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EXTRACTION STUDIES OF THORIUM(IV) WITH TRIPHENYLPHOSPHINE OXIDE

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A simple method is described for the solvent extraction of thorium. Thorium is extracted quantitatively from $5 \cdot 10^{-3}$M sodium salicylate solution at pH 2.5–3.25 using $2.16 \cdot 10^{-2}$M triphenylphosphine oxide as an extractant dissolved in toluene. The extracted metal ion is stripped with hydrochloric acid (0.1M) and determined spectrophotometrically with Thoron-I at 540 nm. The method permits separation of thorium from lanthanum, cerium, neodymium, samarium and uranium from binary mixtures and is applicable to the analysis of monazite sand. The method is precise, accurate and selective.

In view of the increasing demand for thorium as a source of fuel for atomic energy programs and its uses in refractory materials and photoelectric cells, separation and purification of thorium is desired.

Several solvents such as tributyl phosphate (TBP),[1,2] tris-(2-ethylhexyl) phosphate (TEHP),[3] 4-methylpentan-2-one,[4] sulfoxides,[5] mesityl oxide,[6,7] trioctylphosphine oxide (TOPO)[8,9] and a mixture of triphenylphosphine oxide and an aromatic carboxylic acid[10] have been used for the extraction of thorium(IV) but these methods suffer from drawbacks such as multiple extraction,[5,10] critical temperature controlling,[1] long equilibration time,[1,8,10] heating of the aqueous phase and use of high concentrations of salting out agents.[9]

Bis(2-ethylhexyl) hydrogen phosphate[11] and dibutyl hydrogen phosphate[12] have also been used for extraction of thorium from mineral acids but they have few practical applications. High molecular weight amines such as trioctylamine,[13,14] tridodecylamine,[15] Aliquat,[16,17] Alamine 336[18] and Primene JMT[19] have also been used for the extraction of thorium but in all these methods a systematic separation study of thorium is lacking. In this communication we describe a method for binary separation of thorium(IV) from lanthanum(III), cerium(IV), neodymium(III), samarium(III) and uranium(VI).

Experimental

Apparatus: Absorbance measurements were made on a Spectronic 20-D (Milton Roy and Co) and pH was measured on a Control Dynamics digital pH meter with a combined glass electrode.

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Chemicals and reagents: A stock solution of thorium(IV) was prepared by dissolving 0.634 g of thorium nitrate (BDH) in doubly distilled water containing 2 ml of concentrated nitric acid and diluted to 250 ml. The solution was standardized[20] and diluted as required.

A 2.16 · 10^{-2}M solution of triphenylphosphine oxide (Fluka) dissolved in toluene was used for extraction studies.

An 0.1% aqueous solution of Thoron-I (BDH) was used for spectrophotometric determination of thorium.[21] All other reagents were of analytical reagent grade.

General extraction procedure: An aliquot of solution (10 ml) containing 80 μg of thorium(IV) (3.45 · 10^{-5}M) and 8 mg of sodium salicylate (5 · 10;$^{-3}$M) was adjusted to pH 2.5–3.25 with dilute hydrochloric acid and sodium hydroxide solutions. The solution was transferred to a separatory funnel and equilibrated for 30 seconds with 5 ml of 2.16 · 10^{-2}M triphenylphosphine oxide in toluene. After separation of the two phases, thorium was removed from the organic phase by stripping with 10 ml of 0.1M hydrochloric acid and estimated spectrophotometrically with Thoron-I at 540 nm.[21]

Results and discussion

Extraction conditions

The extraction of thorium(IV) was studied at various pH values (1.5–6.0), sodium salicylate concentrations (1.0 · 10^{-3} – 1.0 · 10^{-1}M) and triphenylphosphine oxide concentrations (1.80 · 10^{-3} – 2.87 · 10^{-2}M). The results in Tables 1 and 2 show that the

Table 1
Extraction of thorium(IV) as a function of pH;
Th(IV) = 3.45 · 10^{-5}M, aqueus phase = 5 · 10^{-3}M sodium salicylate, organic phase = 2.16 · 10^{-2}M TPPO in toluene

pH	Extraction, %	Distribution ratio, *D*
1.5	80.75	8.38
1.75	89.74	17.49
2.00	97.06	66.02
2.25	98.08	102.16
2.5–3.25	99.60	498.00
3.50	90.60	19.05
4.00	88.75	15.77
4.50	49.04	1.92
5.00	38.90	1.27
6.00	23.26	0.60

Table 2
Extraction of thorium((IV) as a function of TPPO concentration; Th(IV) = 3.45 · 10^{-5}M, pH 3.0, aqueous phase = 5 · 10^{-3}M sodium salicylate

TPPO concentration, M	Extraction, %	Distribution ratio, (D)
1.80 · 10^{-3}	84.79	11.14
3.59 · 10^{-3}	86.12	12.40
7.19 · 10^{-3}	89.74	17.88
1.08 · 10^{-2}	95.76	45.16
1.44 · 10^{-2}	97.87	91.89
1.80 · 10^{-2}	98.70	151.84
2.16 · 10^{-2}	99.60	498.00
2.51 · 10^{-2}	99.60	498.00
2.87 · 10^{-2}	97.14	67.93

extraction of thorium(IV) is quantitative at pH 2.5–3.25 from 2.5 · 10^{-3} – 2.5 · 10^{-2}M sodium salicylate concentration with 2.16 · 10^{-2}M triphenylphosphine oxide in toluene.

Effect of various diluent

The suitability of several diluents such as toluene, xylene, benzene, chloroform, carbon tetrachloride and hexane for the extraction of thorium was investigated. Extraction was found quantitative with 2.16 · 10^{-2}M solution of triphenylphosphine oxide in toluene. The extraction was incomplete in other diluents (Table 3).

Table 3
Effect of diluent on extraction of thorium(IV); Th(IV) = 3.45 · 10^{-5}:M, pH 3.0, aqueus phase = 5 · 10^{-3}M sodium salicylate, organic phase = 2.16 · 10^{-2}M TPPO

Diluents	Extraction, %	Distribution ratio (D)
Toluene	99.60	498.00
Xylene	99.00	198.00
Benzene	96.85	61.49
Chloroform	83.05	9.79
Carbon tetrachloride	95.76	45.16
Hexane	98.40	61.50

Period of equilibration

Variation of shaking time from 5 to 60 seconds showed that a single extraction for 30 seconds with 5 ml of $2.16 \cdot 10^{-2}$M triphenyl phosphine oxide was adequate for quantitative extraction of thorium(IV). Prolonged shaking had no adverse effect on the extraction.

Choice of stripping agents

Different stripping agents such as mineral acids, sodium hydroxide, ammonium hydroxide and water were tried for back-extraction of thorium from the organic phase (Table 4). It was found that 0.05–1.0M hydrochloric acid and 0.1–0.5M nitric acid back–extract thorium quantitatively from the organic phase. Stripping was incomplete with other agents. Water does not strip thorium from the organic phase.

Table 4
Effect of stripping agents; Th(IV) = $3.45 \cdot 10^{-5}$M, pH 3.0, aqueous phase = $5 \cdot 10^{-3}$M sodium salicylate, organic phase = $2.16 \cdot 10^{-2}$M TPPO in toluene

Stripping agents	Recovery, %				
	0.05M	0.1M	0.5M	1.0M	2.0M
Hydrochloric acid	99.60	99.60	99.60	99.60	88.00
Nitric acid	60.30	99.60	99.60	70.21	–
Sulfuric acid	–	22.72	< 5.0	–	–
Sodium hydroxide	–	< 5.0	20.08	27.43	–
Ammonium hydroxide	–	–	< 5.0	< 10.0	–

Water does not strip thorium(IV) from triphenylphosphine oxide.

Nature of the extracted species

The nature of the extracted species was established using log-log plots (Fig. 1). A plot of log of distribution ratio versus log of triphenylphosphine oxide concentration (at fixed pH and sodium salicylate concentration) and a plot of log distribution ratio versus log of sodium salicylate concentration (at fixed pH and triphenyl phosphine oxide concentration) gave a slope of 2.2 and 2.3, respectively, indicating a molar ratio of 1 : 2 of thorium with respect to both extractant and salicylate. Hence the extracted species must be a neutral complex with the composition $Th(sal)_2 \cdot 2TPPO$, where TPPO is triphenylphosphine oxide and sal is salicylate. TPPO solvates the thorium salicylate

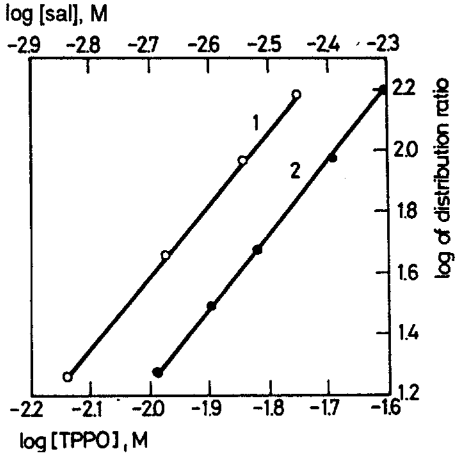

Fig. 1. Plot of log (distribution ratio) versus log (TPPO concentration, M) of thorium(IV) at fixed pH (3.0) and salicylate concentration ($5.0 \cdot 10^{-3}$M) (curve 1), plot of log (distribution ratio) versus log (salicylate concentration, M) of thorium(IV) at fixed pH (3.0) and TPPO concentration ($2.16 \cdot 10^{-2}$M) (curve 2)

chelate and promotes its extraction by forming an adduct. The mechanism of extraction can be written as

$$Th^{4+}(H_2O)_6 + 2sal^{2-} \Leftrightarrow Th(sal)_2 \cdot 2H_2O \qquad (1)$$

$$Th(sal)_2 \cdot 2H_2O + 2TPPO \Leftrightarrow Th(sal)_2 \cdot 2TPPO \qquad (2)$$

TPPO, being more basic, replaces water molecules and renders the thorium salicylate chelate more hydrophobic.

Effect of foreign ions

The extraction was carried out by the recommended procedure in the presence of varying amounts of several foreign ions in order to observe their interference in the extraction and subsequent spectrophotometric determination of thorium. The results in Table 5 show that a large number of cations and anions do not interfere. Notable interferences were given by ions such as vanadium, zirconium, oxalate, tartrate, sulfate and EDTA and these ions must be absent.

Table 5
Effect of foreign ions; Th(IV) = $3.45 \cdot 10^{-5}$M, pH 3.0,
aqueous phase = $5 \cdot 10^{-3}$M sodium salicylate,
organic phase = $2.16 \cdot 10^{-2}$M TPPO in toluene

Added ion	Tolerance limit, μg	Added ions	Tolerance limit, μg
Hg(II)	3500	Rh(III)	500
Pb(II)	2500	Fe(III)	150
Mg(II)	2000	Hf(IV)	100
Mn(II)	2000	Te(IV)	250
Cd(II)	1800	Ce(IV)	100
Ni(II)	1200	Zr(IV)	None
Co(II)	1000	V(V)	None
Pd(II)	800	Cr(VI)	500
Ba(II)	100	U(VI)	1700
Ag(II)	600	Nitrate	2500
Pt(II)	500	Thiourea	600
Cu(II)	1000	Chloride	1000
Au(III)	500	Phosphate	800
Al(III)	400	Oxalate	None
Bi(III)	100	Tartrate	None
Ru(III)	600	EDTA	None
Sb(III)	100	Sulphate	None

Binary separation of thorium(IV) from lanthanum(III), cerium(IV), neodymium(III), samarium(III) and uranium(VI)

16% lanthanum(III), 9% neodymium(III), 10% samarium(III) and 99% of uranium(VI) show coextraction with thorium(IV) when extracted from $5 \cdot 10^{-3}$M sodium salicylate solution with $2.16 \cdot 10^{-2}$M TPPO at pH 3.0.

However, lanthanum(III),. neodymium(III) and samarium(III) are selectively removed from the organic phase by stripping with distilled water and uranium(VI) with 0.05M ammonium hydroxide and estimated spectrophotometrically by standard procedures.[23-25] Thorium does not strip with either water or 0.05M ammonium hydroxide and remains in the organic phase. It was subsequently removed from the organic phase by stripping with 0.1M hydrochloric acid and determined spectrophotometrically with Thoron-I. Cerium(IV) is not extracted by TPPO in these experimental conditions, therefore, it remains completely in the aqueous phase and can be estimated by a standard procedure.[21] The results of separation are reported in Table 6.

This method provides selective separation of thorium(IV) from lanthanum(III), cerium(IV), neodymium(III), samarium(III) and uranium(VI).

Table 6
Separation of thorium from binary mixtures

Composition of mixture, μg	Recovery of thorium from triplicate analysis, %	Relative error, %	Recovery of added ion from triplicate analysis, %	Relative error, %	Spectrophotometric reagent used for added ions
Th, 80.0; La, 80.0	99.4	0.6	99.2	0.8	Thoron-I[23]
Th, 80.0; Ce, 80.0	99.1	0.9	100.0	0.0	Arsenazo III[21]
Th, 80.0; Nd, 80.0	99.3	0.7	99.6	0.4	Xylenol orange[24]
Th, 80.0; Sm, 80.0	99.3	0.7	99.5	0.5	Xylenol orange[24]
Th, 80.0; U, 80.0	99.6	0.4	99.1	0.9	PAR[25]

Application

The proposed method has been used for determination of thorium in monazite sand. The monazite sample (Indian Rare Earths, IRE) is treated as follows.[22]

100 mg of finely ground monazite sand is mixed with 1 g of sodium peroxide in a platinum crucible and heated at 440 °C for about 30 minutes. The mass is leached with 50 ml of water, digested on a steam bath until the precipitate can be filtered through medium speed filter paper. It is washed with 1% potassium hydroxide solution and the residue is dissolved in 20 ml of hot (1 + 1) hydrochloric acid and diluted to 100 ml. An aliquot (2 ml) of this solution is taken for the extraction and determination of thorium by the proposed method. The results are reproducible and are reported in Table 7. The method permits rapid separation and determination of thorium; the average recovery of thorium was >99.0%.

Table 7
Analysis of monazite sand

Sample	Approximate composition	Amount of thorium found by the proposed method, %	Amount of thorium found by the ICP–AES method, %
Monazite sand (IRE)	Th, U, SiO_2 Rare earths, PO_4^{3-}	5.92	5.93

IRE – Indian rare earths.
ICP–AES – Inductively Coupled Plasma – Atomic Emission Spectrophotometer.

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