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Analytical application of poly[dibenzo-18-crown-6] for column chromatographic separation of Nd(III) from Ce(III), U(VI) and other elements

S. N. Lad · B. S. Mohite

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Abstract This research is dedicated to the study of analytical application of poly[dibenzo-18-crown-6] for separation of Nd(III) from possible lanthanides, actinides and other metal ions. A simple and efficient column chromatographic method has been developed using poly [dibenzo-18-crown-6] as stationary phase and hippuric acid as a counter ion. The capacity of crown polymer for Nd(III) was found to be 0.55 ± 0.01 mmol/g. Nd(III) was quantitatively separated from Ce(III), U(VI) and other elements in binary as well as multicomponent mixtures. Separation yields were good and reproducible (±2 %). This method has important application for separation of Nd(III) from Ce(III) rapidly and selectively.

Keywords Chromatographic separation · Neodymium(III) · Hippuric acid · Poly[dibenzo-18-crown-6]

Introduction

The rare earth elements are vastly used in the production of ceramics, electronics, magnets, alloys, catalysts etc. Because of demanding applications in metallurgy and nuclear technologies, recovery of rare earths from nuclear wastes and further use has gained more attention of the separation scientists [1]. Main constituents of nuclear spent fuel are actinides like uranium, thorium and various fission products like Nd, Pu, Zr, Mo, Ce, Ru, La, Pr etc. Whereas Co, Ni, Cd, Ca, Zn and Li show marginal contribution. ^{148}Nd is well known to be used as a burnup monitor. The amount of ^{148}Nd as well as plutonium, uranium, etc. are used for the burnup calculation after the determinations by a mass spectrometry [2, 3]. Burnup measurements are essential for fuel development studies and evaluation of power reactor operation [4]. 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 [5, 6]. The use of methods such as solvent extraction, ion exchange, solid phase extraction using different crown ethers have been reported for the separation of neodymium, uranium, thorium etc. [7–15].

Polymeric crown ethers are well known reagents. They are widely used as extractants and sorbents in chromatography for lanthanides and actinides [16]. Crown ethers have good stability for organic solvents, temperatures and radiolysis. Their reusability is very important characteristic. Most of the extractions are pH independent. Hence in this study use of poly[dibenzo-18-crown-6] as a stationary phase is favorable. It was also used for selective separation of lanthanides and actinides [17–21], but no attempts were made on the sorption study of Nd(III) using poly[dibenzo-18-crown-6] in hippuric acid medium. Hippuric acid shows good results over the wide range of concentration (10^{-2}–10^{-8} M). The use of hippuric acid is beneficial, because it is an amino acid. Therefore it does not cause serious harm to the environment. Present study describes the detailed sorption study of Nd(III) using poly[dibenzo-18-crown-6] and hippuric acid as counter anion. We have reported selective separation of Nd(III) from Ce(III), U (VI) and other metal ions. The method does not require sophisticated instruments and it is very simple.

S. N. Lad (✉) · B. S. Mohite
Analytical and Environmental Research Lab, Department of Chemistry, Shivaji University, Kolhapur 416004, Maharashtra, India
e-mail: lad.sheela@rediffmail.com

Experimental

Apparatus and reagents

All chemicals utilised were of analytical grade. A stock solution of Nd(III) was prepared by dissolving 1.243 g of neodymium chloride hexahydrate (99.9 % purity, BDH, India) in 100 ml distilled deionised water. The solution was standardized gravimetrically [14]. A solution containing 40 μgmL^{-1} of Nd(III) was prepared by appropriate dilution of the standard stock solution. Hippuric acid solution (1×10^{-2} M) was prepared by dissolving 0.1791 g of hippuric acid in distilled deionised water and diluted to 100 mL. Poly[dibenzo-18-crown-6] from Merck (Darmstadt, Germany) was screened to 100–200 mesh and then used. A total of 0.5 g of polymer was slurred with distilled deionised water and poured into a Pyrex glass column (20 × 0.8 cm i.d.). The chromatographic column was preconditioned with hippuric acid solution before use. A digital visible spectrophotometer (215 D, Thermo Electron LLS, India), a digital pH meter (Model LI-120, Elico, India) with glass and calomel electrodes and a digital flame photometer (PI Model No. 041, India) were used.

General procedure

Initially column was equilibrated with hippuric acid solution of concentration 1×10^{-3} M. Then solution containing 40 μgmL^{-1} of Nd(III) was mixed with hippuric acid solution of concentration 1×10^{-3} M in a total volume of 10 mL. The solution was then passed through column at flow rate of 0.5 mL min^{-1}. This flow rate was remained fixed throughout the study. The sorbed Nd(III) was eluted out by different eluting agents. Fractions of 5 mL were collected and acid was evaporated. After extracting with water, Nd(III) content was determined spectrophotometrically with arsenazo(III) [23–26] at 650 nm. The concentration of Nd(III) was calculated from a calibration graph.

Results and discussion

Adsorption of Nd(III) on poly[dibenzo-18-crown-6] as a function of hippuric acid concentration

Adsorption studies of Nd(III) were carried out in presence of hippuric acid using 40 μgmL^{-1} of Nd(III) concentration. The concentration of hippuric acid was varied from 1×10^{-2} to 1×10^{-10} M. It was found that there was quantitative sorption of Nd(III) from 1×10^{-2} to 1×10^{-8} M hippuric acid. After that, there was decrease in concentration of Nd(III). Further sorption studies of Nd(III) were carried out at 1×10^{-3} M hippuric acid concentration.

Elution studies of Nd(III) with various eluting agents

Nd(III) was eluted out from the column with different eluting agents such as HCl, H_2SO_4, $HClO_4$, CH_3COOH and HBr. Neodymium was eluted quantitatively with 0.1–8 M HCl, 0.1–8 M H_2SO_4, 0.5–8 M $HClO_4$, and 0.5–8 M HBr. But for CH_3COOH, even at 0.1–7.5 M concentration, there was 0 % elution. In order to carry out elution study, 25 ml of eluent (Vt) was used for each elution and maximum volume of eluent fraction collected (Vf) was 5.0 ml. From results, it was clear that 15 ml of 4 M HCl solution was sufficient for the complete elution of Nd(III) and therefore for further studies, it was selected as efficient eluent in this work. Elution profile of Nd(III) with different eluting agents showed in Fig. 1.

Sorption capacity of poly[dibenzo-18-crown-6]

In order to find out the capacity of poly[dibenzo-18-crown-6] for Nd(III), the concentration of Nd(III) was varied from 100–1,200 μg/10 mL in 1×10^{-3} M hippuric acid. After sorption, the elution of Nd(III) was carried out with 4 M HCl. Sorption of Nd(III) was quantitative up to 800 μg/mL. The extent of sorption of Nd(III) is decreased with increase in concentration of Nd(III). The capacity of poly[dibenzo-18-crown-6] for Nd(III) was found to be 0.55 ± 0.01 mmol/g of crown polymer.

Effect of foreign ions on recovery of Nd(III)

The effect of foreign ions on the sorption of Nd(III) was determined. Known amount of foreign ion was added to a standard Nd(III) solution and final absorbance was compared with standard. Binary mixture solutions were prepared by mixing 40 μg/ml of Nd(III) with foreign ions and hippuric acid was added so that its concentration was 1×10^{-3} M in total volume of 10 mL. Tolerance limit was set as the amount of foreign ions required to cause ±2 % deviation in the recovery of metal ion. The column was preconditioned with 1×10^{-3} M hippuric acid and binary mixture solution was passed through a poly[dibenzo-18-crown-6] column at flow rate of 0.5 mL min^{-1}. The effluent was collected and analyzed for foreign ion content. The alkaline earth metals were sorbed quantitatively. Most of alkali metals showed higher tolerance limits. But p and d block elements showed low tolerance limits. Actinides like thorium, uranium (VI) and some lanthanides like Ce(III), La(III) were sorbed along with Nd(III). Tolerance limits of anions of inorganic and organic acids were also determined as shown in Table 1.

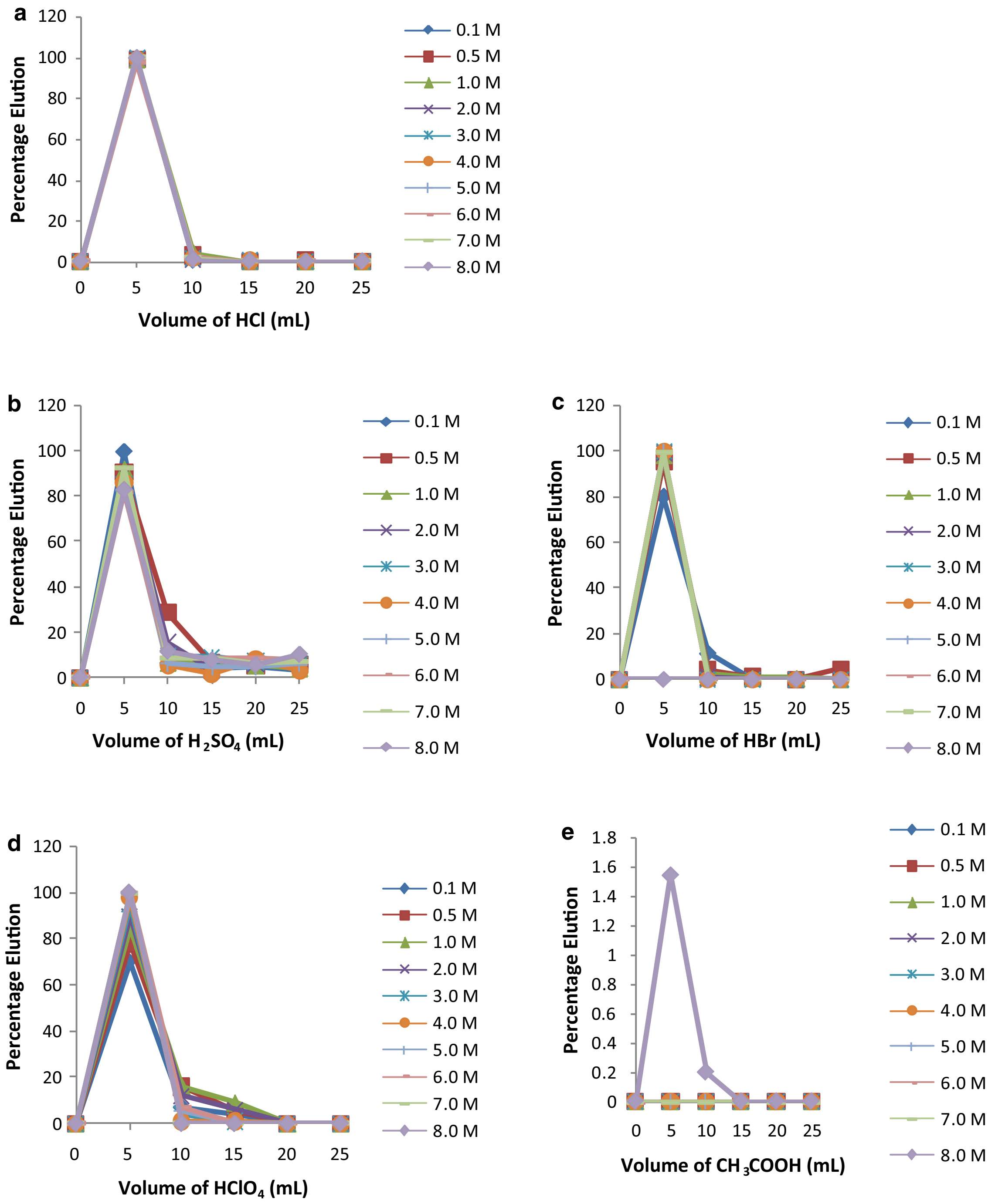

Fig. 1 **a** Elution profile of Nd(III) with HCl. **b** Elution profile of NdIII) with H_2SO_4. **c** Elution profile of Nd(III) with HBr. **d** Elution profile of Nd(III) with $HClO_4$.**e** Elution profile of Nd(III) with CH_3COOH

Separation of Nd(III) from ternary mixtures

Most of the lanthanides were sorbed on the column. We tried to achieve clear cut separation of some lanthanides from Nd(III). But we became successful only in separation of Ce(III) from Nd(III). Again ternary mixtures of Li(I)/Ca(II), U(VI)/Ba(II)/Ni(II)/Co(II)/Cd(II)/Zn(II)/Ce(III) and Nd(III) were prepared by taking known amounts of each metal ion and 1×10^{-3} M hippuric acid in total volume of 10 mL. Then for each mixture, depending upon specific eluent for each metal, separation was carried out at definite sequence of different eluents. It was observed that Li(I) and Ca(II) were not sorbed on the column. Hence they passed down the column first in the effluent while loading mixture

Table 1 Effect of foreign ions on recovery of Nd(III)

Ion	Added as	Total limit (mg)	Ion	Added as	Total limit (mg)
Li^+	LiCl	35	Sb^{3+}	$SbCl_3$	3
Na^+	NaCl	5	Y^{3+}	$Y(NO3)_3\cdot 6H_2O$	0.07
K^+	KCl	4	Cu^{2+}	$CuCl_2$	0.025
Cs^+	CsCl	40	V^{5+}	$VOSO_4\cdot 4H_2O$	0.1
$NH_4{}^+$	NH_4Cl	10	Th^{4+}	$Th(NO_3)_4 6H_2O$	0.1
Be^{2+}	$BeSO_4\cdot 4H_2O$	0.08	Mo^{6+}	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	<0.01
Mg^{2+}	$MgCl_2\cdot 6H_2O$	0.1	W^{6+}	$Na_2WO_4\cdot 4H_2O$	2
Sr^{2+}	$Sr(NO_3)_2$	0.01	Gd^{3+}	$Gd(NO_3)_3\cdot 6H_2O$	0.1
Pr^{3+}	$PrCl_3\cdot 6H_2O$	0.1	Ce^{3+}	$Ce(NO_3)_3 6H_2O$	0.1
U^{6+}	$UO_2(NO_3)_2\cdot 6H_2O$	0.1	Ca^{2+}	$CaCl_2$	5
Ba^{2+}	$Ba(NO_3)_2$	0.5	I^-	HI	5
Co^{2+}	$COCl_2\cdot 6H_2O$	1	BO^-	H_3BO_3	4
Ni^{2+}	$NiCl_2\cdot 6H_2O$	1	Oxalate	Oxalic acid	4
Mn^{2+}	$MnCl_2\cdot 4H_2O$	3	Cl^-	HCl	2
Zn^{2+}	$ZnCl_2$	2	Br^-	HBr	1
Cd^{2+}	$(CH_3COO)_2\cdot Cd\cdot H_2O$	3	SCN^-	NaSCN	4
Pb^{2+}	$Pb(NO_3)_2$	10	$ClO_4{}^-$	$HClO_4$	4
La^{3+}	$LaCl_3$	0.1	CH_3COO^-	CH_3COOH	4
Cr^{6+}	$K_2Cr_2O_7$	3	$SO_4{}^-$	H_2SO_4	4
Fe^{3+}	$FeCl_3\cdot 6H_2O$	0.3	Citrate	Citric acid	0.5
Al^{3+}	$Al_2(SO4)_3\cdot 16H_2O$	0.04	Tartarate	Tartaric acid	5
In^{3+}	$InCl_3$	0.02	H_3PO_4	H_3PO_4	5
Tl^{3+}	$Tl(NO_3)_3\cdot 3H_2O$	0.7	Ascorbate	Ascorbic acid	4

Nd(III)–40 μg mL^{-1}, sorption condition–1 × 10^{-3} M hippuric acid, eluent–4 M HCl

of metals on the column. We explain separation of one representative ternary mixure. Lets discuss separation of mixture containing Li(I), Ce(III) and Nd(III). After equilibration of the column with hippuric acid, mixture of metals was passed through poly[dibenzo-18-crown-6] column under the optimum condition of Nd(III). Li(I) was not sorbed and passed through column, which was determined by standard procedures [23–27]. Then 25 ml 7.5 M acetic acid was passed through column. At this stage, Ce(III) was eluted out of the column, but Nd(III) remains as it is on the column. This eluted Ce(III) was determined spectrophotometrically [23–26]. Then after that 25 mL 5 M HCl was passed through the column. At this stage Nd(III) was eluted out which was determined by standard methods [17–21]. In this way, we can separate further mixtures as shown in Table 2 by using specific eluents for corresponding metals sequentially.

Separation of Nd(III) from multicomponent mixtures

Nd(III) was separated from different mixtures of different metals prepared by taking known volumes of Li(I)/Ca(II), Ce(III),U(VI), Nd(III), Ba(II)/Ni(II)/Co(II)/Cd(II)/Zn(II). For each Mixture preparation, there was different combinations of specific metals which are described above. We explain separation of one representative multicomponent mixture. Lets discuss separation of mixture containing known amounts of Ca(II), U(VI), Ce(III) and Nd(III). After equilibration of the column with hippuric acid, mixture of metals was passed through poly[dibenzo-18-crown-6] column under the optimum condition of Nd(III). Ca(II) was not sorbed and passed through column, which was determined by standard procedures [23–27]. Then 25 mL 0.2 M ammonium carbonate was passed through the column. At this stage, U(VI) was eluted out which was determined spectrophotometrically by standard procedures [23–27], but Ce(III) and Nd(III) remained as it is on the column. After that 25 mL 7.5 M acetic acid was passed through column. At this stage, Ce(III) eluted out of the column, but Nd(III) remains as it is on the column. This eluted Ce(III) was determined spectrophotometrically [23–26]. Finally Nd(III) was eluted out with 5 M HCl and determined by standard methods [17–21]. The results were shown in Table 3 and Fig. 2. In this way, we can separate further mixtures as shown in Table 3 by using specific eluents for corresponding metals sequentially.

Table 2 Separation of Nd(III) from ternary mixture

Sr. no.	Mixture	Recovery[a]%	SD (±)	Eluent
1	Li(I)	100	0	NAPC
	U(VI)	98.57	0.12	0.2 M AC
	Nd(III)	99.21	0.13	4 M HCl
2	Li(I)	100	0	NAPC
	Co(II)	98.73	0.14	0.5 M AA
	Nd(III)	98.88	0.35	4 M HCl
3	Li(I)	100	0	NAPC
	Cd(II)	99.26	0.18	0.5 M AA
	Nd(III)	98.92	0.24	5 M HCl
4	Li(I)	100	0	NAPC
	Nd(III)	99.76	0.25	1 M $HClO_4$
	Ba(II)	98.41	0.38	5 M HCl
5	Li(I)	100	0	NAPC
	Ni(II)	99.13	0.37	0.5 M AA
	Nd(III)	99.81	0.22	5 M HCl
6	Li(I)	100	0	NAPC
	Zn(II)	99.13	0.22	0.5 M AA
	Nd(III)	99.47	0.11	5 M HCl
7	Li(I)	100	0	NAPC
	Ce(III)	99.28	0.35	7.5 M AA
	Nd(III)	97.84	0.28	5 M HCl
8	Ca(II)	100	0	NAPC
	Co(II)	99.25	0.17	0.5 M AA
	Nd(III)	99.82	0.16	5 M HCl
9	Ca(II)	100	0	NAPC
	Zn(II)	99.46	0.38	0.5 M AA
	Nd(III)	98.87	0.11	5 M HCl
10	Ca(II)	100	0	NAPC
	Ni(II)	99.23	0.15	0.5 M AA
	Nd(III)	99.94	0.52	5 M HCl
11	Ca(II)	100	0	NAPC
	Cd(II)	99.19	0.35	0.5 M AA
	Nd(III)	97.31	0.14	5 M HCl
12	Ca(II)	100	0	NAPC
	U(VI)	99.41	0.67	0.2 M AC
	Nd(III)	99.78	0.27	5 M HCl

Sorption condition–1 × 10^{-3} M hippuric acid, Amount of each metal ion taken–50 μg

NAPC no adsorption passing through column, *AA* acetic acid, *AC* ammonium carbonate, *SD* standard deviation

[a] Average of triplicate analysis

Comparison of the present method with other methods for the separation of Nd(III)

It was observed that crown polymer has relatively high sorption capacity as compared to other sorbents like Amberlite XAD-4-bicine resin, grafted resin MCM-CMPO etc. shown in Table 4. Even same crown polymer shows higher sorption capacity for Nd(III) in hippuric acid as compared with Th(IV) in glycine. Sorption capacity is very significant factor in column chromatography. It determines maximum sorption limit of stationary phase for corresponding analyte. More numbers of mixtures containing different elements are separated. Hence our method is superior.

Table 3 Separation of Nd(III) from associated elements (multicomponent mixture)

Sr. no.	Mixture	Recovery[a]%	SD (±)	Eluent
1	Li(I)	100	0	NAPC
	U(VI)	98.16	0.27	0.2 M AC
	Ni(II)	98.84	0.25	0.5 M AA
	Nd(III)	98.66	0.37	5 M HCl
2	Ca(II)	100	0	NAPC
	U(VI)	98.71	0.14	0.2 M AC
	Zn(II)	98.63	0.34	0.5 M AA
	Nd(III)	98.56	0.38	5 M HCl
3	Li(I)	100	0	NAPC
	U(VI)	98.33	0.34	0.2 M AC
	Co(II)	99.15	0.57	0.5 M AA
	Nd(III)	98.74	0.38	5 M HCl
4	Ca(II)	100	0	NAPC
	U(VI)	99.14	0.28	0.2 M AC
	Cd(II)	97.32	0.34	0.5 M AA
	Nd(III)	98.68	0.18	5 M HCl
5	Li(I)	100	0	NAPC
	U(VI)	98.16	0.27	0.2 M AC
	Ce(III)	98.84	0.25	7.5 M AA
	Nd(III)	98.66	0.37	5 M HCl

Sorption condition–1 × 10^{-3} M hippuric acid, Amount of each metal ion taken–50 μg

NAPC no adsorption passing through column, *AA* acetic acid, *AC* ammonium carbonate, *SD* standard deviation

[a] Average of triplicate analysis

Conclusions

Taking into account all above results, we can conclude that the developed method is very useful for selective separation of Nd(III) from Ce(III), U(VI) and other elements which are contributing to spent fuel and are associated with fission product. Poly[dibenzo-18-crown-6] has better capacity for Nd(III) and also has important analytical application as stationary phase for Nd(III). The developed method is superior because of its simplicity, selectivity and reproducibility. Precision in terms of the standard deviation

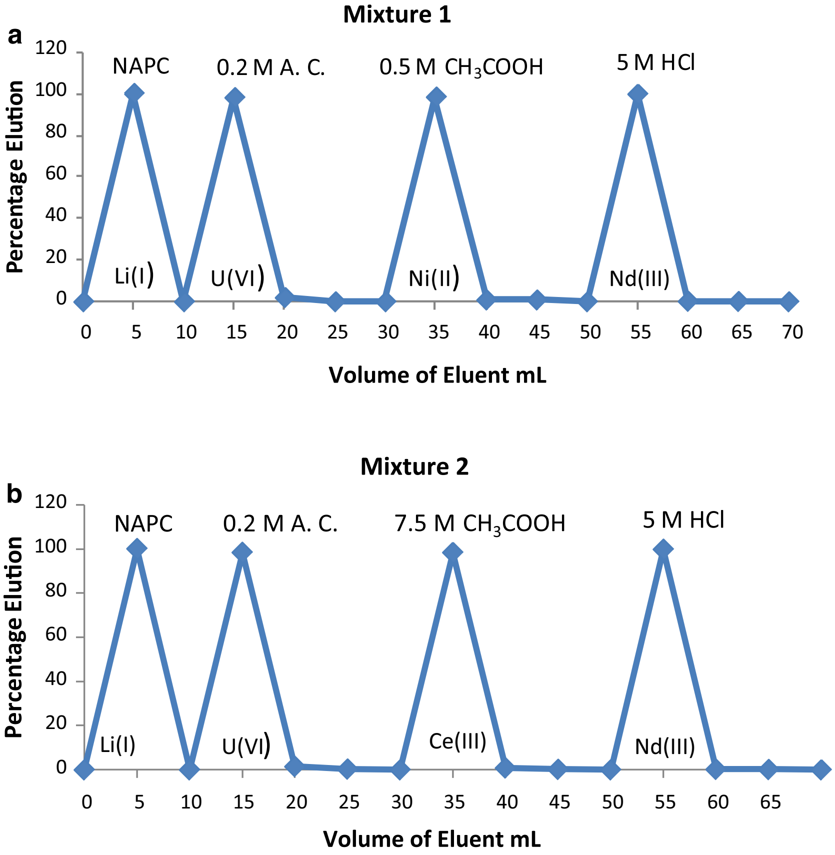

Fig. 2 Chromatograms of multicomponent mixtures **a** Separation of Li(I), U(VI), Ni(III), Nd(III). **b** Separation of Li(I), U(VI), Ce(III), Nd(III)

Table 4 A comparison of the present method with other solid phase extraction and extraction chromatographic method for the separation of Nd(III)

Sr. no.	Sorbent	Condition	Sorption capacity (mmol/g)	Separation	Ref. no
1	Grafted resin MCM-CMPO	4 M HNO_3, 4 M HCl	0.502	U(VI), La(III), Th(IV), Nd(III)	[3]
2	Amberlite XAD-4-bicine resin	pH = 7.58	0.40	Ni(II)/Zn(II)/Co(II)/Cu(II), U(VI)	[28]
2	Poly[dibenzo-18-crown-6]	1×10^{-3} M glycine	0.215	U(VI), Th(IV), K(I)	[22]
3	ICABs modified silica gel	pH = 2.1–3.4	0.0693	La(III), Nd(III), Gd(III), Sm(III), Pr(III)	[29]
4	Poly[dibenzo-18-crown-6]	1×10^{-3} M hippuric acid	0.55	Li(I)/Ca(II), U(VI), Nd(III), Co(II)/Ni(II)/Cd(II)Zn(II)/Ba(II)	Present method

of the present method is very retainable for the determination of Nd(III).

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