

Determination of Uranium and Thorium with Arsenazo III after Sequential Extraction from Acid-deficient Aluminium Nitrate Medium

T. V. RAMAKRISHNA* and R. S. SHREEDHARA MURTHY

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

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Uranium has been quantitatively extracted into IBMK from $\approx 2.2 \text{ mol dm}^{-3}$ aluminium nitrate solution at pH 0.8—0.9. Coextracted thorium ($\approx 10\%$) is returned to the aqueous phase by addition of benzene. Subsequently, thorium is extracted into IBMK in the presence of hexadecyltrimethylammonium bromide (CTAB). This separation method has been applied to the analysis of uranium and thorium content of monazite sand.

Extensive work has been carried out on the extractive separation of uranium and thorium from each other and from accompanying elements.¹⁻⁵ A review of these methods indicates that in many instances the methods are selective either for uranium or thorium, and are therefore useful for the separation of any one of them from accompanying elements. Extraction methods have not been extensively explored for the sequential separation of uranium and thorium probably because their extraction takes place from medium of widely differing composition. This is illustrated by the studies of Cospito and Rigali⁶ who extracted uranium from sulfate medium into trioctylamine in xylene and thorium with Aliquat 336, after making the aqueous phase 4 mol dm^{-3} with respect to nitric acid.

The selectivity of the extraction of uranium from 2.7 mol dm^{-3} acid-deficient aluminium nitrate into isobutyl methyl ketone (IBMK) proposed by Nietzel and De Sesa⁷ was found to be far superior as compared to extraction from highly acid medium.⁸ However, thorium has been coextracted to varying extents, no attempt being made to use this extraction for the separation of uranium from thorium.

The present investigation was undertaken to find suitable conditions for the selective and sequential extraction of uranium and thorium from acid-deficient aluminium nitrate solution into IBMK. The extraction behaviour of these metal ions was spectrophotometrically followed using arsenazo III.⁹ The results indicate that coextracted thorium ($\approx 10\%$) can be selectively returned to the aqueous phase by the addition of benzene. Further, addition of CTAB enabled the quantitative extraction of thorium into IBMK. The method was applied to the analysis of monazite sand.

Experimental

Reagents. Standard uranium and thorium solutions (10 ppm) Saturated aluminium nitrate solution Hexadecyltrimethylammonium bromide solution (0.5%) Arsenazo III solution (0.02%).

Apparatus. A Carl Zeiss PMQ II spectrophotometer with 10 mm quartz cells.

Recommended Procedure. *Separation:* Transfer a 5 cm^3 aliquot of the sample solution to a 25 cm^3 beaker. Add 10 g of aluminium nitrate and stir to dissolve. Adjust the pH to 0.8—0.9 using powdered ammonium carbonate under a pH-meter. Transfer the solution quantitatively to a 60 cm^3 separatory funnel using 1 cm^3 of saturated aluminium nitrate

solution for rinsing. After extraction into 5 cm^3 of IBMK for 3 min, separate the aqueous phase (I) and treat the organic phase with 5 cm^3 each of saturated aluminium nitrate solution and benzene. Shake for 1 min. Separate the aqueous phase (II) and retain the organic phase for the recovery of uranium.

To the combined aqueous phase (I and II) in a 60 cm^3 separatory funnel, add 1 cm^3 of CTAB solution and extract into 10 cm^3 of IBMK for 5 min. Discard the aqueous phase. Retain the organic phase for the recovery of thorium.

Determination: Strip each organic phase containing uranium or thorium twice with 5 cm^3 of 0.1 mol dm^{-3} HCl and collect the resulting aqueous phases separately in a 25 cm^3 standard flask and make upto the mark with distilled water. Discard the organic phases.

Transfer an aliquot of the made-up solution containing not more than $30 \mu\text{g}$ of uranium or thorium to a 25 cm^3 conical flask. Add a few drops of concd H_2SO_4 and evaporate until fumes of sulfur trioxide evolve. For the determination of uranium, treat the residue containing uranium with 1 cm^3 of water, 5 cm^3 of concd HCl and 2 g of zinc granules. Allow the reduction to proceed for 5 min. Filter the solution through glass wool and wash thoroughly with 1:1 HCl, collecting the filtrate and washings in a 25 cm^3 standard flask. Add 5 cm^3 of arsenazo III solution and make upto the mark with 1:1 HCl. For the determination of thorium, dissolve the residue containing thorium in 5 cm^3 of water and transfer the solution to a 25 cm^3 standard flask using 1:1 HCl for rinsing. Add 5 cm^3 of arsenazo III solution and dilute to the mark with 1:1 HCl. Measure the absorbance in a 10 mm cell at 665 nm against a reagent blank. Estimate the concentration of uranium or thorium by reference to the respective calibration graphs prepared by directly subjecting $5\text{--}30 \mu\text{g}$ of uranium or thorium using $0.5\text{--}3.0 \text{ cm}^3$ of standard metal solution for development of coloration.

Results and Discussion

Initial studies on the extractive separation of uranium and thorium were made using $100 \mu\text{g}$ of each element. Extraction was carried out from 10 cm^3 of aqueous phase into 5 cm^3 of IBMK for 5 min, the percentage extraction of uranium or thorium being estimated.

Separation of Uranium: The effect of variation of aluminium nitrate concentration at pH 0.9 on the extraction of uranium and thorium is shown by curves A and B, respectively, in Fig. 1. It is evident that uranium extraction is quantitative provided that the aqueous phase is at least 2 mol dm^{-3} in aluminium nitrate. However, a significant amount of thorium (5—50%) was also extracted when the aluminium nitrate concen-

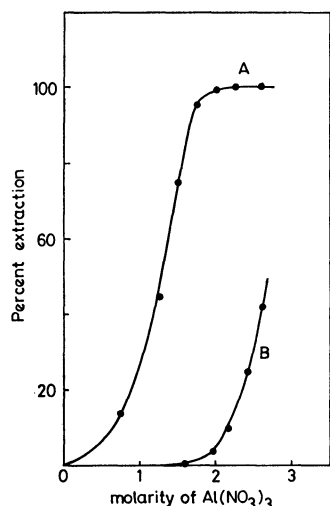


Fig. 1. Effect of aluminium nitrate concentration on the extraction of uranium (curve A) and thorium (curve B) into IBMK; pH of aqueous phase 0.9.

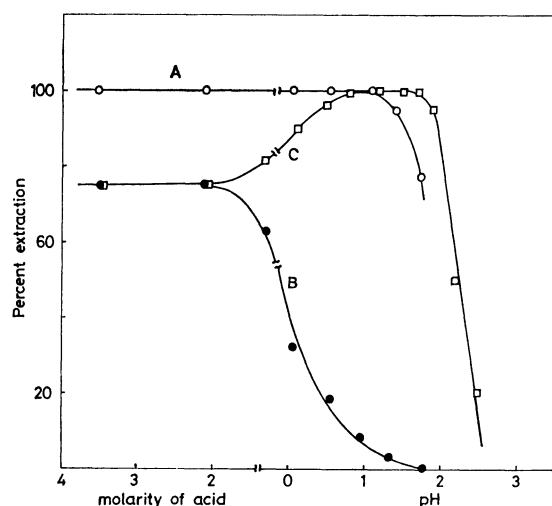


Fig. 2. Effect of acidity on the extraction of uranium (curve A), thorium (curve B), and thorium-CTAB (curve C) from 2.2 mol dm^{-3} aluminium nitrate solution into IBMK.

tration was varied from 2 to 2.6 mol dm^{-3} .

Figure 2 shows the effect of acidity on the extraction of uranium (curve A) and thorium (curve B) from aluminium nitrate solution ($\approx 2.2 \text{ mol dm}^{-3}$). Variation in acidity was brought about by using concd HNO_3 or ammonia solution. It is evident that thorium extraction decreases rapidly with decreasing acidity; at pH 1.2, where uranium extraction is quantitative, only 5% of thorium is extracted. To ensure the quantitative extraction of uranium, the pH should be maintained at 0.8–0.9 where the extraction of thorium is 10–15%. Satisfactory conditions for the extraction can be conveniently brought about by dissolving 10 g of aluminium nitrate in a 5 cm^3 aliquot of the sample solution (whose volume increased to 10 cm^3) and by adjusting the pH to 0.8–0.9 using powdered ammonium carbonate with a pH-meter.

Attempts to make the organic uranium extract

free from thorium revealed that retrograde extraction with a fresh aqueous phase of $\approx 2.2 \text{ mol dm}^{-3}$ aluminium nitrate at pH 0.9 is ineffective, since it did not bring down thorium to the aqueous phase completely. As solvent to the organic extract in order to return the coextracted thorium selectively to the aqueous phase, benzene was chosen since it does not extract uranium or thorium. Equilibration of the phases after the addition of 5 cm^3 benzene, however, caused 10% decrease in the recovery of uranium. This was overcome by replacing the aqueous phase by 5 cm^3 of saturated aluminium nitrate solution (acidity $\approx 1 \text{ mol dm}^{-3}$) and equilibrating for 1 min with the IBMK extract after the addition of 5 cm^3 benzene. Uranium and thorium separation, however, was not quantitative when extraction was carried out from saturated aluminium nitrate solution directly into a 1:1 IBMK: benzene mixture, as uranium upto 20% remained in the aqueous phase along with thorium.

A shaking time of 1 min was found to be sufficient for the quantitative extraction of uranium into IBMK. Later equilibration upto 3 min with saturated aluminium nitrate and benzene did not affect the recovery of uranium.

Other solvents examined for the extraction of uranium included 1-butanol, ethyl acetate, butyl acetate, pentyl acetate, and cyclohexanone. Though extraction was quantitative with ethyl acetate and cyclohexanone, IBMK was preferred because it coextracted only 10% of thorium, while the percentage coextraction of thorium was 30% in ethyl acetate and 42% in cyclohexanone.

Separation of Thorium: Since thorium in nitrate medium would be present as the species $[\text{Th}(\text{NO}_3)_6]^{2-}$ its extraction from aluminium nitrate medium containing a cationic surfactant was considered.¹⁰ This was examined by adding 1 cm^3 of 0.5% solution of CTAB to 10 cm^3 of $\approx 2.2 \text{ mol dm}^{-3}$ of aluminium nitrate solution containing $100 \mu\text{g}$ of thorium. Extraction was carried out for 5 min using 10 cm^3 of IBMK, 1-butanol, ethyl acetate, butyl acetate, or cyclohexanone, of which only ethyl acetate and IBMK quantitatively

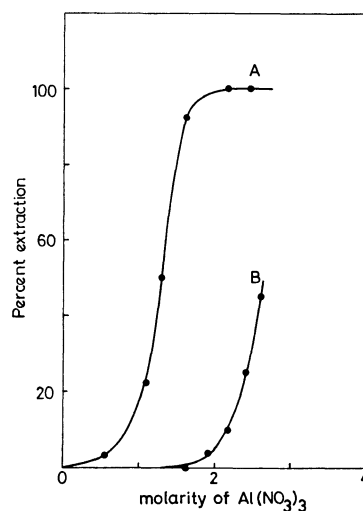


Fig. 3. Effect of aluminium nitrate concentration on the extraction of thorium-CTAB (curve A) and thorium (curve B) into IBMK; pH of aqueous phase 0.9.

extracted thorium. IBMK was preferred because of its lower solubility in the aqueous phase and rapid separation of both phases.

The effect of various parameters on the extraction of thorium indicates that the aqueous phase containing CTAB should be at least $\approx 2.2 \text{ mol dm}^{-3}$ in aluminium nitrate (curve A, Fig. 3) and that the pH maintained over the pH range 0.8–1.6 for the quantitative extraction of thorium (curve C, in Fig. 2). Equilibration for 4 min and addition of at least 1 cm^3 of 0.3% solution of CTAB were sufficient for transferring thorium from the aqueous to organic phase.

TABLE 1. RECOVERY STUDIES FOR THE SEQUENTIAL EXTRACTION OF URANIUM AND THORIUM

Metal taken, μg		Metal found, μg		% Recovery	
U	Th	U	Th	U	Th
100	100	99	99	99	99
20	100	20.3	98	101.5	98
100	20	99.5	19.8	99.5	99
20	20	20	19.6	100	98
500	20	490	19.8	98	99
20	500	20.6	490	102.5	98

Sequential Extraction of Uranium and Thorium: The above results are promising for the sequential extraction of uranium and thorium. The sample solutions were subjected to extraction and determination (Experimental). The results (Table 1) indicate that the proposed method works satisfactorily.

Interference Studies: The extent of extraction of metal ions present in monazite sand which interfere with the arsenazo III procedure like zirconium, titanium and rare earths was examined. One mg of each ion (gadolinium was chosen as a representative rare earth) was subjected to extraction separately in the absence of thorium and uranium. After stripping the organic phases with 1:1 HCl, the concentrations of zirconium and gadolinium were estimated by the arsenazo III⁹ procedure and that of titanium by the hydrogen peroxide method.¹¹ The interfering effect of anions such as sulfate and phosphate which are not removed by the usual means was also studied. The results (Table 2) indicate that the extraction procedure is quite selective, only phosphate inhibiting the extraction of both uranium and thorium.

Iron(III) hydroxide was used for collecting thorium

TABLE 2. INTERFERENCE STUDIES

Ion added	% Extraction of		% Extraction at	
	U	Th	U stage	Th stage
Sulfate (1 mM)	99	98.5	—	—
Phosphate (1 mg)	95	94	—	—
Phosphate (2 mg) ^a	99	98.5	—	—
Titanium (1 mg)	—	—	nil	nil
Zirconium (1 mg)	—	—	nil	0.63
Gadolinium (1 mg)	—	—	0.2	1.10

a) After collection by use of aluminium hydroxide.

and accompanying elements as hydroxide in order to overcome the interference of phosphate.¹² Aluminium hydroxide was also found to be effective for collecting thorium. The precipitate could be dissolved simply by treatment with saturated aluminium nitrate solution, so that subsequent separation and determination could be effected with no particular modification. 5 drops of saturated aluminium nitrate solution was added to samples containing uranium, thorium and phosphate. Dilute ammonia solution was then added until aluminium hydroxide precipitation was complete. The precipitate was centrifuged, washed with dilute ammonia (1:10) and dissolved in 8 cm^3 of saturated aluminium nitrate solution. The pH was then adjusted to 0.8–0.9 with solid ammonium carbonate and subjected to extraction. The results (Table 2) indicate that the method works satisfactorily.

TABLE 3. ANALYSIS OF MONAZITE

	% ThO ₂		% U ₃ O ₈	
	Reported	Found	Reported	Found
Sample 1 ^a	8.83	8.80	0.35	0.34
	—	8.84	—	0.36
	—	8.87	—	0.34
Sample 2	—	8.31	—	0.33
	—	8.34	—	0.35
	—	8.33	—	0.32

a) Supplied by Bhabha Atomic Research Center, Bombay.

Analysis of Monazite Sand: The thorium and uranium content of two monazite sand samples was determined after the removal of phosphate with aluminium hydroxide. 0.500 g of the finely ground sand was heated with 2 cm^3 of concd H_2SO_4 upto fuming of sulfur trioxide on a hot plate for 2 h. The residue was leached with ice-cold water and the leachate made up to 100 cm^3 with distilled water. A 1.0 cm^3 aliquot of the solution thus obtained was subjected to phosphate removal, then to extraction. The results (Table 3) indicate that the method works satisfactorily. In the present study, though the extraction behavior of rare earths other than gadolinium was not investigated, successful application of the extraction procedure to the analysis of monazite sand indicates that other rare earths behave in a similar way to that of gadolinium.

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