DETERMINATION OF THORIUM IN URANIUM ORES AND FEEDS
BY
SOLVENT EXTRACTION EMPLOYING THENOYLTRIFLUOROACETONE.

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ABSTRACT

The thenoyltrifluoroacetone (TTA) extraction method has been investigated for the determination of microgram concentrations of thorium in uranium ores and concentrates. The tolerance limits for eighteen elements commonly found in uranium ore concentrates have been established. The effect of phosphate on extraction of thorium was studied. Cobalt, copper, tin, and bismuth were found to seriously interfere with the Thoron method for the determination of thorium after a TTA extraction. A TTA extraction method is described for the separation of thorium and uranium from the interfering ions, employing preliminary acid sulfide and ammonium hydroxide separations. The method is rapid, and results obtained compare favorably with results obtained with other procedures.

INTRODUCTION

A number of analytical methods have been employed to separate microgram quantities of thorium from uranium and other elements. Nietzel et al.¹ used ion exchange techniques. Sackville² describes the separation of thorium by precipitation of thorium fluoride, using lanthanum as a carrier. Levine and Grimaldi³ employed a mesityl oxide extraction of thorium nitrate from a mixture of other nitrates. In the first two methods, rare earth elements, if present, accompany thorium and interfere with the colorimetric determination of thorium using Thoron.⁴ In the mesityl oxide method, uranium, zirconium, and vanadium are not separated from thorium, and the extract is contaminated with aluminum (aluminum nitrate being used as a salting-out agent) which must be removed prior to the determination of thorium colorimetrically.

The need arose in this laboratory for a rapid and selective analytical method for the determination of from 10 ppm to one per cent of thorium in uranium ore concentrates. This study was undertaken to develop a more satisfactory procedure for the processing of thorium-bearing feed materials.

The chelating agent, thenoyltrifluoroacetone (TTA), has been used to separate thorium from uranium.^{5,6} This method has been found to be satisfactory in this laboratory for determining microgram amounts of thorium in purified uranium materials.

A summary of the extractability of other ions with TTA is given by Morrison and Freiser.⁷ The significant difference in distribution coefficient reported for thorium and the distribution coefficients reported for other elements, (including the rare earths), suggested the application of solvent extraction to more complex materials, such as uranium ore concentrates. A systematic study was necessary to evaluate the method.

THEORETICAL CONSIDERATIONS

In a two-phase system consisting of an aqueous phase and a nonpolar organic phase, thenoyltrifluoroacetone (TTA) is preferentially distributed into the organic phase. TTA is known to form chelates with a large number of metal ions. The following reaction occurs when the organic and aqueous phases containing metal ions are brought together, forming organic-soluble metallic-chelate compounds:⁷

when HT represents TTA, M^{+x} is the metal ion of positive charge x , and (aq) and (org) refer to the phase containing the major portion of that species.

The equilibrium constant, K , for the reaction is given by the following relationship:

$$K = \frac{(MT)_{org} (H^+)_{aq}^x}{(M^{+x})_{aq} (HT)_{org}^x}$$

The dependence of the extraction of the metal ion in Equation (1) on the exponential term, $(H^+)^x$, indicates that sharp changes in the extraction behavior of the metal ion, M^{+x} , may be possible by changing the pH of the solution.

For any particular concentration of the chelating agent, (HT)org, and the anion system, Equation (1) may be more conveniently expressed in terms of the distribution ratio, D , and, the per cent extracted, % E, as follows:

$$D = \frac{E}{100 - E}$$

$$= K (H^+)^{-x}$$

or

$$\log E - \log (100 - E) = \log K' + x \text{pH} \quad (2)$$

The term, K' , is based on the assumptions that the metal ion undergoes no appreciable amount of hydrolysis and forms no intermediate chelate species and that the concentration in the aqueous phase is negligible. A detailed theoretical treatment of the chelate system is given by Morrison and Freiser.⁷

Equation (2) represents a family of symmetrical sigmoid curves for the different metals that react with TTA. The position of the curves on the pH axis is dependent upon the magnitude of the constant, K' , as shown in Figure 1 for thorium, bismuth, uranium, lead, and thallium in a nitrate media.⁸

The dependence of the equilibrium constant, K' , on both ketone and acid concentration creates a flexible condition for sharp changes in the extraction behavior. A particular element may be separated by adjusting the pH and TTA concentration to a value at which the element, plus all those whose pH extraction values are smaller than that of this element, is completely extracted

FIGURE 1 Effect of pH on Extraction of Metals With TTA
(From data presented by F. Hagemann, J. Am. Chem. Soc., 72, 768, 1950)

into the organic phase. The organic phase is then backwashed with an aqueous solution of higher acidity, which returns the desired ion to the aqueous phase. The other elements, whose pH extraction values are smaller, remain in the organic phase. Therefore, selective separations are possible by the use of this technique.

The values for the constant, K' , for a number of metals in a nitric acid media have been reported.⁹ Selective separation of thorium from many metals can be predicted.

However, due to the wide variations in the concentration and in the levels of other metals encountered in uranium ores and refinery feed materials, a detailed study was necessary to establish the tolerance limits for each element.

EXPERIMENTAL PROCEDURE

The effect of individual metal cations, phosphate ion and individual rare earths upon the experimental procedure described below is reported in the following sections:

EXTRACTION WITH 0.5M TTA IN XYLENE⁵

Thorium was extracted from solutions containing phosphate ion or metal ion impurities at a pH of 1.0 ± 0.2 using 0.5M TTA in xylene. The organic phase was backwashed twice with 0.1M HNO_3 . The pH of the extractant was adjusted to 0.5, and thorium was determined colorimetrically.

DETERMINATION OF THORIUM⁴

Five ml of 0.1 per cent aqueous solution of "Thoron" (1-(o-arsonophenylazo)-2 naphthol 3, 6 disulfonic acid) were added to a 50-ml volumetric flask containing the thorium-bearing solution obtained by extraction with TTA in xylene. The sample was diluted to the mark. The absorbance was measured at 545 m μ against a reagent blank carried through all steps of the extraction and colorimetric procedures. A calibration curve was prepared by extracting, in turn, solutions containing 10 to 100 μg thorium.

COMPLEXING ACTION OF PHOSPHATE ON THORIUM EXTRACTION

Since many of the uranium ore materials contain ortho-phosphate, which is difficult to separate quantitatively from the sample, a study was made of the effect of phosphate on the TTA thorium extraction. In this study, the thorium concentration, ionic strength, TTA concentration, and hydrogen ion concentration due to nitric acid were held constant. The concentration of phosphate was varied. Thorium in the aqueous phase was determined by the ion exchange-Thoron method¹ and in the organic phase by the TTA-Thoron method described in the Experimental Procedure.

The results obtained are summarized in Table I.

Various means were employed in an attempt to remove or to complex phosphate and thereby prevent the interference of phosphate in concentrations greater than $8 \times 10^{-3}M$. These methods included the formation of the molybdovanado or molybdotungsto complexes and subsequent extraction of the phosphate complexes with various organic solvents. Thorium was found to accompany the phosphate ion. Precipitation as bismuth phosphate proved unsuccessful, as did removal by use of lead perchlorate as a complexing agent. The formation of the soluble iron phosphate complex with ferric iron and, finally, the reaction of metastannic acid with phosphate were attempted. All of these methods yielded low thorium values when the aqueous phase was analyzed by TTA extraction.

From these experiments and the data presented in Table I, it was concluded that the extraction of thorium as the TTA chelate could be applied only if the phosphate concentration as phosphoric acid is less than $8 \times 10^{-3}M$. Phosphate interference was not encountered in the uranium ore concentrates analyzed in this study.

TABLE I Distribution Coefficient, D, as a Function of Concentration of Phosphoric Acid at Ionic Strength 1.0 in 1.0M Nitric Acid

Molarity of H_3PO_4	Thorium Taken ($\mu g/10$ ml)	Thorium Found ($\mu g/10$ ml)		D
		Aqueous	Organic	
3×10^{-1}	50	48.9	0.0	0.00
2×10^{-1}		46.9	3.1	0.06
5×10^{-2}		25.0	23.1	0.92
3×10^{-2}		18.9	29.9	1.58
1×10^{-2}		4.3	44.5	10.35
3×10^{-3}		1.0	48.2	48.20
5×10^{-3}		0.0	51.1	Infinity

EFFECT OF METAL ION IMPURITIES ON THE EXTRACTION OF THORIUM

A number of elements normally present in uranium ore concentrates form a color with the Thoron reagent. An effort was made to determine which of these elements seriously interfere (necessitating removal) and to establish tolerance limits for elements which do not seriously interfere in the method outlined in the Experimental Procedure.

TABLE II Evaluation of Metal Cation Interference in the TTA Method for Thorium

Element	Amount of Element Added	Thorium Added ($\mu\text{g}/10\text{ ml}$)	Thorium Conc. Found* ($\mu\text{g}/10\text{ ml}$)	Thorium Extracted (%)
Sodium	100 mg	50	49.4	98.8
Potassium	100 mg		50	100
Silver	100 mg		49.8	99.6
Magnesium	100 mg		50.7	101.4
Calcium	100 mg		46.6	93.2
	75 mg		50.2	100.3
Zinc	100 mg		50.6	101.2
Tin	20 to 100 mg		**	
	100 μg		39	78
	50 μg		37	74
	25 μg		38	76
Lead	100 mg		49.8	99.6
Chromium	100 mg		49.4	98.8
Bismuth	100 mg		340	682
	50 mg		400	800
	200 μg		72	144
	50 μg		49	98
Iron	50 to 100 mg		†	
Vanadium	5000 μg		50.2	100.3
	2000 μg		50	100
	1000 μg		50	100
	500 μg		50	100
Cobalt	100 mg		55.5	111
	60 mg		45	90
	40 mg		44	88
	20 mg		44	88
Nickel	100 mg		**	
	20 mg		49.8	99.6
	1000 μg		49	98
	500 μg		48.6	97.2
Zirconium	50 μg	26.6	35	132
	25 μg		32	120
	10 μg		30	113
	5 μg		26	98
Barium	100 mg	50	45.8	91.6
	75 mg		50.2	100.4
Cadmium	100 mg		49.6	99.3
	100 mg		52.3	104.5
	75 mg		52.7	105.4
	50 mg		51.0	102.0

* All results are averages of at least two determinations.

** Precipitates were formed in these cases – refer to the discussion of results below for each element's behavior.

† At 100-mg level, a precipitate formed. For amounts of iron less than 100 mg, see the discussion of results.

Solutions of various metals were prepared from the nitrate wherever possible. Various amounts of these solutions were added to a thorium solution containing 50 μg Th/10 ml. The procedure previously described was followed in evaluating metal cation interference. The results obtained are summarized in Table II.

Examination of Table II shows that when present in concentrations up to 100 mg, sodium, potassium, silver, magnesium, zinc, cadmium, lead and chromium do not interfere.

Bismuth interferes at all concentrations down to 50 μg .

Iron does not interfere in concentrations below 20 milligrams. Above this level, the solubility of the highly colored iron (III) TTA complex in the aqueous phase renders a quantitative separation impossible.

The results obtained for tin show that definite interference can be expected for micro amounts. Samples which contained from 40 to 80 mg of tin formed a precipitate with TTA, presumably tin (II) thenoyltrifluoroacetate. This precipitate was appreciably insoluble in 0.1M HNO_3 , but was quite soluble in 2M HNO_3 . Upon addition of Thoron to the 2M HNO_3 , a red precipitate formed. This solution was filtered, and the optical density of the filtrate was found to be zero. The exact nature of the precipitate was not determined, although it may be presumed to be some coordination compound of tin with Thoron. The fact that concentrations of tin in the microgram range led to low thorium values is consistent with results obtained in the macro range, although the exact nature of the inhibition is not known.

In the study of cobalt interference, an apparent inhibition noted below the 80-mg level was essentially constant down to 20 mg of cobalt. At concentrations above 80 mg, an apparent enhancement occurs. The exact nature of the interference is undefined, but the effect of cobalt must be considered when this element is present.

Zirconium produces interference at levels above 5 μg . In macro amounts, precipitation occurs. Micro amounts lead to enhancement and produce a positive error.

In addition to these elements, copper was studied in some detail. Experiments revealed a positive error for quantities of copper greater than 20 mg. A negative error was observed for quantities of copper less than 5 mg. Interference was noted down to at least 500 μg . In this one case, elimination of the interference was attempted. First, consideration was given to the copper ammonia complex formed in adjustment of the pH to 0.5. Sodium acetate was used in place of ammonium hydroxide for pH adjustment. The results obtained compared with those obtained with ammonium hydroxide. This eliminates the possibility that the interference is caused by the complex copper ammino ion, $\text{Cu}(\text{NH}_3)_4^+$.

Reduction of Cu (II) to Cu (I) with hydroxylamine hydrochloride resulted in a positive error at the 1000 μg level, in contrast to the inhibition noted at the 1000 μg copper (II) level.

A final attempt was made to extract copper. Oxine in chloroform was used. A loss of thorium was noted when solutions containing only thorium were subjected to an oxine-chloroform extraction, and this technique was abandoned.

EXTRACTABILITY OF THE RARE EARTH ELEMENTS BY TTA

Difficulties were experienced in obtaining individual rare earth elements in macro quantities that were free of traces of thorium. Therefore, a detailed study of the effect of rare earth elements on the TTA extraction and Thoron color development of thorium was not possible. However, the following study of the extractability of the rare earth elements with TTA was performed. Weighed amounts of the rare earth oxide or salt were dissolved in nitric acid and were carried through the TTA extraction step outlined in the experimental procedure. The aqueous solution obtained by stripping with 2M HNO_3 was evaporated to dryness and was ignited to the oxide. The results of this study will be found in Table III.

According to Thomason et al.,⁴ the Thoron spectrophotometric method will tolerate milligram concentrations of lanthanum without serious interference with the thorium result. It is evident from the results that the rare earth elements are not extracted with TTA in sufficient quantities to interfere,

TABLE III Extractability of Rare Earths in the TTA Method

Element	mg Added	mg Found
Lanthanum	100	0.4
Neodymium	100	0.1
Gadolinium	91	0.3
Praseodymium	95	0.0
Yttrium	95	0.0
Samarium	99	0.0
Cerium	100	0.0

SEPARATION OF INTERFERING ELEMENTS

From an examination of the results shown in Tables II and III, only bismuth, copper, cobalt, iron, zirconium,* and tin of the elements studied, may be present in uranium ore concentrates in concentrations that are likely to interfere with the method. A preliminary separation was therefore necessary to eliminate these interferences. Since the above elements can all be precipitated as sulfides or hydroxides, the following scheme was devised:

A thioacetamide separation from a 10 per cent sulfuric acid solution was used to remove the sulfide metals (bismuth, copper and tin). An ammonium hydroxide separation was next used to separate thorium and other R_2O_3 group hydroxides from the major portion of ferrous iron, cobalt, and copper. Complete separation of the thorium from iron is not necessary, as noted in the discussion of Table II. The uranium in the sample acts as a carrier to precipitate the thorium (which can then be readily dissolved in nitric acid and separated, using the TTA method).

This scheme of analysis was tested by analyzing duplicate synthetic solutions. The composition of these synthetic solutions is shown in Table IV.

The results obtained by analysis of these solutions are shown in Table V.

These data indicate that the proposed scheme of analysis gives quantitative results and successfully removes interfering elements. A recommended procedure is given in the following section.

TABLE IV Synthetic Solutions, A and B

Element	(mg/100 ml)	Element	(mg/100 ml)
Uranium	700	Aluminum	30
Copper	50	Tin	15
Cobalt	20	Chromium	10
Iron	100	Bismuth	5
Nickel	20	Thorium	0.6
Magnesium	20		

TABLE V Analysis of Synthetic Solutions By Sulfide -Hydroxide -TTA -Thoron Method

Solution A			Solution B		
Aliquot No.	Thorium Taken (μg)	Thorium Found (μg)	Aliquot No.	Thorium Taken (μg)	Thorium Found (μg)
1	60	59	1	60	60
2		59	2		60
3		59	3		59
4		59	4		59
5		60	5		61
6		58	6		58

*Little data is available on the concentration levels of zirconium in ore concentrates. However, if zirconium is encountered in sufficient quantities to interfere, it can be masked by the addition of meso-tartaric acid before the addition of the Thoron reagent.⁹

RECOMMENDED PROCEDURE

Accurately weigh a 0.1 to 1.0-gram sample of the ore concentrate into a 250-ml beaker. The sample size depends on the estimated amount of thorium present. The final aliquot taken for analysis (after sulfide and ammonium hydroxide separations) should contain less than 100 μg of thorium.

Add 50 ml of aqua regia, and evaporate on a hot plate to a small volume. Repeat this step with an additional 50 ml of aqua regia. Wash down the sides of the beaker, and filter through a No. 42 Whatman filter paper. Retain the filtrate. Ignite the residue, and volatilize any silica present by fuming with hydrofluoric and sulfuric acids in a platinum crucible. Fuse the residue with sodium carbonate, leach with dilute hydrochloric acid, and add it to the main filtrate. (One fusion should suffice for most materials.) Add five ml of concentrated sulfuric acid, and evaporate until strong sulfur trioxide fumes are evolved. Dilute to 50 ml with water. Heat the solution to near boiling and add 10 ml of a two per cent thioacetamide solution (w/v) to precipitate the acid-insoluble sulfide group. Boil for a few minutes to remove excess hydrogen sulfide, and filter through a No. 42 filter paper. Discard the residue. To the filtrate add five ml of a 10 per cent solution of l-ascorbic acid (w/v) to reduce ferric iron to the ferrous state. Heat the sample to near boiling. Remove the sample from the hot plate, and precipitate the R_2O_3 group (containing the thorium), using ammonium hydroxide (1:4). Filter through a double No. 41 H Whatman filter paper. Discard the filtrate. Dissolve the residue through the paper with a minimum amount of dilute nitric acid (1:1).

Transfer the sample to a 100-ml volumetric flask, and dilute to the mark. Take an aliquot for analysis containing less than 100 μg thorium (usually 10 ml). Adjust the pH of the sample to 1.0 (using nitric acid or ammonium hydroxide), and transfer to a 125-ml separatory funnel; add five ml of a 0.5M solution of TTA in xylene and shake for three minutes. Discard the aqueous phase, and backwash the organic phase with two 10-ml portions of 0.1M nitric acid, shaking for two minutes each time. Discard the aqueous phases. Add five ml of 2M nitric acid to the organic, and shake for one minute. Separate the phases, and adjust the pH of the aqueous phase to 0.5. Transfer to a 50-ml volumetric flask containing five ml of 0.1 per cent (w/v) Thoron color reagent; dilute to volume, and measure the optical density at 545 $\text{m}\mu$ against a reagent blank carried through all steps of the extraction procedure.

The calibration curve is prepared by extracting from 10 to 100 μg amounts of thorium from a 0.1M nitric acid solution.

EVALUATION OF THE RECOMMENDED PROCEDURE

EVALUATION BY RADIOISOTOPE TRACER ANALYSIS

Thorium-230 (ionium) was used in order to determine the extraction efficiency of the TTA separation outlined in the recommended procedure. In addition to the solvent extraction procedure, the ion exchange method⁷ formerly used in these laboratories was evaluated.

Three typical ore concentrate samples, ranging from 50 ppm to 1000 ppm in thorium content, were dissolved by the method described in the recommended procedure. Final dilution of each sample to 100 ml was made, and an aliquot was taken to determine its alpha counting rate.

An appropriate amount of thorium-230 was then added to each solution, and the volume was readjusted to 100 ml. These solutions were used to evaluate the solvent extraction and ion exchange procedures.

Evaluation of the Recommended Solvent Extraction Procedure

Ten-ml aliquots of the ore concentrate stock solutions were taken for analysis. The recommended procedure was followed for all samples.

The following fractions were counted, using a twenty-channel scintillation counter to determine the alpha counting rates:

1. Filtrates from the NH_4OH precipitation step.
2. Backwash solutions of 0.1M HNO_3 .
3. 2M HNO_3 thorium stripping solution.

The results obtained are summarized in Table VI.

These results indicate that quantitative recovery of thorium can be achieved by the solvent extraction from uranium ore concentrates.

TABLE VI Recovery of Thorium By the Solvent Extraction Procedure

Sample Type	Sample Number	Th ²³⁰ Taken (cpm/ml)	Th ²³⁰ in OH ⁻ Filtrates (cpm/ml)	Th ²³⁰ in 0.1M HNO ₃ (cpm/ml)	Th ²³⁰ in 2M HNO ₃ (cpm/ml)
Pronto	1	112,917	Background	Background	106,640
Pronto	2	113,500	Background	Background	110,620
Denison	1	109,750	Background	Background	108,280
Denison	2	100,950	Background	Background	99,680
INX	1	150,550	Background	Background	148,670
INX	2	142,395	Background	Background	138,260

Evaluation of the Ion Exchange Procedure

The procedure as given by Nietzel et al.⁷ was previously used in these laboratories for the determination of thorium in ore concentrates. Since this is the procedure used to check results obtained by the solvent extraction method, it was considered advisable to also check the recovery of thorium achieved by this method.

The dissolution procedure used in the ion exchange method is the same as that outlined in the recommended procedure. After dissolution, the R_2O_3 group is precipitated by ammonium hydroxide. The residue is dissolved in 100 ml of 2M hydrochloric acid and passed through a 30-cm column of Dowex 50 x 4 resin. Impurities are eluted by 150 ml of 2M hydrochloric acid. Two hundred ml of 3N sulfuric acid is then passed through the column to elute the thorium. The solution is then evaporated to dryness. Nitric and perchloric acids are added, and the evaporation is repeated. The residue is dissolved in hydrochloric acid, and the determination of thorium outlined in the experimental procedure is carried out.

Ten-ml aliquots of the ore concentrate stock solutions containing ionium were analyzed by the above procedure.

The following fractions were counted:

1. Filtrates from the ammonium hydroxide precipitation.
2. Column rinses with 2N hydrochloric acid.
3. Final sulfuric acid eluates.
4. A second sulfuric acid elution to determine if any thorium remained on the resin.

The results obtained are summarized in Table VII.

These results indicate that quantitative recovery of thorium is achieved by the ion exchange procedure.

TABLE VII Recovery of Thorium By the Ion Exchange Procedure

Sample Type	Sample Number	Th ²³⁰ Taken (cpm/ml)	Th ²³⁰ in OH ⁻ Filtrate (cpm/ml)	Th ²³⁰ in HCl Rinses (cpm/ml)	Th ²³⁰ in H ₂ SO ₄ Eluate (cpm/ml)	Th ²³⁰ in Second H ₂ SO ₄ Eluate (cpm/ml)
Pronto	1	112,917	Background	Background	110,775	Background
Pronto	2	113,500	Background	Background	111,257	Background
Denison	1	109,750	Background	Background	109,000	Background
Denison	2	100,950	Background	Background	99,950	Background
INX	1	150,550	Background	Background	147,250	Background
INX	2	142,395	Background	Background	139,000	Background

Any discrepancies which may arise will probably be due to some interference in the final colorimetric procedure for determining thorium. It was not possible to check this possibility by tracer analysis.

ANALYSIS OF URANIUM ORE CONCENTRATES

In order to further evaluate the recommended procedure, a number of different types of samples were analyzed. Thorium values for these samples had been previously established, either by the

TABLE VIII Analysis of Thorium-Bearing Uranium Ore Concentrates

Sample Type	Sample No.	Method	
		Solvent Extraction (Per Cent thorium)	Ion Exchange (Per Cent thorium)
Faraday Concentrate	1	0.50, 0.49, 0.48*	0.49, 0.56*
	2	0.79	0.79
	3	0.89	0.89
	4	0.73	0.76
	5	1.03	1.05
	6	1.01, 1.01*	0.96, 0.99*
Bicroft Concentrate	1 A**	1.45	1.47
	1 B**	1.49	1.46
Metal Oxides	1	0.33	0.38
	2	0.79	0.80
Pronto Concentrate	1 A**	1.00	0.99
	1 B**	1.01	0.94
Porter Brothers Concentrate	1	4.21	4.14†
	2	4.88	4.64†
Rayrock Concentrate	1 A**	(ppm thorium) 72	(ppm thorium) 72
	1 B**	75	
Rum Jungle Concentrate	1 A**	27	22
	1 B**	24	
South African Concentrate	1 A**	357	353
	1 B**	351	
INX Concentrate	1	72, 70*	72, 75*
	2	64, 66*	66, 67*
	3	71, 66*	67, 64*
	4	82, 83*	81, 77*
	5	70, 73*	74, 70*
Radium Hill Concentrate	1 A**	719	620
	1 B**	722	
Portuguese Concentrate	1 A**	80	48
	1 B**	80	
Denison Concentrate	1	519	530
	2	692	690
	3	385	380
	4	345, 343*	340, 330*
	5	287	303
	6	355	365
	7	462	436
	8	1033, 1036*	1200

*Aliquots of the same sample taken for analysis after dissolution.

**A and B refer to separate samples of the same material taken for analysis.

†Analyzed gravimetrically.

ion exchange method or gravimetrically by the classical oxalate method. The results obtained are summarized in Table VIII.

The results given in Table VIII indicate the precision that may be obtained by use of the TTA method. The samples analyzed here covered the range from 20 ppm to 5 per cent thorium. The samples analyzed are representative of the type of samples to be processed at FMPC and contain in varying amounts the elements covered in the interference study. With the exception of the Radium Hill and Portuguese Concentrates, the results obtained using the solvent extraction technique compare favorably with the ion exchange and gravimetric values.

Initial studies on the INX and Denison Concentrates in which the experimental procedure was used showed some discrepancies. (These concentrates contain appreciable amounts of iron.) This may have been due to a poor reduction of iron. Hydroxylamine hydrochloride was initially used to reduce ferric iron to the ferrous state. Substitution of 1-ascorbic acid for hydroxylamine hydrochloride resulted in a much better agreement of the two methods. This substitution was incorporated in the recommended procedure.

CONCLUSION

The results of this study show that thorium can be determined in uranium ore concentrates by solvent extraction, using TTA in xylene. Interfering elements are removed by precipitation of the acid-insoluble sulfide and the hydroxide groups. In addition to good precision, the method offers the advantage of being much more rapid than any other method for the determination of thorium in complex materials, and is presently being used in this laboratory for determining thorium in uranium ore concentrates.

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