Selective Extraction, Preconcentration and Transport Studies of Thorium(IV) Using Octa-Functionalized Calix[4]resorcinarene-Hydroxamic Acid

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A new calix[4]resorcinarene bearing eight hydroxamic acid groups (C4RAHA) has been synthesized and characterized by FT-IR, ^{1}H-NMR and elemental analysis. Its analytical properties were investigated, and showed high affinity and selectivity toward thorium(IV) in the presence of large quantities of associated metal ions. Thorium(IV) was extracted from an ethyl acetate solution of C4RAHA at pH 4.5. The λ_{max} and molar absorptivity (ε) for thorium(IV) were 341 nm and 7120 l mol^{-1} cm^{-1}. The complexation of thorium(IV) with C4RAHA has a 4:1 metal:ligand stoichiometry, which is relatively rare. The extracts were directly aspirated in the plasma for ICP-AES measurements for thorium(IV) in the presence of a diversified matrix. The system obeyed Beer's law over the range 0.1 – 6.5 μg ml^{-1} of thorium(IV) with a Sandell sensitivity of 0.0325 μg cm^{-2}. The preconcentration factor and overall stability constant evaluated at 25°C for thorium(IV) were 133 and 15.86, respectively. The complexation was characterized by a favorable enthalpy change. A liquid-membrane transport study of thorium(IV) was carried out from the source to the receiving phase under controlled conditions, and a mechanism of transport proposed. To check the validity of the proposed method, thorium(IV) was determined in monazite sand, rare earth sand and water samples.

Introduction

The advent of supramolecular chemistry[1] and non-covalent interactive forces has made the synthesis and assembling of a wide range of supramolecules increasingly feasible and efficient for metal inclusion. These supramolecular assemblies[2] possess remarkable structural versatility, and allow an examination of co-operative interaction between the metal centers. Hence, such synthetic supramolecular receptors are in great demand in the extraction and complexation chemistry of large numbers of cationic and anionic species and neutral organic molecules.

Among the different supramolecules, calix[4]resorcinarenes[3-6] have been widely employed as changeable units with well-defined structures and easy accessibility. Calix[4]resorcinarenes are large cyclic tetramers, and belong to a class of [1$_4$]metacyclophanes, which have found applications as host molecules,[4-10] components in liquid crystals,[11] photoresists,[12] selective membranes,[13] surface reforming agents,[14] HPLC stationary phase,[15] ion channel mimics,[16] and metal ion extraction agents.[17,18]

The main source of Th(IV) is monazite sand, mainly associated with cerium, lanthanum, yttrium, iron, *etc*. It has found extensive applications in nuclear fuels, used in dissipating static electricity and the gas mantle industry. Thorium(IV) compounds are hazardous, causing environmental pollution. Because of these realities, the processing of nuclear waste before disposal relies most often on solvent-extraction procedures, and a large number of extracting agents have been synthesized and tested with the aim of separating Th(IV) more effectively. There are several reagent (thoron-I, arsenazo-III, arsenazo-I, *p*-bromochlorophosphonazo, tribromoarsenazo, *etc*.) that have been reported for the spectrophotometric determination of Th(IV).[19-21] The separation of Th(IV) is done either by liquid–liquid extraction or by solid-phase extraction techniques. A large number of extractants, such as tributylphosphate, trioctyl phosphineoxide, organophosphoric acid, *etc*., have been reported for the extraction.[22-24] However, these reagents are either less sensitive, or non-specific, or a large number of diverse ions interfere in their determination. In ion-exchange chromatography, a number of resins have been reported, but they have less specificity, and also low sorption capacities due to the poor loading of metal ions.[25-29]

The macrocycles form the host-guest complex and are used for the complexation of several metal ions; however, complexation with Th(IV) is scanty.[30] With this in view, designing a new ligand that can selectively bind Th(IV), one has to overcome a difficult problem, *i.e.* the ligand must strictly discriminate Th(IV) from other metal ions present in great excess in monazite sand and other samples. Hydroxamic acids have achieved considerable importance as analytical tools for the separation and determination of a large number of metal ions, including Th(IV).[31–35]

In this communication, we describe the synthesis of octaarmed calix[4]resorcinarene-hydroxamic acid, C4RAHA, and its analytical application for the extraction and simultaneous determination of Th(IV) in the presence of several interfering ions. The extraction removes the bulk of the major elements and, at the same time, preconcentrates Th(IV) into a small

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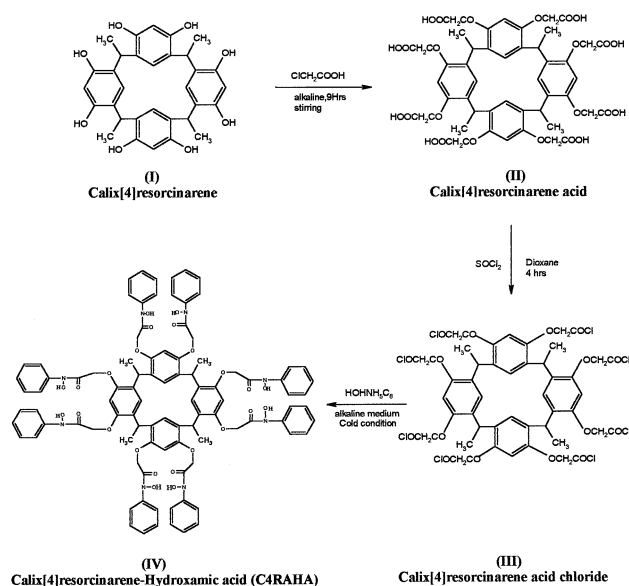E-mail: drvkjain@hotmail.com; shibupillai@indiatimes.com

Fig. 1   Synthetic route for calix[4]resorcinarene-hydroxamic acid (C4RAHA).

Source Phase (SP)	: 50 ml, 1.08×10^{-4} M thorium(IV)
Liquid Membrane Phase (LMP)	: 75 ml, 1.08×10^{-4} M C4RAHA in Ethyl Acetate
Receiving Phase (RP)	: 50 ml, 0.1 M HCl

Fig. 2   Apparatus for transport studies.

volume. The extract is directly aspirated into ICP-AES, which increases the sensitivity and detection limit by many fold.

## Experimental

Instruments and measurements

Electronic spectra were recorded on a Hitachi 3210 UV-visible spectrophotometer with matching 10 mm quartz cells. A plasma scan Model 710 sequential inductively coupled plasma atomic emission spectrometer along with a plasma scan multitasking computer and peristaltic pump was used. The following operating conditions were set for ICP-AES: Rf, 27.12 MHz; incident power, 2000 W; GMK nebulizer; sample concentration, 1 ppm; RF power, 5 W; observation height, 14 mm; argon coolant flow rate, 10 l min^{-1}; argon carrier flow rate, 10 l min^{-1}; intergraph period, 10 s; resolution, 0.004 nm; peristaltic pump flow rate, 1 ml min^{-1}; wavelength, 283.73 nm.

Materials and solutions

All of the chemicals used were of analytical reagent grade of E. Merck or BDH. All aqueous solutions were prepared with quartz distilled deionized water, which was further purified by a Millipore Milli-Q water purification system. The standard stock solution of thorium(IV) was prepared by dissolving 2.5 g of thorium nitrate tetrahydrate in 1000 ml of doubly deionized water and standardized spectrophotometrically.[36] A 0.02% (1.2 $\times 10^{-4}$ M) stock solution of C4RAHA was prepared in ethyl acetate. A working solution was subsequently prepared by appropriate dilution of the stock solution.

Synthesis of calix[4]resorcinarene-hydroxamic acid (C4RAHA)

Calix[4]resorcinarene **I** was synthesized by the acid-catalyzed condensation of resorcinol and acetaldehyde.[3] The calix[4]resorcinarene **I** was functionalized by chloroacetic acid in an alkaline medium to form calix[4]resorcinarene acid **II**.[37,38] The calix[4]resorcinarene acid **II** (10.08 g, 0.01 mol) was refluxed with thionyl chloride (11.9 g, 0.1 mol) in a dioxane medium for 4 h, excess thionyl chloride was distilled, and calix[4]resorcinarene acid chloride **III** was obtained.
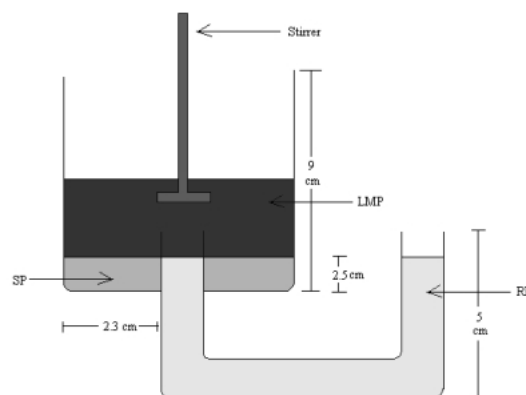
The calix[4]resorcinarene acid chloride **III** was added dropwise in a 100 ml conical flask containing an etheral solution of phenyl hydroxylamine and a saturated aqueous solution of sodium bicarbonate. The mixture was stirred continuously for 3 h at –5°C. The reaction mixture was then brought to room temperature and solvent ether was evaporated to obtain the crude product **IV**, recrystallized from ethyl acetate-hexane medium. The yield of **IV** 55%, mp >240°C dec.; IR (KBr), 3184, 1622 and 900 cm^{-1}; ^{1}H NMR (DMSO) δ 1.65 ppm (d, CHCH$_3$), δ 3.4 ppm (q, CH), δ 4.7 ppm (s, CH$_2$), δ 7 – 8 ppm (s, ArH), δ 8.8 ppm (s, N–OH); *Anal*. Calcd. for C$_{96}$H$_{88}$N$_8$O$_{24}$: C, 66.35; H, 5.10; N, 6.45; O, 22.10. Found: C, 66.43; H, 4.83; N, 6.27, O, 22.47 (Fig. 1).

Liquid–liquid extraction procedure

An aliquot of a sample solution containing 1.0 – 65.0 µg of thorium(IV) was transferred into a 25 ml separatory funnel. The pH of the solution was adjusted to 4.5 for thorium(IV) with the buffer solutions. The mixture was shaken with 3 ml of 1.08 $\times 10^{-4}$ M C4RAHA in ethyl acetate for 15 – 18 min. The organic extract was separated, dried over anhydrous sodium sulphate and transferred into a 10 ml volumetric flask. To ensure complete recovery, the extractions were repeated with 1 ml of C4RAHA. The combined extracts and washings were diluted to the mark with ethyl acetate. The absorbance of the organic phase was measured against the reagent blank at 341 nm. The total concentration of the thorium ion [ThO^{2+}] species remaining in the aqueous phase [ThO^{2+}]$_{(aq)}$ was measured by ICP-AES.

The concentration of the thorium(IV) extracted into the organic phase, [ThO$_2$]$_{(org)}$, as a complex was estimated by [ThO^{2+}]$_{(org)}$ = [ThO^{2+}]$_{(aq,initial)}$ – [ThO^{2+}]$_{(aq)}$, where [ThO^{2+}]$_{(aq,initial)}$ is the initial concentration of the metal ion in the aqueous phase. The percent extraction (%E) for thorium(IV) was calculated by

$$\%E_{Th} = [ThO^{2+}]_{(org)}/[ThO^{2+}]_{(aq,initial)} \times 100.$$

The extracted C4RAHA-thorium(IV) complex in ethyl acetate after appropriate dilution was also determined by ICP-AES.

Transport of thorium(IV)

The transport of ThO^{2+} was carried out in a glass assembly, as shown in Fig. 2. The reaction cell was 6.6 cm in inner diameter

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Table 1   Effect of solvents on the extraction of C4RAHA-thorium(IV) complex

Solvent	Dielectric constant	Extraction, %	Molar absorptivity/ l mol^{-1} cm^{-1}
Benzene	2.28	11	7.83×10^2
Toluene	2.30	36	2.56×10^3
Chloroform	4.80	85	6.05×10^3
Ethyl acetate	6.40	100	7.12×10^3

Thorium(IV), 2.0 μg ml^{-1}; C4RAHA, 3.0 ml, 1.08×10^{-4} M; pH, 4.5; λ_{max}, 341 nm.

Thorium   : 2 μg ml^{-1}
C4RAHA   : 3 ml, 1.08×10^{-4} M
Solvent   : Ethyl acetate
λ_{max} : 341 nm

Fig. 3   Effect of the pH on the extraction of C4RAHA-thorium complex.

Fig. 4   Comparative spectra of reagent C4RAHA 1.08×10^{-4} M (A) and its thorium complex (B).

and 9.0 cm in height with a total capacity of 305 ml. A U-tube (2.0 cm diameter, 20 cm length) was fused from the base of the cell. The height of the tube inside the cell was 4.0 cm from the basal plane. The whole assembly was kept in a thermostat maintained at 30°C. Transport experiments were performed with 50 ml of 1.08×10^{-4} M thorium(IV) solution at pH 4.5 as a source phase, and 50 ml 0.1 M HCl as a receiving phase. The liquid membrane consisted of 75 ml, 1.08×10^{-4} M C4RAHA in ethyl acetate. A synchronous motor (200 rpm) provided constant reproducible stirring from the top. The amount of thorium(IV) transported from the source phase to the receiving phase was measured by ICP-AES. The transport data were the average of 5 runs with an experimental error of less than 2%.

Results and Discussion

Spectral interpretations

The structure of **IV** was characterized by FT-IR and ^{1}H-NMR spectroscopy and elemental analysis. The IR spectrum showed characteristic absorption at 3184 cm^{-1} due to O–H stretching vibration. It is well known that absorption bands due to O–H stretching vibrations, when free, appear at around 3600 cm^{-1}; hydrogen bonding shifts these bands to lower frequencies.[39-41] In hydroxamic acids, the acidic O–H group is placed in a very close proximity of the polar carbonyl group C=O. The band at 1622 cm^{-1} is assigned for the C=O of the hydroxamic acid group. This assignment is made with respect to the region of amide and anilide. In unsubstituted amide RCONH$_2$, this band is located between 1690 and 1650 cm^{-1}, while in substituted amides RCONHR it is observed at 1680 and 1650 cm^{-1}. The position of the C=O stretching band is greatly influenced by the molecular structure, and is generally shifted to lower frequencies.[42] Thus, hydrogen bonding lowers the C=O band by 10 – 45 cm^{-1}.[42] A sharp band at 900 cm^{-1} is attributed to N–O stretching vibration in **IV**.[43-45] The ^{1}H-NMR spectrum of **II** showed five prominent sharp peaks at 1.6, 3.2, 4.6, 7.6 and 10.2 ppm, which were assigned to methyl, methine, methene, aromatic and carboxylic groups. After phenyl hydroxylamine groups were attached to **III**, the ^{1}H NMR spectrum of **II** changed dramatically; a new peak that appeared by the formation of hydroxamic acid groups was observed at 8.8 ppm,[46] and diminished the carboxylic acid signal, of 10.2 ppm.[37,38] The results obtained from an elemental analysis of **IV** confirm the presence of eight hydroxamic acid groups.

Complexation studies and statistical significance

The complexation of thorium(IV) with C4RAHA was studied under the optimum conditions of the pH, solvent, and reagent (C4RAHA) concentration. Figure 3 shows that the maximum extraction of thorium(IV) was possible in the pH range of 4.0 –
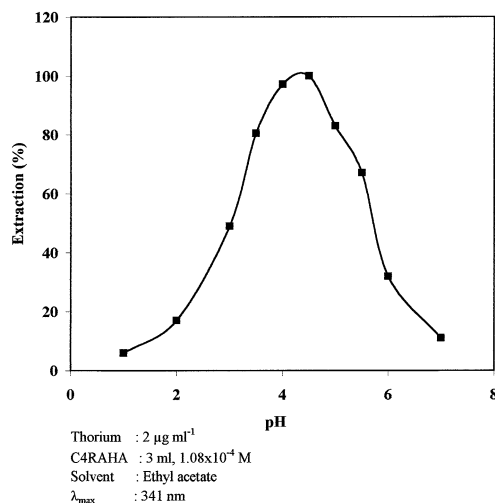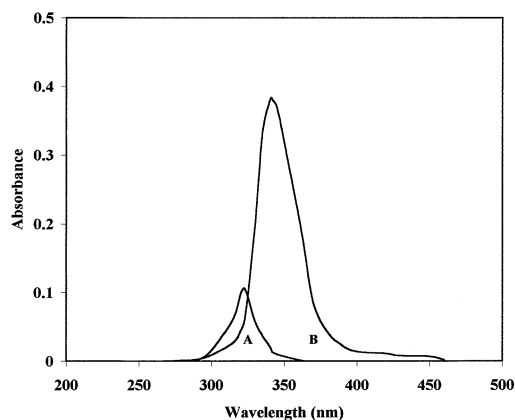
4.5; however, above and below this range extraction of the complex were incomplete. It was also found that 15 – 18 min of shaking was sufficient for the quantitative extraction of thorium(IV). The extractions were not affected by further shaking, indicating that the equilibrium state had been attained. The effect of a solvent, as shown in Table 1, on the extraction of the C4RAHA-thorium(IV) complex was restricted to ethyl acetate, chloroform, toluene and benzene due its limited solubility in other organic solvents, and it was found that quantitative extraction is possible in ethyl acetate. The spectra of the complex of thorium(IV) showed a bathochromic shift of 18 nm from that of the reagent C4RAHA in ethyl acetate, as shown in Fig. 4.

Under the optimum conditions, quantitative extraction was possible with 3.0 ml, 1.08×10^{-4} M C4RAHA in ethyl acetate. The molar absorptivity measured at the wavelength of the maximum absorption (λ_{max} 341 nm) for the extracted complexes was 7120 l mol^{-1} cm^{-1}. The system obeyed Beer's law over the range of 0.1 – 6.5 μg ml^{-1}, and the regression analysis equation obtained from the calibrated standard solution of thorium(IV) can be represented as Abs. = 0.153 × Conc. – 0.0001645 with a correlation coefficient of r = 0.997. Sandell's sensitivity, calculated for the proposed method, was 0.0335 μg cm^{-2}. The
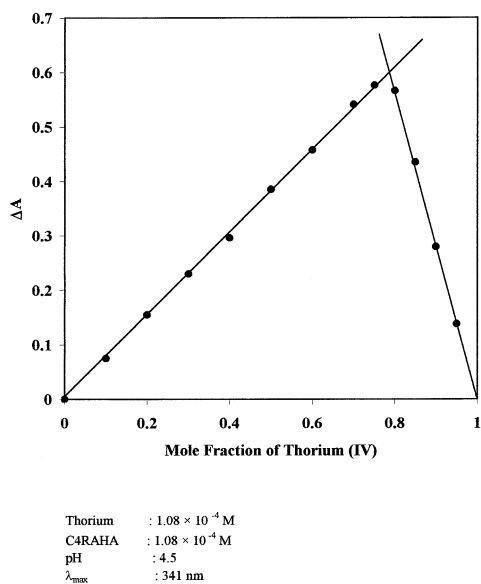
Thorium   : 1.08×10^{-4} M
C4RAHA   : 1.08×10^{-4} M
pH   : 4.5
λ_{max} : 341 nm

Fig. 5   Stoichiometry of the C4RAHA-thorium(IV) complex.

A: Thorium in the source phase (SP)
B: Thorium in the receiving phase (RP)

Source Phase (SP)   : 50 ml, 1.08×10^{-4} M thorium
Liquid Membrane Phase (LMP)   : 75 ml, 1.08×10^{-4} M C4RAHA in Ethyl Acetate
Receiving Phase (RP)   : 50 ml, 0.1 M HCl

Fig. 6   Transport profile of thorium (ThO^{2+}) through a liquid membrane containing C4RAHA at 30°C.

precision of the proposed method was investigated based on the optimum condition of thorium(IV) extraction, and expressed as a relative standard deviation of 1.9%. The limit of detection (LOD is 3.3 ppb) was defined as that analyte concentration giving a signal equal to three-times the standard deviation of a blank signal.[47] The limit of quantification (LOQ is 10.97 ppb) was then set as ten-times the standard deviation of the blank signal.

Stoichiometry of the complex

The stoichiometric ratio of the thorium(IV) complex was determined by a modified Job's method of continuous variation. The absorbance of complex A_c of a series of solutions containing thorium ion (ThO^{2+}) a and C4RAHA b at a constant total concentration $a + b$, but different concentration ratios, was measured at 341 nm. The absorbance of b was subtracted from the observed absorbance, A_c, to obtain the difference absorbance ΔA,

$$\Delta A = A_c - A_b.$$

The ΔA values were plotted against the molar ratio of thorium(IV) ion $a/(a + b)$ (Fig. 5). The maximum value for ΔA was clearly obtained at $a/(a + b) = 0.81$, indicating a 4:1 stoichiometric ratio of ThO^{2+} and C4RAHA. The accuracy of this result is possible if only a single complex is formed. To verify this, measurements were taken at different selected wavelengths, which gave the same value for the $a/(a + b)$ ratio.

To obtain more information about the nature of the extracted complex, attempts were made to isolate it from ethyl acetate extract. The extract was evaporated to dryness and subjected to elemental analysis. Further, a known weight of the dry complex was digested with a perchloric and nitric acid mixture. It was centrifuged, and the thorium(IV) content was determined by ICP-AES. The obtained results are in conformity with the complex formulae. The experimental results obtained for the elemental analysis of the C4RAHA–thorium(IV) complex is: carbon, 42.27%; nitrogen, 4.07%; hydrogen, 2.97%; and thorium, 34.11%, which is comparable to their theoretical values: carbon, 42.34%; nitrogen, 4.12%; hydrogen, 2.96%; and thorium, 34.11%.
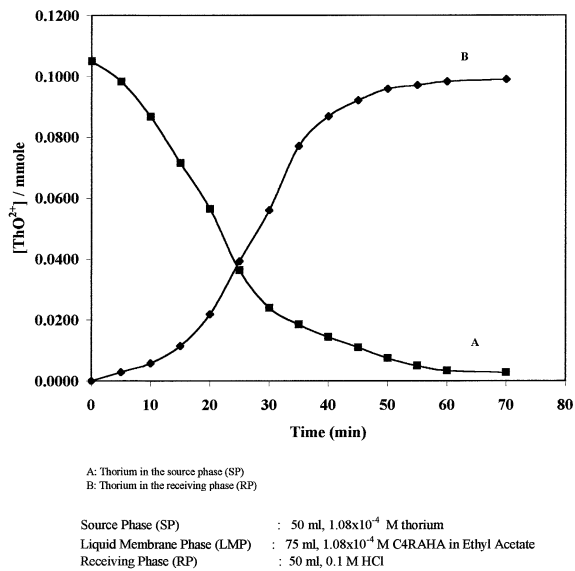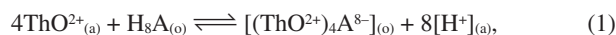
Extraction studies and equilibria

To evaluate the binding ability of C4RAHA (H_8A) with thorium(IV), a liquid–liquid extraction (water–ethyl acetate system) was carried out, and the extraction constants were determined.

The extraction equilibria for thorium(IV) can be expressed by

$$4ThO^{2+}{}_{(a)} + H_8A_{(o)} \rightleftharpoons [(ThO^{2+})_4A^{8-}]_{(o)} + 8[H^+]_{(a)}, \qquad (1)$$

where the species in the organic and aqueous phases are denoted by subscripts (o) and (a), respectively.

The extraction constant, K_{ex}, is given by

$$K_{ex} = \frac{[(ThO^{2+})_4A^{8-}]_{(o)} + [H^+]^8{}_{(a)}}{[ThO^{2+}]^4{}_{(a)}[H_8A]_{(o)}}. \qquad (2)$$

Also, the distribution ratio of thorium(IV) in the two phases can be given by

$$D = \frac{[(ThO^{2+})_4A^{8-}]_{(O)}}{[ThO^{2+}]^4{}_{(a)}}. \qquad (3)$$

From Eqs. (2) and (3), we obtain

$$K_{ex} = \frac{D[H^+]^8{}_{(a)}}{[H_8A]_{(o)}}. \qquad (4)$$

Equation (4), can be written as

$$\log K_{ex} = \log D + 8\log[H^+] - \log[H_8A]. \qquad (5)$$

The extraction constant, K_{ex}, may be obtained from the above Eq. (5), where

$$[H_8A] = \frac{(C_{H_8A} \cdot P_{H_8A})}{1 + P_{H_8A} + (k_a/[H^+])}. \qquad (6)$$

In this expression, C_{H_8A} is the analytical concentration of the reagent, H_8A; P_{H_8A} and k_a are its respective distribution constant

Table 2   Stability constant and thermodynamic parameters for the C4RAHA-thorium(IV) complex

Temp./K	pK_a of H_8A	$\log P_{H_8A}$	$\log \beta_4 \cdot P_{Th-H_8A}$	$\log K_{ex}$	ΔG/kJ mol^{-1}	ΔH^a/kJ mol^{-1}	ΔS/kJ^{-1} mol^{-1}
298	8.90	23.00	15.86	9.12×10^{-17}	−90.41	—	−391.37
303	8.85	23.05	16.45	3.55×10^{-16}	−95.35	−203.82	−368.61
308	8.74	23.16	17.03	1.35×10^{-15}	−100.34	−207.09	−346.42
313	8.65	23.25	17.59	4.90×10^{-15}	−105.32	−206.55	−324.97
318	8.57	23.33	18.14	1.74×10^{-14}	−110.35	−209.45	−304.40
323	8.51	23.39	18.67	5.88×10^{-14}	−115.36	−208.28	−283.83

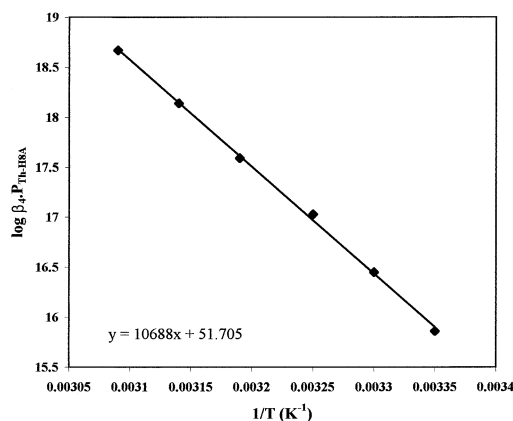a. Mean ΔH = −207.038 kJ mol^{-1}.

Fig. 7 Variation of the two-phase stability constant with the temperature (T^{-1}).
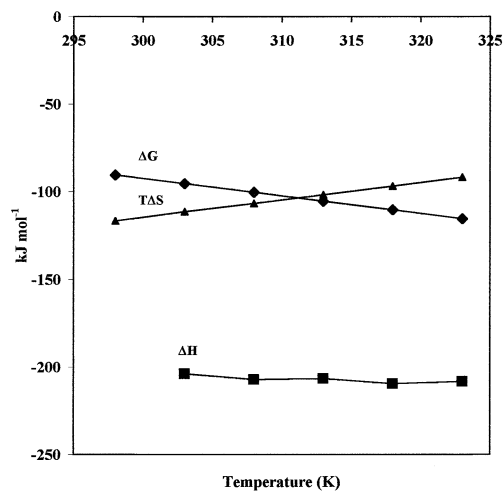

Fig. 8   Variation in the thermodynamic parameter with temperature.

and acid dissociation constant. With the aid of Eq. (6) and the values of pK_a = 8.9 and $\log P_{H_8A}$, the K_{ex} values were calculated by a least-squares procedure. Also, the two-phase stability constant ($\log \beta_4 \cdot P_{Th-H_8A}$) was obtained from the relation

$$\log \beta_4 \cdot P_{Th-H_8A} = \log K_{ex} + pK_a + \log P_{H_8A}, \qquad (7)$$

where β_4 and P_{Th-H_8A} are the respective overall formation constant and the distribution constant of the $[(ThO^{2+})_4A^{8-}]$ complex in the two phases. Table 2 summarizes the value of $\log \beta_4 \cdot P_{Th-H_8A}$ and $\log K_{ex}$ at different temperatures.

Liquid membrane transport studies

Considerable effort has been directed over the last two decades to the transport of metal ions across a liquid membrane.[48] A liquid membrane is a liquid phase, which separates two other liquid phases with which it is immiscible. These liquid membranes are of interest both for possible technological applications and for fundamental studies of the transport process.   The transport of $[ThO^{2+}]$ through a membrane containing 1.08×10^{-4} M C4RAHA from the source phase of $[ThO^{2+}]$ = 1.08×10^{-4} M to the receiving phase of 0.1 M HCl was carried out.   As evident from Fig. 6, the concentration of ThO^{2+} in the source phase started to decrease continuously, and reached a lower concentration than the detection limit after 22 min (curve A). On the other hand, the concentration of ThO^{2+} in the receiving phase incurred, as shown in the curve B. Therefore, it is clear that ThO^{2+} moved from the source to receiving phase through the liquid membrane. The carrier in the membrane reacted with ThO^{2+} in the source phase at the interface of these phases, and formed a complex $[(ThO^{2+})_4 A^{8-}]$ while releasing 8 moles of proton into the source phase. At the other interface of the membrane and

the receiving phase, the complex reacted with 8 moles of protons while releasing 4 moles of ThO^{2+} in the receiving phase.

Effect of the temperature and thermodynamic parameters

The extractions of thorium(IV) from aqueous solution were studied at different temperatures between 298 K and 323 K; the results show that the extraction equilibrium constant ($\log K_{ex}$) and two-phase stability constants for thorium(IV) ($\log \beta4 \cdot P_{Th-H_8A}$) increased with an increase in temperature (Table 2).   The change in the extraction equilibrium constant (ln K_{ex}) with temperature can be expressed by the Van't Hoff equation,

$$d(\ln(K_{ex}))/dT = \Delta H^0/RT^2.$$

In order to utilize this equation for calculations, it must be integrated while assuming that the heat of reaction (ΔH) remains constant over a small range of temperature,

$$\ln(K_{ex}) = -\Delta H^0/RT + \text{constant (intercept)}.$$

Plots of ($\log \beta_4 \cdot P_{Th-H_8A}$) against $1/T$ yield a straight-line equation, $10688x + 51.705$, with slope(x) – $\Delta H^0/2.303R$ (Fig. 7).   The enthalpy change accompanying complexation was found to be −207.038 kJ mol^{-1} in the given range of temperatures.   An inspection of Fig. 8 (ΔH^0, −$T\Delta S^0$, $\Delta G^0 \rightarrow T$) reveals that the complexation is driven by a favorable enthalpy change.   The negative values of the free energy suggest that the reaction is exothermic and favorable for complexation.

Effect of diverse ions

The extraction of a single metal ion under controlled condition

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Table 3   Effect of diverse ions on the extraction of C4RAHA-thorium(IV) complex

Ion	Amount added/mg	Recovery of thorium(IV)/ppm	
		Spectrophotometry	ICP-AES
Ag^+	40	9.9	9.99
Be^{2+}	40	10.1	9.99
Pb^{2+}	45	9.8	9.98
Mn^{2+}	40	9.9	9.99
Ni^{2+}	60	9.9	10.03
Cu^{2+}	50	10.2	10.01
Zn^{2+}	45	10.1	9.99
Cd^{2+}	40	9.8	9.98
Hg^{2+}	50	10.0	9.99
Pd^{2+}	40	9.7	9.99
Al^{3+}	50	9.8	10.02
Sn^{2+}	40	9.9	9.97
La^{3+}	50	10.2	9.99
Ce^{4+}	50	10.1	9.97
Zr^{4+}	50	9.8	9.99
Mo^{6+}	50	9.7	9.99
UO_2^{2+}	50	10.2	10.00
V^{5+}	50	10.3	10.00
Fe^{2+}	45	9.96	10.00
Cr^{3+}	40	9.9	10.00
Mg^{2+}	60	9.9	10.00

Thorium(IV), 10.0 $\mu g\ ml^{-1}$; pH, 4.5; solvent, ethyl acetate; C4RAHA, 3 ml, 1.08×10^{-4} M; λ_{max}, 341 nm.

Table 4   Analysis of thorium(IV) in standard samples from the United States Geological Survey (USGS) and monazite sand

Sample	Certified value/ $\mu g\ ml^{-1}$	Present method[b]/$\mu g\ ml^{-1}$ thorium(IV) found	
		Spectrophotometry	ICP-AES
BCR-1 (52/19)	6.00	5.95 ± 0.5	5.985 ± 0.016
WI	2.42	2.50 ± 0.08	2.430 ± 0.010
AGV-1 (74/19)	24.20	24.15 ± 0.05	24.200 ± 0.007
GSP-1 (17/22)	104.00	105.1 ± 0.05	105.078 ± 0.010
Soil-5	11.30	11.20 ± 0.15	11.298 ± 0.005
Monazite sand[a] (%)	—	8.00 ± 0.03	8.00 ± 0.005
Rare earth-silicon-magnesium alloy-(88.8)	0.196	0.20 ± 0.01	0.198 ± 0.002
Water sample[c] 1	—	0.56 ± 0.05	0.515 ± 0.003
2	—	0.09 ± 0.03	0.088 ± 0.005

a. The samples from Travancore, India.
b. The results are the average of ten determinations.
c. The samples are from Mumbai seawater.

gives an indication of the potential sensitivity of the proposed method. However, the selectivity of a reagent can be more realistically determined under condition where the extraction is carried out from a solution containing different metal ions. In order to examine this by the present method, the effect of various cations and anions in the separation and determination of thorium(IV) was studied.   Interference studies were performed by measuring the absorbance of the extracted organic phase and the aqueous phase by ICP-AES. The tolerance limit was set as the amount of foreign ion causing a change of ± 0.021 in absorbance, or a 2% error in the recovery of thorium(IV).

Thorium(IV) was extracted in the presence of a large number of competitive ions at the optimum pH of 4.5; none of them
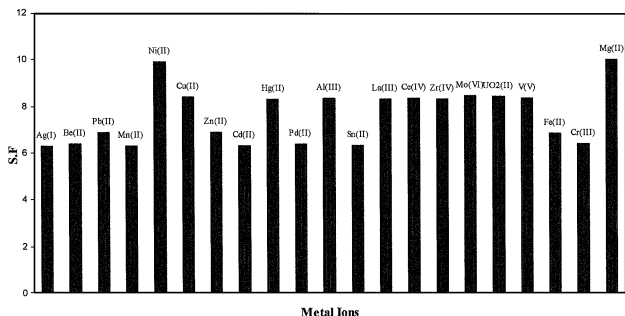

Fig. 9   Stability constants of thorium(IV) compared to other competitive metal ions.

affected the absorbance of the C4RAHA-thorium(IV) complex. The separation factor for thorium(IV) over these commonly associated metal ions (M^{n+}) may be given by

$$S.F = \frac{D_{Th}}{D_M},$$

where D_{Th} and D_M are the distribution ratios of thorium (ThO^{2+}) and other metal (M^{n+}) ions, respectively. As is evident from the Fig. 9 and Table 3, the proposed method has a high selectivity for thorium compared to other metal ions.

Preconcentration of thorium

The concentration of thorium(IV) in natural water samples is too low for its direct determination.   Therefore, a preconcentration or enrichment step is necessary to bring the sample to the detectable limits of the existing instrumental method. The method was studied for the preconcentration of thorium(IV) in terms of its preconcentration factors.

$$PF = \frac{\text{Concentration of metal in organic phase}}{\text{Initial concentration of metal in aqueous phase}}$$

A preconcentration study was carried out by extracting 20 μg of thorium(IV) in 1000 ml of the aqueous phase with 7.5 ml of 0.005% C4RAHA in ethyl acetate. To evaluate the efficiency of preconcentration, expressed as recovery, the concentrations of thorium(IV) in the organic phase and the aqueous phase were determined by ICP-AES. A quantitative determination was possible with recovery up to 98% with a concentration factor of 133.

Determination of thorium(IV) in standard and natural samples

Standard rock samples from the United States Geological Survey (USGS) were analyzed to test the reliability of the present method. The samples were digested in a mixture of perchloric acid and nitric acid, and evaporated to dryness. The residue was redissolved in 0.1 M perchloric acid and diluted to 250 ml with distilled water. An aliquot of the solution was taken for the extraction and determination of thorium(IV).

For the analysis of thorium(IV) in a rare earth silicon-magnesium alloy, a weight quantity of 0.1 – 0.2 g of a powder sample (rare earth silicon-magnesium alloy) was heated for 30 min in a dried platinum crucible. After it was cooled and 1 – 2 ml hydrofluoric acid was added, it was heated to dissolve and 2 ml of conc. H_2SO_4 was added. The contents were then heated to dryness, and the residue was dissolved in 5 ml of 2 M HCl. Finally, it was diluted to 100 ml with distilled water and determined by ICP-AES. Matrix interferences were verified by

comparing the slopes of the calibration graphs with those using the standard addition method. The results for the analysis of rocks, alloys, and seawater samples are given in Table 4.

Conclusion

The results obtained from the analysis of standard geological samples, monazite sand and seawater samples proved the reliability of the proposed method for their application to various samples. The proposed method is simple, specific, and sensitive for thorium(IV). Thorium(IV) is first preconcentrated by a liquid–liquid extraction technique, and then aspirated to ICP-AES with a detection limit of 3.3 ppb and a quantification limit of 10.97 ppb for thorium(IV) from a diverse matrix. Moreover, the molar absorptivity of 7120 l mol^{-1} cm^{-1} achieved in the present method is high compared to most of the analogous methods cited in the literature.

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