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Extraction and Separation Studies of Th(IV) from Salicylate Media Using Neutral Organophosphorous Extractant

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The neutral extractant, Cyanex-923 has been used for the extraction and separation of Th(IV) from sodium salicylate media. The metal ion was found to be quantitatively extracted with Cyanex-923 in toluene at pH 7.0 and from the organic phase they can be stripped with 2.0 M $HClO_4$ solution. The effect of pH, sodium salicylate concentration, reagent concentration, equilibration period, diluents, diverse ions and stripping agent on the extraction of Th(IV) has been studied. The stoichiometry of the extracted species of this metal ion was determined on the basis of the slope analysis method. The reaction proceed by solvation and the probable extracted species found were $Th(Sal)_2$. 2Cyanex-923.

Key Words: Extraction, Separation, Th(IV), Salicylate, Cyanex-923, Stripping.

INTRODUCTION

Thorium is used in the production of refractory materials, electronic components, alloys utilized for components in jet engines and as catalysts in chemical industry. Its oxide is used in the electrodes for arc welding and in manufacturing of ceramics. In view of this, the separation and determination of thorium is of great importance.

Neutral organophosphorus extractants such as tributylphosphate (TBP), trioctylphosphine oxide (TOPO), triphenylphosphine oxide (TPPO) were used for extraction of Th(IV) and U(VI)[1-7]. Reprocessing of spent Th-U fuel and extraction of U(VI) and Th(IV) from dilute HNO_3 media was carried out using di(2-ethylhexyl) sulfoxide [DEHSO][8]. Preston *et al.*[9] carried out the extraction of U(VI) and Th(IV) using N-alkylcarboxylic acid amide from $NaNO_3$ media. Quantitative extraction of Th(IV) and U(VI) was investigated by Dhadke *et al.*[10] using *bis*(2-ethylhexyl) phosphinic acid (PIA-8) and *bis*(2-ethylhexyl)phosphoric acid (HDEHP) from HNO_3 media.

The extraction of Th(IV) with U(VI) was studied from nitrate media using various other extractants like N,N'-tetrahexylbipicolinamide (THBPA) and N,N'-tetra-(2-ethylhexyl) bipicolinamide, O-methyleneoxyphenyldiphosphine dioxide and butyl *bis*(dibutoxyphosphinylmethyl) phosphinate[11-13]. The separation of Th, La, Eu ions has been carried by acidic extractant *bis*(2-ethylhexyl) phosphoric acid

(DEHPA) in cyclohexane using 2-nitrobenzo-18-crown-6 as a selective masking agent[14]. 2-Hydroxy-1-naphthaldehyde thiosemicarbazone is also used to study the extraction behaviour of Th(IV) from HNO_3 in the presence of donors, like trioctylphosphine oxide (TOPO), Calix[3] OH[3] OMe[6] arene, trioctyl amine (TOA) and DMSO in ethyl acetate solvent[15].

In the present work, the extraction of Th(IV) with neutral phosphine oxide, Cyanex-923 diluted in toluene from sodium salicylate media was studied in detail. It is worthwhile here to stress the advantages of organic acid media over mineral acid media. One distinct advantage of organic acid media is facility of controlling the concentration of complexing ligand, the ease of pH adjustment and the widely differing pH values at which various metals form anionic complexes. Stripping the complexes from the organic phase can be achieved comparatively easily by fully exploiting the differences in the reactivity of various metals to backwash in the aqueous phase by a mineral acid. It is known that organic acid media offer better separation of metals, possibly due to the high stability of metal-organic acid complexes[16].

EXPERIMENTAL

The extractant, Cyanex-923 supplied by Cytec Industries Inc. Canada, were used without further purification. A known amount of $Th(NO_3)_4 \cdot 4H_2O$ was dissolved and diluted with double distilled water as per requirement. All other chemical used were of analytical grade. EQUIP-TRONIC model EQ-614 pH meter with combined electrode was used for H^+ ions concentration studies and ELICO UV-visible SL-27 spectrophotometer with 10 mm cortex quartz cuvettes for absorbance measurements.

Procedure: An aliquot containing Th(IV) (40 mg) was taken and equilibrated with Cyanex-923 dissolved in toluene for the required shaking time of 10 min after adjusting the pH to 7.0 and sodium salicylate concentration to 1×10^{-3} M. The two phases were allowed to separate, the organic phase containing the metal extracted species was stripped with different stripping agent such HCl, HNO_3, H_2SO_4 and $HClO_4$. It was found that Th(IV) can be stripped quantitatively with 2.0 M $HClO_4$ and determine spectrophotometrically by Thoron-I indicator, respectively[17]. All the experiment were carried out at room temperature except the effect of temperature on distribution equilibria.

RESULTS AND DISCUSSION

Effect of pH: Extraction of Th(IV) was carried out in the pH range of 1.0-7.0 containing 1×10^{-3} M sodium salicylate. With the increase in pH the extraction goes on increasing and found to be quantitative in the pH range 5.0-7.0. Hence all the extraction of Th(IV) with Cyanex-923 was carried out at a fixed pH of 7.0 (Fig. 1).

Effect of reagent concentration: In order to determine the minimum amount of reagent required for complete extraction of Th(IV), an experiment was carried out by varying the reagent concentration from 2.5×10^{-4} M to 1×10^{-1} M. It was found that the extraction increased with increase in the reagent concentration. Quantitative extraction of Th(IV) was found in the range 2.5 × 10^{-3} M to 1 × 10^{-1} Cyanex-923 in toluene. Therefore 2.5 × 10^{-3} M of Cyanex-923 is used for all further experiments (Fig. 2).

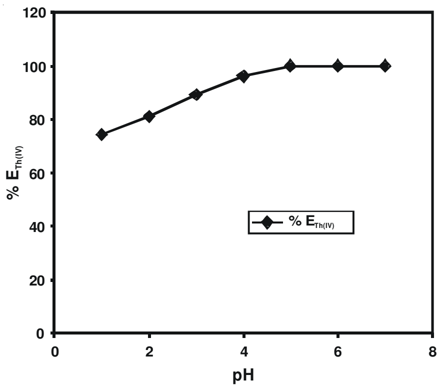

Fig. 1. Effect of pH on percentage extraction of Th(IV) with Cyanex-923 in toluene

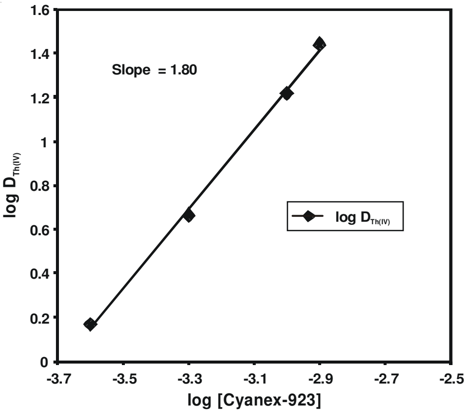

Fig. 2. Effect of reagent concentration on distribution ratio of Th(IV) with Cyanex-923 in toluene

Effect of sodium salicylate concentration: The effect of sodium salicylate concentration on the percentage extraction of Th(IV) with 2.5 × 10^{-3} M Cyanex-923 in toluene at fix pH of 7.0 was studied in the sodium salicylate range from 1.0 × 10^{-5} M - 5.0 × 10^{-3} M. As the sodium salicylate concentration increases the extraction goes on increasing and becomes quantitative in the range 5 × 10^{-4} M - 5.0 × 10^{-3} M with Cyanex-923 in toluene. Hence all the extractions were carried out at 1 × 10^{-3} M sodium salicylate with Cyanex-923 in toluene (Fig. 3).

Effect of stripping agents: The metal loaded organic phase of Cyanex-923 was stripped with different strengths of acids like HCl, HNO_3, H_2SO_4 and $HClO_4$. The complete recovery of Th(IV) from metal loaded Cyanex-923 was found with 2.0-3.0 M $HClO_4$ solution (Table-1).

Influence of diluents: Th(IV) was extracted quantitatively with toluene, cyclohexane, xylene, chloroform and carbon tetrachloride whereas with *n*-hexane (98.1 %) it was incomplete. Toluene was preferred as the best diluents for the extraction of Th(IV) since it provided better phase separation (Table-2).

Effect of equilibration period: Extraction equilibrium was studied for different periods of shaking ranging from 1-30 min. It was observed that 10 min of shaking period was sufficient for quantitative extraction of Th(IV) with 2.5 × 10^{-3} M Cyanex-923 in toluene respectively. However there was no adverse effect by increasing the extraction period upto 0.5 h.

TABLE-1
EFFECT OF STRIPPING AGENTS ON THE PERCENTAGE RECOVERY OF Th(IV) FROM METAL LOADED ORGANIC PHASE OF CYANEX-923 IN TOLUENE
Th(IV) = 40 µg, Cyanex-923 = 2.5 × 10^{-3} M in toluene,
Sodium salicylate = 1 × 10^{-3} M, pH = 5.0

Percentage recovery (%R) of thorium(IV) from organic phase of Cyanex-923				
Acids (mol dm^{-3})	1.0	2.0	3.0	4.0
HCl	40.8	45.6	55.6	54.0
HNO_3	57.3	26.2	0.0	0.0
H_2SO_4	26.2	4.8	3.9	0.0
$HClO_4$	98.1	99.9	99.9	67.0

TABLE-2
EFFECT OF VARIOUS DILUENTS ON PERCENTAGE EXTRACTION OF Th(IV) WITH CYANEX-923
Th(IV) = 40 µg, Cyanex-923 = 2.5 × 10^{-3} M in toluene,
Sodium salicylate = 1 × 10^{-3} M, pH = 5.0

Diluent	Percentage extraction (%E) Th(IV)
Toluene	99.9
Cyclohexane	99.9
n-Hexane	98.1
Xylene	99.9
Chloroform	99.9
Carbon-tetrachloride	99.9

Effect of diverse ion: The extraction of Th(IV) was carried out in presence of a large number of foreign ions. The tolerance limit of individual foreign ions was set so that error in percentage recovery was not more than ± 2 %. It was found that, in case of Th(IV), the ions such as thiocyanate, thiourea, Al^{3+}, Be^{2+}, Zr^{4+}, V^{6+} interfere to the maximum in the percentage extraction of Th(IV) while ions such as Na^+, K^+, Cs^+, Rb^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Cl^-, Br^-, I^-, SO_3^{2-} are tolerated to larger extent (Table-3).

TABLE-3
EFFECT OF VARIOUS DIVERSE IONS ON PERCENTAGE EXTRACTION OF Th(IV) WITH CYANEX-923 IN TOLUENE
Th(IV) = 40 µg, Cyanex-923 = 2.5 × 10^{-3} M in toluene,
Sodium salicylate = 1 × 10^{-3} M, pH = 5.0

1:32	1:27	1:22	1:17	1:10	1:6	Strongly interfere
Na^+, K^+, Cs^+, Rb^+, Mg^{+2}, Ca^{+2}, Ba^{+2}, Sr^{+2}	Mn^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}	Cr^{3+}, Fe^{3+}, Zn^{2+}, Bi^{3+}	Pt^{2+}, Pd^{2+}, Os^{8+}, Ru^{3+}	Ce^{3+}, La^{3+}	SO_3^{-2}, Cl^-, I^-, Br^-, Citrate, Oxalate	Thiocynate, Thiourea, Al^{3+}, Be^{3+}, Zr^{4+}, V^{6+}

Influence of temperature: Extraction of thorium(IV) with 2.5 × 10^{-3} M Cyanex-923 in toluene at a pH 7 having salicylate concentration of 1 × 10^{-3} M, were carried out at different temperature (upto 343 K). The distribution ratio decreased with increase in temperature. The Van't Hoff equation is:

$$\log D_{Th(IV)} = -\frac{\Delta H}{2.303RT} + C$$

where $D_{Th(IV)}$ represent the distribution ratio, ΔH is the enthalpy change for the reaction and C is the constant. The slope obtained from plot of log $D_{Th(IV)}$ *vs.* 1/T × 1000 is 2.73 (Fig. 4). The ΔH values obtained is - 52.3 kJ/mol indicating that the reaction is exothermic in nature.

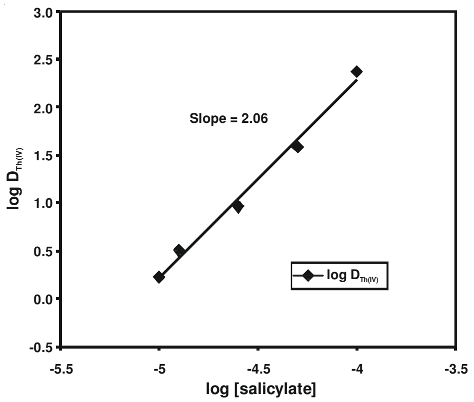

Fig. 3. Effect of sodium salicylate concentration on distribution ratio of Th(IV) with Cyanex -923 in toluene

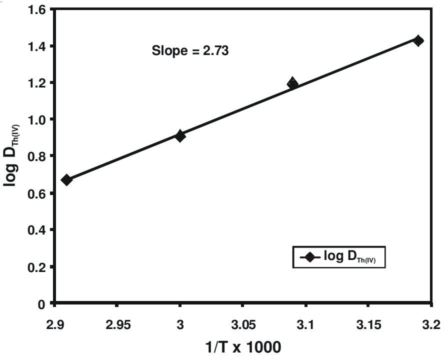

Fig. 4. Effect of temperature on distribution ratio of Th(IV) with Cyanex-923 in toluene

Stoichiometry 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 Cyanex-923 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 Cyanex-923 concentration) gave a slope of 1.80 and 2.06, 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 $Th(Sal)_2$. 2Cyanex-923, where Sal is salicylate which is similar to the early reported with triphenylphosphine oxide[6]. Cyanex-923 solvates the thorium salicylate chelate and promotes its extraction by forming and adduct. The mechanism of extraction can be written as:

$$Th^{4+}(H_2O)_6 + 2Sal^{2-} \rightleftharpoons Th(Sal)_2{\cdot}2H_2O$$
$$Th(Sal)_2{\cdot}2H_2O + 2\ \text{Cyanex-923} \rightleftharpoons Th(Sal)_2.\ 2\ \text{Cyanex-923}$$

Cyanex-923, being more basic, replaces water molecules and renders thorium salicylate chelate more hydrophobic.

Separation of thorium(IV) from other metal ions: In order to separate Th(IV) from U(VI) the difference in their pH and stripping agents was exploited. U(VI) and Th(IV) were first extracted with 2.5 × 10^{-3} M Cyanex-923 in toluene at a fixed pH of 5.0 and the solution having sodium salicylate concentration of 5 × 10^{-4} M, when both the metal ions get quantitatively extracted. U(VI) was then stripped completely with 4.0 M H_2SO_4, Th(IV) was then stripped with 2.0 M $HClO_4$. Thus U(VI) was completely separated from Th(IV).

Thorium(IV) was also separated from various other metal ions such as Be(II) and Zr(IV). U(VI) was also separated from closely associated metal ions such as Zr(IV) and Pd(II). The solution containing all the three metal ions were equilibrated with 2.5×10^{-3} M Cyanex-923 in toluene at pH 7.0 having sodium salicylate concentration of 5×10^{-4} M, when all the three metal ions were extracted in the organic phase. Thorium(IV) was first stripped with 2.0 M $HClO_4$, while Be(II) was completely back extracted with 1.0 M NaOH and Zr(IV) was finally stripped out with 0.5 M NaF.

Similarly other related important metal ions were separated from Th(IV) by using the differences in their respective extraction and stripping conditions as shown in Table-4.

TABLE–4
SEPARATION OF Th(IV) FROM MULTICOMPONENT MIXTURES WITH CYANEX-923 IN TOLUENE

Sr. No.	Metal ions	Amount taken (μg)	pH	Sodium salicylate in (mol/dm^3)	Extractant Cyanex-923	Stripping agents	Recovery (%)
1	U(VI)	40	5	5×10^{-4}M	2.5×10^{-3}M	4.0 M H_2SO_4	99.5
	Th(IV)	40		–		2.0 M $HClO_4$	99.4
2	Th(IV)	40	7	1×10^{-3}M	2.5×10^{-3}M	2.0 M $HClO_4$	99.4
	Be(II)	50		–		1.0 M NaOH	99.2
3	La (III)	50	7	1×10^{-3}M	2.5×10^{-3}M	2.0 M HCl	99.2
	Th(IV)	40		–		2.0 M $HClO_4$	99.4
4	U(VI)	40	5	5×10^{-4}M	2.5×10^{-3}M	4.0 M H_2SO_4	99.5
	Th(IV)	40		–		2.0 M $HClO_4$	99.4
	Zr (IV)	40		–		0.5 M NaF	98.8
5	U(VI)	40	5	5×10^{-4}M	2.5×10^{-3}M	4.0 M H_2SO_4	99.5
	Th(IV)	40		–		2.0 M $HClO_4$	99.4
	Ce (IV)	50		–		Unextracted	99.1
6	La (III)	50	7	1×10^{-3}M	2.5×10^{-3}M	2.0 M HCl	99.2
	Th(IV)	40		–		2.0 M $HClO_4$	99.4
	Ce(IV)	50		–		unextracted	99.1
7	Pd(II)	50	7	1×10^{-3}M	2.5×10^{-3}M	1:1 HCl + $HClO_4$	99.3
	Th(IV)	40		–		2.0 M $HClO_4$	99.4
8	Fe(III)	100	7	1×10^{-3}M	2.5×10^{-3}M	Water	99.9
	Th(IV)	40		–		2.0 M $HClO_4$	99.4

Conclusion

(**1**) The results obtained show that commercially available neutral phosphine oxide, Cyanex-923 in toluene can be used effectively for quantitative extraction of Th(IV) from sodium salicylate media in the pH range 5-7. The minimum reagent concentration required for the complete extraction of Th(IV) was 2.5×10^{-3} M Cyanex-923 in toluene. (**2**) The minimum equilibration time required for quantitative extraction was mere 10 min. (**3**) The thermodynamic study of the extraction reaction of Th(IV) with Cyanex-923 in toluene was also performed. It revealed that the extraction reaction is exothermic in nature with an enthalpy change (ΔH) value -52.3 kJ/mol, respectively. (**4**) Limitations like multistep extraction, multistep stripping and longer equilibration period was found with tributylphosphate (TBP), trioctylphosphine oxide (TOPO), triphenylphosphine oxide (TPPO)[1-7]. However such limitations were not observed with Cyanex-923. (**5**) For complete extraction of Th(IV) with di-2-ethyhexyl isobutaramide (D2EHIBA) in *n*-dodecane, the reagent concentration required for the quantitative extraction was 1.0 M[18]. Also quantitative extraction of Th(IV) was possible with 0.5 M of TOA[19] but with Cyanex-923, concentration required for the quantitative extraction was 2.5×10^{-3} M in toluene.

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REFERENCES

1. V.V. Sergievskii, L.V. Evdokimova and G.A. Yogodin, *Radiokhimiya*, **23**, 512 (1981).
2. H.A.C. Micky and R.J.W. Streeton, *J. Inorg. Nucl. Chem.*, **27**, 879 (1965).
3. C.A. Horton and J.C. White, *Anal. Chem.*, **30**, 1779 (1975).
4. M. Mojski, *J. Radioanal. Nucl. Chem.*, **35**, 3315 (1975).
5. M. Rajan and V.M. Shinde, *J. Radioanal. Nucl. Chem.*, **154**, 243 (1991).
6. N.G. Bhilare and V.M. Shinde, *J. Radioanal. Nucl. Chem.*, **185**, 243 (1994).
7. V.I. Volk, A.Yu. Vakhrushin and S.L. Mamaev, *Radiochemistry*, **41**, 120 (1999).
8. B. Borong, B. Yazhi, S. Chaohong, W. Gaodong, J. Qian and C. Zhengbai, *J. Radioanal. Nucl. Chem.*, **162**, 391 (1992).
9. J.S. Preston and A.C.du Preez, *Solvent Extr. Ion. Exch.*, **13**, 391 (1995).
10. D.V. Koladkar and P.M. Dhadke, *J. Radioanal. Nucl. Chem.*, **253**, 297 (2002).
11. E.A. Mowafy, A.M. Shalash and I.M. El-Naggar, *Indian J. Chem.*, **42A**, 3012 (2003).
12. A.N. Turanov, V.K. Karandashev, A.M. Fedoseev, N.I. Rodygina and V.E. Baulin, *Radiochemistry*, **47**, 177 (2005).
13. A.N. Turanov, V.K. Karandashev and A.N. Yarkevich, *Radiochemistry*, **47**, 570 (2005).
14. A.A. Zamani and M.R. Yaftian, *Separ. Purific. Technol.*, **40**, 115 (2004).
15. R.G. Vibhute and S.M. Khopkar, *J. Chem. Thermodyn.*, **25**, 861 (1993).
16. M.M. Rajamane, B.M. Sargar, S.V. Mahamuni and M.A. Anuse, *J. Serb. Chem. Soc.*, **71**, 223 (2006).
17. W.W. Philip and C. Maria, *Anal. Chem.*, **21**, 628 (1949).
18. P.N. Pathak, R. Veeraraghavan, P.B. Ruikar and V.K. Manchanda, *Radiokhim. Acta*, **86**, 129 (1999).
19. T.I. Bukina, Z.K. Karalova and B.F. Myasoedov, *Radiokhimiya*, **34**, 32 (1992).

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