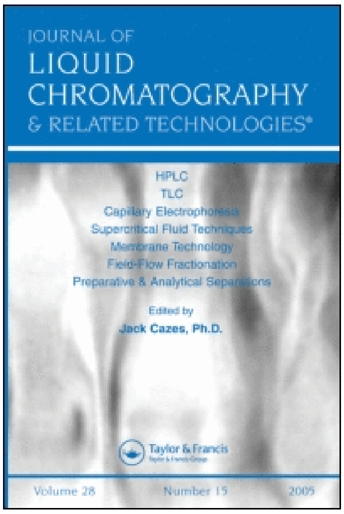

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P. G. Jaison[a]; Pranaw Kumar[a]; Vijay M. Telmore[a]; Suresh K. Aggarwal[a]
[a] Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India

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Comparative Study of Ion Interaction Reagents for the Separation of Lanthanides by Reversed-Phase High Performance Liquid Chromatography (RP-HPLC)

P. G. Jaison, Pranaw Kumar, Vijay M. Telmore, and Suresh K. Aggarwal

Fuel Chemistry Division, Bhabha Atomic Research Centre,
Trombay, Mumbai, India

Abstract: A study of two ion interaction reagents (IIRs) viz. *n*-octadecane sulphonate (C_{18}-sulphonate) and eicosyl sulphate (C_{20}-sulphate) was carried out for the separation of lanthanides by reversed-phase high performance liquid chromatography (RP–HPLC). The objective of the study was to identify a suitable IIR offering long term adsorption onto the RP column, thereby obviating the need to introduce the IIR in the mobile phase during the separation of lanthanides. This avoids the rigorous treatment of purified fractions before their mass spectrometric analysis. Resolution was used for comparing different IIRs for separation of lanthanides under identical chromatographic conditions, employing α-hydroxy isobutyric acid (α-HIBA) as an eluent. The volume and composition of IIR solution required for the modification of the column, as well as their long term adsorption, were studied. Columns coated with C_{18}-sulphonate and C_{20}-sulphate allowed the separation of lanthanides without introducing the IIR in the mobile phase. Between these two IIRs, C_{18}-sulphonate offered higher resolution and provided good long term adsorption stability. A RP column modified with C_{18}-sulphonate, as per the optimised procedure, was used for the separation of lanthanides from a geological reference sample without the need to include IIR into the mobile phase.

Keywords: HPLC, Ion interaction reagents, Lanthanides, Modification, Resolution, Reversed-phase

Correspondence: Suresh K. Aggarwal and P. G. Jaison, Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India. E-mail: skaggr2002@rediffmain; pg_jaison@yahoo.com

INTRODUCTION

Separation and determination of lanthanides is of interest in geochemistry, environmental sciences, mineral exploration, material science, and in the nuclear industry.[1–8] Individual separation of lanthanides is a challenging task due to the similarities in their ionic radii and the existence of most of these metal ions in trivalent oxidation state.[9–12] Among the analytical scale techniques for individual separation of lanthanides, the widely used methods are based on high performance liquid chromatography (HPLC) based either on bonded phase cation exchangers[13–15] or on ion interaction chromatography (also known as ion pair chromatography or dynamically modified reversed-phase chromatography).[16–19] Though bonded ion exchanger columns offer high capacity, they yield poor resolution due to peak broadening and longer retention times. Ion interaction chromatography offers the advantages such as high resolution resulting from faster mass transfer at the surface of the ion exchanger and the possibility for replenishment of damaged exchange groups due to radiolysis when dealing with radioactive samples.[20] Thus, ion interaction chromatography in combination with post-column detection has been used for the determination of lanthanides in complex matrices.[21–23]

One of the applications demanding individual separation of lanthanides is the isolation of La and Nd used as burnup monitors for irradiated nuclear fuels.[24–27] Previously, studies have been carried out in our lab on the comparison of three homologues of hydroxy carboxylic acids for the separation of lanthanides; sequential separation of lanthanides, Th and U; and separation of lanthanides in the presence of large amounts of Th employing particulate C_{18} column as stationary phase and C_8 sulphonate as the IIR.[16,26,27] The IIRs employed are not easily destroyed by chemical treatments, and their presence in the separated lanthanide fractions lowers the ionization efficiency during subsequent isotope ratio measurements by thermal ionization mass spectrometry (TIMS). Elaborate treatment of the collected fractions with HNO_3 and H_2O_2 is needed for the destruction of the IIR prior to loading of solution onto the filament for analysis by TIMS.[28] The objective of the present study was to identify an IIR, which would remain sorbed on the column for a considerably long time and thus, subsequently, need not be added to the mobile phase when running the samples. Use of C_{20}-sulphate prepared in 25% acetonitrile as IIR was reported for the separation of lanthanides for the determination of burnup of irradiated nuclear fuel samples.[17,20] This paper presents the detailed studies carried out using the two IIRs viz. n-octadecane sulphonate (C_{18}-sulphonate) and eicosyl sulphate (C_{20}-sulphate) for the separation of lanthanides. Since the two IIRs contain two different functional groups, C_8-sulphate and C_8-sulphonate were also included in the comparative study to find out the effect of different functional groups on the separation of lanthanides. In chromatography, separation efficiency is assessed by determining the reduced plate height.[29] In the present work, we have used resolution, which is related to number of theoretical plates, as a measure of column efficiency.[30] Volume and composition of the IIR and volumes of washings with water and mobile phase etc., for the proper equilibration of the column were optimized for each IIR. The long term adsorption of these IIRs onto the stationary phase was also studied. Better resolutions for the separation of lanthanides were obtained with a RP column, modified using C_{18}-sulphonate as compared to C_{20}-sulphate. The preference of the stationary phase for C_{18}-sulphonate over C_{20}-sulphate is believed to be due to the similarity in the number of carbon atoms in the carbon chain. In order to support this assumption, comparative studies have been carried out using C_8-sulphonate and n-nonane sulphonate (C_9-sulphonate) employing C_8 and C_{18} stationary phases. The column modified with C_{18}-sulphonate was demonstrated for the separation of lanthanides in a synthetic mixture and also in a geological reference material.

EXPERIMENTAL

Instrumentation

The HPLC setup consisted of an L-7100 (LaChrom) low pressure quaternary gradient pump and an L-7420 (LaChrom) variable wavelength detector. A C_{18} monolith RP column (100 mm × 4.6 mm, Merck Chromolith) and a C_8 Purospher STAR particulate column (150 mm × 4.6 mm, 5 μm particle size) were used as stationary phases. Samples were injected into the column using a Rheodyne injector (Model 7725i) with 100 μL sample loop. The eluted components were monitored after post-column reaction (PCR) with a metallochromic reagent, which was added with a reciprocating pump (Eldex Laboratories Inc.) into a low dead volume mixing tee (Valco). The signal from the detector was processed by HSM software package.

Reagents

All solutions were prepared using the deionised water obtained from the Milli-Q system (Millipore). α-Hydroxy IsoButyric Acid (α-HIBA) purchased from Lancaster was used as an eluent. The reagents used as IIRs are sodium n-octane sulphonate (Fluka), sodium n-octane sulphate (Alfa-Aesar), sodium n-nonane sulphonate (Fluka), n-octadecyl sulphonate

(Alfa-Aesar), and sodium n-eicosyl sulphate (Regis Technologies Inc). A mixture of 14 lanthanides was prepared from the stock solutions of individual lanthanides using the procedure mentioned elsewhere.[26] High purity reagents such as HNO_3, HF, NH_4OH, MeOH, CH_3CN etc., used during the sample treatment and preparation of IIRs, were obtained from Merck. Arsenazo(III) (Fluka) was used as a post-column reagent. Geological reference material (SY-3) of Canadian Geological Survey was used for the validation of the separation procedure.

Procedure

All the experiments were conducted at room temperature (25°C). Different IIRs viz. C_8-sulphonate, C_8-sulphate, C_9-sulphonate, C_{18}-sulphonate and C_{20}-sulphate were used for the separation of lanthanides with one IIR at a time. Appropriate quantities of C_8-sulphonate, C_8-sulphate, and C_9-sulphonate were dissolved in water to prepare 0.1 M solutions. The mobile phase used for the elution of lanthanides under dynamically modified conditions, consisted of 7% (v/v) (0.007 M) of these IIRs. Each 2.5×10^{-4} M of C_{18}-sulphonate and C_{20}-sulphate were prepared in 30% MeOH. All the solutions were filtered through a 0.45 µm Millipore membrane filter before use. HPLC columns were equilibrated by passing required volume of the specific IIR before carrying out the separation studies. α-HIBA solution (0.5 M) of pH 5.0 was used as the eluent. The PCR solution was prepared using Arsenazo (III) as reported elsewhere.[31] Flow rates of the mobile phase and PCR solution were $1\,\mathrm{mL\,min^{-1}}$ and $0.3\,\mathrm{mL\,min^{-1}}$, respectively. Geological standard material was digested and processed as per the procedure given elsewhere.[26]

RESULTS AND DISCUSSION

The objective of the present study was to find out the effect of carbon chain length of IIRs on the efficiency of separation of lanthanides under ion interaction chromatographic conditions. For this purpose, resolution was determined among various lanthanide pairs under identical chromatographic conditions. The resolution between two adjacent peaks of lanthanides was calculated using the equation:

$$R = 1.18\frac{(R_{t2} - R_{t1})}{(W_{(1/2)_1} + W_{(1/2)_2})}$$

where, R_{t1} and R_{t2} are the retention times of the two adjacent peaks 1 and 2, respectively, and W's denote their peak widths at half maximum heights. When the resolution between two adjacent peaks is less than 1, the resolution was estimated based on comparison with a standard set of resolution curves.[32]

Optimization of IIR Composition

Table 1 shows a comparison of resolution among lanthanides separated by C_{18} RP column (Monolith) modified with C_{20}-sulphonate prepared in 30, 40, and 50% of MeOH with those obtained by the same column modified with C_{20}-sulphonate prepared in 25% acetonitrile. Resolution data obtained for the column modified with C_{20}-sulphate prepared in acetonitrile were found to be poorer as compared to those obtained by the IIR prepared in all the three compositions of MeOH-water.[17,20]

Table 1. Effect of composition of C_{20}-sulphate solution used as IIR on the separation of lanthanides

	Resolution			
Ln pairs	50% MeOH	40% MeOH	30% MeOH	25% Acetonitrile
Lu-Yb	0.83	1.18	1.21	0.42
Yb-Tm	1.01	1.62	1.65	0.69
Tm-Er	1.12	1.47	1.59	0.81
Er-Ho	1.40	1.50	1.58	1.02
Ho-Dy	1.28	1.36	1.39	0.90
Dy-Tb	1.69	1.83	1.92	1.32
Tb-Gd	2.20	2.39	2.61	1.55
Gd-Eu	0.97	0.98	1.15	0.50
Eu-Sm	1.24	1.56	1.86	0.76
Sm-Nd	2.39	3.38	4.08	1.38
Nd-Pr	0.82	1.18	1.42	not resolved
Pr-Ce	1.04	1.63	2.04	1.46
Ce-La	2.08	2.69	3.52	1.44

Resolutions calculated from the chromatograms recorded after modifying the RP column by passing 200 mL each of 2.5×10^{-4} M C_{20}-sulphate solution prepared in 50, 40 and 30% of MeOH and 25% acetonitrile.

Chromatographic condition: C_{18} (100 mm × 4.6 mm) Chromolith column; α-HIBA of pH 5.0 concentration was changed from 0.03 to 0.18 M in 20 min.

Mobile phase flow rate: 1mL $\min^{-1}$; Post-coloum reagent [0.15 mM Arsenazo (III) and 0.01 M urea in 0.1 M HNO_3] flow rate: 0.3 mL $\min^{-1}$.

Also, it is obvious from data in Table 1 that the efficiency of separation of lanthanides decreases with the increase in percentage of MeOH in the IIR loading solution. Thus, passing of sufficiently large volume of the IIR solution prepared in higher percentage of MeOH through the column could result in the bleeding of IIR, rather than its adsorption onto the RP surface. The bleeding of IIR is prominent for solutions prepared in acetonitrile, as it is more non-polar than MeOH. Hence, further studies were carried out by using C_{18}-sulphonate and C_{20}-sulphate prepared in 30% MeOH, since this is the minimum percentage of MeOH required to dissolve the IIRs (2.5×10^{-4} M) in aqueous solution.

Optimization of the IIR Volume

The data on the changes in the resolution among lanthanides separated by a RP column modified with varying volume of C_{18}-sulphonate solution (2.5×10^{-4} M in 30% MeOH) are given in Table 2. It was found that there was a steady improvement in resolution with increase in volume of IIR solution, up to 600 mL. Beyond this volume, no appreciable increase in the resolution was observed. Thus 600 mL was chosen as

Table 2. Effect of volume of C_{18}-sulphonate IIR solution on the separation of lanthanides

	Resolution obtained after passing different volume of C_{18}-sulphonate (mL)				
Ln pairs	100	300	500	600	800
Lu-Yb	1.10	1.27	1.37	1.62	1.61
Yb-Tm	1.39	1.71	1.83	2.22	2.25
Tm-Er	1.44	1.77	1.63	2.20	2.18
Er-Ho	1.70	2.10	1.73	2.33	2.33
Ho-Dy	1.66	2.10	1.82	2.27	2.32
Dy-Tb	2.23	2.74	2.57	3.09	3.09
Tb-Gd	2.75	3.57	3.80	4.08	3.95
Gd-Eu	1.16	1.63	1.95	1.91	1.82
Eu-Sm	1.39	2.01	2.68	2.30	2.23
Sm-Nd	2.14	3.68	5.29	4.20	3.79
Nd-Pr	0.51	1.27	2.26	1.81	1.73
Pr-Ce	0.70	1.56	2.79	2.11	2.05
Ce-La	0.91	2.80	4.47	3.30	3.18

A RP column modified by passing different volumes of C_{18}-sulphonate (2.5×10^{-4} M prepared in 30% of MeOH).
Chromatographic conditions: same as those given in Table 1.

Table 3. Effect of volume of C_{20}-sulphate solution on the separation of lanthanides

	Resolution obtained after passing a volume of C_{20}-sulphate passed (mL)			
Ln pairs	200	400	600	800
Lu-Yb	1.13	1.18	1.21	1.19
Yb-Tm	1.46	1.62	1.65	1.63
Tm-Er	1.35	1.47	1.59	1.42
Er-Ho	1.34	1.50	1.58	1.40
Ho-Dy	1.23	1.36	1.39	1.26
Dy-Tb	1.68	1.83	1.92	1.70
Tb-Gd	2.22	2.39	2.61	2.24
Gd-Eu	0.91	0.98	1.15	1.02
Eu-Sm	1.49	1.56	1.86	1.69
Sm-Nd	3.45	3.38	4.08	3.65
Nd-Pr	1.18	1.18	1.42	1.30
Pr-Ce	1.60	1.63	2.04	1.87
Ce-La	2.69	2.69	3.52	3.08

A RP column modified using different volumes of C_{20}-sulphate (2.5×10^{-4} M prepared in 30% of MeOH).
Chromatographic conditions: same as those given in Table 1.

the volume of the C_{18}-sulphonate solution to be passed for modifying the column for carrying out comparative studies with other IIRs. A volume of the IIR solution larger than the optimized volume causes a slight decrease in the resolution, especially for lighter lanthanides. This is possibly due to the removal of the adsorbed modifier by the MeOH present in the modifier solution.

Similarly, the effect of volume of C_{20}-sulphate IIR solution (2.5×10^{-4} M in 30% MeOH) on the resolution for the separation of lanthanides was determined, and the data are given in Table 3. The optimum volume of the C_{20}-sulphate IIR solution required for conditioning the column to obtain good resolution for the separation of lanthanides was found to be 600 mL.

Optimization of Washings with Water

The stationary phase coated with IIR was washed with different volumes of water and the change in the resolution for the separation of lanthanides at regular intervals of washing was noticed. Table 4 shows the changes in the resolution among the lanthanide pairs separated by

Table 4. Effect of volume of water passed through C_{18}-sulphonate coated column on the separation of lanthanides

Ln pairs	Resolution values obtained after passing volume of water (mL)				
	100	200	400	700	1600
Lu-Yb	1.67	1.75	1.92	1.99	1.73
Yb-Tm	2.22	2.36	2.61	2.77	2.49
Tm-Er	2.33	2.47	2.73	3.04	2.64
Er-Ho	2.59	2.84	3.03	3.49	3.01
Ho-Dy	2.55	2.82	3.07	3.37	3.01
Dy-Tb	3.33	3.41	3.95	4.35	4.01
Tb-Gd	4.24	4.46	5.23	5.68	5.63
Gd-Eu	1.93	2.05	2.36	2.67	2.73
Eu-Sm	2.44	2.78	3.03	3.63	3.78
Sm-Nd	4.43	5.24	5.81	6.92	7.05
Nd-Pr	1.80	1.89	2.22	2.65	3.02
Pr-Ce	2.12	2.42	2.79	3.45	4.13
Ce-La	3.26	3.46	4.14	5.18	6.12

A RP column modified by passing 600 mL of C_{18}-sulphonate (2.5×10^{-4} M prepared in 30% of MeOH) followed by washings with different volume of water.

Chromatographic conditions: same as those given in Table 1.

the column modified with C_{18}-sulphonate with progressive washings with water. It is seen that the resolution improves after washing the C_{18}-sulphonate coated column with water. This improvement in the efficiency of the coated column with the passage of water was observed to continue up to 700 mL of water washings and was attributed to the increase in the available surface area, resulting from better orientation of the IIR molecules on the RP surface. However, when a very large volume (>700 mL) of water is passed, the hydrophobic moiety of the IIR molecules could undergo shrinkage and this might be the reason for the slight decrease in resolution. In a similar way, the volume of water required to be passed through the C_{20}-sulphate coated column for the efficient separation of lanthanides was optimised and was found to be 1000 mL.

While studying the effect of washings with water, it was observed that the relative change in the resolution among the lighter lanthanide (late eluting) pairs is 5–20 times higher than the corresponding change observed with heavier (early eluting) lanthanides. Since lighter lanthanides reside longer in the column, they have the opportunity for better equilibration with the mobile phase containing the eluent (0.03 M α-HIBA), resulting in an enhanced improvement in resolution as compared to heavier lanthanides. This observation indicated that there is a need for optimizing the eluent mobile phase volume required for conditioning the coated column for maximizing the resolution possible with a given IIR.

Optimization of Washings with Mobile Phase

Table 5 shows the changes in the resolution among the lanthanides with progressive washings using mobile phase containing α-HIBA. A RP column coated by passing 600 mL of C_{18}-sulphonate solution and subjected to 1600 mL of water washing (from experiment described in Table 5) was employed for this study. It was found that lanthanides were separated with enhanced resolution when chromatographic runs were performed after conditioning the C_{18}-sulphonate coated column with 30 mL & 70 mL of the mobile phase (0.03 M α-HIBA). Though conditioning of the column with 70 mL of the mobile phase gave slightly better resolution

Table 5. Effect of mobile phase conditioning of C_{18}-sulphonate coated column on the separation of lanthanides

	Resolution obtained after passing volume of mobile phase for conditioning (in mL)		
Ln pairs	10	30	70
Lu-Yb	1.77	1.84 (4)*	1.84 (4)*
Yb-Tm	2.40	2.50 (4)	2.49 (4)
Tm-Er	2.52	2.73 (8)	2.74 (9)
Er-Ho	3.01	3.09 (2)	3.12 (4)
Ho-Dy	3.16	3.12 (1)	3.16 (0)
Dy-Tb	4.05	4.09 (1)	4.30 (6)
Tb-Gd	5.46	5.63 (3)	5.82 (7)
Gd-Eu	2.65	2.64 (0)	2.53 (4)
Eu-Sm	3.74	3.53 (6)	3.48 (7)
Sm-Nd	7.11	6.81 (4)	6.75 (5)
Nd-Pr	2.82	2.74 (3)	2.84 (1)
Pr-Ce	3.87	3.92 (1)	3.95 (2)
Ce-La	6.05	6.05 (0)	6.14 (2)

A RP column modified by passing 1600 mL C_{18}-sulphonate (2.5×10^{-4} M prepared in 30% of MeOH) followed by sequential washing with 700 mL of water and different volumes of mobile phase.

*Percentage change with respect to the resolution obtained by conditioning with 10 mL of the mobile phase.

Chromatographic conditions: same as those given in Table 1.

(>5%) than that obtained by using 30 mL, the relative improvement in resolution for various pair of lanthanides is less than 5%. Considering that each chromatographic run is to be taken after conditioning with the mobile phase, this improvement in resolution is not a significant gain. Thus, 30 mL of 0.03 M α-HIBA was chosen for the final conditioning of the C_{18}-sulphonate coated column.

Comparison of Resolution Data using Different IIRs

Table 6 presents a comparison of resolution values obtained for the separation of lanthanides using C_8-sulphate, C_8-sulphonate, C_{18}-sulphonate and C_{20}-sulphate under identical chromatographic conditions. Both C_8-sulphate and C_8-sulphonate gave comparable performances indicating that no significant improvement in separation is contributed by functional group difference (i.e., sulphate and sulphonate).

Table 6. Comparison of resolution for the separation of lanthanides using column modified with different IIRs

	Resolution			
Ln pairs	C_8-sulphonate	C_8-sulphate	C_{18}-sulphonate	C_{20}-sulphate
Lu-Yb	1.61	1.55	1.99	1.21
Yb-Tm	1.81	1.79	2.77	1.65
Tm-Er	1.77	1.70	3.04	1.59
Er-Ho	1.90	1.91	3.49	1.58
Ho-Dy	1.86	1.96	3.37	1.39
Dy-Tb	2.42	2.47	4.35	1.92
Tb-Gd	3.42	3.52	5.68	2.61
Gd-Eu	1.63	1.72	2.67	1.15
Eu-Sm	2.31	2.48	3.63	1.86
Sm-Nd	4.72	4.63	6.92	4.08
Nd-Pr	1.75	1.79	2.65	1.42
Pr-Ce	2.32	2.29	3.45	2.04
Ce-La	3.73	3.70	5.18	3.52

IIRs used: 0.007 M each of C_8-sulphate and C_8-sulphonate; 2.5×10^{-4} M each of C_{18}-sulphonate and C_{20}-sulphate (prepared in 30% MeOH).

Column: C_{18} (100 mm × 4.6 mm) Chromolith column; Mobile phase flow rate: 1 mL min^{-1}; other chromatographic conditions: same as those given for Table 1.

C_{20}-sulphate was expected to have the strongest adsorption onto the stationary phase and provided the highest resolution as compared to C_{18}-sulphonate. However, C_{18}-sulphonate was found to give higher resolutions for the separation lanthanides compared to C_{20}-sulphate. The chemically bonded octadecyl group in the reversed phase of the monolith column and the C_{18}-sulphonate used for the ion exchange modification contain the same number of carbon atoms. This similarity would cause better adsorption and orientation of the modifier on the stationary phase.

In order to confirm this interpretation, RP columns based on C_8 and C_{18} were compared for the improvement in separation of lanthanides when the IIR was changed from C_8-sulphonate to C_9-sulphonate. Table 7 shows the data on the resolution of lanthanides separated on RP columns based on C_8 and C_{18} under dynamically modified conditions

Table 7. Comparison of resolution for the separation of lanthanides using C_8 and C_{18} columns modified with C_8-sulphonate and C_9-sulphonate

	Resolution obtained for the C_8 column using the IIR			Resolution obtained for the C_{18} column using the IIR		
Ln pairs	C_8-sulphonate (R_8)	C_9-sulphonate (R_9)	(R_9/R_8)	C_8-sulphonate (R_8^1)	C_9-sulphonate (R_9^1)	(R_9^1/R_8^1)
Lu-Yb	2.4	1.94	0.81	1.61	1.71	1.06
Yb-Tm	2.88	2.87	1.00	1.81	2.4	1.33
Tm-Er	3.04	3.15	1.04	1.77	2.36	1.33
Er-Ho	2.42	3.58	1.48	1.9	2.63	1.38
Ho-Dy	2.7	3.89	1.44	1.86	2.66	1.43
Dy-Tb	4.17	4.91	1.18	2.42	3.47	1.43
Tb-Gd	5.72	6.52	1.14	3.42	4.96	1.45
Gd-Eu	2.98	3.38	1.13	1.63	2.42	1.48
Eu-Sm	3.99	4.41	1.11	2.31	3.25	1.41
Sm-Nd	7.55	8.70	1.15	4.72	6.22	1.32
Nd-Pr	2.32	3.92	1.69	1.75	2.67	1.53
Pr-Ce	3.48	5.08	1.46	2.32	3.23	1.39
Ce-La	7.93	8.00	1.01	3.73	5.16	1.38

Resolutions calculated from the chromatograms recorded under dynamically modifying condition by passing 0.007 M each of C_8-sulphonate and C_9-sulphonate.

Columns used: C18 (100 mm × 4.6 mm) Chromolith column and C_8 (150 mm × 4.6 mm, 5 μm particle size) Purosher STAR column.

Gradient condition; α-HIBA of pH 5.0 concentration was changed from 0.03 to 0.18 M in 20 min.

Mobile phase flow rate: 1 mL min^{-1}; Post-column reagent flow rate: 0.3 mL min^{-1}.

employing C_8-sulphonate and C_9-sulphonate as IIRs. For both types of stationary phases, C_9-sulphonate gave better resolution for the separation of lanthanide ions indicating the dominance of hydrophobicity. However, it is seen that for most of the adjacent lanthanide pairs, relative change in resolution obtained using C_9-sulphonate with respect to C_8-sulphonate (R_9^1/R_8^1) is higher for the C_{18} column as compared to the corresponding values obtained for the C_8 column (R_9/R_8). This observation supports our interpretation of enhancement in resolution due to increased hydrophobicity, while changing from C_8-sulphonate to C_9-sulphonate using a C_{18} column. In the case of the C_8 column, the preference of the C_8 stationary phase for an IIR having an equal number of carbon atoms in its chain could be responsible for partially offsetting the expected enhancement in (R_9/R_8). When C_{18}-sulphonate and C_{20}-sulphate were used as the IIRs in combination with C_{18} stationary phase, the degree of hydrophobicity is comparable for these two modifiers. Hence, the resolution for the separation of lanthanides is influenced more by the preference of the stationary phase for the IIR having equal number of carbon atoms in its chain.

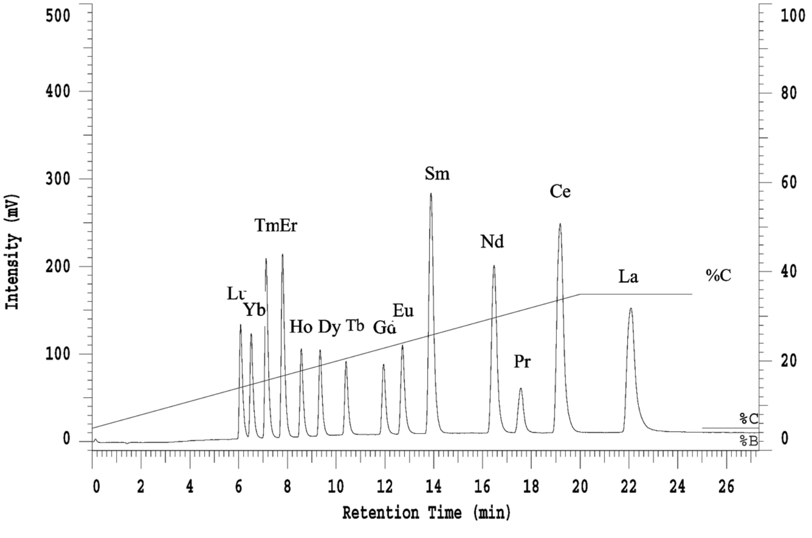

Figure 1. Separation of 14 lanthanides on a C_{18} column coated with C_{18}-sulphonate. Chromatographic condition: C_{18} Chromolith (100 mm × 4.6 mm), washed with 700 mL water and 30 mL of mobile phase. Concentration of α-HIBA of pH 6.0 [C] was changed from 0.03 to 0.35 M in 20 min; flow rate: 1 mL min^{-1}; Post-column reagent [0.15 mM Arsenazo(III) and 0.01 M urea in 0.1 M HNO_3] flow rate: 0.3 mL min^{-1}; monitoring wavelength: 650 nm. Injected 100 µL of the synthetic mixture solution containing 1 ppm each of lanthanide.

In view of the high separation efficiency and stability of adsorption, C_{18}-sulphonate was chosen as the IIR for carrying out the further separation studies. The chromatogram of separation of 14 lanthanides on a RP column modified with C_{18}-sulphonate and conditioned as per the procedures discussed above, is given in Figure 1. It is seen that all the peaks are baseline separated and display good peak shape indicative of excellent mass transfer of lanthanide ions between the mobile phase and coated ion exchanger.

Figure 2 shows the chromatogram obtained for the separation of Fe, lanthanides, Th and U carried out on a C_{18}-sulphonate modified column using a geological reference material (SY-3). The gradient condition was modified to dual (concentration and pH) gradient conditions given in Table 8 to allow the sequential separation of Fe, lanthanides, Th and U. Table 9 shows the data on the concentration of lanthanides determined by this method. Dy could not be determined in this sample due to its overlapping with Y when α-HIBA is used as the complexing agent. As the

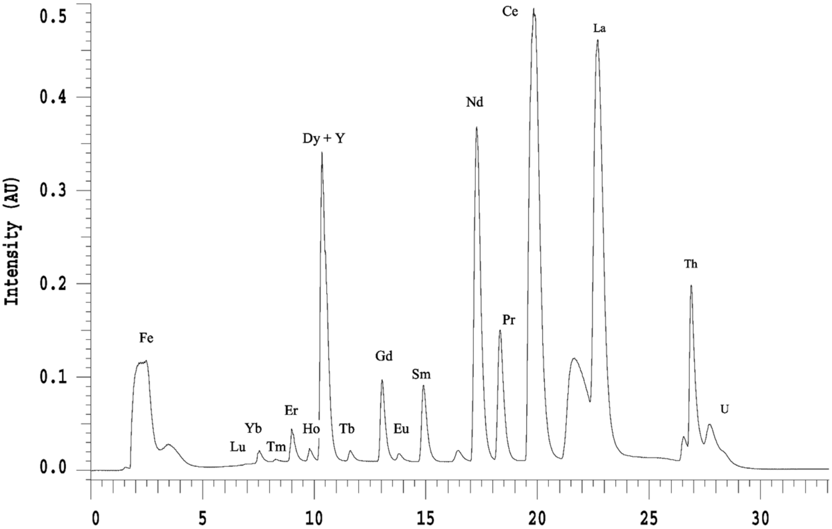

Figure 2. Sequential separation of Fe, lanthanides, Th and U from a geological reference material (SY-3) on C_{18}-sulphonate coated C_{18} column. Expected concentrations of lanthanides and actinides (ppmw): Lu: 0.07, Yb: 0.05, Tm: 0.11, Er: 0.62, Ho: 0.27, Dy: 1.08, Tb: 0.16, Gd: 0.96, Eu: 0.16, Sm: 1.00, Nd: 6.13, Pr: 2.04, Ce: 20.40, La: 12.26, Th: 9.17, U: 5.95. Chromatographic condition: C_{18} (100 mm × 4.6 mm), washed with 700 mL water and 30 mL of mobile phase. α-HIBA gradient as given in Table 8. Mobile phase flow rate: $1\,\mathrm{mL\,min^{-1}}$; Post-column reagent [0.15 mM Arsenazo(III) and 0.01 M urea in 0.1 M HNO_3] flow rate: $0.3\,\mathrm{mL\,min^{-1}}$; monitoring wavelength: 650 nm.

Table 8. Gradient conditions used for the separation of Fe, lanthanides, Th and U

Time (min)	Concentration (M) of α-HIBA at pH 3.0 [%B]	Concentration (M) of α-HIBA at pH 6.0 [%C]
0	0	0.03
20	0	0.15
23	0.18	0
30	0.18	0

digested sample was not subjected to extensive purification procedure for the isolation of rare earth fractions, the chromatogram contains other peaks also. Good resolution obtained by the optimised procedure allows the separation of lanthanides, which are present in widely differing proportions.

Long Term Adsorption and Reproducibility of Coating

Long term stability of adsorption of C_{18}-sulphonate modifier on to the RP stationary phase was confirmed by monitoring the separation of

Table 9. Determination of lanthanides in SY-3 sample

Elements	Recommended concentration (ppm)	Determined concentration (ppm)*	RSD (%)*
La	1340	1432	16
Ce	2230	2195	4
Pr	223	219	10
Nd	670	661	1
Sm	109	105	7
Eu	17	18	3
Gd	105	104	3
Tb	18	20	6
Dy	118	ND	–
Ho	29.5	27	7.8
Er	68	65	3.7
Tm	11.6	10	4.6
Yb	62	58	8.1
Lu	7.9	6	10.3

ND: Not determined.

*Average and Relative standard deviation from triplicate runs.

Table 10. Long-term performance of C_{18} monolith column coated with C_{18}-sulphonate

Ln pairs	Mean value of resolution	RSD (%)
Lu-Yb	1.7	8
Yb-Tm	2.4	6
Tm-Er	2.5	8
Er-Ho	2.7	5
Ho-Dy	2.7	6
Dy-Tb	3.7	3
Tb-Gd	4.9	2
Gd-Eu	2.3	2
Eu-Sm	3.4	5
Sm-Nd	6.9	7
Nd-Pr	2.7	5
Pr-Ce	3.8	6
Ce-La	6.2	6

Relative Standard Deviation (RSD) calculated from eight chromatograms recorded over a period of two months.

Chromatographic conditions: same as given in Table 1.

lanthanides under identical separation conditions over a period of two months. The modified column showed consistent resolution for all the pairs of lanthanides indicating the efficacy of C_{18}-sulphonate for the long term modification of reversed-phase to obtain high resolution separation of individual lanthanides. Table 10 shows the average resolution for lanthanides obtained from chromatograms recorded over a period of two months. It is seen that the C_{18}-sulphonate coating over the stationary phase is quite stable, as indicated by the reproducibility (RSD 2–8%) of resolutions among lanthanide peaks. The reproducibility of the coating procedure using C_{18}-sulphonate was verified by removing the coating completely from the column by washing with methanol, remodifying the column by passing the IIR solution, followed by water and mobile phase washings. Reproducible data (better than 10%) on resolution were obtained for the separation of lanthanides performed with these recoated columns.

CONCLUSIONS

A comparative study of C_{18}-sulphonate and C_{20}-sulphate as interaction reagents was carried out for the separation of lanthanides. Different parameters in the modification process, like composition and volume of the IIR solution, volume of washings with water, and mobile phase, etc., demonstrated significant changes in the performance of the column for the separation of lanthanides. After carefully optimizing the experimental parameters, it was found that columns coated with C_{18}-sulphonate provide higher resolutions as compared to C_{20}-sulphate. C_{18}-sulphonate was also found to exhibit excellent adsorption stability and hence, need not be added to mobile phase during the separation of lanthanides by HPLC. This reagent can be employed as a potential modifier for the separation of lanthanides in complex samples requiring high resolution. The absence of modifier (IIR) in the eluted fractions of lanthanides will allow unaffected ionization of lanthanides during TIMS analysis.

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