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Liquid–liquid extraction of thorium(IV) with *N*-*n*-heptylaniline from acid media

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Abstract The extraction behavior of thorium(IV) from sulphuric acid medium with *N*-*n*-heptylaniline in xylene. Various parameters like reagent concentration, acid concentration, equilibration time, diverse ions and effect of diluents were studied. Thorium(IV) was selectively extracted and separated from many metal ions. The nature of the extracted species was determined. Thorium(IV) was analyzed from monazite ore and gas mantle.

Keywords Thorium(IV) · Liquid–liquid extraction · H_2SO_4 · *N*-*n*-Heptylaniline

Introduction

Thorium is a naturally occurring, radioactive metal. Nowadays thorium is used in nuclear power generation. So it is the need of time that it should be extracted and finally in pure form. Vary many amines have been used for the extraction of thorium(IV) like Amberlite LA-1 or LA-2 [1], *N*-*n*-octylaniline [2], mixture of *N*-*n*-octylaniline and trioctylamine [3], 2-octylaminopyridine [4] and various extractants like di-(2-ethylhexyl) 2-ethylhexyl phosphonate [5], bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) [6], organo phosphoric compounds from various media [7–15], TODGA in ionic liquids have been successfully employed for the recovery of thorium(IV) in industry [16]. Extraction of uranium(VI) and thorium(IV) by triphenylarsine oxide from salicylate media has been carried out [17]. Liquid–liquid extraction of uranium(VI) and thorium(IV) by two open-chain crown ethers with two terminal quinolyl groups in chloroform were studied [18].

Extraction of uranium(VI), zirconium(IV) and thorium(IV) by PC-88A from perchlorate media have been carried out [19]. Extraction of thorium(IV) from nitrate solution by bis-2-(butoxyethylether) was reported [20]. The extraction studies of uranium(VI) and thorium(IV) with TBPO in toluene from sodium salicylate medium were studied [21]. The extractive separation of thorium(IV) and praseodymium(III) with Cyanex 301 and Cyanex 302 from nitrate medium were studied [22]. The extraction behaviors of uranium(VI), thorium(IV) and lanthanides were studied using Cyanex 923 in toluene from different mineral acid media [23]. Further, high molecular weight amines are also used for the extraction and determination of a variety of other metal ions [24–26].

Previously we have reported the solvent extraction methods for the quantitative extraction of platinum group metals with amines [27–30]. In the present study extraction behavior of thorium(IV) from sulphuric acid media by *N*-*n*-heptylaniline is undertaken. Various parameters such as reagent concentration, acid concentration, effect of diluents, phase ratio, shaking period, loading capacity and diverse ions were studied. Separation of thorium(IV) from binary as well as multicomponent mixtures was achieved and also from associated elements in geological and real samples. The proposed method is relatively simple, rapid and selective used for the separation from many metal ions successfully.

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Table 1 Effect of concentrations of *N-n*-heptylaniline on thorium(IV)

N-n-heptylaniline (M)	Percentage extraction (*%E*)	Distribution ratio (*D*)
0.05	9.5	0.10
0.10	47.2	0.89
0.15	59.4	1.46
0.20	75.5	3.08
0.25	79.2	3.81
0.30	94.3	16.5
0.35	99.1	110.1
0.40	99.8	499
0.45	99.8	499
0.50	99.8	499
1.0	99.8	499

Conditions: thorium(IV) = 1 mg, aq.:org. = 1:1, H_2SO_4 = 1 M, shaking time = 3 min, strippant = 0.1 M HNO_3 (2 × 10 mL)

Table 2 Effect of sulphuric acid concentrations on thorium(IV) distribution ratio

Sulphuric acid (M)	Percentage extraction (*%E*)	Distribution ratio (*D*)
0.1	9.5	0.10
0.3	47.4	0.90
0.5	87.9	7.26
0.7	99.8	499
0.9	99.8	499
1.0	99.8	499
1.2	99.8	499
1.5	99.8	499
2.0	72.4	2.62
3.0	23.2	0.30
4.0	12.1	0.14
5.0	–	–

Conditions: thorium(IV) = 1 mg, aq.:org. = 1:1, H_2SO_4 = 1 M, shaking time = 3 min, strippant = 0.1 M HNO_3 (2 × 10 mL)

Table 3 Effect of various diluents on extraction of thorium(IV)

Diluent	Dielectric constant	Percentage extraction (*%E*)	Distribution ratio (*D*)
Xylene	2.30	99.8	499
Toluene	2.38	99.6	249
Benzene	2.28	99.8	499
Chloroform	4.81	98.0	49
Carbon tetrachloride	2.24	99.4	165
Nitrobenzene	34.8	63.0	1.70

Conditions: thorium(IV) = 1 mg, *N-n*-heptylaniline = 0.4 M, H_2SO_4 = 1 M, shaking time = 3 min, strippant = 0.1 M HNO_3 (2 × 10 mL)

Experimental

The pH of the solution was measured with the help of Elico digital pH meter model Li-120. 1.0 mg mL^{-1} solution of thorium(IV) was prepared by dissolving adequate amount of $Th(NO_3)_4{\cdot}4H_2O$ in double distilled water containing 5 mL of concentrated HNO_3 and diluted to 1 L and standardized gravimetrically [31]. The *N-n*-heptylaniline was synthesized by method of Gardlund [32] and its solution (% v/v) was prepared in xylene. All

Table 4 Effect of aqueous to organic volume ratio

Aq:org	Percentage extraction (*%E*)	Distribution ratio (*D*)
10:10	99.8	499
15:10	99.8	499
20:10	99.0	99.0
30:10	50.0	1.00
40:10	15.0	0.18
50:10	7.0	0.08
100:10	2.0	0.02

Conditions: thorium(IV) = 1 mg, *N*-*n*-heptylaniline = 0.4 M in xylene, H_2SO_4 = 1 M, shaking time = 3 min, strippant = 0.1 M HNO_3 (2 × 10 mL)

Table 5 Effect of stripping agents

Stripping agent	HCl		HNO_3	
(M)	(*%E*)	(*D*)	(*%E*)	(*D*)
0.1	76.2	3.20	99.8	499
0.5	78.0	3.55	99.8	499
1.0	84.0	5.25	92.0	11.5
2.0	91.1	10.2	90.0	9.0
3.0	92.0	11.5	78.2	3.59
4.0	84.2	5.33	–	–
5.0	78.2	3.59	–	–

Conditions: thorium(IV) = 1 mg, *N*-*n*-heptylaniline = 0.4 M in xylene, H_2SO_4 = 1 M, aq.:org. = 1:1, shaking time = 3 min *%E* percentage extraction, *D* distribution ratio

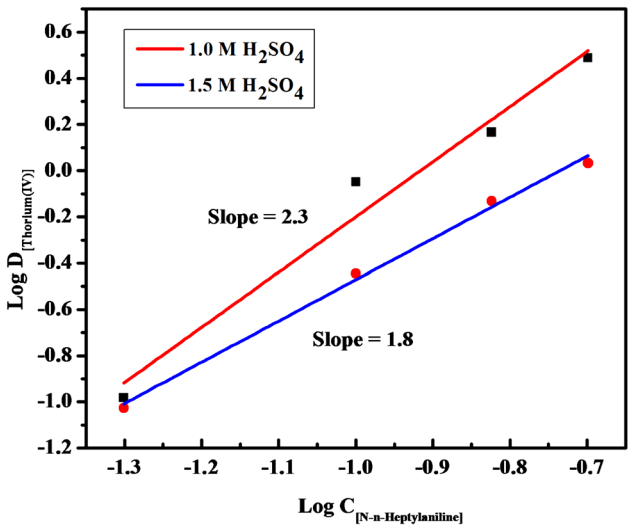

Fig. 1 Log–log plot of log $D_{[Thorium(IV)]}$ versus log $C_{[N\text{-}n\text{-}Heptylaniline]}$. Conditions: thorium(IV) = 1 mg, H_2SO_4 = 1.0 and 1.5 M, aq.:org. = 1:1, shaking time = 3 min, strippant = 0.1 M HNO_3 (2 × 10 mL)

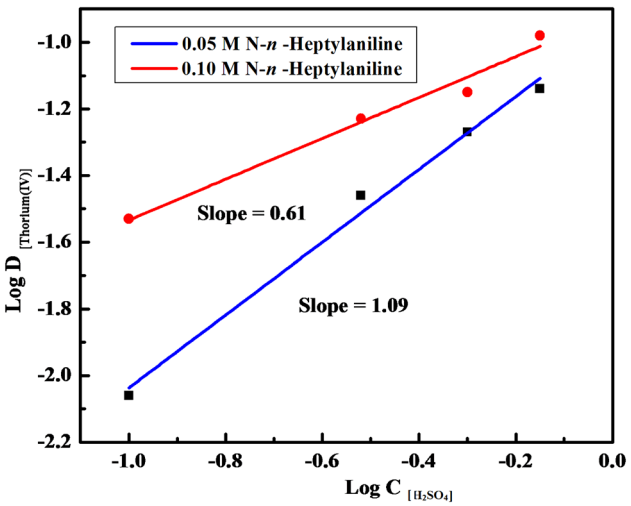

Fig. 2 Log–log plot of log $D_{[Thorium(IV)]}$ versus log$C_{[H_2SO_4]}$. Conditions: thorium(IV) = 1 mg, *N*-*n*-heptylaniline = 0.05 and 0.10 M in xylene, aq.:org. = 1:1, shaking time = 3 min, strippant = 0.1 M HNO_3 (2 × 10 mL)

chemicals and solvents used were of analytical reagent (AR) grade purity.

General extraction and determination procedure

To an aliquot of solution containing 1 mg of thorium(IV), sufficient quantity of sulphuric acid was added to make a concentration of 0.1–5 M in a volume of 10 cm^3 and then transferred to 125 cm^3 separatory funnel. The solution was shaken with 10 mL of (0.05–0.5 M) *N*-*n*-heptylaniline in xylene for 3 min. The two layers were allowed to separate. The organic phase was stripped with 20 mL (2 × 10 mL) of 0.1 M nitric acid. The stripped solution containing thorium(IV) was concentrated to moist dryness and diluted with water and the pH of the solution was adjusted to 2 with dilute solutions of nitric acid and sodium hydroxide and titrated against 0.001 M EDTA using 0.5 % xylenol orange as an indicator.

Results and discussion

Effect of the concentration of *N*-*n*-heptylaniline and sulphuric acid on thorium(IV) extraction

The extraction of thorium(IV) was studied from sulphuric acid media in the range of 0.1–5 and 0.05–0.5 M *N*-*n*-heptylaniline in xylene keeping the aqueous to organic volume ratio 1:1. It was observed that the extraction of thorium(IV) increases with increase in acid concentration and becomes quantitative in 0.7–1.5 M sulphuric acid and 0.35–1.0 M *N*-*n*-heptylaniline concentration. Hence, 1 M concentration of sulphuric acid and 0.4 M *N*-*n*-heptylaniline concentration was used throughout the work (Tables 1, 2).

Effect of various diluents on extraction of thorium(IV)

Various solvents such as xylene, toluene, benzene, chloroform, carbon tetrachloride and nitrobenzene were used as diluents for *N*-*n*-heptylaniline. It was noted that non-polar diluents were more efficient. The following percentage extractions were obtained. Nitrobenzene (63.00) < chloroform (98.00) carbontetrachloride (99.00) < toluene = benzene = xylene (100.00). The extraction of thorium(IV) was quantitative with xylene, benzene, toluene, carbon tetrachloride, Chloroform as diluents. It was incomplete with nitrobenzene. We were selected xylene a diluent for quantitative extraction because of its low dielectric constant, clear-cut separation of the phases and cost. Table 3 summarizes a solvent study for quantitative extraction.

Effect of aqueous to organic volume ratio

The effect of contact of different volumes of aqueous to organic ratio was studied by keeping the volume of organic phase constant. The study was carried between volumes of aqueous phase from 10 to 100 mL. The study shows that quantitative extraction takes place with volume ratio only 1:1 to 2:1. Beyond it this may be attribute extraction decreases due to the less stability of ion pair formed under conditions (Table 4).

Effect of time of equilibrium

When two immiscible phases were equilibrated for a period of 15 s to 15 min the extraction was quantitative over a period of 2–5 min. Therefore, for the proposed method 3 min equilibration time was recommended in order to insure the complete extraction of thorium(IV). However, the prolonged shaking period (<5 min) was found to have an adverse effect on the extraction and should be avoided.

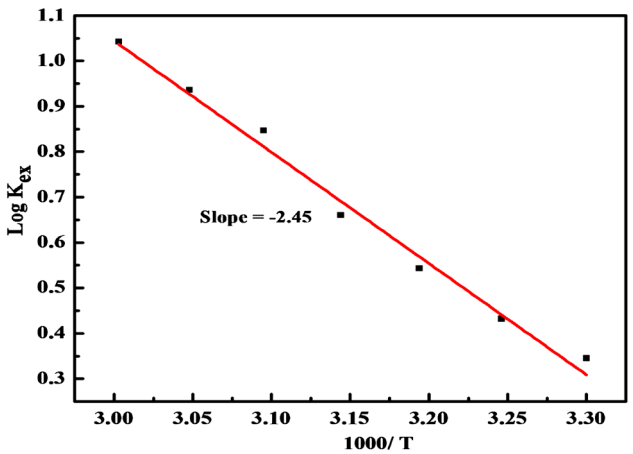

Fig. 3 Extraction behaviour of thorium(III) as a function of temperature. Conditions: thorium(IV) = 1 mg, *N*-*n*-heptylaniline = 0.4 M in xylene, H_2SO_4 = 1 M, aq.:org. = 1:1, shaking time = 3 min, strippant = 0.1 M HNO_3 (2 × 10 mL)

Effect of stripping agents

In solvent extraction back extraction is one of the important step to remove thorium(IV) from the loaded organic phase by suitable stripping agents. Various stripping agents studied were HNO_3, HCl, ammonia, acetic acid and ammonia buffer. Thorium(IV) was stripped with different strengths of nitric acid and hydrochloric acids after its extraction. It was observed that quantitative stripping was not possible with hydrochloric acid (0.1–0.5 M). Thorium(IV) was quantitatively stripped with 0.1–0.5 M nitric acid (Table 5). At higher concentrations of nitric acid (1–3 M) stripping was incomplete probably due to the formation of an anionic nitrate complex of thorium(IV). There was no complete stripping with acetic acid, ammonia and ammonia buffer.

Nature of the extracted species

The extraction mechanism of thorium(IV) was determined by analyzing the experimental data and conventional slope analysis method. The composition of the ion association complex of thorium(IV), sulphuric acid and *N*-*n*-heptylaniline was carried out from the plots of log $D_{[\text{Thorium(IV)}]}$ versus log $C_{[N\text{-}n\text{-heptylaniline}]}$ the slopes obtained at 1 and 1.5 M of sulphuric acid are 2.3 and 1.8, respectively (Fig. 1) and from the plots of log $D_{[\text{Thorium(IV)}]}$ versus log $C_{[\text{H2SO4}]}$ the slopes obtained at 0.05 and 0.1 M of *N*-*n*-heptylaniline are 1.09 and 0.61, respectively (Fig. 2). Hence, from the slope analysis method the probable composition of the species was found to be 1:2:1 (metal:extractant:acid).

The probable extraction mechanism is as follows:

$$\mathrm{Th}^{4+} + 3\mathrm{SO}_4^{2-} \rightleftharpoons [\mathrm{Th}(\mathrm{SO}_4)_3]^{2-} \quad (1)$$

$$2[RR'\text{–NH}]_{\text{org}} + \mathrm{H_2SO_4} \rightleftharpoons [(RR'\text{–NH}^{+2})_2\mathrm{SO}_4^{2-}]_{\text{org}} \quad (2)$$

$$[(RR'\text{–NH}_2^{+})_2\mathrm{SO}_4^{2-}]_{\text{org}} + [\mathrm{Th}(\mathrm{SO}_4)_3]^{2-} \rightleftharpoons [(RR'\text{–NH}_2^{+})_2\mathrm{Th}(\mathrm{SO}_4)_3^{2-}] + \mathrm{SO}_4^{2-} \quad (3)$$

where $R = \mathrm{C_6H_5}$ and $R' = \mathrm{C_7H_{15}}$.

Metal loading capacity

The extraction behaviour of thorium(IV) as a function of metal loading capacity was investigated at various concentrations of thorium(IV) between 500 and 4000 µg. The study shows that the quantitative extraction takes place between 500 and 3000 µg. It means up to 3000 µg of thorium, 10 mL of 0.4 M *N*-*n*-heptylaniline is sufficient

Table 6 Effect of temperature

Temp (K)	1000/T	Percentage extraction (%E)	D	Log D	Log K_{ex}	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J k mol^{-1})
303	3.300	68.75	2.2	0.3424	0.3445	−1.998	46.94	0.1615
308	3.246	72.91	2.69	0.4297	0.4319	−2.547		0.1606
313	3.194	77.08	3.47	0.5403	0.5425	−3.254		0.1603
318	3.144	81.25	4.33	0.6364	0.6383	−3.884		0.1598
323	3.095	87.90	7.00	0.8450	0.8472	−5.238		0.1615
328	3.048	89.58	8.59	0.9342	0.9364	−5.878		0.1610
333	3.003	91.66	10.99	1.040	1.043	−6.650		0.1609

Conditions: thorium(IV) = 1 mg, *N-n*-heptylaniline = 0.4 M in xylene, H_2SO_4 = 1 M, aq.:org. = 1:1, shaking time = 3 min, strippant = 0.1 M HNO_3 (2 × 10 mL)

T Temperature, *%E* Percentage extraction, *D* Distribution ratio, *ΔG* Gibb's free energy, *ΔH* Enthalpy, *ΔS* Entropy

Table 7 Effect of diverse ions

Diverse ions added	Tolerance limit (mg)
Tl(I)	03
Ce(IV)	05
Mg(II)	05
Co(II)[a]	10
Cr(II)[d]	10
Mn(II)	10
Fe(III)[c]	10
Mo(VI)	10
Hg(II)	15
Cd(II)	20
Cu(II)[c]	20
U(VI)	20
Ba(II)[e]	25
Pb(II)	25
Ni(II)[b]	30
Zn(II)	30
Acetate	100
Thiourea	100
Ascorbate	100
Citrate	100
Tartarate	100
Succinate	100

Conditions: thorium(IV) = 1 mg, *N-n*-heptylaniline = 0.4 M in xylene, H_2SO_4 = 1 M, shaking time = 3 min, strippant = 0.1 M HNO_3 (2 × 10 mL)

[a] Citrate

[b] Tartrate

[c] Thiourea

[d] Acetate

[e] Thiocyanate

and at higher concentration of thorium(IV), extraction decreases which demonstrates that there is deficiency of *N-n*-heptylaniline. Thus, this study indicates that 3000 µg of thorium was a loading capacity of 10 mL *N-n*-heptylaniline.

Effect of temperature

The extraction of thorium(IV) from aqueous solution was carried out at 1 M H_2SO_4 using 0.4 M *N-n*-heptylaniline in xylene at temperatures varying from 303 to 333 K. It was found that in the extraction of thorium(IV) by *N-n*-heptylaniline in xylene the distribution coefficient increases with a rise in temperature. The change of the extraction equilibrium constant (K_{ex}) with temperature is expressed by the Van't Hoff equation

$$D(\log K_{ex})/d(1/T) = -(\Delta H)/(2.303\ \mathrm{R}) \quad (4)$$

The plot of log K_{ex} versus 1000/T is linear with slope −2.45 (Fig. 3) and the enthalpy change of the extraction reaction carried out at constant pH 2 was evaluated as $\Delta H = 46.94$ kJ mol^{-1} which suggests the reaction is an endothermic process. The free energy ΔG and entropy ΔS were calculated from Eqs. (5) and (6), results are shown in (Table 6).

$$\Delta G = -2.303\ \mathrm{RT}\ \log K_{ex} \quad (5)$$

$$\Delta S = \Delta H - \Delta G/\mathrm{T} \quad (6)$$

The negative value of free energy ΔG implies the reaction is spontaneous. The positive enthalpy value indicates that the extraction of thorium(IV) with *N-n*-heptylaniline in xylene is favourable with a rise in temperature.

Effect of diverse ions

The solutions containing 1 mg of thorium(IV) and varying amounts of diverse ions were prepared and the content of thorium(IV) was determined after extraction. The tolerance limit of each individual ion was set, required to cause ±2 % error in the extraction of thorium(IV) using the proposed

Table 8 Separation and determination of thorium(IV) from binary mixtures

Metal ions	Amount taken (mg)	Average percentage recovery[a]	Chromogenic ligand	Ref.
Thorium(IV)	1	99.6		
Ba(II)	20	99.4	Eriochrome black-T	[33]
Thorium(IV)	1	99.5		
Pb(II)	20	99.4	Eriochrome black-T	[33]
Thorium(IV)	1	99.6		
U(IV)	20	99.4	Arsenazo-I	[34]
Thorium(IV)	1	99.5		
Mo(VI)	10	99.5	Thiocyanate	[34]

Conditions: thorium(IV) = 1 mg, *N*-*n*-heptylaniline = 0.4 M in xylene, H_2SO_4 = 1 M, shaking time = 3 min, strippant = 0.1 M HNO_3 (2 × 10 mL)

[a] Average of five determinations

Table 9 Separation of thorium(IV) from synthetic mixtures

Metal ions	Amount taken (mg)	Amount found (mg)	Recovery %
Thorium(IV)	1	0.99	99.4
Cd(II)	20	19.80	
Pb(II)	20	19.60	
Thorium(IV)	1	0.99	99.6
Ce(II)	5	4.94	
Mg(II)	5	4.94	
Thorium(IV)	1	0.99	99.5
Pb(II)	20	19.60	
Ba(II)	20	19.70	
Thorium(IV)	1	0.99	99.7
U(VI)	20	19.74	
Ce(IV)	5	4.94	
Thorium(IV)	1	0.99	99.5
U(VI)	20	19.76	
Zn(II)	30	29.76	

Conditions: thorium(IV) = 1 mg, *N*-*n*-heptylaniline = 0.4 M in xylene, H_2SO_4 = 1 M, shaking time = 3 min, strippant = 0.1 M HNO_3 (2 × 10 mL)

method. The results shown in the table illustrates that many metal ions do not interfere. Phoshate, oxalate and thiocyanate interfered seriously. With the extraction and determination. The interfering ions were masked to enhance their tolerance limit with suitable masking agent as shown in (Table 7).

Applications

Separation of thorium(IV) from associated metal ions

Thorium(IV) was extracted with 0.4 M *N*-*n*-heptylaniline in xylene from 1 M H_2SO_4 in the presence of a large number of foreign ions. The tolerance limit of different anions and cations already set under diverse ion study required to cause allowed ±2 % error in the recovery of thorium(IV). Thorium(IV) was successfully extracted from its associated metal ions. Amongst those very few metal ions were interfered which are masked by the suitable masking agent. Each associating ion was determined by a specific method and specific chromogenic reagent [33, 34] whereas thorium(IV) was determined complexometrically by 0.001 M EDTA which is summarized in (Table 8).

Separation of thorium(IV) from ternary mixture

A ternary mixtures of thorium(IV) and metals like, U(VI), Cd(II), Pb(II), Ba(II), etc. were prepared and are subjected to extraction by developed method. All associated metal ions remain in aqueous phase, whereas thorium(IV) from organic phase was stripped with 0.1 M HNO_3 and determined by 0.001 M EDTA by using xylenol orange as an indicator (Table 9) summarizes the study of ternary mixtures.

Analysis of thorium(IV) from monazite sand

A sample solution of 100 μg mL^{-1} monazite was prepared by prescribed procedure. An aliquot of sample solution was used for extraction of thorium(IV) as per our developed procedure. The number of determinations were six and finally thorium(IV) was determined. The amount of thorium(IV) detected by our procedure was 8.54 % against 8.6 %.

Separation of thorium(IV) from gas mantle

1 g of gas mantle of commercial grade was digested with 20 mL of concentrated sulphuric acid (A.R.) for about 4 h.

The mixture was extracted with 0.1 M hydrochloric acid and diluted to 100 mL. An aliquot of solution was extracted as usual with *N*-*n*-heptylaniline. Magnesium was not extracted but Cerium and Beryllium which were extracted but not stripped with 20 mL of 0.1 M nitric acid. The extracted thorium(IV) was stripped with HNO_3 and determined by general method. The content of thorium(IV) was 23.8 % against a standard value of 24 %.

Conclusions

The proposed method is relatively simple, reliable, selective and reproducible method used for the extraction and separation of thorium(IV) from ternary mixtures and also from temperature studies it is clear that the method is spontaneous and favourable with rise in temperature. Separation of thorium from real samples such as monazite sand and gas mantles has been carried out by using this method.

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