

# Sequential separation of lanthanides, thorium and uranium using novel solid phase extraction method from high acidic nuclear wastes

Ch. Siva Kesava Raju, M.S. Subramanian\*

Department of Chemistry, Indian Institute of Technology, Chennai 600036, India

Received 22 August 2006; received in revised form 17 October 2006; accepted 15 November 2006

Available online 18 November 2006

## Abstract

A novel grafted polymer for selective extraction and sequential separation of lanthanides, thorium and uranium from high acidic wastes has been developed by grafting Merrifield chloromethylated (MCM) resin with octyl(phenyl)-*N,N*-diisobutylcarbamoyl-methylphosphine oxide (CMPO) (MCM-CMPO). The grafting process is well characterized using FT-IR spectroscopy,  $^{31}\text{P}$  and  $^{13}\text{C}$  CPMAS (cross-polarized magic angle spin) NMR spectroscopy and CHNPS elemental analysis. The influence of various physico-chemical parameters during metal ion extraction by the resin phase are studied and optimized by both static and dynamic methods. The resin shows very high sorption capacity values of  $0.960\text{ mmol g}^{-1}$  for U(VI),  $0.984\text{ mmol g}^{-1}$  for Th(IV),  $0.488\text{ mmol g}^{-1}$  for La(III) and  $0.502\text{ mmol g}^{-1}$  for Nd(III) under optimum  $\text{HNO}_3$  medium, respectively. The grafted polymer shows faster rate exchange kinetics (<5 min is sufficient for 50% extraction) and greater preconcentration ability, with reusability exceeding 20 cycles. During desorption process, sequential separation of the analytes is possible with varying eluting agents. The developed grafted resin has been successfully applied in extracting Th(IV) from high matrix monazite sand, U(VI) and Th(IV) from simulated nuclear spent fuel mixtures. All the analytical data is based on triplicate analysis and measurements are within 3.5% rsd reflecting the reproducibility and reliability of the developed method.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Merrifield chloromethylated polymer; CMPO; Preconcentration; Acidic waste; Actinides

## 1. Introduction

Main constituents in the nuclear spent fuels are actinides like uranium, thorium and various fission products. Recovery of these metal ions is a challenging task because of high acidic environment associated with them [1–3]. Extraction and preconcentration of these valuable metal ions from other fission products is extremely important not only from the point of view of their limited resource availability, but also to reduce their quantum for disposal as radioactive wastes [4].

Various methods were adopted for separation of actinides, which include precipitation [5] and co-precipitation [6] and ion-exchange chromatography systems [7]. But over the years solvent extraction (SE) has been proved to be promising in this aspect because of simple operation and using this technique several extractants have been developed with various organic

ligands like phosphonic acid based ligands [8], *N,N*-dialkyl amides [9], crown ethers [10],  $\beta$ -diketones [11], picolinamides [12], calixarenes [13]. Amongst them, octyl(phenyl)-*N,N*-diisobutylcarbamoyl-methylphosphine oxide (CMPO) is regarded as one of the best ligand for extraction of transuranium elements and used in TRUEX (Trans Uranium Extraction) process [14–18].

Even though SE technique is the widely adopted process, it suffers from limitations like the third phase formation, disposal of large volumes of extractants and diluents and tedious extraction procedures.

More recently, the use of solid phase extractants (SPE) have been proved to be more advantageous in view of their total insolubility in aqueous phase, low rate of physical degradation, no disposal of toxic organic solvents as waste and it can be recycled. In SPE, the organic extractants are anchored to an inert polymeric support and several methods have been developed for actinide extractions [19–26].

Thus keeping the positive features of CMPO ligand a novel grafted polymer was developed by modifying Merrifield

\* Corresponding author. Fax: +91 44 2257 4202.

E-mail address: [mssu@rediffmail.com](mailto:mssu@rediffmail.com) (M.S. Subramanian).

chloromethylated resin with CMPO ligand. Various physicochemical parameters were optimized and discussed in detail for extraction of U(VI) and Th(IV). Studies were also performed on La(III) and Nd(III) as their chemical behavior is similar to Am(III) and also they are used in burn up measurements. The applicability was tested for the recovery of U(VI) and Th(IV) from synthetic mixtures mimicking nuclear spent fuel and monazite sand.

## 2. Experimental

### 2.1. Instrumentation

The characterization of grafted polymer was done using a Perkin-Elmer Spectrum One model FT-IR spectrometer, a Bruker-Avance 400 model CPMAS NMR Spectrometer and Perkin-Elmer 2400 model CHNS/O analyzer. A Jasco V-530 model UV–vis spectrophotometer was used for the estimation of U(VI), Th(IV), La(III) and Nd(III). Trace amounts of U(VI) from real and synthetic samples were determined using Hitachi F-4500 model fluorescence spectrophotometer. A Varian SpectrAA-20 model flame atomic absorption spectrometer was used for the estimation of transition metal ions during interference studies. Flow rates during column operations were adjusted with a Ravel Hi-Tech S-50 model peristaltic pump. Static equilibrium studies were performed using an Orbitek DL model mechanical shaker with shaking rate of 200 rpm.

### 2.2. Chemicals and reagents

U(VI) and Th(IV) standard individual metal ion solutions were prepared from  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  (AR grade, Fluka Chemicals) by dissolving appropriate amounts in slightly acidified double distilled water. La(III) and Nd(III) solutions were prepared from the corresponding oxides obtained from Indian Rare earths Ltd. Merrifield chloromethylated styrene-divinylbenzene resin (capacity [Cl]:  $\sim 5.5 \text{ mmol g}^{-1}$  resin, 16–50 mesh) obtained from Fluka chemicals was purified by washing with distilled water, 1:1 ethanol and water mixture followed by washing with absolute ethanol to remove the monomer impurities. Finally, the beads were filtered, dried and vacuumized prior to usage. The ligand octyl(phenyl)-*N,N*-

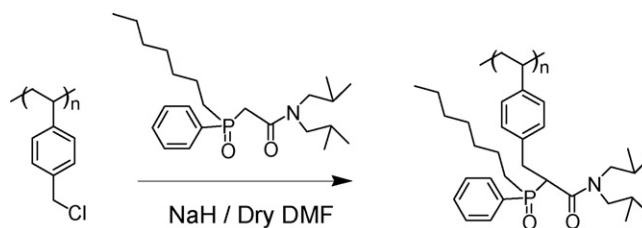


Fig. 1. Modification of chloromethylated resin with CMPO.

diisobutylcarbamoyl-methylphosphine oxide (CMPO) with purity greater than 99.5% was obtained from Fuel Chemistry Division, IGCAR, Kalpakkam, India and all other reagents and solvents were purchased from E-Merck chemicals which are of AR grade.

### 2.3. Synthesis of the resin

The vacuum dried Merrifield resin (5 g) was reacted with CMPO (1.5 equiv.) for 30 h at 70 °C, which was initially treated with NaH in dry DMF medium. The grafted polymer was washed with acetone and ethanol and vacuum dried. To remove the adsorbed CMPO, the grafted polymer was packed in mini glass column and hexane was passed through the column. Finally the grafted polymer was filtered and vacuum dried. The synthetic scheme leading to the formation of resin is shown in Fig. 1.

### 2.4. Methods adopted for metal ion extraction and preconcentration

#### 2.4.1. Batch 'static' method

Batch method was performed to optimize the basic experimental conditions for quantitative analyte extraction such as acid concentration dependence, kinetic studies and diverse ion tolerance. For this study, known amounts of resin beads (50 mg) was equilibrated with known concentrations of metal ion solution (40 mL,  $10 \mu\text{g mL}^{-1}$ ) in 125 mL reagent bottles for 90 min using a mechanical shaker at 200 rpm under different acid conditions. The extracted metal ions were desorbed using 15 mL of 1 M ammonium carbonate. The amount of metal ions extracted were estimated spectrophotometrically using Arsenazo (III) as

Table 1  
Optimized experimental parameters for metal ion sorption and desorption

Experimental parameters	U(VI)	Th(IV)	La(III)	Nd(III)
$t_{1/2}$ (min) <sup>a</sup>	3.0	3.0	4.0	4.0
Metal sorption capacity ( $\text{mmol g}^{-1}$ )				
At optimum $\text{HNO}_3$ concentration <sup>b</sup>	0.960	0.984	0.488	0.502
At optimum HCl concentration <sup>c</sup>	0.420	0.435	–	–
Maximum sample flow rate ( $\text{mL min}^{-1}$ )	15	15	10	10
Lower limit of detection ( $\mu\text{g L}^{-1}$ )	20	20	15	15
Sample breakthrough volume (L)	6.0	6.0	5.0	5.0
Preconcentration factor	400	400	333	333

<sup>a</sup>  $t_{1/2}$  is minimum time taken for 50% extraction.

<sup>b</sup> Optimum  $\text{HNO}_3$  concentration: 4 M for U, Th and lanthanides.

<sup>c</sup> Optimum HCl concentration: 4 M for U and Th.

chromogen for U(VI) (7 M HNO<sub>3</sub>) [27] and La(III) (pH 3) [28] at 655 nm and using Thoron as chromogen for Th(IV) (0.5 M HCl) [28] at 545 nm, respectively.

#### 2.4.2. Column 'dynamic' method

A glass column (15 cm × 0.4 cm) was packed uniformly with 1 g of preconditioned resin beads by slurry method and the sample solution was passed through at a constant flow rate using a peristaltic pump. All column parameters such as break through volume, sample flow rate and lower limit of analytes quantification were optimized using this method. Based on the data obtained from dynamic method, the practical applicability of the resin matrix was tested for the preconcentration of U(VI) from synthetic mixture mimicking nuclear spent fuels in acid medium and sea water in near neutral conditions and also Th(IV) from monazite sand. The optimum parameters for both static and dynamic methods are listed in Table 1.

### 3. Results and discussion

#### 3.1. Characterization of the resin matrix

The <sup>13</sup>C CPMAS NMR spectra showed resonance signal at 208.7 ppm corresponds to the amide carbonyl group present in the ligand moiety of the grafted polymer, as shown in Fig. 2a. Also, it could be seen that the more number of resonance signals were observed in the 70–20 ppm range indicating the presence of alkyl groups and also resonance signal at 129 ppm confirms the presence of phenyl group in the CMPO. The presence of P=O moiety in the grafted polymer was inferred from <sup>31</sup>P solid state NMR spectra as shown in Fig. 2b, whose resonance signal were observed at 53.8 ppm along with side bands at 3.4 and 103.2 ppm.

Each step of the grafting process was monitored using FT-IR spectra. From the spectra it was observed that band

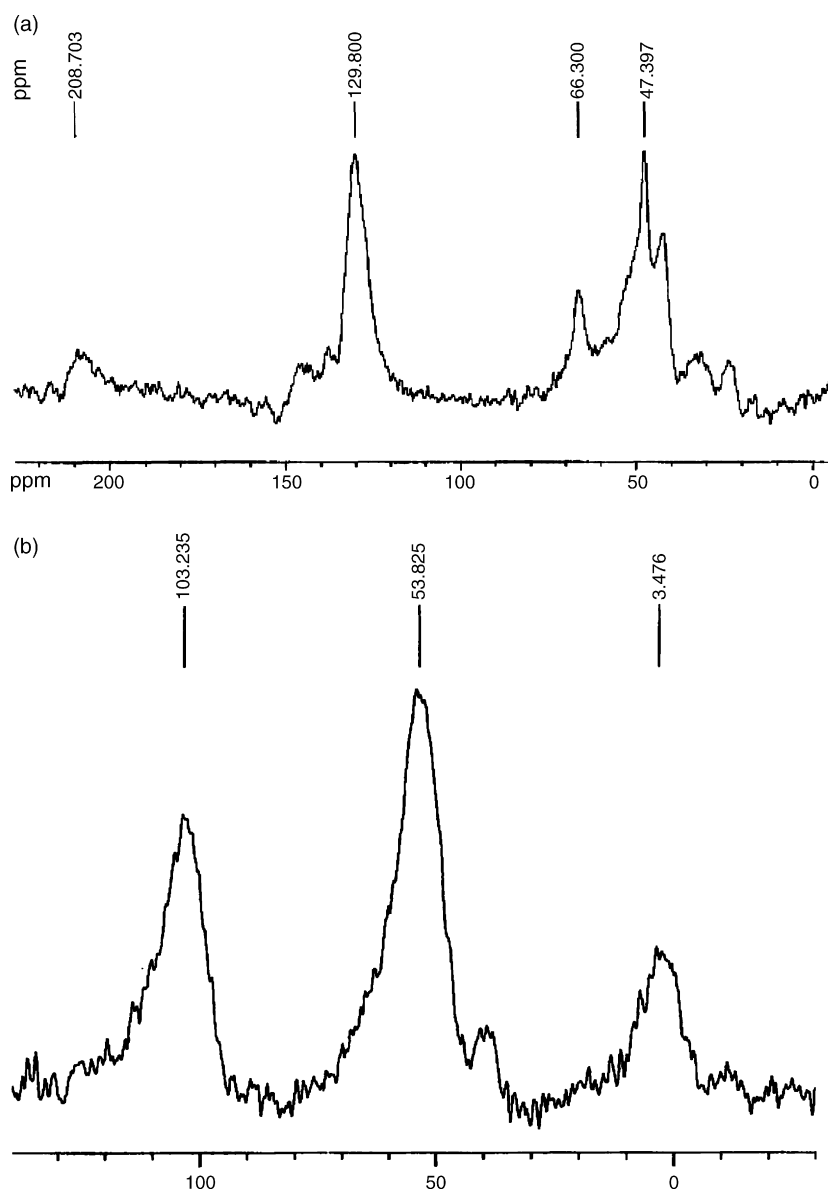


Fig. 2. (a) <sup>13</sup>C CPMAS NMR spectrum of CMPO grafted polymer. (b) <sup>31</sup>P solid state NMR spectrum of CMPO grafted polymer.

Table 2  
Characterization at various stages of functionalization

Item characterized	FT-IR spectral data (cm <sup>-1</sup> )	(%) C:H:N:P elemental data
CMPO ligand	—CH <sub>2</sub> — aliphatic side chain (2926), P=O (1025), C=O (1635, amide)	Theoretical: 70.7,10.3,3.4,7.6; experimental: 71.0, 10.1, 3.5, 7.2
Merrifield chloromethylated resin	—CH <sub>2</sub> Cl (672.0), —CH <sub>2</sub> wagging (1263.5)	Theoretical: 72.0, 6.1; experimental: 72.9, 6.1
CMPO-grafted polymer	—CH <sub>2</sub> — aliphatic side chains (2928), —C=O (1636), P=O (1023)	Theoretical: 76.2, 10.7, 2.4, 5.7; experimental: 75.8, 10.9, 2.8, 5.2

at 672 cm<sup>-1</sup> corresponding to C–Cl stretching frequency in unmodified chloromethylated resin has completely disappeared in the CMPO grafted polymer and new set of bands are observed at 1028 cm<sup>-1</sup> (P=O), 1264 cm<sup>-1</sup> (C–N str), 1643 cm<sup>-1</sup> (C=O), thereby confirming the grafting process Table 2 and also there is considerable shift in FT-IR spectra of grafted polymer when compared to free ligand (1028 cm<sup>-1</sup> (P=O), 1264 cm<sup>-1</sup> (C–N str)) in fingerprint region proves the effective anchoring of functional group in to the polymeric matrix.

CHNPS elemental analysis was performed during each stage of the grafting process and the data obtained are given in Table 2. From the table it is observed that the experimental (%) values are in close agreement with the corresponding theoretical values, which suggests the presence of one ligand moiety per polymer repeat unit and also confirms quantitative ligand grafting.

### 3.2. Metal extraction studies by Batch method

#### 3.2.1. Influence of acidity for the metal extraction

Nitric acid is the major constituent in nuclear waste as most of the reprocessing was done in high acid medium. So metal ion extraction was studied with varying concentrations of HNO<sub>3</sub>. The effect of HCl concentration was also studied because most of the analytical procedures for metal ion separation and pre-concentration from environmental, biological and geological samples are performed in this medium.

For this study, 0.05 g of the resin beads were batch equilibrated with metal ion solutions (40 mL, 10 μg mL<sup>-1</sup>) of different acid concentrations, for 90 min. The results were expressed in terms of the distribution ratio (*D*) using the following expression [29]:

$$D \text{ (mL g}^{-1}\text{)} = (A_0 - A_f) \frac{V}{A_f W}$$

where *A*<sub>0</sub> and *A*<sub>f</sub> are the metal ion concentration before and after equilibration, *V* refers to the overall volume (mL) and *W* is the dry weight of the resin matrix (g). It is evident from Fig. 3 that the grafted polymer is more suitable for extraction of hexavalent U and tetravalent Th compared to trivalent lanthanides. The extraction of actinides takes place even in high acid medium and it is because of the high acidic property of carbamoyl-methylphosphine oxide group which shows high affinity towards actinides. At high acid conditions, these metal ions will form stable neutral complexes with CMPO ligand and therefore are extracted in to polymeric phase.

In HCl medium, both U(VI) and Th(IV) showed similar extractive behavior and their extraction decreases after higher

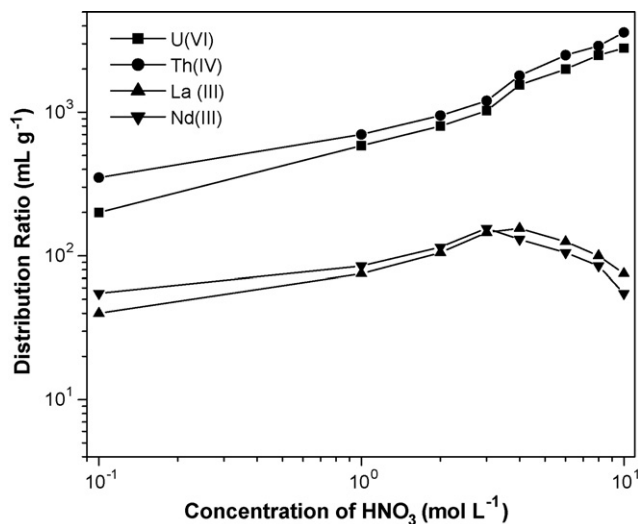


Fig. 3. Nitric acid dependency on analytes extraction; amount of metal ion: 400 μg, amount of resin used: 50 mg, total volume of aqueous phase: 40 mL.

HCl concentrations as shown in Fig. 4. However at lower concentrations of HCl (<2 M), there is no extraction of lanthanides which may be due to the inability to form strong chloro complexes. However, at these HCl concentrations, there is still appreciable extraction of uranium and thorium which form stable neutral extractable complexes. This observation paved the way for the separation of lanthanides from uranium and thorium at these lower HCl concentrations.

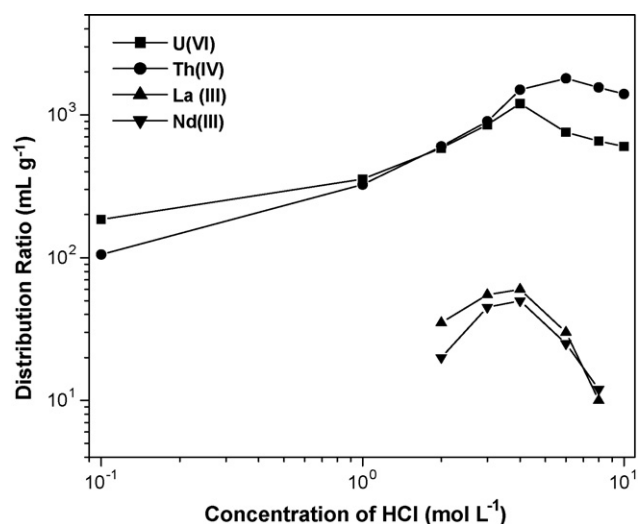


Fig. 4. Hydrochloric acid dependency on analytes extraction; amount of metal ion: 400 μg, amount of resin used: 50 mg, total volume of aqueous phase: 40 mL.

Table 3  
Comparison of sorption capacities and preconcentration factors with other solid phase extractants

Sl. no.	Polymeric sorbent	Resin sorption capacity (mmol g <sup>-1</sup> )		Preconcentration factors		References
		U(VI)	Th(IV)	U(VI)	Th(IV)	
1.	Merrifield polymer-CMPO	<b>0.960</b>	<b>0.984</b>	<b>400</b>	<b>400</b>	–
2.	Merrifield polymer-TTA	0.138	0.117	350	350	[21]
3.	Amberlite XAD-4-Bicene	0.380	0.250	50	50	[22]
4.	Amberlite XAD-2-Tiron	0.032	–	150	–	[23]
5.	Amberlite XAD-4-OVSC	0.012	0.013	125	120	[24]
6.	Amberlite XAD-4-octa carboxy methyl- <i>c</i> -methyl Calix [4] resorcinarene	0.270	0.290	100	105	[25]
7.	Merrifield polymer- <i>N,N,N',N'</i> -tetrahexyl malonamide	0.645	0.558	400	350	[26]

### 3.2.2. Resin metal sorption capacity

The maximum metal sorption capacity of the developed resin matrix was studied by equilibrating 0.02 g of the grafted polymer with a solution of excess metal ion concentration (100 mL, 100 μg mL<sup>-1</sup>) for time duration of 6 h. For this study 4 M HNO<sub>3</sub> and 4 M HCl medium was employed for U(VI), Th(IV) and 4 M HNO<sub>3</sub> medium was employed for La(III) and Nd(III). The metal sorption capacities were compared with other literature reported values as given in Table 3, from the values it can be seen that the grafted polymer is able to sorb high amount of metal concentration even in high acid medium.

### 3.2.3. Elution studies

Quantitative desorption of U(VI), Th(IV), La(III) and Nd(III) was performed with various eluting agents as shown in Table 4. Among various eluting agents, ammonium carbonate was found to be successful in quantitatively recovering all the analytes. The desorption process involves the formation of soluble strong anionic carbonate complexes of both actinides and lanthanides. However with 1 M HCl lanthanides alone are quantitatively eluted. It can also be seen from the figure that with (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> as eluting agent only Th is quantitatively removed leaving U in the resin phase. Thus with 1 M HCl as an eluting agent lanthanides could be selectively eluted out. The elution can then be continued with 0.5 M (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> to selectively remove Th from the resin phase. The retained U in the resin phase can be finally eluted with 0.5 M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>. From these observations we have performed sequential separation of lanthanides, thorium and uranium using 1 M HCl, 0.5 M (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> respectively as eluents and their profile is shown in Fig. 5.

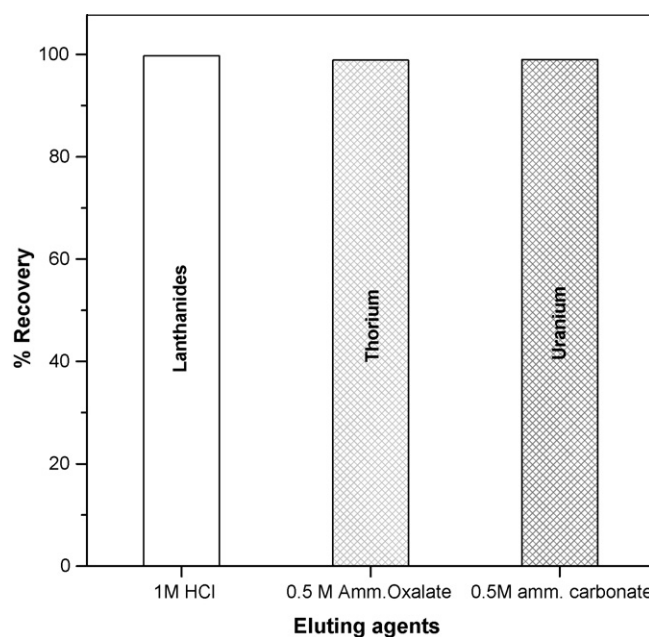


Fig. 5. Sequential separation of La(III), Th(IV) and U(VI); amount of metal ion: 400 μg, amount of resin used: 50 mg, amount of 1 M HCl taken: 20 mL; amount of 0.5 M Amm.oxalate taken: 20 mL; amount of 0.5 M Amm.carbonate taken: 15 mL.

### 3.2.4. Kinetic studies

The rate of transfer of metal ions from the aqueous to solid phase was studied at various time durations by equilibrating 0.05 g of resin beads with a series of metal ion solutions (40 mL, 10 μg mL<sup>-1</sup>) in 4 M HNO<sub>3</sub>. The kinetic data were plotted in terms of (1 - F) values as function of equilibration time where, F is the fractional attainment of equilibrium, which is expressed as [30]:

$$F = \frac{[M^R]_t}{[M^R]_{eq}}$$

where  $[M^R]_t$ ,  $[M^R]_{eq}$  are the metal ion concentration in the resin phase at time  $t$  to that at equilibrium. From Table 1 it is evident from  $t_{1/2}$  values, 3 min is sufficient for 50% extraction of U(VI) and Th(IV) and it will take 4 min for La(III) and Nd(III). However complete equilibrium is attained within 10 min of duration for all the analytes.

Table 4  
Analytes recovery with various eluants

Eluants	Eluant volumes (mL)	Recovery (%)		
		U(VI)	Th(IV)	La(III)
0.1 M (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	15	99.9	99.8	99.5
0.1 M EDTA (pH ≥ 5)	20	78.0	88.0	95.0
1 M HCl	20	2.0	4.0	99.8
0.1 M (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	20	5.0	98.5	95.0

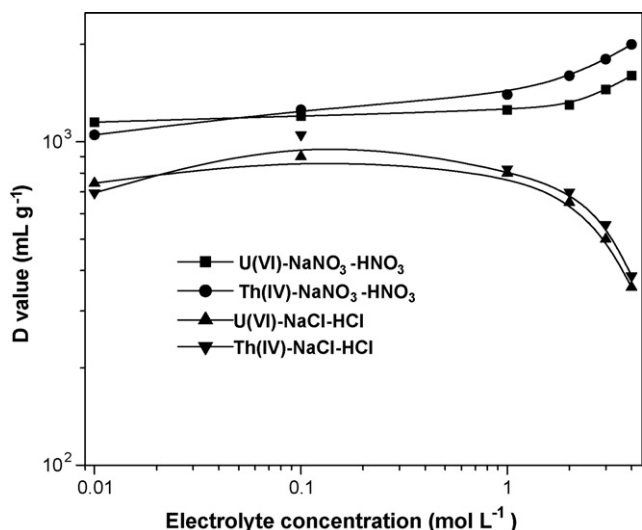


Fig. 6. Effect of salt concentration on extraction of analytes; amount of metal ion: 400 µg, amount of resin used: 50 mg.

### 3.2.5. Effect of NaNO<sub>3</sub> and NaCl on metal ion extraction

As NaNO<sub>3</sub> and NaCl are the main electrolytes present nuclear spent fuels and environmental samples, respectively, their influence on the quantitative extraction of U(VI) and Th(IV) was studied at varying concentrations (0.01–4 M) of NaNO<sub>3</sub> and NaCl in 2 M HNO<sub>3</sub> and 2 M HCl, respectively. From Fig. 6, it can be observed that there exists a positive trend with increasing NaNO<sub>3</sub> concentration (up to 2 M) and thereafter there is slight increase in extraction. This perhaps may be due to the reduction of hydration sphere around the metal ions through salting out effect. The negative trend on increasing NaCl concentration may be due to the formation of more stable metal anionic chloro complexes, which are non-extractable by the phosphoryl oxygen of the carbomoyl methyl phosphineoxide group.

### 3.2.6. Tolerance limit towards interfering ions and common metal ions

The resin's tolerance limits towards various electrolytes and diverse metal ions was studied by equilibrating 0.05 g of the resin beads with analytes concentration (40 mL, 1.25 µg mL<sup>-1</sup>) along with varying concentrations of individual diverse ions under 4 M HNO<sub>3</sub> conditions. The resin showed no uptake for common transition metal ions. The degree of tolerance for some post-transition ions, rare earths and electrolyte species, are shown in Table 5. From the tolerance data, it can be seen that the resin shows high selectivity towards the studied analytes when compared to other diverse ions.

### 3.2.7. Stability of the chelating matrix

The resin's reusability was tested by shaking 50 mg of the resin beads with metal ion solution (40 mL, 10 µg mL<sup>-1</sup>) in 4 M HNO<sub>3</sub> medium and the sorbed metal ions were eluted and analyzed. The metal ions were desorbed from the resin and were washed with distilled water till neutral pH. The same experiment was repeated with the same resin beads a number of times and it was found that the grafted polymer was able to extract metal ions

Table 5  
Resin tolerance towards interfering electrolytes/metal ion species

Metal ions	Tolerance limits for electrolytes (mol L <sup>-1</sup> )					
	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>3</sub> PO <sub>4</sub>	NaF	CH <sub>3</sub> COO <sup>-</sup>	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	
U(VI)	0.88	0.42	0.32	0.31	0.45	
Th(IV)	0.74	0.32	0.35	0.26	0.05	
La(III)	0.33	0.15	0.28	0.14	0.05	
Nd(III)	0.36	0.18	0.22	0.28	0.05	
Metal ions	Tolerance limits for interfering metal ions (mmol L <sup>-1</sup> )					
	Zr(IV)	Mo(VI)	Cd(II)	Ce(IV)	Sm(III)	Gd(III)
U(VI)	9.2	8.8	12.5	5.5	2.8	3.2
Th(IV)	8.0	7.2	11.1	2.2	2.5	2.8
La(III)	4.2	4.5	11.0	1.8	1.0	1.2
Nd(III)	4.5	5.2	10.2	1.5	0.9	0.8

Volume and concentration of metal ion solution (40 mL, 1.25 µg mL<sup>-1</sup>), amount of resin used: 50 mg.

quantitatively more than 20 cycles showing the reproducibility and durability of the resin even under high acidic conditions. The reusability profile for U(VI) up to 30 cycles is shown in Fig. 7.

### 3.3. Metal extraction studies by dynamic method

#### 3.3.1. Influence of sample flow rate on metal ion sorption

The rate at which the quantitative sorption was possible was studied using a packed resin bed column by varying the sample flow rate using a peristaltic pump. The metal ion solution (1000 mL, 0.5 µg mL<sup>-1</sup>, bed volume –1.2 mL) was passed through the column with varying flow rates from 1 to 25 mL min<sup>-1</sup>. The results showed that quantitative extraction of analytes was achieved even with high flow rates of 20 mL min<sup>-1</sup> for U(VI), and Th(IV), 15 mL min<sup>-1</sup> for La(III) and Nd(III), respectively.

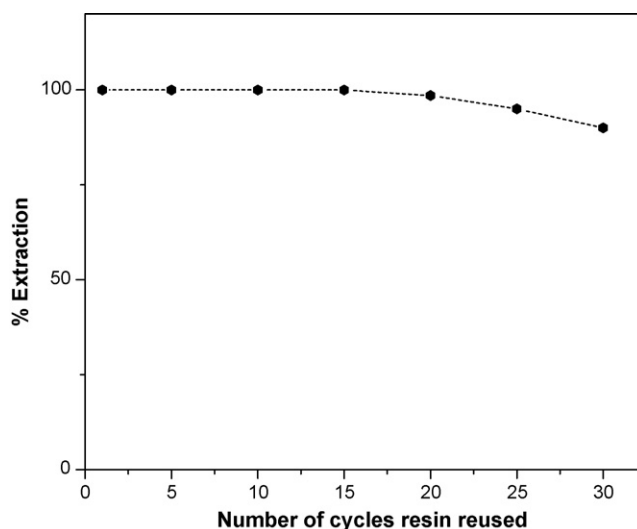


Fig. 7. Reusability profile grafted polymer; amount of metal ion: 400 µg, amount of resin used: 50 mg, total volume of aqueous phase: 40 mL; concentration of HNO<sub>3</sub>: 4 M.

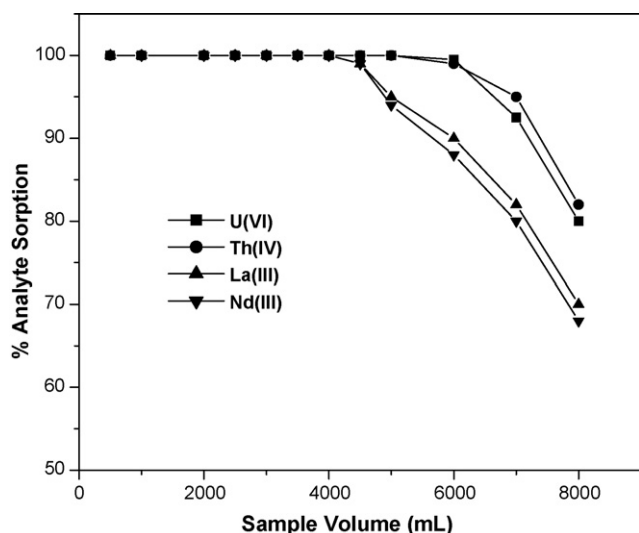


Fig. 8. Breakthrough volume studies; amount of individual metal ion added: 50  $\mu\text{g}$ , amount of resin used: 500 mg.

### 3.3.2. Sample breakthrough volume studies

The sample breakthrough volume studies were performed to know the ability of resin matrix to extract quantitatively trace amounts of metal analytes of interest from large sample volumes. For this study, various sample volumes (500–6000 mL) containing 50  $\mu\text{g}$  of each individual analytes were passed through the column bed equilibrated with 4 M  $\text{HNO}_3$  and 15 mL of eluting agent is used for elution of each metal ion. Breakthrough volumes of 6000 mL for U(VI) and Th(IV) and 5000 mL for La(III) and Nd(III) (Fig. 8) were observed thereby giving good preconcentration factors 400, 400, 333 and 333, respectively for U(VI), Th(IV), La(III) and Nd(III) and these values are comparatively higher with other solid phase extractants as shown in Table 3.

### 3.3.3. Lower limit of analytes quantification

To test the grafted polymers ability to extract trace quantities of metal ions studies were performed by passing 1000 mL of sample solution containing varying analyte concentrations from 10 to 100  $\text{ng mL}^{-1}$ . The sorbed metal ions were eluted and estimated. The limits of quantification were found to be 20  $\mu\text{g L}^{-1}$  for U and 80  $\text{ng mL}^{-1}$  for U(VI), La(III) and Th(IV), respectively thereby, indicating the resin's sensitivity to extract the trace metal ions of interest even at ppb level.

## 4. Applications

### 4.1. Synthetic mixture mimicking reprocessing streams

The applicability of the grafted polymer for the real samples was tested using synthetic mixture mimicking nuclear spent fuels similar to nuclear reprocessing solutions. Three liters of the synthetic mixture [31] spiked with 100  $\mu\text{g}$  of analyte was passed through the chromatographic column at 4 M  $\text{HNO}_3$ . The sorbed metal ions were eluted and estimated. It was found that the resin was successful in quantitatively extracting the actinides of interest even in the presence of various diverse ions. The amount of U(VI) extracted was found to be  $98.80 \pm 0.35$  for

direct analysis and  $99.12 \pm 0.32$  for standard addition methods with rsd values corresponding to 3.8 and 3.5, respectively, based on triplicate analysis. The amount of Th(IV) extracted was found to be  $96.50 \pm 0.44$  for direct analysis and  $97.20 \pm 0.40$  for standard addition methods with rsd values corresponding to 4.2 and 4.0, respectively, based on triplicate analysis.

### 4.2. Extraction of thorium from monazite sand (Travancore, India)

The resin's applicability in extracting Th(IV) from monazite sand was studied. 0.1 g of monazite sand sample was digested with conc.  $\text{H}_2\text{SO}_4$  at 250  $^\circ\text{C}$  for 4 h. Subsequently, it was digested using 5 mL of HF followed by conc.  $\text{HNO}_3$ . The residue was redissolved in minimal volumes of dil. HCl and passed through the resin column. The amount of Th(IV) extracted was found to be  $79.80 \pm 0.50$  mg/g for direct analysis and  $80.12 \pm 0.48$  mg/g for standard addition methods with rsd values corresponding to 4.0 and 3.6, respectively, based on triplicate analysis. These values are well comparable with the certified value of 81  $\text{mg g}^{-1}$ .

## 5. Conclusions

The CMPO grafted polymer is suitable for selective and sequential separation of lanthanides, thorium and uranium. The significant features of the developed resin matrix are its superior metal sorption capacity even under highly acidic conditions. The synthesized resin has shown good enrichment factor values at high extraction rates. The grafted polymer showed good durability and reusability even up to 20 cycles. The polymer also showed good selectivity and sensitivity towards analytes down to ppb levels.

## Acknowledgements

We are thankful to BRNS, Board of Research in Nuclear Sciences, India for the financial assistance and Fuel Chemistry Division, IGCAR, Kalpakkam, India for providing required chemicals for the experimental purposes.

## References

- [1] E.P. Horwitz, M.L. Dietz, D.M. Nelson, J.J. La Rosa, W.L. Fairman, Concentration and separation of actinides from urine using a supported organophosphorus extractant, *Anal. Chim. Acta* 238 (1990) 263–271.
- [2] Y. Sasaki, S. Tachimori, Extraction of actinides (III), (IV), (V), (VI) and lanthanides (III) by structurally tailored diamides, *Sol. Extr. Ion Exch.* 20 (2002) 21–34.
- [3] L. Spjuth, J.O. Liljenzin, M.J. Hudson, M.G. Drew, P.B. Iveson, C. Madic, Comparison of extraction behavior and basicity of some substituted malonamides, *Sol. Extr. Ion Exch.* 18 (2000) 1–23.
- [4] K.K. Gupta, V.K. Manchanda, M.S. Subramanian, R.K. Singh, Solvent extraction studies on U(VI), Pu(IV) and fission products using *N,N*-dihexyloctanamide, *Sol. Extr. Ion Exch.* 1 (2000) 273–292.
- [5] S. Lawrosky, Survey of separation processes other than solvent extraction, *Chem. Eng. Prog.* 51 (1955) 461.
- [6] V.I. Grebenshikova, R.V. Bryzgalova, A study of the co-precipitation of Pu(IV) with lanthanum oxalate, *Radiokhimiya* 2 (1960) 265–273.

- [7] J. Korkish, Handbook of Ion Exchange resins: Their Application to Inorganic Analytical Chemistry, vol. II, CRC Press, Inc., 1989.
- [8] M.R. Yaftian, R. Taheri, A.A. Zamani, D. Matt, Thermodynamics of the solvent extraction of thorium and europium nitrates by neutral phosphorylated ligands, *J. Radioanal. Chem.* 262 (2004) 455–459.
- [9] N. Condamines, C. Musikas, The extraction by *N,N*-dialkylamides. I. Nitric and other inorganic acids, *Sol. Extr. Ion Exch.* 6 (1988) 1007–1034.
- [10] K.L. Nash, A review of the basic chemistry and recent developments in trivalent f-element separations, *Sol. Extr. Ion Exch.* 11 (1993) 729.
- [11] D.D. Ensor, G.D. Jarvinen, B.F. Smith, The use of soft donor ligands, 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione and 4,7-diphenyl-1,10-phenanthroline for improved separation of trivalent americium and europium, *Sol. Extr. Ion Exch.* 6 (1988) 439.
- [12] P.Y. Coredier, N. Condamines, De Nouvelles Molécules pour la separation des actinides: les Picolinamides, CEACONF-11759, 1993.
- [13] C.D. Gutsche, Calixarenes, Royal Society of Chemistry, Cambridge, 1989.
- [14] W.W. Schulz, E.P. Horwitz, The TRUEX process and the management of liquid TRU waste, *Sep. Sci. Technol.* 23 (1988) 1191–1210.
- [15] E.P. Horwitz, D.G. Kalina, H. Diamond, G.F. Vandegrift, W.W. Schulz, Behavior of americium in the strip stages of the TRUEX process, *Sol. Extr. Ion Exch.* 3 (1985) 75–109.
- [16] E.P. Horwitz, R. Chiarizia, R.C. Gatrone, Behaviour of americium in the strip stages of the TRUEX process, *Sol. Extr. Ion Exch.* 6 (1988) 93–110.
- [17] J.N. Mathur, M.S. Murali, G.H. Rizvi, R.H. Iyer, K.M. Michael, S.C. Kapoor, A. Ramanujam, L.P. Badheka, A. Banerji, Extraction chromatographic separation and recovery of plutonium from oxalate supernatant using CMPO, *J. Nucl. Sci. Technol.* 30 (1993) 1198–1200.
- [18] A. Suresh, C.V.S. Brahmananda Rao, R. Devanayaki, T.G. Srinivasan, P.R. Vasudeva Rao, Studies on the extraction behavior of octyl (phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide in polymeric adsorbent resins, *Sol. Extr. Ion Exch.* 21 (2003) 449–463.
- [19] Ch. Siva Kesava Raju, M.S. Subramanian, DAPPA grafted polymer: an efficient solid phase extractant for U(VI), Th(IV) and La(III) from acidic waste streams and environmental samples, *Talanta* 67 (2005) 81–89.
- [20] Ch. Siva Kesava Raju, S. Srinivasan, M.S. Subramanian, New multi-dentate ion-selective AXAD-16-MOPPA polymer for the preconcentration and sequential separation of U(VI), Th(IV) from rare earth matrix, *Sep. Sci. Technol.* 40 (2005) 2213–2230.
- [21] D. Prabhakaran, M.S. Subramanian, Extraction of U(VI), Th(IV), and La(III) from acidic streams and geological samples using AXAD-16-POPDE polymer, *Anal. Bioanal. Chem.* 380 (2004) 578–585.
- [22] K. Dev, R. Pathak, G.N. Rao, Preparation and analytical properties of a chelating resin containing bicine groups, *Talanta* 48 (1999) 576–584.
- [23] M. Kumar, D.P.S. Rathore, A.K. Singh, Metal ion enrichment with Amberlite XAD-2 functionalized with tiron: analytical applications, *Analyst* 125 (2000) 1221–1226.
- [24] M. Merdian, M.Z. Duz, C. Hamamci, Sorption behavior of uranium(VI) with *N,N*-dibutyl-*N'*-benzoylthiourea impregnated in Amberlite XAD-16, *Talanta* 16 (2001) 639–645.
- [25] V.K. Jain, A. Handa, S.S. Sait, P. Shrivastav, Y.K. Agarwal, Preconcentration, separation and trace determination of lanthanum(III), cerium(III), thorium(IV) and uranium(VI) on polymer supported *o*-vanillinsemicarbazone, *Anal. Chim. Acta* 429 (2001) 237–246.
- [26] Ch. Siva Kesava Raju, M.S. Subramanian, Selective preconcentration of U(VI) and Th(IV) in trace and macroscopic levels using malonamide grafted polymer from acidic matrices, *Microchim. Acta* 150 (2005) 297–304.
- [27] P.R.V. Rao, S.K. Patil, A spectrophotometric method for the determination of neptunium and plutonium in process solutions, *J. Radioanal. Chem.* 42 (1978) 399–410.
- [28] F.D. Snell, Photometric and Fluorometric Methods of Analysis Metals, John Wiley & Sons, Inc., New York, 1978.
- [29] R. Chiarizia, E.P. Horwitz, S.D. Alexandratos, Uptake of metal ions by a new chelating ion-exchange resin. Part 1. Acid dependencies of actinide ions, *Sol. Extr. Ion Exch.* 11 (1993) 943–966.
- [30] R. Chiarizia, E.P. Horwitz, S.D. Alexandratos, Uptake of metal ions by a new chelating ion-exchange resin. Part 4. Kinetics, *Sol. Extr. Ion Exch.* 12 (1994) 211–217.
- [31] S. Maji, K. Sundarajan, G. Hemamalini, K.S. Viswanathan, Fluorimetric Estimation of Uranium: Applications in Nuclear Technology, IGC 228, Indira Gandhi Center for Atomic Research, India, 2001.