Reversed Phase Partition Chromatographic Separation of Gd(III) From Hippuric Acid on Poly[Dibenzo-18-Crown-6]

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Abstract

A simple method has been developed for the separation of Gd(III) in hippuric acid medium by using poly[dibenzo-18-crown-6] as stationary phase. The effect of hippuric acid concentration, different eluting agent, foreign ions etc. was studied and the optimum conditions were established. Breakthrough capacity of poly[dibenzo-18-crown-6] for Gd(III) was found to be 0.572±0.01 mmol/g of crown polymer. The separation of Gd(III) from other elements in multicomponent mixtures has been achieved. The method was extended for determination of Gd(III) in real sample. The method is simple, rapid and selective with good reproducibility (approximately ±2%).

Keywords: Gd(III); poly[dibenzo18-crown-6]; hippuric acid; sorption; separation.

1. Introduction

In recent years, the separation chemistry of rare earth elements (REE) continues to receive a growing interest. The major reasons for this stems from, the importance of rare earths not only in their industrial applications, but also in energy generation related activities as well as their environmental mitigation. Gadolinium is useful in nuclear technique in fuel element fabrication and as control rods and as refractory materials and in ceramic industries [1,2]. In view of all above applications the separation and purification of Gd(III) is important.

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 [3].Various methods were adopted for separation of lanthanides and actinides, which include precipitation [4] and co-precipitation [5] and ion exchange chromatography systems [6]. But over the years extraction chromatography (EC) has been proved to be promising in this aspect because of simple operation.

Macrocyclic polyethers generally called as “crown ethers” have gained attention due to their special selectivity arising presumably from their ring-size comparable with the ionic radii of certain alkali metals [7–11]. The resistance to certain chemicals like organic solvents e.g. acetone, alcohols, chloroform as well as mineral acids like hydrochloric, sulfuric, bromic acid by poly[dibenzo-18-crown-6] could potentially be advantageous with respect to the sorption of various cations using column chromatography. Crown ethers are widely popular and used as complexing agents that can selectively capture certain metal cations in their cavity based on their size. This special chemical property exhibited by poly [dibenzo-18-crown-6] has been continuously explored in our laboratory for selective cation exchanger by column chromatography [12-14].

To our knowledge, no successful attempts were reported in the literature for the separation of Gd (III) using hippuric acid media and column chromatography. The present communication describes a simple and sensitive method for the determination of Gd(III) using poly[dibenzo-18-crown-6] as stationary phase in hippuric acid medium. In our study we use hippuric acid as the counter ion. The counter ion plays an important role in the complexation of crown ether and the metal ion. The proposed method affords an attractive feature as compared to the solvent extraction technique i.e. it is free from any organic diluents, leading to potential green chemistry applications.

2. Methods

2.1. Apparatus and reagents

A Ziess (Germany) spectrophotometer, 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. All chemicals used are of analytical grade.

A stock solution of Gd(III) was prepared by dissolving 1.09 g of Gadolinium nitrate (AnalR grade, BDH, Poole, UK) in 100 mL of distilled deionised water and standardized gravimetrically [16]. A solution containing 100 μg/mL of Gd(III) was prepared by appropriate dilution of the standard stock solution. Hippuric acid solution (1×10^{-1} M) was prepared by dissolving 1.798 g of hippuric acid in distilled deionised water and diluted to 100 mL.

Poly[dibenzo-18-crown-6] from (Merck Darmstadt, Germany) was used after screening to 100-200 mesh. A total of 0.5 g of polymer was slurred with distilled deionised water and poured into a Pyrex glass chromatographic column (20×0.8 cm i.d.). The column was used after preconditioning with hippuric acid solution.

2.2. General procedure

100 μg of Gd(III) was mixed with hippuric acid solution in the concentration range of 1×10^{-2} to 1×10^{-7} M in a total volume of 10 mL. The solution was passed through poly[dibenzo-18-crown-6] column preconditioned with same concentration of hippuric acid as that of the sample solution at flow rate of 0.5 mL/min. Afterwards the column was washed with the same concentration of hippuric acid, and the sorbed Gd(III) was then eluted with different eluting agents at the flow rate of 0.5 mL/min. 5.0 mL fractions were collected and the Gd(III) content was determined spectrophotometrically with Arsenazo(III) [17] at 650 nm. The concentration of Gd(III) was calculated from a calibration graph.

3. Results and Discussion

3.1. Sorption of Gd(III) on poly[dibenzo-18-crown-6] as a function of hippuric acid concentration

Sorption studies of Gd(III) were carried out from hippuric acid medium using 100 μg of Gd(III). The concentration of hippuric acid varied from 1×10^{-2} to 1×10^{-7} M. It was found that there was quantitative sorption of Gd(III) from 1×10^{-2} to 1×10^{-5} M hippuric acid as shown in table 1. Sorbed Gd(III) was eluted with 2.0 M HBr. The subsequent sorption studies of Gd(III) were carried out with 1×10^{-4} M hippuric acid.

Table 1: Sorption of Gd(III) as a function of hippuric acid concentration. Gd(III) - 100 μg/mL, Eluent - 2.0 M HBr

Hippuric acid concentration (M)	Sorption of Gd(III) (%)
1×10^{-2}	98.5
1×10^{-3}	100
1×10^{-4}	100
1×10^{-5}	100
1×10^{-6}	96.0
1×10^{-7}	92.5

3.2. Elution studies of Gd(III) with various eluting agents

Gd(III) was eluted out from the column with different strength of acids such as HCl, H_2SO_4, $HClO_4$, CH_3COOH and HBr. The concentration of eluting agents were varied from 0.1 to 8.0 M. Gd(III) was eluted quantitatively with 1-8.0

M $HClO_4$, and 0.5-3.0 M HBr. However, in our studies we found that HCl, H_2SO_4, CH_3COOH were found to be an inefficient eluents for Gd(III). Further the elution study of Gd(III) in this work was carried out with 1.0 M HBr, as shown in Figure 1. We choose 1.0 M HBr for metal ions separation in multicomponent mixtures because it forms strong bromo- complex. Elution profile of various eluting agents is shown in Figure 2.

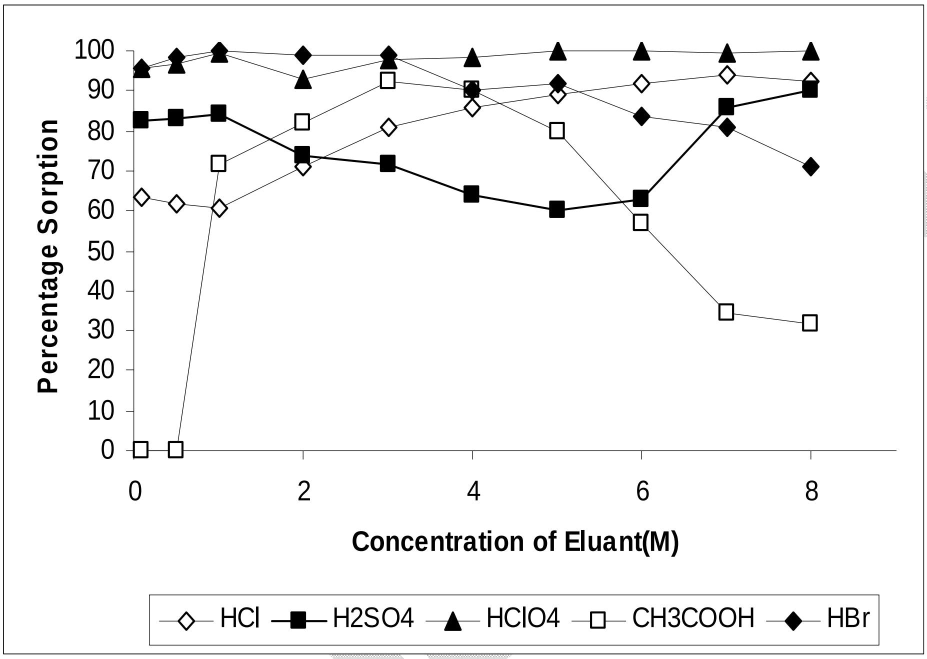

Figure 1: Elution profile of Gd(III) with various eluting agents.

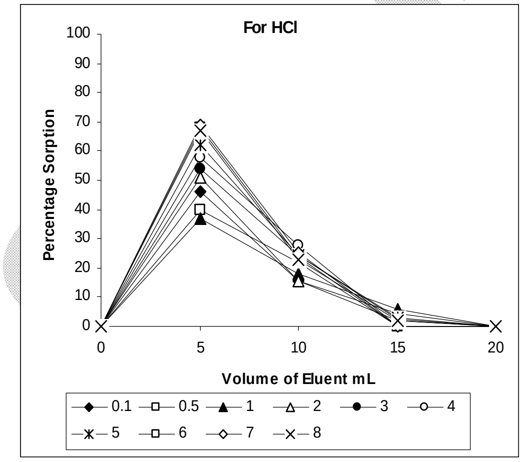

Figure 2a: Elution profile of HCl.

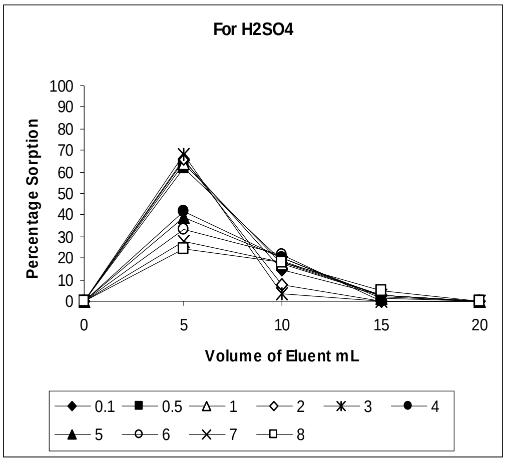

Figure 2b: Elution profile of H_2SO_4.

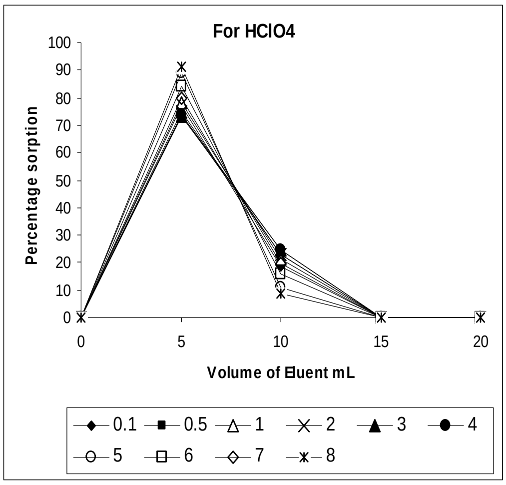

Figure 2c: Elution profile of $HClO_4$.

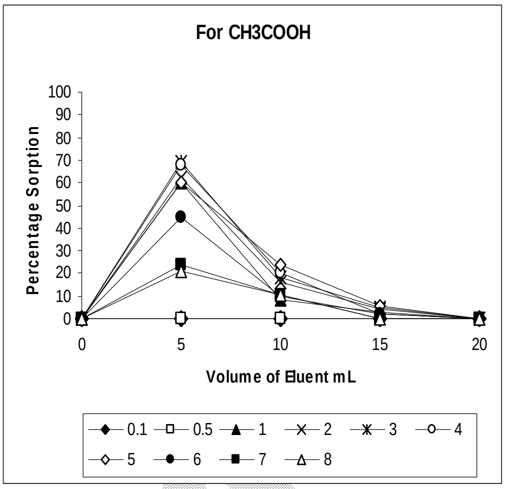

Figure 2d: Elution profile of CH_3COOH.

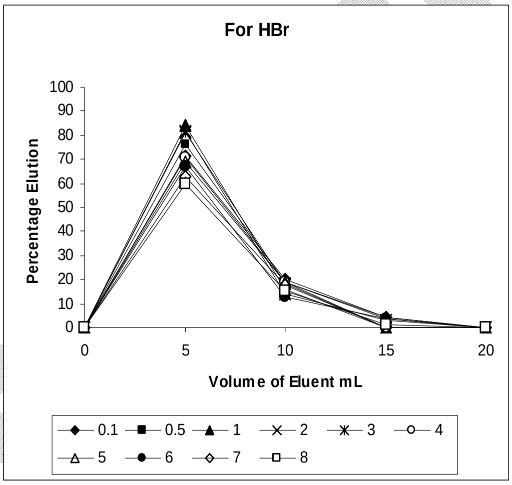

Figure 2e: Elution profile of HBr.

3.3. Breakthrough capacity of poly[dibenzo-18-crown-6]

The breakthrough capacity for Gd(III) was carried out on 1.0 g of poly[dibenzo-18-crown-6] with 1×10^{-4} M hippuric acid. The volume of Gd(III) sample solution employed was 10.0 mL. The concentration of Gd(III) was varied from 100 to 800 μg of Gd (III)/10.0 mL solution. After sorption, the elution of Gd(III) was carried out with 1.0 M HBr at a flow rate of 0.5 ml/ min. From the results shown in Figure 3, it is clear that the sorption of Gd(III) was quantitative up to 450 μg/10 mL. The extent of sorption of Gd(III) is decreased with increase in concentration of Gd(III). From the study it was found that the breakthrough capacity of poly[dibenzo-18-crown-6] for Gd(III) was found to be 0.572±0.01 mmol/g of crown polymer.

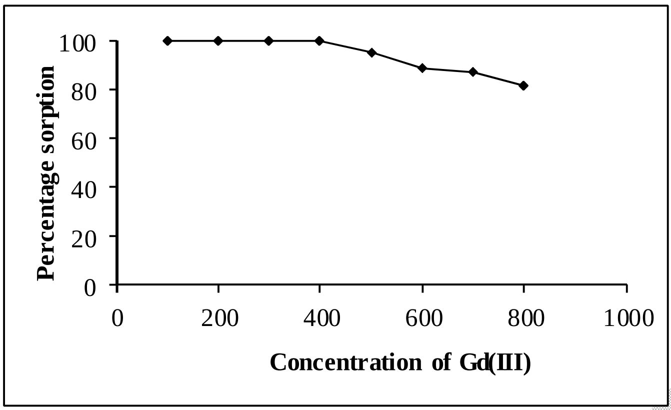

Figure 3: Effect of varying concentration of Gd(III).

3.4. Diverse ion effect

The effect of foreign ions on the sorption of Gd(III) was investigated by adding known amount of foreign ion to a standard Gd(III) solution and by comparing the final absorbance with standard. An aliquot of solution containing 100 µg of Gd(III) was mixed with foreign ions and hippuric acid was added so that its concentration was 1×10^{-4} M in total volume of 10 mL. The tolerance limit of other ions which do not cause a deviation of more than 2% in the absorbance in determination of Gd(III) is given in table 2. The column was equilibrated with 1×10^{-4} 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. Various foreign ions were not sorbed and hence passed through the column. The results show that most common ions do not interfere with the determination. The effluent was collected and analyzed for foreign ion content. Zn(II), Cd(II), Ni(II) and Th(IV) were sorbed quantitatively and there separation is carried out in our subsequent study employing multicomponent mixtures.

Table 2: Separation of Gd (III) from binary mixtures.

Gd(III) - 100 µg, sorption - 1×10^{-4} M hippuric acid, eluent - 1.0 M HBr

Ion	Added as	Tol. Limit (mg)	Ion	Added as	Tol. Limit (mg)
Li^+	LiCl	4	Al^{3+}	$Al_2(SO_4)_3.16H_2O$	1
Na^+	NaCl	8	Zr^{4+}	$Zr(NO_3)_4.4H_2O$	0.5
K^+	KCl	3	La^{3+}	$La(NO_3)_3$	0.5
Rb^+	RbCl	1	Ce^{3+}	$CeCl_2.6H_2O$	1
Cs^+	CsCl	3	V^{4+}	$VOSO_4.4H_2O$	2
NH_4^+	NH_4Cl	2	Th^{4+}	$Th(NO_3)_4$	0.5
Be^{2+}	$BeSO_4.4H_2O$	0.5	W^{6+}	$Na_2WO_4.4H_2O$	3
Ca^{2+}	$CaCl_2$	0.1	U^{6+}	$UO_2(NO_3)_2.6H_2O$	0.2
Sr^{2+}	$Sr(NO_3)_2$	0.2	Cl^-	HCl	2
Ba^{2+}	$Ba(NO_3)_2$	0.8	Br^-	HBr	2
Co^{2+}	$CoCl_2.6H_2O$	1	SCN^-	NaSCN	4
Ni^{2+}	$NiCl_2.6H_2O$	0.5	ClO_4^-	$HClO_4$	4
Mn^{2+}	$MnCl_2.4H_2O$	2	CH_3COO^-	CH_3COOH	3
Zn^{2+}	$ZnCl_2$	2	SO_4^{2-}	H_2SO_4	0.6
Cd^{2+}	$(CH_3COO)_2Cd.H_2O$	5	Tartrate	Tartaric acid	3
Pb^{2+}	$Pb(NO_3)_2$	1	EDTA	EDTA	10
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	0.5	Ascorbate	Ascorbic acid	12
Fe^{3+}	$FeCl_3.6H_2O$	0.5	Citrate	Citric acid	6
Cu^{2+}	$CuCl_2$	2			

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3.5. Sequential separation of Gd(III) from other elements (multicomponent mixtures)

The mixture of Sr(II), Mg(II), Ca(II), Zn(II), Ni(II), Cd(II),Th(IV) and Gd(III) was mixed with 1×10^{-4} M hippuric acid in a total volume of 10ml. Sr(II)/ Mg(II)/Ca(II) were not sorbed and passed through column. Zn(II), Ni(II), Cd(II) and Th(IV) sorbed on the column along with Gd(III). Th(IV) was eluted with 0.2 M ammonium oxalate at this condition Zn(II)/ Ni(II)/ Cd(II) and Gd(III) were not eluted and remained on the column. Then Zn(II)/ Ni(II)/ Cd(II) eluted with 0.5 M CH_3COOH and the remaining Gd(III) on the column was eluted with 1.0 M HBr and determined by standard methods [15,16] as shown in table 3 and chromatograms of all metal ions shown in Figure 4.

Table 3: Separation of Gd(III) from other elements (multicomponent mixtures).

Mixture	Taken µg	Recovery* %	SD	Eluent
Sr(II)	50	98.16	±0.25	NSPC**
Th(IV)	50	98.78	±0.07	0.2 M A.O.
Zn(II)	50	97.83	±0.01	0.5 M CH_3COOH
Gd(III)	50	98.94	±0.01	1.0 M HBr
Ca(II)	50	99.01	±0.06	NSPC
Th(IV)	50	97.86	±0.37	0.2 M A.O.
Ni(II)	50	98.12	±0.10	0.5 M CH_3COOH.
Gd(III)	50	100.00	±0.01	1.0 M HBr
Mg (II)	50	99.01	±0.20	NSPC
Th(IV)	50	99.21	±0.94	0.2 M A.O.
Cd(II)	50	98.60	±0.26	0.5 M CH_3COOH
Gd (III)	50	98.10	±0.06	1.0 M HBr
Mg(II)	50	98.41	±0.41	NSPC
Th(IV)	50	98.12	±0.10	0.2 M A.O.
Ni(II)	50	97.51	±0.11	0.5 M CH_3COOH
Gd(III)	50	100.00	±0.06	1.0 M HBr
Sr(II)	50	99.11	±0.05	NSPC
Th(IV)	50	98.61	±0.50	0.2 M A.O.
Ni(II)	50	97.56	±0.03	0.5 M CH_3COOH
Gd(III)	50	99.31	±0.12	1.0 M HBr
Ca(II)	50	100.00	-	NSPC
Th(IV)	50	98.11	±0.64	0.2 M A.O.
Zn(II)	50	97.92	±0.65	0.5 M CH_3COOH
Gd(III)	50	99.12	±0.06	1.0 M HBr

*Average of triplicate analysis
**NSPC - No Sorption Passing through the Column
A.O. - Ammonium oxalate

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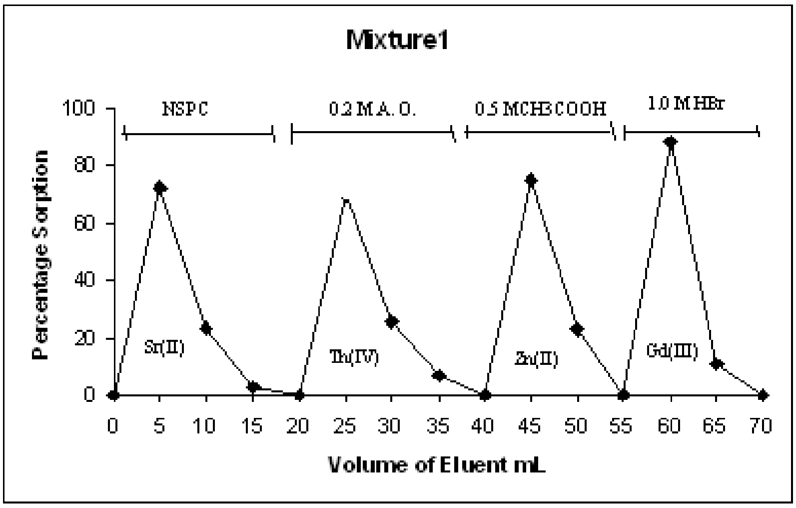

Figure 4a: Separation of Sr(II), Th(IV), Zn(II), Gd(III).

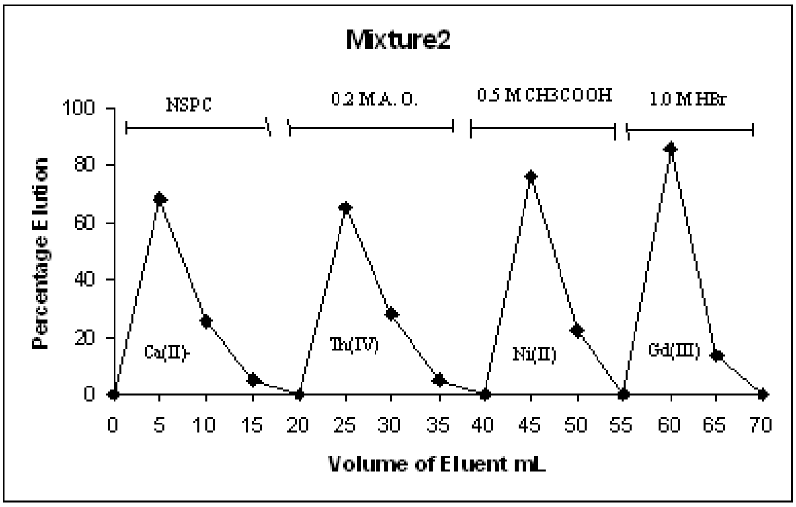

Figure 4b: Separation of Ca(II), Th(IV), Ni(II), Gd(III).

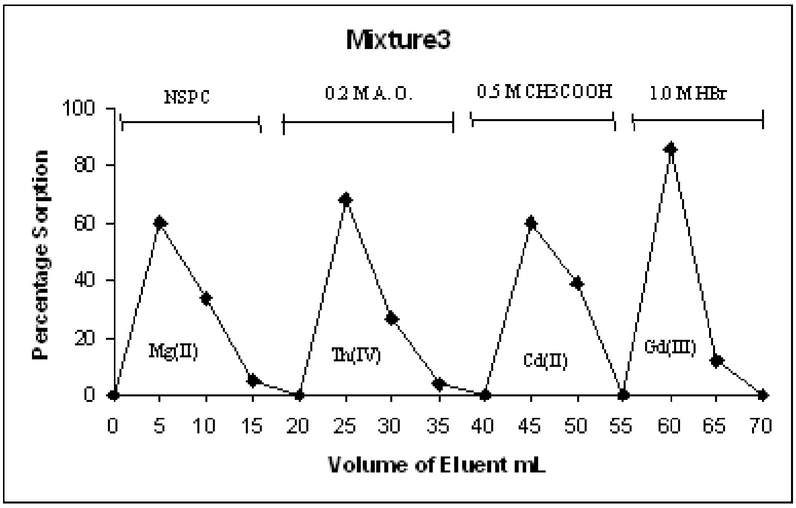

Figure 4c: Separation of Mg(II), Th(IV), Cd(II), Gd(III).

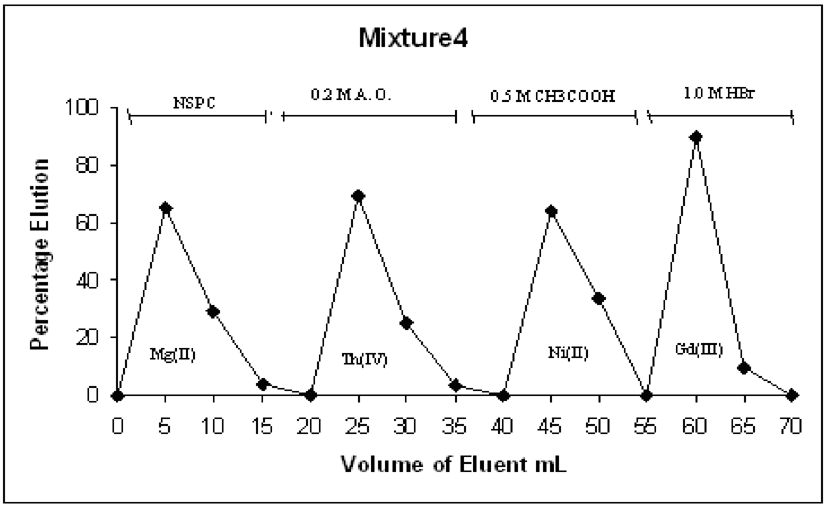

Figure 4d: Separation of Mg(II), Th(IV), Ni(II), Gd(III).

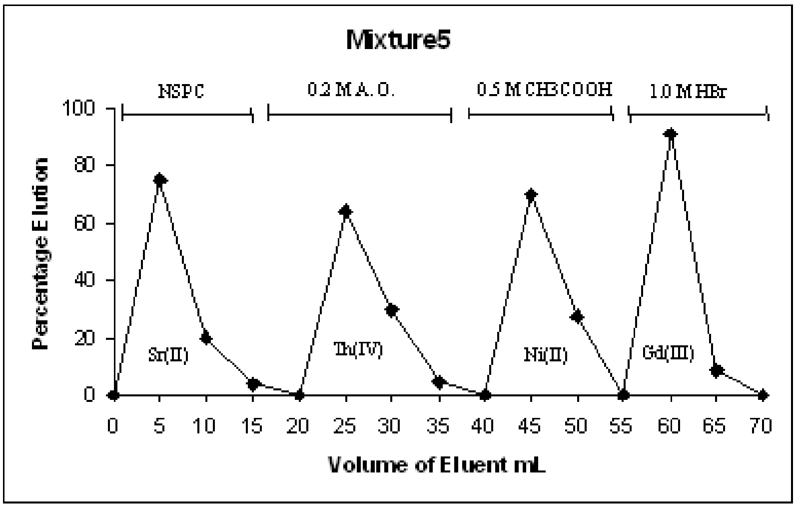

Figure 4e: Separation of Sr(II), Th(IV), Ni(II), Gd(III).

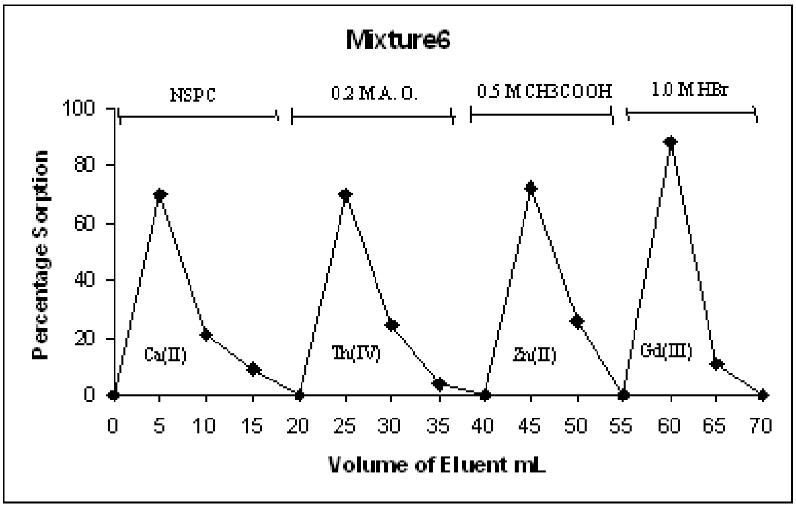

Figure 4f: Separation of Ca(II), Th(IV), Zn(II), Gd(III).

Figure 4 (a-f): Chromatograms of multicomponent mixture separation.

3.6. Reproducibility of method

Reproducibility of the method was checked by thirty replicate analysis of a standard Gd(III) solution. The results indicate the method to be fairly reproducible. The poly[dibenzo-18-crown-6] could be recycled many times without affecting its sorption capacity. The reusability of poly[dibenzo-18-crown-6] with standard deviations is shown in table 4.

Table 4: Reproducibility of method.

S. No.	Gd(III) 100 µg	Recovery (%)	S.D.
1	100	99.86	±0.06
2	100	99.60	±0.07
3	100	99.32	±0.38
4	100	98.90	±0.61
5	100	99.96	±0.33
6	100	98.96	±0.05
7	100	99.70	±0.27
8	100	99.61	±0.11
9	100	99.39	±0.05
10	100	99.73	±0.17
11	100	98.60	±0.79
12	100	99.86	±0.43
13	100	99.81	±0.36
14	100	99.62	±0.21
15	100	100	±0.09
16	100	99.71	±0.76
17	100	100	±0.51
18	100	99.16	±0.01
19	100	98.86	±0.20
20	100	99.61	±0.17
21	100	99.52	±0.43
22	100	98.9	±0.17
23	100	99.16	±0.02
24	100	99.9	±0.01
25	100	100	±0.01
26	100	100	±0.21
27	100	99.66	±0.66
28	100	99.89	±0.08
29	100	99.98	±0.41
30	100	99.56	±0.01

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3.7. Determination of Gd(III) from real samples (composite materials)

The composite material samples after acid treatment are subjected to proposed method for the determination of Gd(III). The percentage of Gd(III) found after triplicate analysis is shown in table 5.

Table 5: Determination of Gd(III) from real sample.

Sample	Percentage of Gd(III)	
	Certified value	Proposed method
$GdSrO_2$	10.0 %	9.88 % (±0.21)

4. Conclusion

Proposed method is simple, rapid, highly selective and easily reproducible for the separation and determination of Gd(III). Low reagent and acid concentration are required for quantitative recovery of Gd(III). The poly[dibenzo-18-crown-6] could be recycled many times without affecting its sorption capacity i.e. it has higher stability as a stationary phase. It permits the separation of Gd(III) from other elements. Precision in terms of the standard deviation of the present method are very retainable for the determination of Gd(III).

Competing Interests

We have no competing interests.

Authors' Contributions

BSM, SRS, KRM made the plan, explained data. KRM dissected the results involved in the preparation of manuscript, carried out experimental work. NSM, GHN provided literature survey.

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