the spectrographic method; hence it was tested for its applicability in this case.

#### Colour development of neodymium and lanthanum with the colorimetric reagent

Amounts of lanthanum oxide and neodymium oxide from one mg. to 10 mg. were tested under the conditions of colour development. The final volumes for colour development were 10 ml. and 25 ml., with one ml. of 0.1 per cent colorimetric reagent present per 10 ml. of solution. The acidity of the solution was adjusted to about 0.3 N. with hydrochloric acid and the colour read against a reagent blank.

## Results

Lanthanum appeared to be the more promising carrier. The colorimetric values with lanthanum were more consistent than with neodymium and the physical structure of lanthanum oxide ( $\text{La}_2\text{O}_3$ ) is more suitable than that of neodymium oxide ( $\text{Nd}_2\text{O}_3$ ) when the sample is to be analysed spectrographically, as well as colorimetrically. Results indicated that neodymium oxide would not be suitable for this purpose as it appeared to melt upon ignition at  $800^\circ\text{C}$ - $900^\circ\text{C}$ . Indications were that a working volume of 25 ml. would be more satisfactory than a 10 ml. volume (Figure 2).

### The oxalate precipitation of small amounts of thorium

Four samples (1-4) containing amounts of thorium oxide from 11.3 micrograms to 226.0 micrograms were subjected to an oxalate precipitation in 25 ml. of solution. In four cases (5-8) 10 mg. of lanthanum oxide was used as a carrier for the thorium. The volume for the oxalate precipitation was 25 ml. 10 mg. of lanthanum oxide was chosen as a convenient amount for the oxalate precipitation.

## Results

A carrier is necessary to recover small amounts of thorium during the oxalate precipitation. Lanthanum appears to be adequate for this purpose (see Table 2). The minimum amount of lanthanum oxide required to assure complete precipitation of the thorium is not known. It is expected that amounts greater than 5 mg. lanthanum oxide will be satisfactory for this purpose.

EFFECTS OF LANTHANUM AND NEODYMIUM ON THE  
COLORIMETRIC DETERMINATION OF THORIUM.

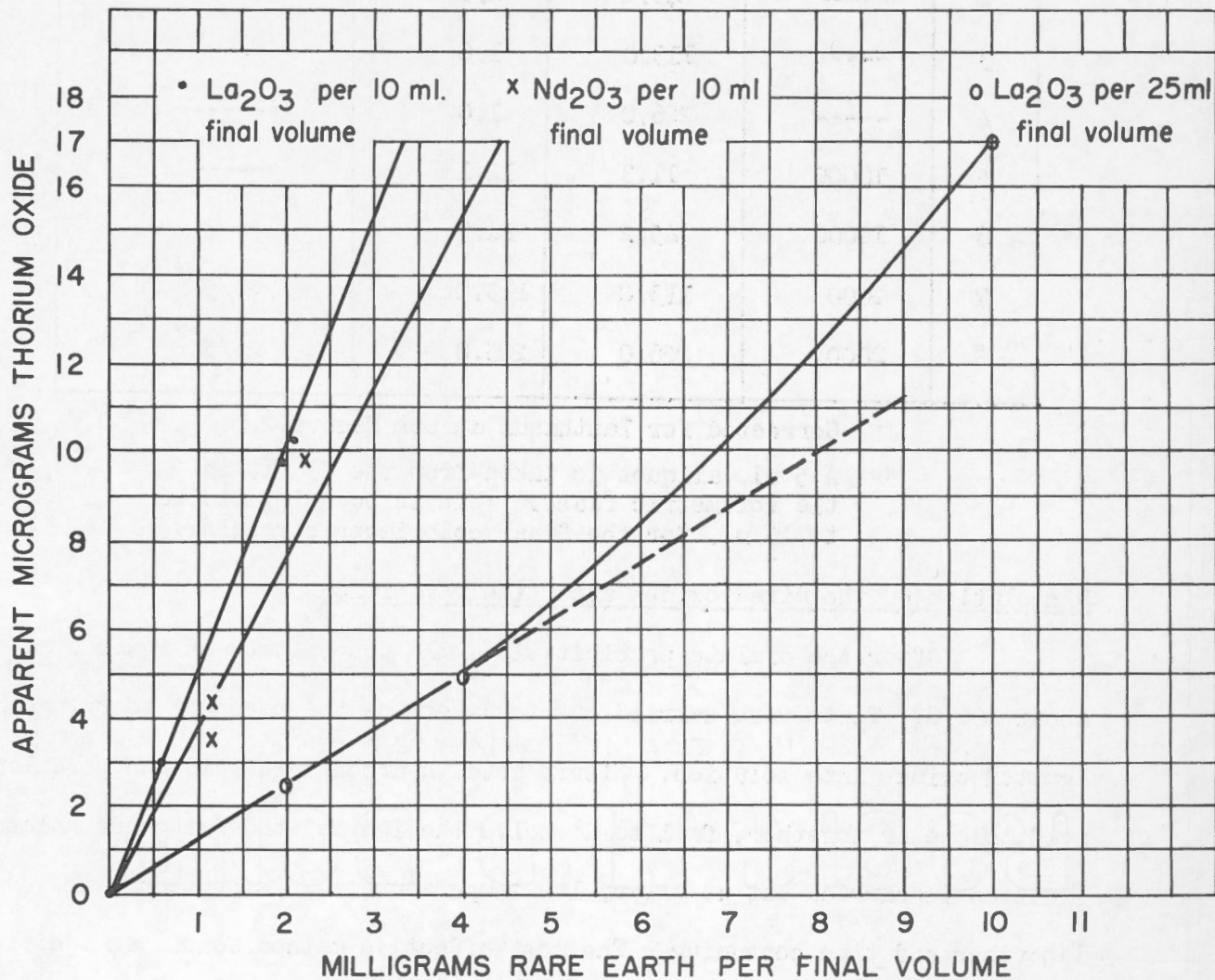


FIGURE 2

Table 2

Use of lanthanum as a carrier

Test	La <sub>2</sub> O <sub>3</sub> present micrograms	ThO <sub>2</sub> present micrograms	ThO <sub>2</sub> <sup>*</sup> found micrograms	Aliquot before colorimetric determination
1	-----	11.3	none det.	-----
2	-----	45.2	2.5	-----
3	-----	113.0	1.0	-----
4	-----	226.0	1.0	-----
5	10000	11.3	12.1	-----
6	10000	45.2	44.7	-----
7	2000	113.0	113.0	25/5 <sup>**</sup>
8	2000	226.0	225.0	25/5 <sup>**</sup>

\* Corrected for lanthanum as per Figure 2.

\*\* A 5 ml. aliquot is taken from the 25 ml. in the volumetric flask. This in turn is diluted to 25 ml. for the final colorimetric reading.

Dissolution of the mixed oxides after their ignition

After the oxalate precipitation, the precipitate is ignited at about 800°C. Tests were carried out to determine the best way to bring the ignited oxides into solution. Nitric acid, hydrochloric acid and perchloric acid, alone or together, fail to dissolve the ignited thorium oxide unless ignition is carried out at a very low temperature. This procedure is laborious and time consuming. The most effective method found was ignition of the oxides at 800°-900°C. and their dissolution by concentrated nitric acid containing 2-3 drops of 1:40 hydrofluoric acid. Fluorides are then removed by fuming the sample with perchloric acid.

### Effect of lanthanum on colorimetric values for thorium

Several samples containing varying amounts of thorium were analysed colorimetrically in the presence of varying amounts of lanthanum. An oxalate precipitation was carried out first in all cases.

#### Results

If the quantity of lanthanum oxide in the final volume is kept at 2.0 mg. or lower, recovery of thorium appears to be quantitative up to at least 200 micrograms of thorium oxide. In actual practice, the dilution is arranged so that not more than 2.0 mg. of lanthanum oxide are present in the final volume for colorimetric determination. A small correction is made for the amount of lanthanum present (Figure 3 and Note 3).

The amount of Thoron reagent in the final volume is not adequate to take care of large amounts of thorium and lanthanum together. This is shown in Figure 3. For example, if 50 micrograms of thorium oxide are analysed colorimetrically in the presence of 10,000 micrograms of lanthanum oxide, a correction can be applied for lanthanum (from Figure 2) and a quantitative result for thorium obtained. In the case of a sample containing 150 micrograms of thorium oxide and 10,000 micrograms of lanthanum oxide, thorium results will be low if the lanthanum correction is applied from Figure 2. The combined lanthanum-thorium curve approaches the true thorium curve for thorium values greater than 100 micrograms when 10,000 micrograms of lanthanum oxide are present. As will be seen from Figure 3 this effect is not noted when as much as 225 micrograms of thorium oxide are present as long as lanthanum oxide content is limited to 2,000 micrograms. The final volume for the colorimetric determination was 25 ml. in all cases.



EFFECT OF LANTHANUM ON THE THORIUM - THORON COLOUR

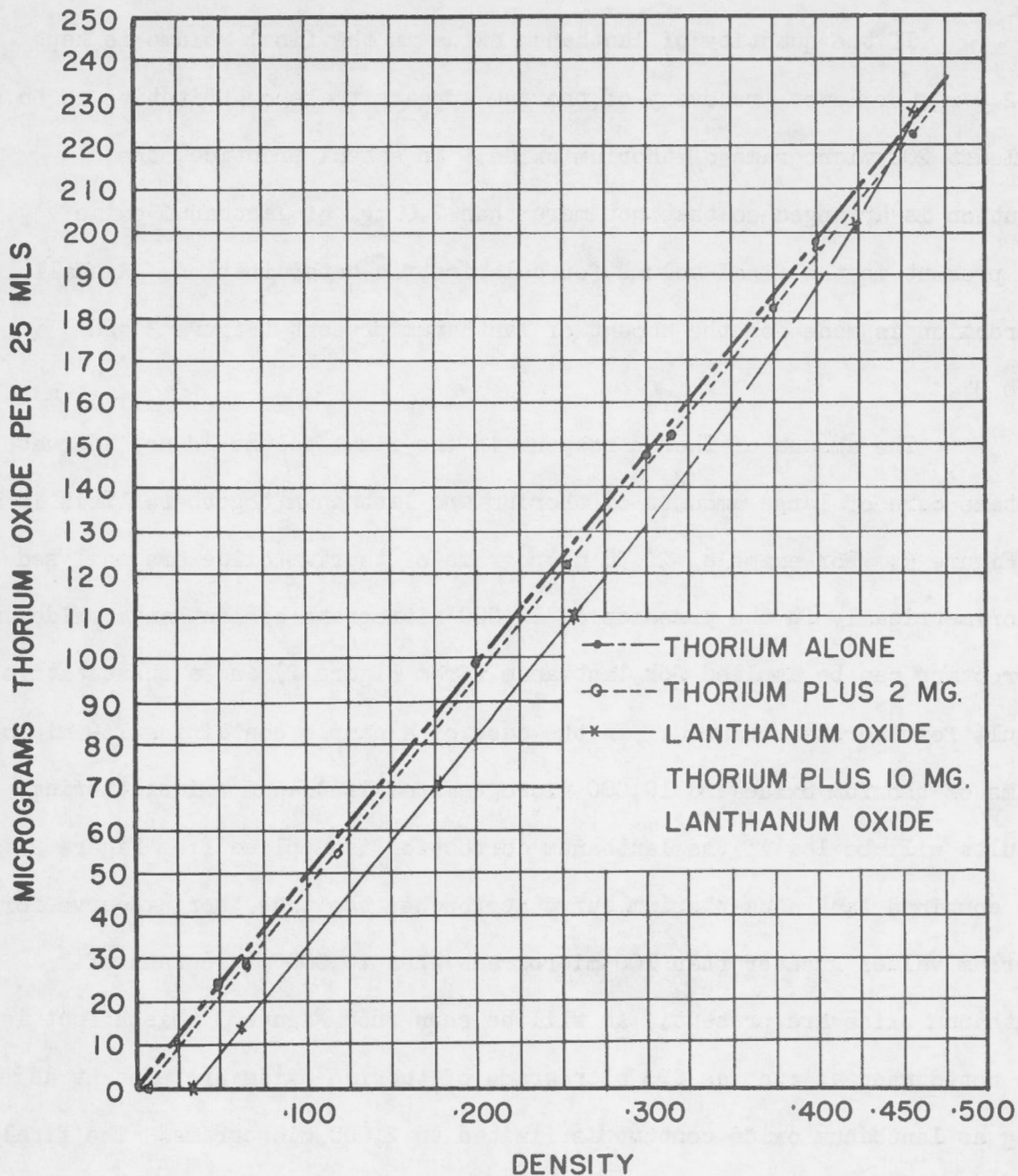


FIGURE 3

PROCEDURE

After the column extraction, remove the ether from the effluent and transfer the solution to a 250 ml. beaker. Add 5 ml. hydrochloric acid and evaporate the solution to dryness. Take the sample to dryness with 1:1 hydrochloric - nitric acid mixture until all the ammonium salts and organic matter are removed. If the thorium is expected to be below one per cent, add 10 mg. lanthanum oxide in solution form and take up the salts in a small amount of hydrochloric acid and water.

Carry out an oxalate precipitation in 25 ml. to 50 ml. of solution in a 250 ml. beaker. A control sample containing lanthanum alone is carried along at the same time. Add one ml. concentrated hydrochloric acid for every 25 ml. of solution present. Bring sample to boil and add one gm. of oxalic acid for every 25 ml. of solution present. Boil 3-5 minutes. If precipitation is slow add a drop or two of concentrated ammonium hydroxide to induce precipitation. Allow the precipitate to stand for about 4 hours and then filter on #42 Whatman paper. Dry the paper and precipitate in a tared crucible and ignite at 800°C (see Note 1). Weigh the precipitate. If the amount of thorium is appreciable the percentage thorium may be calculated by weight. If lanthanum has been added the thorium may be calculated by weight difference.

Place several ml. of concentrated nitric acid in the crucible. Add 2-3 drops of 1:40 hydrofluoric acid solution to the hot mixture and heat gently until dissolution of the precipitate is complete. The solution is transferred to a 50 ml. beaker and 2 ml. perchloric acid added. Fume the sample to dryness. Wash down the sides of the beaker, add one ml. perchloric acid and a few drops of concentrated nitric acid. Fume the sample to dryness.

Take up the residue with several drops of hydrochloric acid and water and make up to volume in a volumetric flask. Take an appropriate aliquot for the colorimetric determination.

Place the chosen aliquot in a 25 ml. volumetric flask. Add enough hydrochloric acid to make the final acidity from 0.3 N - 0.4 N (about 12 drops conc. acid) and dilute to about 20 ml. Add 2.5 ml. of 0.1 per cent Thoron reagent and make up to the mark with distilled water. Allow the sample to stand for 10-15 minutes and then read it against a reagent blank at 545 millimicrons on the Beckman spectrophotometer. A small correction is made for the lanthanum present in the final volume (see Note 3). The amount of thorium present is read from a standard curve.

#### ALTERNATIVE PROCEDURE

After a double column extraction remove the ether and evaporate the solution to dryness. Only thorium should now be present. Add a little nitric acid and 2 ml. perchloric acid, taking the sample to fumes. Repeat the fuming, taking the sample to dryness. Continue as above, following the colorimetric procedure.

#### NOTE 1

If the sample is to be analysed both spectrographically and colorimetrically the mixed oxides are ground in a small mortar and transferred to a small sample bottle. A portion of the sample is then weighed out for colorimetric analysis and the remainder of the sample reserved for spectrographic analysis. In this case it is advisable to add 20 mg. of lanthanum oxide before the oxalate precipitation, rather than the 10 mg. usually added.

NOTE 2

If the sample contains between 0.1 per cent and 1.00 per cent thorium oxide, gravimetric, colorimetric and spectrographic values can be obtained on the same sample. On samples below 0.1 per cent thorium oxide the gravimetric results are of doubtful value.

NOTE 3

The colour development of lanthanum with Thoron reagent is plotted in Figure 2 under the conditions of the colorimetric determination. The density reading produced by the amount of lanthanum present in the sample is subtracted from the total density reading. The resulting density value is then read as thorium oxide from the standard thorium curve. Alternatively, a lanthanum blank containing the amount of lanthanum in the sample may be analysed at the same time as the sample. A correction is then made for the density reading produced by the lanthanum blank.

RESULTS AND DISCUSSION

Several synthetic samples containing lanthanum and thorium were made up and run through the colorimetric procedure. An oxalate precipitation was carried out in all cases.

Complete analysis, including a column separation, was carried out on 4 standard samples. In one case a double column separation was performed and the oxalate precipitation omitted. A colorimetric finish was used in all cases. Results are shown in Table 3.

These results indicate that thorium can be determined colorimetrically with Thoron reagent in the presence of lanthanum. If the amount of lanthanum oxide is kept below 2 mg. when as much as 0.2 mg. of thorium oxide is present, the effectiveness of the method is unimpaired. By adding a large excess of reagent, the

Table 3

Colorimetric and gravimetric analyses of representative samples

Sample	La <sub>2</sub> O <sub>3</sub> present in final volume micrograms	ThO <sub>2</sub> present micrograms	Dilution before colorimetric det.	Per cent ThO <sub>2</sub> present	Per cent ThO <sub>2</sub> found		Column separation	Oxalate precipitation
					colorimetric	gravimetric		
Synthetic	1700	22.6	25/5	0.0011	0.0009	----	----	✓
Synthetic	1700	45.2	25/5	0.0022	0.0022	----	----	✓
Synthetic	1700	113.0	25/5	0.0056	0.0058	----	----	✓
Synthetic	1000	226.0	25/5	0.0110	0.0109	----	----	✓
Synthetic	1000	1,130	50/5	0.056	0.055	0.05	----	✓
Synthetic	200	5,650	100/2	0.282	0.289	0.27	----	✓
Dunite- monazite	----	440	25/5	0.023	0.024	----	(double column) ✓	----
Dunite- monazite	1200	440	100/5	0.023	0.024	----	✓	✓
Dunite- monazite	1000	2,200	25/1	0.114	0.108	0.13	✓	✓
Radiation Laboratory Standard	----	10,000	100/1	1.00	0.97	0.99	✓	✓

range of the method could probably be increased, but it has been found convenient to keep the amount of lanthanum oxide as low as possible. The colorimetric method is applicable after a double column separation. In a case where more than 4 determinations are being carried out, a considerable saving in time is accomplished by using the procedure employing a single column extraction and an oxalate precipitation.

The colour development of thorium with Thoron reagent under the conditions of the procedure is at least 500 times as great as that shown by lanthanum. Little or no change in colour intensity has been found over a period of about 4 hours. Samples should be allowed to stand for 10-15 minutes before reading the colour intensity on the spectrophotometer.

Many cations and anions affect the colorimetric method. Thomason et al. (5) tabulate the effect of a number of these. Amounts of uranium up to 20 times the thorium content can be tolerated. The presence of cations other than thorium has not presented a problem so far. After a column separation and an oxalate precipitation, or a double column separation, no cation except thorium should be present in other than trace amounts.

Anions such as phosphates, oxalates and fluorides should be absent or removed. The bleaching effect of fluorides is very strong and this characteristic has been made the basis of a spectrophotometric method for fluoride.<sup>(4)</sup> Special care should be taken to remove all the fluoride present during the perchloric acid fuming.

#### SUMMARY AND CONCLUSIONS

A rapid and accurate colorimetric method for the determination of small amounts of thorium has been described. The method is applicable in the presence of a considerable amount of lanthanum. The working range of the method is between 0.001 per cent and 1.00 per cent thorium oxide. Provision is made in the procedure for gravimetric, colorimetric and spectrographic determinations on the same sample thus providing a double check on analytical results.

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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.

