

## Octafunctionalized Calix[4]resorcinarene-N-fenil-acetohydroxamic acid for the Separation, Preconcentration and Transport Studies of Cerium(IV)

Vinod K. Jain,\* Shibu G. Pillai and Parin H. Kanaiya

Chemistry Department, School of Sciences, Gujarat University, Ahmedabad, 380009 India

Um novo método para extração líquido-líquido, separação e pré-concentração de cério(IV) com um derivado ácido do calix[4]resorcinareno [C4RAHA] é descrito. Cério foi extraído em pH 9 com etilacetato, e recuperado de areias monazíticas, na presença de tório, urânio, lantânio e um grande número de cátions e ânions. Cério(IV) forma um complexo colorido, amarelo,  $\lambda_{\text{max}}$  381 nm, absorvidade molar de  $1,06 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$  e obedece a lei de Beer no intervalo entre 0,4 e 15 mg mL<sup>-1</sup>. A razão metal-ligante encontrada para cério(IV) foi de 4:1 (M:L). Estudos de transporte foram realizados em um sistema de três fases, através de uma membrana líquida contendo C4RAHA. Para medidas por ICP OES, o extrato pode ser diretamente aspirado, o que aperfeiçoa a sensibilidade em 25 vezes e os limites de estimativa são 5-150 µg L<sup>-1</sup> de cério. O método foi aplicado para a determinação de cério em materiais geológicos de referência, areia monazítica e amostras de água de mar.

A new method for liquid-liquid extraction, separation and preconcentration of cerium(IV) with a calix[4]resorcinarene acid derivative [C4RAHA] is reported. Cerium was extracted at pH 9 in ethyl acetate and recovered from monazite sands in the presence of thorium, uranium, lanthanum and large number of cations and anions. Cerium(IV) forms yellow coloured complex,  $\lambda_{\text{max}}$  381 nm, molar absorptivity  $1.06 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$  and obeys Beer's law over the range 0.4-15 mg mL<sup>-1</sup>. The metal ligand ratio for cerium (IV) was found to be 4:1 (M:L). Transport studies were carried out in a three phase system across a liquid membrane containing C4RAHA. For ICP OES measurements, the extract can be directly aspirated, which enhances the sensitivity 25-fold and the limits for estimation are 5-150 µg L<sup>-1</sup> of cerium. The method was applied for the determination of cerium in standard geological samples, monazite sand and sea water samples.

**Keywords:** cerium(IV), calix[4]resorcinarene-N-fenil-acetohydroxamic acid(C4RAHA), transport studies, spectrophotometry

### Introduction

The chemistry of bowl shaped macrocyclic compounds that can complex organic and inorganic guests has been receiving significant attention in the field of supramolecular chemistry.<sup>1</sup> Among the different macrocyclic compounds, calix[4]resorcinarenes and calixarenes<sup>2</sup> have been widely employed as changeable units with a well defined structure and easy accessibility. The calixresorcinarenes are unique three-dimensional cyclic tetramer and hexamer that belong to a class of metacyclophanes in which resorcinol units are linked by methylene bridges.<sup>3</sup>

The interest towards this class of compounds which are capable of forming host guest complexes is stimulated

by the development of supramolecular chemistry which uses them for the possible creation of synthetic receptors and carriers of cations, anions and neutral molecules.<sup>4</sup> The host properties of calix[4]resorcinarenes continue to draw research interests due to its potential application as macrocyclic receptors,<sup>5</sup> as dendrimers in biological systems,<sup>6</sup> nano-capsule,<sup>7</sup> nanoparticles,<sup>8</sup> optical chemosensors,<sup>9</sup> supramolecular tectons,<sup>10</sup> host molecules,<sup>11</sup> as components in liquid crystals,<sup>12</sup> photoresists,<sup>13</sup> selective membranes,<sup>14</sup> surface reforming agents,<sup>15</sup> HPLC stationary phases,<sup>16</sup> as ion channel mimics,<sup>17</sup> and metal ion extraction agents.<sup>18</sup>

High purity cerium is required for nuclear power production and as catalyst for automobile and nuclear industries. The analysis of environmental samples, like monazite sand, for rare earth elements is an important topic for geochemical and geological research, which

\*e-mail: drvkjain@hotmail.com

allows solving the problems of genesis of ore deposits.<sup>19</sup> Cerium is the major element present in monazite sands associated with lanthanum, thorium and uranium. Generally monazite sand is treated with an alkali followed by acid digestion and extraction with tetra butyl phosphate for the separation of lanthanides. However, the process is time consuming and needs further purification for isolation of high purity elements. A large number of reagents have been reported for the separation of cerium, however, several closely related ions including thorium and traces of uranium interfere.<sup>20-24</sup> Highly versatile techniques like atomic absorption spectrometry (AAS) and also inductively coupled plasma optical emission spectrometry (ICP OES) cannot be applied directly for the trace determination of cerium as they have high detection limits of  $10 \mu\text{g mL}^{-1}$ ,<sup>25,26</sup> and a prior separation is mandatory.<sup>27,28</sup> Hydroxamic acids are well known to be efficient extractants that find wide applications in analytical,<sup>29</sup> and agricultural fields.<sup>30</sup> Hydroxamic acids have achieved significant importance as analytical tools for the separation and determination of a large number of metal ions.<sup>31-35</sup> Thus still remains a need of a specific ligand that discriminate Ce(IV) from La(III), Th(IV), and U(VI) from other metal ions, present in great excess in sea water, monazite sand, and other environmental samples.

Since we had recently prepared a series of novel Calix[4]resorcinarene-N-fenil-acetohydroxamic acid derivatives to study the extraction of uranium and thorium from acidic media,<sup>36,37</sup> we thought to extend our investigations to include the extraction of cerium under similar conditions. In the present study we have used Calix[4]resorcinarene-N-fenil-acetohydroxamic acid (C4RAHA) for the liquid-liquid extraction, preconcentration and transport of cerium across a liquid membrane. The extraction removes the bulk of the elements and at the same time preconcentrates Ce(IV) into small volumes. The extract is directly aspirated into ICP OES improving the sensitivity and detection limit. To check the applicability of the proposed method, cerium was determined in monazite sand, standard geological materials and sea water samples.

## Experimental

### Instrumentation and measurements

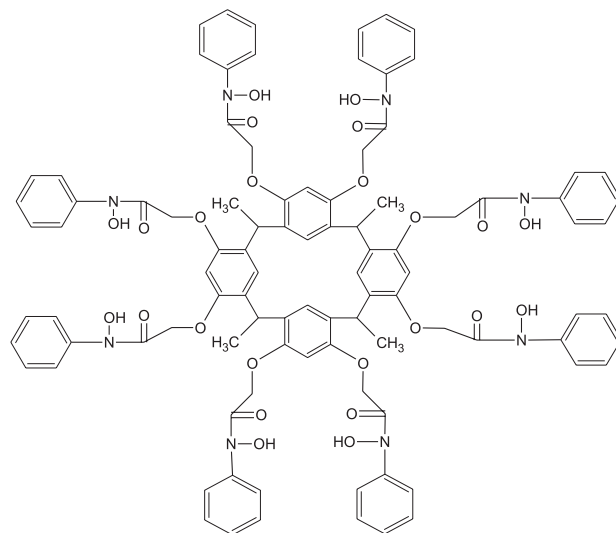
Spectrophotometric determinations were done with a Hitachi 3210 UV/Vis spectrophotometer using 10 mm quartz cells. Plasma scan model 710 sequential inductively coupled plasma optical emission spectrometer with plasma scan multitasking computer and peristaltic pump was used

for emission measurements applying the following conditions.

Radio frequency (Rf) 27.12 MHz; incident power, 2000 W; Labtam GMK nebulizer; Reflected power, 5 W; observation height, 14 mm; argon coolant flow rate, 10 L  $\text{min}^{-1}$ ; argon carrier flow rate, 1.0 L  $\text{min}^{-1}$ ; integration time (period): 10 s; resolution of mono chromator used 0.004 nm; peristaltic pump flow rate 1.0 mL  $\text{min}^{-1}$ ; analytical wavelength for cerium 413.77 nm.

### Chemicals and solutions

All chemicals used were of analytical reagent grade of BDH, E-Merck or Qualigens unless otherwise specified. All aqueous solutions were prepared with quartz distilled deionized water, which was further purified by a Millipore Milli-Q plus water purification system. The standard stock solution of cerium(IV) ( $1000 \mu\text{g mL}^{-1}$ ) was prepared by dissolving 4.511 g of  $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$  in water containing 2 mL  $\text{H}_2\text{SO}_4$  in a 1000 mL volumetric flask and standardized spectrophotometrically.<sup>38</sup> The buffer solutions in the pH range 3-10 were prepared from 0.2 mol  $\text{L}^{-1}$  ethanoic acid/0.2 mol  $\text{L}^{-1}$  sodium ethanoate or triethanolamine buffer (mix 200 mL of 15% v/v triethanolamine, 160 mL of 1 mol  $\text{L}^{-1}$   $\text{HNO}_3$ , and 40 mL of water). The C4RAHA (Figure 1) was synthesized as reported earlier.<sup>36,37</sup> Its  $7.14 \times 10^{-5}$  mol  $\text{L}^{-1}$  solution was prepared in ethyl acetate.



**Figure 1.** Structure of Calix[4]resorcinarene-N-fenil-acetohydroxamic acid (C4RAHA).

### Liquid-liquid extraction of cerium(IV)

An aliquot of sample solution containing 4.0-150.0  $\mu\text{g}$  of Ce(IV) was transferred into a 25 mL separatory funnel.

pH was adjusted between 8-9 by adding the buffer solution. The mixture was shaken with 3 mL of  $7.14 \times 10^{-5} \text{ mol L}^{-1}$  C4RAHA in ethyl acetate for 8-9 min. The organic extract was separated, dried over anhydrous sodium sulphate and transferred into a 10 mL volumetric flask. To ensure complete recovery, the extraction was 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 381 nm. The total concentration of the cerium ion  $[\text{Ce}^{4+}]$  species remaining in the aqueous phase  $[\text{Ce}^{4+}]_{(\text{aq})}$  was measured by ICP OES.

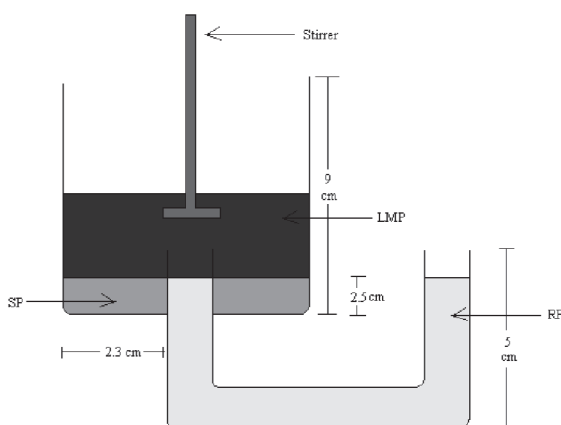
The concentration of the metal ion extracted into the organic phase  $[\text{Ce}^{4+}]_{(\text{org})}$  as complex was estimated by  $[\text{Ce}^{4+}]_{(\text{org})} = [\text{Ce}^{4+}]_{(\text{aq, initial})} - [\text{Ce}^{4+}]_{(\text{aq, final})}$ , where  $[\text{Ce}^{4+}]_{(\text{aq, initial})}$  and  $[\text{Ce}^{4+}]_{(\text{aq, final})}$  are the initial and final concentration of the metal ion in the aqueous phase respectively. The percent extraction (%E), was calculated by

$$\%E = [\text{Ce}^{4+}]_{(\text{org})} / [\text{Ce}^{4+}]_{(\text{aq, initial})} \times 100$$

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

#### Transport studies of cerium(IV)

Transport of Ce(IV) through the liquid membrane in a three phase system was carried out in a glass assembly as shown in Figure 2. The reaction cell was 6.6 cm in inner diameter and 9.0 cm in height with a total capacity of 305 mL. 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



Source Phase (SP): 50 mL,  $7.14 \times 10^{-5} \text{ mol L}^{-1}$  Ce(IV) at pH 9.0  
Liquid Membrane Phase (LMP): 75 mL,  $7.14 \times 10^{-5} \text{ mol L}^{-1}$  C4RAHA in ethyl acetate  
Receiving Phase (RP): 50 mL, 0.1 mol L<sup>-1</sup> HCl

Figure 2. Apparatus for transport of cerium(IV) studies.

was kept in a thermostat maintained at 30 °C. The transport experiments were performed with 50.0 mL of  $7.14 \times 10^{-5} \text{ mol L}^{-1}$  Ce(IV) solution at pH 9.0 as source phase and 50.0 mL of 0.1 mol L<sup>-1</sup> HCl as receiving phase. The liquid membrane consisted of 75 mL of  $7.14 \times 10^{-5} \text{ mol L}^{-1}$  C4RAHA in ethyl acetate. A synchronous motor (200 rpm) provided constant reproducible stirring from the top. The amount of Ce(IV) transported from the source phase to the receiving phase was measured by ICP OES. The transport data's are the average of 5 runs with an experimental error of less than 2%.

## Results and Discussion

### Complexation studies and statistical significance

The synthesized Calix[4]resorcinarene-N-fenil-acetohydroxamic acid was used for the extraction and spectrophotometric determination of Ce(IV). The complexation of Ce(IV) with C4RAHA was studied under optimum conditions of pH, solvent, and reagent (C4RAHA) concentration. Maximum extraction of Ce(IV) was reached in the pH range of 8.0-9.0, however, above and below this range, the extraction of the complex was incomplete. It was also found that 5 min of shaking is sufficient for quantitative extraction of Ce(IV). The extraction was not affected by further shaking, indicating that the equilibrium state had been attained. The effect of solvent on the extraction of Ce(IV)- C4RAHA complex was restricted to ethyl acetate, chloroform, toluene and benzene due its limited solubility in other organic solvents and was found that quantitative extraction is possible in ethyl acetate with molar absorptivity  $1.06 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The spectra of the complex of Ce(IV) showed a bathochromic shift of 58 nm from that of the reagent C4RAHA in ethyl acetate as shown in Figure 3.

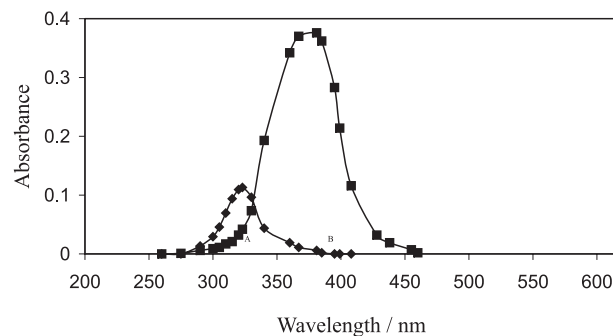


Figure 3. Comparative spectra of reagent C4RAHA (A) and its cerium complex (B).

Under the optimum conditions, quantitative extraction was possible with 3.0 mL,  $7.14 \times 10^{-5} \text{ mol L}^{-1}$  C4RAHA

in ethyl acetate. The molar absorptivity measured at the wavelength of maximum absorption ( $\lambda_{\max}$  381 nm) for the extracted complexes was  $1.06 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The system obeys Beer's law over the range of 0.4-15.0 mg  $\text{mL}^{-1}$  and the regression analysis equation obtained using reference solutions can be represented as  $A = 0.0765 \times \text{Conc.} - 0.000057$  with the a linear correlation coefficient of  $r = 0.9988$ . The Sandell's sensitivity calculated for the proposed method is  $0.013 \mu\text{g cm}^{-2}$ . The precision of the proposed method was investigated based on the optimum condition of Ce(IV) extraction and expressed as relative standard deviation of 1.8%. The limit of detection (LOD,  $2.3 \mu\text{g L}^{-1}$ ) was defined as that analyte concentration giving a signal equal to three times the standard deviation of blank signal.<sup>39</sup> The limit of quantification (LOQ,  $7.6 \mu\text{g L}^{-1}$ ) was then set as ten times the standard deviation of the blank signal.

#### Stoichiometry of the complex

The stoichiometric ratio of the complex was determined by the modified Job's method of continuous variation. The absorbance of complex  $A_c$  of a series of solution containing cerium ion ( $\text{Ce}^{4+}$ ) a and C4RAHA b at a constant total concentration a+b, but different concentration ratios were measured at 381 nm. The absorbance of b was subtracted from the observed absorbance  $A_c$  to obtain the true absorbance  $\Delta A$ .

$$\Delta A = A_c - A_b$$

$\Delta A$  values were plotted against the molar ratio of Ce(IV) ion a / (a+b). The maximum value for  $\Delta A$  was clearly obtained at a / (a+b) = 0.78, indicating 4 : 1 stoichiometric ratio of  $\text{Ce}^{4+}$  and C4RAHA. The accuracy of this result is possible if only a single complex is formed. To verify this, measurements were taken at a different selected wavelength, which gave same value for a / (a+b) ratio.

To get more information about the nature of the extracted complex, the extract was evaporated to dryness and subjected to elemental analysis. Further, a known mass of the dry

complex was digested with perchloric and nitric acid mixture. It was centrifuged and cerium content was determined by ICP OES. The results obtained are in conformity with the complex formulae. The experimental results obtained for elemental analysis of the complex are: carbon 47.44%, nitrogen 4.57%, hydrogen 3.58% and cerium 23.01% and are comparable with the theoretical values: carbon 47.50%, nitrogen 4.62%, hydrogen 3.66% and cerium 23.11%.

#### Extraction equilibrium

To evaluate the binding ability of C4RAHA ( $\text{H}_8\text{A}$ ) with Ce(IV), a liquid-liquid extraction in water-ethyl acetate system was carried out and the extraction constants were determined.

The  $\beta_4$  and  $P_{\text{Ce-H8A}}$  are the respective overall formation constant and distribution constant of  $[\{\text{Ce}(\text{OH})_2\}_4\text{A}^{8-}]_{(o)}$  complex in the two phases and the values of  $\log \beta_4 \cdot P_{\text{Ce-H8A}}$  and  $\log K_{\text{ex}}$  at different temperatures are summarized in Table 1.

#### Effect of temperature and thermodynamic parameters

The extraction of Ce(IV) from aqueous solution was studied at different temperatures between 298 K and 318 K and the results show that the extraction equilibrium constant ( $k_{\text{ex}}$ ) and two-phase stability constant ( $\log \beta_4 \cdot P_{\text{Ce-H8A}}$ ) increases with increase in temperature (Table 1). The plot of ( $\log \beta_4 \cdot P_{\text{Ce-H8A}}$ ) against  $1/T$  yields a straight line equation  $9167.4 \times + 47.379$  with slope(x) =  $-\Delta H^\circ / 2.303 R$ . The mean enthalpy change accompany the complexation is found to be  $-177.52 \text{ kJ mol}^{-1}$  for cerium in the given range of temperature. The inspection of Figure 4 ( $\Delta H^\circ$ ,  $-T\Delta S^\circ$ ,  $\Delta G^\circ \rightarrow T$ ) reveals that the complexation is driven by negative values of free energy and favorable enthalpy change.

#### Liquid membrane transport studies

The transport of  $\text{Ce}^{4+}$  through the membrane containing  $7.14 \times 10^{-5} \text{ mol L}^{-1}$ , C4RAHA from source phase of  $[\text{Ce}^{4+}] = 7.14 \times 10^{-5} \text{ mol L}^{-1}$  to the receiving

**Table 1.** Stability constant and thermodynamic parameters for Ce(IV)- C4RAHA Complex

T / (K)	pka of $\text{H}_8\text{A}$	$\log P_{\text{H8A}}$	$\log \beta_4 \cdot P_{\text{Ce-H8A}}$	$k_{\text{ex}}$	$\Delta G / (\text{kJ mol}^{-1})$	$\Delta H^* / (\text{kJ mol}^{-1})$	$\Delta S / (\text{J K}^{-1} \text{ mol}^{-1})$
298	8.90	23.00	16.63	$5.37 \cdot 10^{-16}$	-94.80	-	-277.58
303	8.85	23.05	17.14	$1.74 \cdot 10^{-15}$	-99.35	-176.19	-257.98
308	8.74	23.16	17.64	$5.49 \cdot 10^{-15}$	-103.94	-178.53	-238.88
313	8.65	23.25	18.12	$1.66 \cdot 10^{-14}$	-108.49	-177.04	-220.54
318	8.57	23.33	18.59	$4.9 \cdot 10^{-14}$	-113.10	-178.98	-202.58
323	8.51	23.39	19.04	$1.38 \cdot 10^{-13}$	-117.65	-176.84	-185.35

\*Mean  $\Delta H = -177.52 \text{ kJ mol}^{-1}$ .

phase of 0.1 mol L<sup>-1</sup> HCl was carried out. As it can be seen in Figure 5, the concentration of Ce<sup>4+</sup> in the source phase decreases continuously and reached a lower concentration than the detection limit after 20 min (curve A), on the other hand concentration of Ce<sup>4+</sup> in the receiving phase increases (curve B). Therefore, it is clear that Ce<sup>4+</sup> moved from the source to receiving phase through the liquid membrane. The carrier in the membrane reacts with Ce<sup>4+</sup> in the source phase at the interface and forms a complex [ $\{Ce(OH)_2\}_4A^{-8}$ ]<sub>(o)</sub> while releasing 8 moles of proton into the source phase. At the other interface of the membrane and the receiving phase the complex reacts with 8 moles of protons while releasing 4 moles of Ce<sup>4+</sup> in the receiving phase.

#### Effect of diverse ions

Cerium was selectively separated and determined in presence of various metal ions at pH 9.0 and none of them affected the absorbance of cerium complex. The tolerance

limit was set as the amount of foreign ions causing a change of  $\pm 0.02$  absorbance. However, a large concentration of vanadium(V) and molybdenum(VI) can be eliminated by stripping them with 0.075 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 0.2 mol L<sup>-1</sup> oxalic acid. Moderate amount of various metal ions associated with Ce(IV) were tolerated and also some common anions (Table 2).

#### Preconcentration of Ce(IV)

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

The preconcentration study was carried out by extracting 20  $\mu$ g of Ce(IV) in 1000 mL aqueous phase with 8.5 mL of 0.015% C4RAHA in ethyl acetate. To evaluate the efficiency of preconcentration, expressed as

**Table 2.** Effect of diverse ions on the extraction of Ce(IV)- C4RAHA complex

Ce(IV):	10 mL, 2.0 $\mu$ g mL <sup>-1</sup>	pH:	9.0
Solvent:	Ethyl acetate	C4RAHA:	3 mL, $7.14 \times 10^{-5}$ mol L <sup>-1</sup>
$\lambda$ max:	381 nm		

Ions	Added as	Amount added / (mg)	Concentration of Cerium / (mg L <sup>-1</sup> )	
			Spectrophotometry	ICP OES
Al <sup>3+</sup>	AlCl <sub>3</sub>	40	1.98	1.99
Mg <sup>2+</sup>	MgCl <sub>2</sub>	35	1.96	1.98
Ag <sup>+</sup>	AgNO <sub>3</sub>	35	1.98	1.99
As <sup>3+</sup>	As <sub>2</sub> O <sub>3</sub>	35	1.99	2.00
Zr <sup>4+</sup>	Zr(NO <sub>3</sub> ) <sub>4</sub>	30	1.97	1.99
Be <sup>2+</sup>	BeCl <sub>2</sub>	30	1.96	1.98
Ca <sup>2+</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub>	35	1.97	1.99
Hg <sup>2+</sup>	HgCl <sub>2</sub>	30	1.99	2.00
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	30	1.97	1.99
Mn <sup>2+</sup>	MnCl <sub>2</sub>	35	1.96	1.97
Co <sup>2+</sup>	CoCl <sub>2</sub>	35	1.98	1.99
Ba <sup>2+</sup>	BaCl <sub>2</sub>	35	1.98	2.00
Cd <sup>2+</sup>	CdCl <sub>2</sub>	35	1.97	2.00
Cu <sup>2+</sup>	CuCl <sub>2</sub>	30	1.97	1.99
Sn <sup>2+</sup>	SnCl <sub>2</sub>	35	1.98	1.99
Fe <sup>3+</sup>	FeCl <sub>3</sub>	30	1.97	1.98
Ni <sup>2+</sup>	NiCl <sub>2</sub>	30	1.99	2.00
Zn <sup>2+</sup>	ZnCl <sub>2</sub>	35	1.98	1.99
<sup>a</sup> Mo <sub>7</sub> O <sub>24</sub> <sup>6-</sup>	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub>	30	1.97	1.98
Ti <sup>4+</sup>	TiO <sub>2</sub>	30	1.98	1.99
<sup>b</sup> V <sup>5+</sup>	NH <sub>4</sub> VO <sub>3</sub>	30	1.98	2.00
Ta <sup>5+</sup>	Ta <sub>2</sub> O <sub>5</sub>	25	1.99	2.00
UO <sub>2</sub> <sup>2+</sup>	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	40	1.97	2.00
Th <sup>4+</sup>	Th(NO <sub>3</sub> ) <sub>4</sub>	60	1.99	2.00
<sup>c</sup> Ce <sup>4+</sup>	(NH <sub>4</sub> ) <sub>4</sub> Ce(SO <sub>4</sub> ) <sub>1</sub> .2H <sub>2</sub> O	80	1.98	2.00
Cl <sup>-</sup>	NaCl	40	1.98	1.99
Br <sup>-</sup>	NaBr	40	1.97	1.99
I <sup>-</sup>	NaI	40	1.97	1.99

<sup>a</sup>stripped with 0.2 mol L<sup>-1</sup> oxalic acid, <sup>b</sup>stripped with 0.075 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

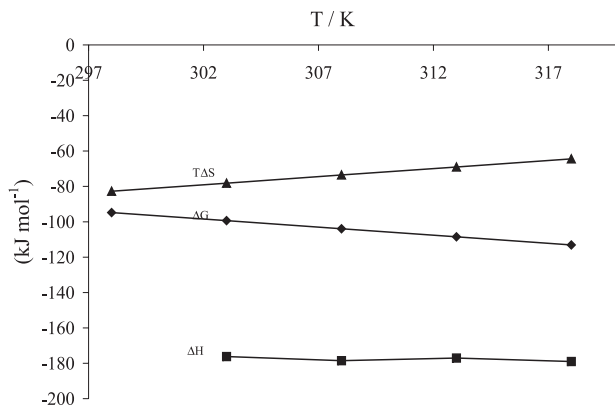
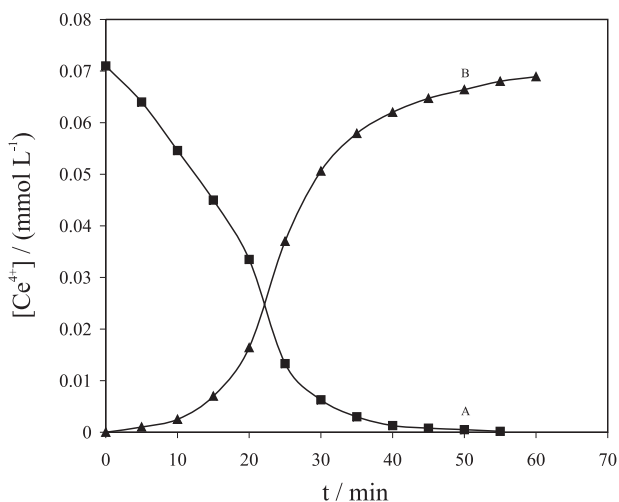


Figure 4. Variation in thermodynamic parameters with temperature.



A: [Cerium] in the source phase (SP)  
B: [Cerium] in the receiving phase (RP)

Source Phase (SP): 50 mL,  $7.1 \times 10^{-5}$  mol L<sup>-1</sup> cerium  
Liquid Membrane Phase (LMP): 75 mL,  $7.1 \times 10^{-5}$  mol L<sup>-1</sup> C4RAHA in ethyl acetate  
Receiving Phase (RP): 50 mL, 0.1 mol L<sup>-1</sup> HCl

Figure 5. Transport profile of cerium(IV) through the liquid membrane containing C4RAHA at 30 °C.

recovery, the concentration of cerium in organic phase and the aqueous phase was determined by ICP OES. Quantitative determination was possible with recovery up to 98% with a preconcentration factor of 118.

#### Determination of Ce(IV) in standard samples

To check the applicability and reliability of the method, cerium(IV) was determined in monazite sand, standard geological samples (USGS) and sea water samples. Cerium was extracted from monazite sand after digesting 0.5 g sand with a mixture of concentrated HCl and HClO<sub>4</sub> (1:1 v/v) and diluting it to 250 mL with deionized water. An appropriate volume of aliquot of it was extracted at pH 9.0 with 10 mL of C4RAHA in ethyl acetate. Cerium was then stripped with 1-3 mL of 0.5 mol L<sup>-1</sup> HNO<sub>3</sub> and the organic layer containing C4RAHA was recycled for recovery. The results for the analysis are summarized in Table 3.

#### Conclusions

The present method is selective for the determination of cerium(IV) in presence of large quantities of associated metal ions by Calix[4]resorcinarene-N-fenil-acetohydroxamic acid. The Calix[4]resorcinarene-N-fenil-acetohydroxamic acid (C4RAHA) shows high affinity for cerium(IV) and binds in a 4:1 (metal:C4RAHA) ratio as evaluated by the Job's method. Transport studies for Ce(IV) are reported for the first time with liquid membrane in a three phase system. The preconcentration factor of 118 suggests the utility of C4RAHA in trace analysis. The results obtained from the analysis of monazite sand, standard geological and seawater samples proved the reliability of the proposed method for their application to various standard and natural samples.

Table 3. Determination of Ce(IV) in Monazite Sand, Geological samples (USGS) and Sea Water

Sample	Standard Value	Ce(IV) found by present method	
		Spectrophotometry	ICP OES
Monazite sand <sup>a</sup>	32.0(%)	31.5 ± 0.2	31.7 ± 0.02
BCR-1 (52/19)	54 mg kg <sup>-1</sup>	53.9 ± 0.09	54.0 ± 0.05
G2	150 mg kg <sup>-1</sup>	149.8 ± 0.06	150.0 ± 0.04
W1	25 mg kg <sup>-1</sup>	24.9 ± 0.09	25.0 ± 0.05
GSP-1 granodiorite	423 mg kg <sup>-1</sup>	422.9 ± 0.09	423.0 ± 0.05
Bombay sea water <sup>b</sup>		(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )
Belapur	—	0.97 ± 0.3	0.98 ± 0.02
Thane Bridge	—	1.58 ± 0.5	1.59 ± 0.06
Apollo Bunder	—	1.23 ± 0.3	1.24 ± 0.05
Mahim	—	0.81 ± 0.7	0.82 ± 0.04
Marine Lines	—	0.79 ± 0.2	0.80 ± 0.02

<sup>a</sup> Samples from Travancore, India, <sup>b</sup>average ± standard deviation (12 determinations). The values obtained by spectrophotometry and ICP OES are established at confidence level of 95%.

## Acknowledgments

The authors are thankful to GUJCOST, Gujarat for their financial assistance. The authors also acknowledge CDRI, Lucknow for providing instrumental facilities and INFLIBNET, Ahmedabad for providing online journals.

## References

1. Atwood, J. L.; Steed, J. W.; *Encyclopedia of Supramolecular Chemistry*, Marcel Dekker: New York, 2004.
2. Cram, D. J.; Cram, J. M.; *Monographs in Supramolecular Chemistry*, The Royal Society of Chemistry: London, 1989, vol. 4, p. 162.
3. Sliwa, W.; Zujewska, T.; Bachowska, B.; *Pol. J. Chem.* **2003**, *77*, 1079.
4. Rudkevich, D. M.; Verboom, W.; Reinhoudt, D. N.; *J. Org. Chem.* **1994**, *59*, 3683.
5. Botta, B.; Cassani, M.; D'Acquarica, I.; Misiti, D.; Subissati, D.; Monache, G. D.; *Curr. Org. Chem.* **2005**, *9*, 337.
6. Ge, Y.; Yan, C.; *J. Chem. Res.* **2004**, *33*, 279.
7. Heaven, M. W.; Raston, C. L.; Atwood, J. L.; *Chem. Commun.* **2005**, *7*, 892.
8. Gualbert, J. E.; Shahgaldian, P.; Lazar, A.; Coleman, A.W.; *J. Inclusion Phenom. Macrocyclic Chem.* **2004**, *48*, 37.
9. Bell, T. W.; Hext, N. M.; *Chem. Soc. Rev.* **2004**, *33*, 589.
10. MacGillivray, L. R.; Atwood, J. L.; *J. Solid State Chem.* **2000**, *152*, 199.
11. Martinez, G. M.; Teran, C. R.; Tlapanco, O. A.; Toscano, A.; Cruz-Almanza, R.; *Fullerene Sci. Technol.* **2000**, *8*, 475.
12. Yonetake, K.; Nakayama, T.; Ueda, M.; *J. Mater. Chem.* **2001**, *11*, 761.
13. Nakayama, T.; Takhashi, D.; Takeshi, K.; Ueda, M.; *J. Photopolym. Sci. Technol.* **1999**, *12*, 347.
14. Tbeur, N.; Rhlalou, T.; Hlaibi, M.; Langevin, D.; Metayer, M.; Verchere, J.-F.; *Carbohydr. Res.* **2000**, *329*, 409.
15. Ichimura, K.; Kurita, E.; Ueda, M.; *Eur. Pat.*, EP 671220, **1995**.
16. Pietraszkiewicz, O.; Pietraszkiewicz, M.; *J. Inclusion Phenom. Macrocyclic Chem.* **1999**, *35*, 261.
17. Yoshino, N.; Satake, A.; Kobuke, Y.; *Angew. Chem., Int. Ed.* **2001**, *40*, 457.
18. Gaunert, E.; Barnier, H.; Nicod, L.; Favre-Reguillon, A.; Foos, J.; Guy, A.; Bardot, C.; Lemaire, M.; *Sep. Sci. Technol.* **1997**, *32*, 2309.
19. Smakhtin, L.A.; Mekhryusheva, L. I.; Filipova, N. V.; Miglina, N. V.; Sinitysna, T. S.; *J. Radioanal. Nucl. Chem.*, **1991**, *154*, 293.
20. Krea, M.; Khalaf, H.; *Hydrometallurgy* **2000**, *58*, 215.
21. Banerjee, S.; Basu, S.; *Indian J. Chem.* **2001**, *40*, 848.
22. Georgiev, G.; Zakhariyeva, M.; *Solvent Extr. Ion Exch.* **2003**, *21*, 735.
23. Czakis-Sulikowska, D.; Pustelink, N.; *Solvent Extr. Ion Exch.* **2003**, *21*, 751.
24. Ludwing, R.; Lentz, D.; Nguyen, T. K. D.; *Radiochim. Acta* **2000**, *88*, 335.
25. Cullen, M.; *Atomic Spectroscopy in Elemental Analysis*, Blackwell Publishing: Oxford, 1999.
26. Hill, S. J.; *Inductively Coupled Plasma Spectroscopy and Its Application*, CRC Press: Boca Raton, 1999.
27. Hirata, S.; Kajiva, T.; Aihara, M.; Honda, K.; Shikino, O.; *Talanta* **2002**, *58*, 1185.
28. Huang, W.; Hu, B.; Jiang, Z.; Wang, L.; *Fresenius' J. Anal. Chem.* **2000**, *366*, 36.
29. Agrawal, Y. K.; *Russ. Chem. Rev.* **1979**, *48*, 948.
30. Davis, C. S.; Ni, X.; Quisenberry, S. S.; Foster, J. E.; *BioOne*, **2000**, *93*, 989.
31. Agrawal, Y. K.; *Rev. Anal. Chem.* **1980**, *3*, 51.
32. Agrawal, Y. K.; Patel, S. A.; *Rev. Anal. Chem.* **1980**, *4*, 237.
33. Agrawal, Y. K.; Jain, R. K.; *Rev. Anal. Chem.* **1982**, *6*, 49.
34. Agrawal, Y. K.; Sanyal, M.; *Analyst* **1995**, *120*, 2759.
35. Rao, K. S.; Sarangi, D.; Dash, P.; Chaudhury, G. R.; *J. Chem. Technol. Biotechnol.* **2003**, *78*, 555.
36. Jain, V. K.; Pillai, S. G.; Pandya, R. A.; Agrawal, Y. K.; Shrivastav, P. S.; *Talanta* **2005**, *65*, 466.
37. Jain, V. K.; Pillai, S. G.; Pandya, R. A.; Agrawal, Y. K.; Shrivastav, P. S.; *Anal. Sci.* **2005**, *21*, 129.
38. Perkampus, H. H.; *UV-Vis Spectroscopy and its Applications*, Springer-Verlag: New York, 1982.
39. Lajunen, L. H. J.; *Spectrochemical Analysis by Atomic Absorption and Emission*, Royal Society of Chemistry: Cambridge, 1992, p. 9.

Received: April 10, 2006

Published on the web: September 13, 2006