Solid Phase Extraction, Preconcentration and Sequential Separation of U(VI), Th(IV), La(III) and Ce(III) by Azocalix[4]resorcinarenes Amberlite XAD-2 Chelating Resins
Resume

This chapter explores the ability of the resin for solid phase extraction, preconcentration and sequential separation of U(VI), Th(IV), La(III) and Ce(III) by azocalix[4]resorcinarenes Amberlite XAD-2 by column chromatography prior to their determination by UV/VIS spectrophotometry, graphite furnace atomic absorption spectrophotometer (GF-AAS) or ICP-AES. The resins have been studied under the optimum conditions of pH, flow rate, sorption capacity, breakthrough studies, distribution coefficient, pre-concentration factor, concentration of eluting agents for the simultaneous separation and determination of metal ions from their binary and ternary mixtures. Tests are conducted to establish the efficiency and stability of the synthesized resin. The proposed method has been applied to the separation and determination of these metal ions in synthetic/natural samples and monazite sand.
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1. Introduction

There is considerable interest in the behavior of actinides as trace levels in environmental and biological samples due to the increasing public attention to radioactive waste disposal and potential public health effects of releases of radioactive materials into the environment. Thorium and Uranium are present in nuclear fuel and their determination is of great significance. Numerous methods have been described for their effective separation and preconcentration; procedures based on ion exchange\textsuperscript{[1,2]}, solvent extraction\textsuperscript{[3-5]} and solid phase extraction\textsuperscript{[6-18]} are among them. In recent times solid phase extraction (SPE) has emerged as a versatile and effective method for analytical and preparative-scale metal ion separations\textsuperscript{[19,20]}. Solid phase extraction is now widely used for the preconcentration and clean up of various chemicals and for applications such as the removal of toxic or valuable substances from a variety of predominantly aqueous solutions.

Chelating resins are of immense value for selective trace metal analysis. Appropriate chelating reagents can be chemically bonded to or impregnated onto polymeric or other supports and used for the solid phase extraction of metal ions from aqueous solution. Many procedures involving rare-earth elements preconcentration can be found in literature employing a variety of materials such as silica, activated carbon and Amberlite resins. Amberlite XAD series resins have shown promise for designing chelating resins. Several previous studies have been reported for the XAD series resins in which an inert support is impregnated (e.g., bifunctional organophosphorus\textsuperscript{[13]}, $N,N$-dibutyl-$N$-benzoylthiourea\textsuperscript{[14]}, diamylphosphonate\textsuperscript{[17]}), or immobilized (e.g., 4-(2-thiazolylazo)resorcinol\textsuperscript{[10]}, bicine\textsuperscript{[11]}, pyrogallo\textsuperscript{[12]}, quinoline-8-ol\textsuperscript{[15]}, o-vanillinsemicarbazone\textsuperscript{[16]}, Tiron\textsuperscript{[18]}), to produce a polymeric support for their analytical applications.

Calix[4]resorcinarenes are well documented in their ability to complex cations and extensive reviews may be found on the subject\textsuperscript{[21]}. For certain applications such as separation of metal ions from aqueous media or fabrication of devices, it is important for a resorcinarene derivative to be available in
insoluble form. Therefore, calix[4]resorcinarenes are modified chemically to control the solubility characteristics by their immobilization on the polymer supports. The preparation of such insoluble polymeric calix[4]resorcinarenes is made either by covalently linking the calixarene derivative to the polymeric framework or by connecting two resorcinarenes by some spacer or functionality to give resin-like substances. In recent years, polymer supported resorcinarenes have been synthesized and used for the separation of metal ions[22-29]. Munakata et al.[30] have studied the reactions of open dimeric and capped polymeric resorcinarenes containing molecules with Ag (I) salt. Dimeric hydrogen bonded resorcinarenes molecule capsule featuring aryl urea or sulfonylurea urea have been synthesized and utilized as hosts that reversibly bind smaller molecular guests in organic media[31].

A part from several analytical methods, the neutron activation analysis (INAA)[32-34], multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS)[35], inductively coupled plasma atomic emission spectrophotometry (ICP-AES)[36,37], isotope dilution thermal mass spectrophotometry (ID-TIMS), inductively coupled plasma mass spectrophotometry (ICP-MS)[38-41] and ion chromatography have been[37, 42] applied for the determination of trace amounts of rare earth elements in environmental and pharmaceutical samples. However, most of these techniques require the use of costly instruments, several hours of analytical time and an expert for their handling and interpretation of the obtained data. Even liquid-liquid extraction technique needs plenty of reagents and time.

So far no data concerning preconcentration of trace metal ions on the calix[4]resorcinarene based XAD-2 chelating resin has been published. Therefore this chapter describes the use of two novel azocalix[4]resorcinarene Amberlite XAD-2 polymeric chelating resins (resin A and resin B) for extraction, preconcentration and sequential separation of metal ions such as U(VI), Th(IV), La(III) and Ce(III) in a column prior to their determination by spectrophotometry/GFAAS/ICP-AES. Various factors influencing the separation and preconcentration of trace metal ions, such as pH, concentration of eluting agents, flow rate, total sorption capacity, exchange kinetics, preconcentration
factor, distribution coefficient, breakthrough capacity, resin stability, effect of electrolytes, and associated metal ions have been investigated. The newly developed method has also been applied for the determination of U(VI), Th(IV), La(III) and Ce(III) from natural water samples of Ahmedabad city.

2. Experimental

2.1. Instruments

All pH measurements were performed using an Elico digital pH-meter, model L1 614, equipped with a combined pH electrode. The flow of the liquid through the column was controlled by Miclins Peristaltic pump PP-10 EX. Spectral measurements were done using a JASCO 570 UV/VIS/NIR spectrophotometer using 10 mm quartz cells. GFAAS measurements were performed using Perkin Elmer Model 420 with pyrolytically coated HGA-76 graphite furnace (GFAAS). A Uranium hollow cathode lamp was used at 358.5 nm wavelength with a spectral width of 0.2 nm. Atomization temperature of 2700°C and an argon gas purge was used. Labtam Plasma Scan model 710 sequential inductively coupled plasma-atomic emission spectrophotometer with the plasma scan multitasking computer and a peristaltic pump was used for lanthanum, cerium, thorium and uranium determinations under optimum working conditions: Radio frequency (rf)-27.12 MHz; incident power-2000W; Labtam GMK nebulizer; rf power-5W; observation height-14 mm; argon coolant flow rate-10 dm³ min⁻¹; argon carrier flow rate-1.0 dm³ min⁻¹; intergraph period-10 s; resolution-0.004 nm; peristaltic pump flow rate-1.0 ml.min⁻¹; wavelengths: Thorium-283.73 nm, Lanthanum-394.91 nm and Cerium-413.77 nm.

2.2. Reagents

All the reagents used were of AR grade, purchased from Sigma-Aldrich, Fluka and were used without further purification. All aqueous solutions were prepared with quartz distilled deionized water, which was further purified by a Millipore Milli-Q water purification system (Millipack 20, Pack name: Simpak 1, Synergy). Glassware were soaked in 10% HNO₃ overnight before use and cleaned repeatedly with double distilled deionized water. The pH was adjusted with the following buffer solutions[43]: PO₄³⁻/HPO₄²⁻ buffer for pH 2.0 and 3.0; CH₃COO⁻¹/
CH$_3$COOH buffer for pH 4.0 and 6.0; HPO$_4^{2-}$/H$_2$PO$_4^{-1}$ buffers for pH 7.0 and 7.5; NH$_3$/NH$_4^+$ buffers of pH 8 and 10. Standard stock solutions (2000 µg ml$^{-1}$) of U(VI), Th(IV), La(III) and Ce(III) were prepared as given below.

- **U(VI):** Dissolve 4.218 gm UO$_2$(NO$_3$)$_2$.6H$_2$O in water containing 1 ml concentrated HNO$_3$ and dilute upto 1000 ml with water in volumetric flask.
- **Th(IV):** Dissolve 4.8 gm Th(NO$_3$)$_4$.4H$_2$O in water containing 5 ml concentrated HNO$_3$ and dilute upto 1000 ml with water in volumetric flask.
- **La(III):** Dissolve 2.34 gm La$_2$O$_3$ in water containing 5 ml hot concentrated HCl and dilute upto 1000 ml with water in volumetric flask.
- **Ce(III):** Dissolve 6.2 gm Ce(NO$_3$)$_3$.6H$_2$O in water containing 2 ml concentrated HNO$_3$ and dilute upto 1000 ml with water in volumetric flask.

Their final concentrations were then standardized spectrophotometrically\[144\].

**UV-Vis Spectrophotometric Determination of U(VI), Th(IV), La(III) and Ce(III)**

- **U(VI) forms** blue colored water soluble complex with Arsenazo-I reagent.
  pH = 8.5, $\lambda_{max} = 596$ nm, $\varepsilon = 23000$

- **Th(IV) forms** grey-green colored water soluble complex with Arsenazo-III reagent.
  3N HCl concentration, $\lambda_{max} = 655$ nm, $\varepsilon = 115000$

- **La(III) forms** pink-violet colored water soluble complex with Arsenazo-I reagent.
  pH = 8.0, $\lambda_{max} = 580$ nm, $\varepsilon = 27000$

- **Ce(III) forms** green colored water soluble complex with Arsenazo-III reagent.
  pH = 2.6, $\lambda_{max} = 650$ nm, $\varepsilon = 27000$

Working solutions were subsequently prepared by appropriate dilution of the stock solutions.

2.3. Recommended column method for separation, preconcentration and determination of metal ions

A glass column (10 cm long, 1 cm inner diameter) equipped with a stopcock and a porous disk was used. 1.0 gm of the azocalix[4]resorcinarene Amberlite XAD-2 polymeric chelating resin (A/B) was mixed with CH₃OH:H₂O (1:1) to obtain a slurry and then poured onto the column. The resin was washed with dilute acid, dilute base, deionized water and finally, it was conditioned with 10-15 ml of a buffer solution of desired pH prior to the passage of a suitable aliquot of the sample solution containing U(VI) and/or Th(IV) and/or La(III) and/or Ce(III) at an optimum flow rate, controlled by a peristaltic pump. The bound metal ions were stripped from the column with suitable eluting agents such as HCl or HNO₃. The eluants were collected and its volume was made up to the mark with doubly distilled water in a 25 ml volumetric flask. Metal content in the eluant was determined by spectrophotometry/GFAAS/ICP-AES. After each experiment, the column was regenerated by washing it with desired acid and large amount of distilled water and stored for the next use.

2.4. Recommended batch method for preconcentration and determination of metal ions

After adjusting optimum pH, the sample solution (100 ml), containing U(VI) or Th(IV) or La(III) or Ce(III) was placed in a glass stopper bottle (250 ml). The azocalix[4]resorcinarene Amberlite XAD-2 polymeric chelating resin (A/B) (0.5 gm) was added to the above solution. The bottle was tightly stoppered and shaken for 1 hour and the chelated resin was filtered. The filtrate and the resins were treated separately for metal content determination. Metal content in chelated resin was determined by shaking it again with a suitable eluating agent (HCl/HNO₃) for atleast 10 minutes. The resin was then filtered, the eluant was collected and its volume was made up to the mark in a 25 ml volumetric flask. Metal content in filtrate and eluant were determined by spectrophotometry/GFAAS/ICP-AES.
3. Results and discussion

3.1. Parameters optimized for separation and preconcentration of U(VI), Th(IV), La(III) and Ce(III)

In order to achieve quantitative recoveries of U(VI), Th(IV), La(III) and Ce(III) on the azocalix[4]resorcinarene Amberlite XAD-2 polymeric chelating resin (A/B), separation and preconcentration procedures were optimized with respect to various parameters such as pH, flow rate, concentration and volume of the eluting agents, total sorption capacity, distribution coefficient (Kd), exchange kinetics, breakthrough studies, preconcentration factor, reusability of the resin and effect of electrolytes.

3.1.1. Metal sorption as a function of pH

The pH of the solution which influences the absorption of metal ions onto the resin is one of the most significant parameters as the formation of metal ion complexes and maximal efficiency for a given separation can be established by optimization of the pH. The influence of the pH on absorption was examined using the batch method. 100 ml of solutions containing 6 µg ml⁻¹ of metal ion [U(VI) or Th(IV) or La(III) or Ce(III)] were placed in different 250 ml capacity stoppered glass bottles at different pH and shaken for 1 hour. The percentage of metal sorption was evaluated by determining the metal content in raffinate by spectrophotometry/GFAAS/ICP-AES.

The optimum pH for sorption for U(VI), Th(IV), La(III) and Ce(III) was found to be 8.0, 3.0, 6.0 and 7.0 respectively (Table 1, Figure 1). Their selectivity in pH of maximum sorption suggests the possibility of separation of these metal ions in presence of each other in the column.

3.1.2. Effect of flow rate on metal sorption

The sorption of metal ion on 1.0 gm resin (A/B) in a packed column was studied at various flow rates. Feed solutions containing 6 µg ml⁻¹ U(VI)/Th(IV)/La(III)/Ce(III) were passed through the column at different flow rates (1-5 ml min⁻¹) maintained by peristaltic pump. Optimum flow rate may be defined as the rate of flow of the effluent through the column at which more than 98 %
sorption takes place. The optimum flow rates obtained for resins (A/B) were 1.0, 1.5, 2.0 and 2.0 ml min⁻¹ for U(VI), Th(IV), La(III) and Ce(III) respectively (Figure 3).

It was observed that, as the flow rate increases the sorption of metal ion decreases. This is because the time required for the metal ion to come in contact with the chelating resin is less (Table 1, Figure 2).

3.1.3. Effect of concentration of eluting agents

One more important factor that affects the separation procedure and reusability of resin is the type and concentration of the eluant used for stripping metal ions from the chelating resin (A/B). In order to obtain maximum recovery of metal at the minimum concentration of the eluant, the effect of eluting agents like HCl and HNO₃ were studied at different concentrations. 1.0 gm sample of resin (A/B) in the column was conditioned at pH of maximum sorption and then fed with 100 ml solutions containing 6 μg ml⁻¹ U(VI)/Th(IV)/La(III)/Ce(III). It was observed that quantitative elution was possible with 15 ml of 0.1 N HCl, 2.0 N HCl, 0.1 N HNO₃, 0.1 N HNO₃ and 20 ml of 0.2 N HCl, 2.5 N HCl, 0.1 N HNO₃, 0.1 N HNO₃ for U(VI), Th(IV), La(III) and Ce(III) on resin A and resin B, respectively. The desorbed metal ions were then determined by spectrophotometry/GFAAS/ICP-AES (Table 1 and Table 2).

3.1.4. Sorption capacity and distribution coefficients

Sorption capacity determines the amount of the sorbent required for quantitative determination of analytes in a given solution. Sorption capacity of the modified resins was determined for each metal ion by using batch method. The chelating resin (A/B) (1.0 gm) was equilibrated in the excess of metal ion solution (100 ml, 2000 μg ml⁻¹) by shaking for 1 hour at optimum pH conditions. Then, the solid resin was filtered and the filtrate was diluted. Concentration of metal ions in the filtrate was determined by GFAAS/ICP-AES. The amount of metal ions sorbed on resin (A/B) was calculated from the difference in the metal ion concentration before and after sorption (Table 1). For resin A sorption capacity for U(VI), Th(IV), La(III) and Ce(III) was found to be 1,22,900, 94,200, 81,920 and 93,100 μg g⁻¹, respectively. For resin B sorption capacity for U(VI), Th(IV),
La(III) and Ce(III) was found to be 1,23,200, 99,300, 87,520 and 96,900 μg g⁻¹, respectively. Sorption capacity for various metal ions differed due to their size, degree of hydration and their binding constants with the ligand immobilized onto the resins (A/B).

Exchange equilibria are very often expressed in terms of the distribution coefficient $K_d$. This quantity is given by the ratio of the equilibrium concentrations of the same metal ion in the resin phase and in the solution.

$$K_d = \frac{\text{Amount of the metal ion taken up by the resin}}{\text{Amount of the metal ion remaining in the solution}} \times \frac{\text{Volume of the solution}}{\text{Amount of resin taken}}$$

The distribution coefficient $K_d$ of the metal ions between resin (A/B) and aqueous phase was determined by batch method.

0.5 gm resin (A/B) was equilibrated with 100 ml solution containing not more than 615, 471, 410, 466 μg ml⁻¹ and 616, 497, 438, 485 μg ml⁻¹ of U(VI), Th(IV), La(III) and Ce(III), respectively, for 1 hour at 30°C. The solution was filtered to remove resin (A/B) and the filtrate was subjected to spectrophotometry/FAAS/ICP-AES for determination of the metal ion content (Table 1). $K_d$ for U(VI), Th(IV), La(III) and Ce(III) were found to be 15362, 13450, 11702, 13300 and 16426, 14185, 12503, 14907, for resin A and resin B, respectively.

3.1.5. Exchange kinetics

The kinetics of sorption was studied by batch method for resin A and resin B. 1.0 gm resin (A/B) was shaken with 100 ml of solution containing 1229, 942, 819, 931 and 1232, 993, 875, 969 μg ml⁻¹ of U(VI), Th(IV), La(III) and Ce(III) respectively, for resin A and resin B with different equilibration times (e.g., 5, 10, 15, 20 minutes) under optimum conditions. 5 ml of solution was withdrawn at predetermined intervals and analyzed. The concentration of metal ions in the supernatant solution was determined by FAAS. The sorption as a function of time for all the metal ions is shown in (Figure 3). The time taken for the sorption of 50% of the metal ions ($t_{1/2}$) for resin A was found to be 9.0, 11.0, 12.0 and 13.0 minutes and for resin B, it was found to be 8.0, 10.0, 11.0 and 11.0 minutes for U(VI), Th(IV), La(III) and Ce(III) respectively, which indicates very good
accessibility of these metal ions towards chelating sites. The faster uptake of these metal ions on resin B probably reflects more accessibility to the chelating sites in resin B in comparison to resin A.

3.1.6. Breakthrough studies

The breakthrough capacities are more significant and useful than the total sorption capacities in ion exchange chromatographic applications as it gives actual working capacity of the resin in the column. Breakthrough capacity or the effective capacity may be defined as the capacity at the moment when the analyte starts appearing in the effluent. It is one of the most critical parameters when working under dynamic conditions. Breakthrough studies were carried out by taking 1.0 gm resin (A/B) in the column and passing 10 µg ml\(^{-1}\) of metal ions [U(VI) or Th(IV) or La(III) or Ce(III)] at their optimum pH and flow rate. An aliquot of 2.0 ml eluant was collected each time and analyzed by ICP-AES for the determination of metal ion content (Figure 4). Breakthrough capacities of resin A and resin B for U(VI), Th(IV), La(III) and Ce(III) were found to be 24580, 19771, 18022, 19551 and 25256, 22839, 20129, 21318 µg g\(^{-1}\) respectively (Table 1).

3.1.7. Reusability of the resin

Accuracy and reproducibility in analytical data is a challenging task when reusing the same resin. To test the resin stability, it was subjected to several loading and elution by batch method. The conditions employed for the studies were: 1.0 gm of resin (A/B) beads were stirred with 100 ml, 1229 µg ml\(^{-1}\) solution containing metal ions [U(VI) or Th(IV) or La(III) or Ce(III)] for 1 hour at room temperature. The elution operations were carried out by shaking the resin with 50 ml of suitable eluant for 10 minutes to ensure complete desorption. The operating capacity was calculated from the loading and elution tests. The results from both tests agreed within 2-4% error for all the metal ions up to 9-10 cycles of sorption and desorption experiments (Figure 5). The resin (A/B) showed better reusability and stability towards these metal ions.

3.1.8. Preconcentration of U(VI), Th(IV), La(III) and Ce(III)

The concentration of trace metal ions in water is too low for its direct determination. Therefore, the preconcentration or enrichment step is necessary
to bring the sample to the detectable limit of existing detection method. Resin (A/B) was studied for column concentration of U(VI), Th(IV), La(III) and Ce(III) in terms of their preconcentration factor (PF).

\[
P_F = \frac{\text{Concentration of metal in stripping solution}}{\text{Initial concentration of metal in feed solution}}
\]

1000 ml solutions containing 6, 8, 10, 12 µg L\(^{-1}\) U(VI), Th(IV), La(III) and Ce(III) at pH 8.0, 3.0, 6.0 and 7.0 respectively, were passed through the column containing 1.0 gm resin (A/B). Metal contents in the stripped solution were determined by spectrophotometry and ICP-AES. The preconcentrating ability of resin (A/B) was assessed from the elution profile of metal ions by plotting the concentration of effluents as a function of the volume of stripping solutions. For resin A: 10 ml, 0.1 N HCl for U(VI); 8.5 ml, 2.0 N HCl for Th(IV); 9.5 ml, 0.1 N HNO\(_3\) for La(III); and 9.0 ml, 0.1 N HNO\(_3\) Ce(III) respectively. For resin B: 11.0 ml, 0.2 N HCl for U(VI); 10.5 ml, 2.5 N HCl for Th(IV); 10.0 ml, 0.1 N HNO\(_3\) for La(III); and 9.5 ml, 0.1 N HNO\(_3\) Ce(III) respectively. The preconcentration factors for resin A were found to be 105, 135, 100, 105 and for resin B were found to be 100, 129, 98, 101 for U(VI), Th(IV), La(III) and Ce(III) respectively, with 97-98% recovery (Tables 1, 3 and Figure 6).

3.1.9. Effect of electrolytes

One of the main problems in the spectrometric determination of metal ions is interference from matrix components. To evaluate the selectivity of the synthesized resins, several interfering electrolytes were tested. The limit of tolerance of anions on the sorption of U(VI), Th(IV), La(III) and Ce(III) is defined as that concentration which causes an error of 2-3% in the recovery of these metal ions. The effect of anions and their limit of tolerance on the sorption of U(VI), Th(IV), La(III) and Ce(III) by resin (A/B) were studied by taking different concentrations of electrolytes and the results presented in (Table 4). All electrolytes did not interfere between 1.5-3.5 M concentration ranges, which further augment the potential application of resin (A/B) for the analysis of real samples.
3.2. Chromatographic separations

As synthesized resin B was found to be better than resin A in terms of sorption capacity, distribution coefficient and exchange kinetics, therefore only resin B was used for the separation of U(VI), Th(IV), La(III) and Ce(III) from their binary and ternary mixtures by column method. The ternary mixtures of U(VI), Th(IV), La(III) and Ce(III) can be separated by selective adjustment of the pH and eluting agents. Hence, the following mixtures (each 100 μg in 25 ml buffer solution) were passed through the column at pH of maximum sorption and at optimum flow rate. The column effluents were analyzed for the metal ions by spectrophotometry/ GFAAS/ICP-AES.

3.2.1. In the separation of a binary mixture:

100 μg of both Th(IV) and U(VI) in 25 ml of buffer solution of pH 3.0 was passed through the column at flow rate of 2.0 ml min⁻¹. At this pH, U(VI) was not sorbed on resin B and it came out with the effluent while Th(IV) was retained in the column. Th(IV) was eluted with 20 ml, 2.5 N HCl. Quantitative separation was achieved in the binary mixture as shown in the separation pattern in (Figure 7(a)).

3.2.2. In the separation of a ternary mixture:

100 μg each of U(VI), Th(IV) and La(III) in 25 ml of buffer solution of pH 7.0 was passed through the column at flow rate of 2.0 ml min⁻¹. At this pH, Th(IV) was not sorbed on resin B and it came out with the effluent while U(VI) and La(III) was retained in the column. U(VI) and La(III) were then separated on the basis of selective eluting agents. U(VI) was eluted first with 20 ml, 0.2 N HCl followed by La(III) with 25 ml, 0.1 N HNO₃. Quantitative separation was achieved in the ternary mixture as shown in the separation pattern in (Figure 7(b)).

3.3. Limit of quantification

Selectivity and sensitivity are two important factors in the extraction and separation processes. To test the resins capability to detect trace amounts of metal ions, studies were performed passing 1000 ml sample solutions in the range of 5–50 μg through the optimized column. The quantification limit for U(VI),
Th(IV), La(III) and Ce(III) for resin B were found to be 6.0, 7.0, 9.0 and 11 µg L\(^{-1}\), respectively, indicating the resin's capability to extract the trace metal ions of interest from the real samples.

3.4. Applications

The application of the proposed method was checked by subjecting resin B to various water samples, monazite sand and standard geological samples. The ground water samples were collected from the University area of Ahmedabad and then passed through the column as described in the general column concentration. The geological sample 0.5 g monazite sand was digested with concentrated HCl and HNO\(_3\) (2:1) for 1 hour on a sand bath. The solution was then evaporated to dryness. The residue was boiled with 10 ml 0.1 N HCl and after filtration, the solution was diluted to 100 ml with distilled water. The appropriate quantity of aliquot was passed through the column after adjustment of pH and the given rare earth metal ions were eluted with the suitable eluting agent. The eluants were then analyzed by spectrophotometry/ GFAAS/ICP-AES. The results are given in (Tables 5).

3.5. Comparison with other solid phase extraction methods

Comparison of sorption capacity and preconcentration factor of various adsorbents (Table 6) showed that resin (A/B) have high sorption capacity and good preconcentrating ability for U(VI), Th(IV), La(III) and Ce(III) metal ions.
Table 1. Parameters optimized for sorption and desorption of U(VI), Th(IV), La(III) and Ce(III) on resin (A/B)

<table>
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<th>Parameters</th>
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<th>Resin B</th>
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<td>5</td>
<td>Distribution Coefficient (Kₐ)</td>
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<td>Preconcentration factor</td>
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<td>Breakthrough capacity (μg g⁻¹ of resin)</td>
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<td>Average Recovery (%)</td>
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<td>t₁/₂ for exchange (minute)</td>
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<td>Relative standard deviation (%)</td>
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* Average of 6-8 determination.
Table 2. Effect of concentration of eluting agents for desorption of U(VI), Th(IV), La(III) and Ce(III) from resin (A/B). [Experimental conditions: Resin (A/B): 1.0 gm; Volume of solution passed: 100 ml; Metal ions: 6 μg ml⁻¹ { U(VI): pH 8.0; Th(IV): pH 3.0; La(III): pH 6; Ce(III): pH 7.0}]

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<th>Concentration (N)</th>
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<td></td>
<td>U(VI) (%)</td>
<td>Th(IV) (%)</td>
<td>La(III) (%)</td>
</tr>
<tr>
<td>0.01</td>
<td></td>
<td>22.0</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>0.02</td>
<td></td>
<td>45.5</td>
<td>3.9</td>
<td>9.0</td>
</tr>
<tr>
<td>0.05</td>
<td></td>
<td>72.5</td>
<td>6.1</td>
<td>12.8</td>
</tr>
<tr>
<td>0.1</td>
<td></td>
<td>98.6</td>
<td>10.8</td>
<td>18.5</td>
</tr>
<tr>
<td>0.2</td>
<td></td>
<td>---</td>
<td>21.1</td>
<td>21.3</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>---</td>
<td>58.3</td>
<td>33.5</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>---</td>
<td>74.6</td>
<td>67.2</td>
</tr>
<tr>
<td>2.0</td>
<td></td>
<td>---</td>
<td>97.9</td>
<td>79.8</td>
</tr>
<tr>
<td>2.5</td>
<td></td>
<td>---</td>
<td>88.2</td>
<td>87.4</td>
</tr>
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</table>
Table 3. Preconcentration factors for the sorption of U(VI), Th(IV), La(III) and Ce(III) on resin (A/B). [Experimental conditions: For resin A: 1.0 gm; U(VI): pH 8.0; Elution by 0.1 N HCl; Th(IV): pH 3.0; Elution by 2.0 N HCl; La(III): pH 6; Elution by 0.1 N HNO₃; Ce(III): pH 7; Elution by 0.1 N HNO₃. For resin B: 1.0 gm U(VI): pH 8.0; Elution by 0.2 N HCl; Th(IV): pH 3.0; Elution by 2.5 N HCl; La(III): pH 6; Elution by 0.1 N HNO₃; Ce(III): pH 7; Elution by 0.1 N HNO₃]

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Volume of solution passed (ml)</th>
<th>Concentration of solution passed (µg L⁻¹)</th>
<th>Volume of eluted solution (ml)</th>
<th>Recovery (%)</th>
<th>Preconcentration factor (PF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U(VI)</td>
<td>1000</td>
<td>6.0</td>
<td>10.0</td>
<td>98</td>
<td>105</td>
</tr>
<tr>
<td>Th(IV)</td>
<td>1000</td>
<td>8.0</td>
<td>8.5</td>
<td>97</td>
<td>135</td>
</tr>
<tr>
<td>La(III)</td>
<td>1000</td>
<td>10.0</td>
<td>9.5</td>
<td>98.5</td>
<td>100</td>
</tr>
<tr>
<td>Ce(III)</td>
<td>1000</td>
<td>12.0</td>
<td>9.0</td>
<td>97.5</td>
<td>105</td>
</tr>
<tr>
<td>Resin B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U(VI)</td>
<td>1000</td>
<td>6.0</td>
<td>11.0</td>
<td>98.5</td>
<td>100</td>
</tr>
<tr>
<td>Th(IV)</td>
<td>1000</td>
<td>8.0</td>
<td>10.5</td>
<td>98</td>
<td>129</td>
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<tr>
<td>La(III)</td>
<td>1000</td>
<td>10.0</td>
<td>10.0</td>
<td>97</td>
<td>98</td>
</tr>
<tr>
<td>Ce(III)</td>
<td>1000</td>
<td>12.0</td>
<td>9.5</td>
<td>98</td>
<td>101</td>
</tr>
</tbody>
</table>

Values given are average of ten determinations.
Table 4. Tolerance limits of electrolytes on the sorption of U(VI), Th(IV), La(III) and Ce(III) on resin (A/B).[Experimental conditions: Resin: 1.0 gm; Volume of solution passed: 100 ml; U(VI): pH 8.0; Th(IV): pH 3.0; La(III): pH 6; Ce(III): pH 7.0]

<table>
<thead>
<tr>
<th>Metal ions (2.5 (µg ml⁻¹))</th>
<th>Concentration of electrolytes (mol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaF</td>
</tr>
<tr>
<td>Resin A</td>
<td></td>
</tr>
<tr>
<td>U(VI)</td>
<td>1.1</td>
</tr>
<tr>
<td>Th(IV)</td>
<td>1.4</td>
</tr>
<tr>
<td>La(III)</td>
<td>1.6</td>
</tr>
<tr>
<td>Ce(III)</td>
<td>2.1</td>
</tr>
<tr>
<td>Resin B</td>
<td></td>
</tr>
<tr>
<td>U(VI)</td>
<td>1.0</td>
</tr>
<tr>
<td>Th(IV)</td>
<td>1.3</td>
</tr>
<tr>
<td>La(III)</td>
<td>1.5</td>
</tr>
<tr>
<td>Ce(III)</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Values given are average of ten determinations.
Table 5. Determination of U(VI), Th(IV), La(III) and Ce(III) in monazite sand and natural water samples on chelating resin B. [Experimental conditions: Resin: 1.0 gm]

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Monazite Sand, Travancore, India (%)</th>
<th>Ground water, Gujarat University area, Ahmedabad (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium (VI)</td>
<td>0.019± 0.0004</td>
<td>17.8 ± 0.04</td>
</tr>
<tr>
<td>Thorium(IV)</td>
<td>8.41± 0.60</td>
<td>-</td>
</tr>
<tr>
<td>Lanthanum (III)</td>
<td>23.96± 0.72</td>
<td>-</td>
</tr>
<tr>
<td>Cerium(III)</td>
<td>42.82± 0.50</td>
<td>-</td>
</tr>
</tbody>
</table>

* Average and Standard Deviation from triplicate run conducted with a single column
Table 6. Comparable methods for preconcentration and determination of U(VI), Th(IV), La(III) and Ce(III)

<table>
<thead>
<tr>
<th>Polymeric sorbent</th>
<th>Resin sorption capacity (μg g⁻¹)</th>
<th>Preconcentration factors</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U(VI)</td>
<td>Th(IV)</td>
<td>La(III)</td>
</tr>
<tr>
<td>Amberlite XAD-4-Bicene</td>
<td>90451</td>
<td>58009</td>
<td>-</td>
</tr>
<tr>
<td>Amberlite XAD-2-Tiron</td>
<td>76169</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Amberlite XAD-4-OVSC</td>
<td>2890</td>
<td>3230</td>
<td>2300</td>
</tr>
<tr>
<td>Amberlite XAD-4-octa carboxy methyl-c-methyl Calix [4] resorcinarene</td>
<td>64268</td>
<td>67291</td>
<td>-</td>
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<tr>
<td>Merrifield polymer-DMDBMA</td>
<td>18780</td>
<td>15740</td>
<td>-</td>
</tr>
<tr>
<td>Amberlite XAD-16-ADHA</td>
<td>164700</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Merrifield polymer-DB2EHMA</td>
<td>62500</td>
<td>38200</td>
<td>-</td>
</tr>
<tr>
<td>Polymer supported calix[4]arene-semicarbazone</td>
<td>3033</td>
<td>2831</td>
<td>1875</td>
</tr>
<tr>
<td>Present Method Resin A</td>
<td>122900</td>
<td>94200</td>
<td>81920</td>
</tr>
<tr>
<td>Resin B</td>
<td>123200</td>
<td>99300</td>
<td>87520</td>
</tr>
</tbody>
</table>
Figure 1(a). Effect of pH on the sorption of U(VI), Th(IV), La(III) and Ce(III) by the resin A [Experimental conditions: Amount of resin A in the column: 1.0 gm; Volume of metal ion solution passed: 100 ml; U(VI): 6 μg ml⁻¹, Elution by: 0.1 N HCl; Th(IV): 6 μg ml⁻¹, Elution by: 2.0 N HCl; La(III): 6 μg ml⁻¹, Elution by: 0.1 NHNO₃; Ce(III): 6 μg ml⁻¹, Elution by: 0.1 N HNO₃]

Figure 1(b). Effect of pH on the sorption of U(VI), Th(IV), La(III) and Ce(III) by the resin B [Experimental conditions: Amount of resin B in the column: 1.0 gm; Volume of metal ion solution passed: 100 ml; U(VI): 6 μg ml⁻¹, Elution by: 2.0 N HCl; Th(IV): 6 μg ml⁻¹, Elution by: 2.5 N HCl; La(III): 6 μg ml⁻¹, Elution by: 0.1 N HNO₃; Ce(III): 6 μg ml⁻¹, Elution by: 0.1 N HNO₃]
Figure 2. Effect of flow rate on the sorption of U(VI), Th(IV), La(III) and Ce(III) on the resin A and resin B. [Experimental conditions: Amount of resin (A/B) in the column: 1.0 gm; 6 μg ml⁻¹ { U(VI): pH 8.0; Th(IV): pH 3.0; La(III): pH 6; Ce(III): pH 7.0}]

Figure 2(a) Resin A

Figure 2(b) Resin B
Figure 4. Breakthrough curve for U(VI), Th(IV), La(III) and Ce(III) on the resin (A/B). [Experimental conditions: Amount of the resin (A/B): 1.0 gm; Concentration of the metal ion solution passed: 10 µg ml⁻¹; U(VI): pH 8.0; Th(IV): pH 3.0; La(III): pH 6; Ce(III): pH 7.0]
Figure 5(a). Evaluation of the stability of the resin A for U(VI), Th(IV), La(III) and Ce(III) by sorption and elution [Experimental condition: Amount of the resin A in the column: 1.0 gm; Volume of the feed solution: 100 ml; Concentration of feed solution: 1229 μg ml⁻¹; U(VI): pH 8.0; Elution by 0.1 N HCl; Th(IV): pH 3.0; Elution by 2.0 N HCl; La(III): pH 6; Elution by 0.1 N HNO₃; Ce(III): pH 7; Elution by 0.1 N HNO₃]

Figure 5(b). Evaluation of the stability of the resin B for U(VI), Th(IV), La(III) and Ce(III) by sorption and elution [Experimental conditions: Amount of the resin B in the column: 1.0 gm; U(VI): pH 8.0; Elution by 0.2 N HCl; Th(IV): pH 3.0; Elution by 2.5 N HCl; La(III): pH 6; Elution by 0.1 N HNO₃; Ce(III): pH 7; Elution by 0.1 N HNO₃]
Figure 6(a). The elution profile of U(VI), Th(IV), La(III) and Ce(III) on the resin A
[Experimental conditions for resin A: Amount of the resin: 1.0 gm; Concentration of the solution passed: 1000 ml; U(VI): 6 µg L⁻¹; pH 8.0; Elution by 0.1 N HCl; Th(IV): 8 µg L⁻¹; pH 3.0; Elution by 2.0 N HCl; La(III): 10 µg L⁻¹; pH 6; Elution by 0.1 N HNO₃; Ce(III): 12 µg L⁻¹; pH 7; Elution by 0.1 N HNO₃]

Figure 6(b). The elution profile of U(VI), Th(IV), La(III) and Ce(III) on the resin B
[Experimental conditions for resin B: Amount of the resin: 1.0 gm; Concentration of the solution passed: 1000 ml; U(VI): 6 µg L⁻¹; pH 8.0; Elution by 0.1 N HCl; Th(IV): 8 µg L⁻¹; pH 3.0; Elution by 2.0 N HCl; La(III): 10 µg L⁻¹; pH 6; Elution by 0.1 N HNO₃; Ce(III): 12 µg L⁻¹; pH 7; Elution by 0.1 N HNO₃]
Figure 7(a). Separation of Th(IV) and U(VI) on the resin B [Experimental conditions: Amount of resin: 1.0 gm; Column maintained at pH 3.5; Th(IV): 100 μg in 25 ml buffer; U(VI): 100 μg in 25 ml buffer]

Figure 7(b). Separation of Th(IV), U(VI) and La(III) on the resin B [Experimental conditions: Amount of resin: 1.0 gm; Column maintained at pH 7; Th(IV): 100 μg in 25 ml buffer; U(VI): 100 μg in 25 ml buffer; La(III): 100 μg in 25 ml buffer]
Conclusion

The newly synthesized azocalix[4]resorcinarene Amberlite XAD-2 polymeric chelating resins (A/B) were successfully applied to preconcentration and determination of U(VI), Th(IV), La(III) and Ce(III) metal ions. Resins (A/B) showed good potential for the enrichment of these metal ions from various matrix as is evident from the column studies. The separation of binary/ternary mixtures is possible by control of pH or gradient elution. The proposed method provides a simple, sensitive, precise, reliable and accurate method for the preconcentration and determination of U(VI), Th(IV), La(III) and Ce(III) metal ions. The reusability of resins was as high as 9-10 cycles without any considerable loss in its sorption behavior. Resin B showed greater affinity and sorption capacity as compared to resin A which may probably be due to more azo functional groups in the calix[4]resorcinarene macrocycle.
References


