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Comparative evaluation of three α -hydroxycarboxylic acids for the separation of lanthanides by dynamically modified reversed-phase high-performance liquid chromatography

Narendra M. Raut, P.G. Jaison, Suresh K. Aggarwal*

Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

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Abstract

The resolution for the three homologues of α -hydroxycarboxylic acids viz. lactic acid, α -hydroxyisobutyric acid (α -HIBA) and α -hydroxy- α -methylbutyric acid (α -H- α -MBA), was compared for the individual separation of 14 lanthanide elements under identical experimental conditions. α -HIBA was found to be the best for separation of heavier lanthanides (Tb to Lu) while α -H- α -MBA led to a better separation for lighter lanthanides (La to Eu). All the 14 lanthanides were separated by gradient HPLC employing both α -HIBA and α -H- α -MBA so that there was reasonable resolution among all the peaks and the separation was completed in a short time. © 2002 Published by Elsevier Science B.V.

Keywords: α -Hydroxycarboxylic acids; Lanthanides

1. Introduction

The separation of lanthanides is important in nuclear technology for the burn-up determination of irradiated fuels and for the characterisation of nuclear fuels with respect to trace constituents. Especially, efficient separation of lighter lanthanides e.g. Ce, Nd, Sm etc. is desirable in a short time for the above task. A number of analytical techniques have been reported [1] for the determination of lanthanides in various matrices. Several methods have been reviewed on the utilisation of chromatographic techniques for lanthanide separation and determination [2–4]. Amongst these techniques, the high-

performance liquid chromatography (HPLC) with on-line detection is a well established method which has shortened the analysis time from days to a few minutes because of its speed, good sensitivity and multi-elemental analysis capability using single injection [5,6]. It is well recognised that dynamically modified reversed-phase (RP)-HPLC offers better resolution, efficiency and flexibility with regard to choice of separation conditions than that obtainable with bonded ion-exchangers [7–9]. Dynamically modified RP-HPLC is based on dynamic sorption of a hydrophobic anion, present in the mobile phase, onto the hydrophobic surface of the column, to provide a negatively charged surface that functions as a cation-exchanger. Eluents like α -hydroxyisobutyric acid (α -HIBA) [5,6,8–10], mandelic acid [11], oxalic acid [12], glycolic acid [13], lactic acid [14] etc. have been tested for separation of lanth-

*Corresponding author. Fax: +91-22-550-5151/551-9613.

E-mail address: skaggr@magnum.barc.ernet.in (S.K. Aggarwal).

anides. A mixed gradient of two eluents e.g. diglycolic acid+oxalic acid has been used for separation of lanthanides in YbF_3 [15] as well as for yttrium in mixtures of lanthanides. Other examples of mixed eluents include use of oxalic acid+ α -HIBA for the separation of 13 lanthanides in 25 min [16] and α -HIBA+glycolic acid to separate yttrium from dysprosium [17]. Amongst different hydroxycarboxylic acids, the most popular eluting agent used for the separation of lanthanides by HPLC is α -HIBA and has been shown to provide a good degree of separation between adjacent lanthanides in reversed-phase–liquid chromatography. Another eluting agent reported for separation of lanthanides by column chromatography is α -hydroxy- α -methylbutyric acid (α -H- α -MBA) [18]. Separation of lanthanides from Eu to Lu was also demonstrated using α -H- α -MBA in a cation-exchanger [19]. Separation of selected lanthanide pairs using the two eluting agents (α -HIBA, α -H- α -MBA) was also reported previously using column chromatography [20] and paper chromatography [21]. Studies for the separation efficiency of eluents consisting of a series of aliphatic α -hydroxy acids viz. glycolic acid, lactic acid, α -HIBA and α -H- α -MBA, for the separation of transplutonium elements, were also reported and the highest values of the separation factors were observed with α -H- α -MBA [22]. These results prompted us to carry out a systematic study of three homologues of α -hydroxycarboxylic acids viz. lactic acid, α -HIBA and α -H- α -MBA, as eluents for separation of 14 lanthanides (La to Lu except Pm) using HPLC in a short time and to evaluate their performance under identical conditions. In this paper, we report resolution of these α -hydroxycarboxylic acids for 14 lanthanides using RP–HPLC under identical experimental conditions. It is shown that the resolution of lanthanides improves with the presence of the longer alkyl group in α -hydroxycarboxylic acid for lighter lanthanides (i.e. La to Eu) as shown in the structures.

Table 1

Stability constants (Log K at an equilibrium of $\text{ML}_3/\text{M.L}^3$) of lanthanides with different eluents used as complexing agents

Lanthanide	Lactic acid 20 °C	α -HIBA 20 °C	α -H- α -MBA 25 °C
La	5.74	5.53	5.20
Ce	5.95	5.95	5.43
Pr	6.10	6.21	5.42
Nd	6.37	6.30	5.81
Sm	6.35	6.77	6.46
Eu	6.43	7.32	6.80
Gd	6.24	7.19	6.86
Tb	6.35	7.43	7.31
Dy	6.67	7.87	7.42
Ho	6.83	7.96	7.72
Er	7.20	8.13	8.03
Tm	7.43	8.39	8.05
Yb	7.58	8.69	8.29
Lu	7.78	8.82	8.35

See Ref. [26].

The $\text{p}K_a$ value of the above acids increases with the increase in the number of methyl groups due to the inductive effect [23]. This explains the decrease in the order of metal–eluent complex stability (lactic acid > α -HIBA > α -H- α -MBA) as given in Table 1.

2. Experimental

2.1. Apparatus

The HPLC system consisted of a L-7100 (Merck Hitachi) gradient pump, a Rheodyne sampling valve (Model 7725i) with a 20 μl sample loop, a 1 cm guard column and an analytical column (150 \times 4.6 mm, Supelcosil LC-18, Supelco, 5 μm , column temperature 25 °C), both packed with C_{18} reversed-phase material and a 512 diode array detector (DAD) L-7450A (Merck Hitachi). The eluted components were monitored after a post-column reaction with a metallochromic reagent. Post-column reagent (PCR)

$\begin{array}{c} \text{OH} \\ \\ \text{H}-\text{C}-\text{COOH} \\ \\ \text{CH}_3 \end{array}$ [Lactic acid $\text{p}K_a$ 3.86]	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3-\text{C}-\text{COOH} \\ \\ \text{CH}_3 \end{array}$ [α -HIBA $\text{p}K_a$ 3.97]	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{COOH} \\ \\ \text{CH}_3 \end{array}$ [α -H- α -MBA $\text{p}K_a$ 4.05]
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was added with a piston pump (Hurst, Princeton Industries) into a low dead volume mixing tee (Valco) via a pulse dampener. The signal from the detector was processed by the HSM D-7000 software package and the chromatograms were monitored using a PC. The HPLC system was computer controlled through an interface with D-7000 (Merck Hitachi).

2.2. Reagents and materials

Freshly deionised water (18.2 M Ω cm) purified with a Milli Q system (Gradient, Millipore) was used for all the dissolutions and dilutions. Lactic acid 85–90% (Merck), α -HIBA (Fluka) and α -H- α -MBA (Sigma–Aldrich) were used as eluents. Sodium salt of *n*-octane sulphonic acid monohydrate (Sigma–Aldrich) was used as the cationic modifier. The oxides of lanthanides La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Yb were obtained from Indian Rare Earths, Alwaye, Kerala, India and those of Ho, Er, Tm and Lu were from Fluka with a chemical purity greater than 99.99%. The oxides were dissolved in high purity nitric acid, evaporated to near dryness and stock solutions were prepared in dilute nitric acid (0.01 M). Ce solution was prepared by treating cerium oxide with nitric acid and reducing Ce(IV) to Ce(III) with hydrogen peroxide [24].

The exact concentration of lactic acid (85–90% w/v) solution was determined by pH titration against standardised NaOH solution prior to its use in the mobile phase. Appropriate quantities of lactic acid, α -HIBA, α -H- α -MBA and sodium *n*-octane sulphate were dissolved in water to obtain the desired concentrations. The pH of the solutions was adjusted using ammonium hydroxide and dilute HNO₃. Arsenazo(III) (Fluka) was used as a PCR. All HPLC mobile phases were filtered through 0.45 μ m Millipore membrane filters.

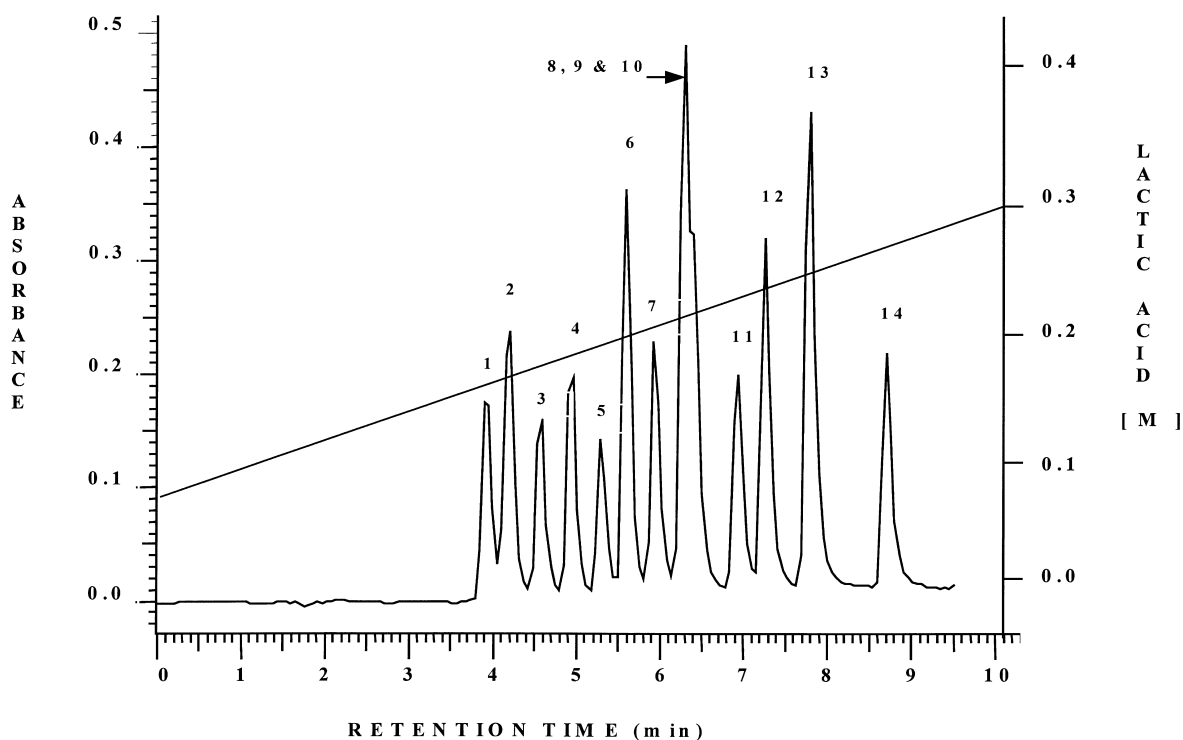
2.3. Procedure

All the experiments were conducted at room temperature (25 °C). A comparative study of three eluents viz. lactic acid, α -HIBA and α -H- α -MBA was carried out for the separation of 14 lanthanides with one eluent at a time. The eluent was pumped through a RP C₁₈ column pre-modified to a cation-

exchanger by sodium *n*-octane sulphonate using a gradient HPLC pump until a constant pH of the effluent was observed. This indicated equilibrium conditions for the column. Throughout the experiment, flow-rate of the mobile phase was maintained at 1 ml min⁻¹. The PCR solution (1.5 \times 10⁻⁴ M Arsenazo(III) and 0.01 M urea in 0.1 M HNO₃) was delivered at a flow-rate of 0.3 ml min⁻¹. Urea was added to the Arsenazo(III) solution to prevent its oxidation in the presence of nitric acid [7]. The mixture of 14 lanthanides, 10 μ g ml⁻¹ of each, was injected through the Rheodyne injector with a 20 μ l loop and the separated lanthanides were detected by the DAD detector at 645 nm after their post-column derivatisation with Arsenazo(III). For the detailed study, the 14 lanthanides were divided into two sets, seven in each and designated as heavy lanthanide group (HREE) for Tb to Lu and lighter lanthanide group (LREE) for La to Gd. The effect of pH for different eluents was studied separately using La, Nd, Gd and Lu representing the lighter and heavier lanthanides groups. Comparative studies for separation were carried out at pH 4.0.

3. Results and discussion

The elution pattern of lanthanides depends on the stability constants of the Ln–eluent complexes. The more the stability constant of Ln–eluent complex, the faster will be its elution. Generally for all the eluents, the stability constant increases from La to Lu and this explains the elution pattern in the order of decreasing atomic number from Lu to La in the cation-exchanger. The formation of a complex between metal ion and complexing agent (eluent) can be affected by their nature as well as the environmental factors such as solvent or medium, concentration, temperature and pressure [25]. Hence the stability constants for a given metal–eluent complex under different environmental conditions can be different. Stability constant values (Log *K*) reported in the literature for lactates, α -hydroxyisobutyrate and α -hydroxy- α -methylbutyrate for lanthanides (La to Lu) are given in Table 1 [26]. These give only a qualitative picture of the behaviour during separation of lanthanides; however, the exact performance can be different. Figs. 1–3 present the chro-



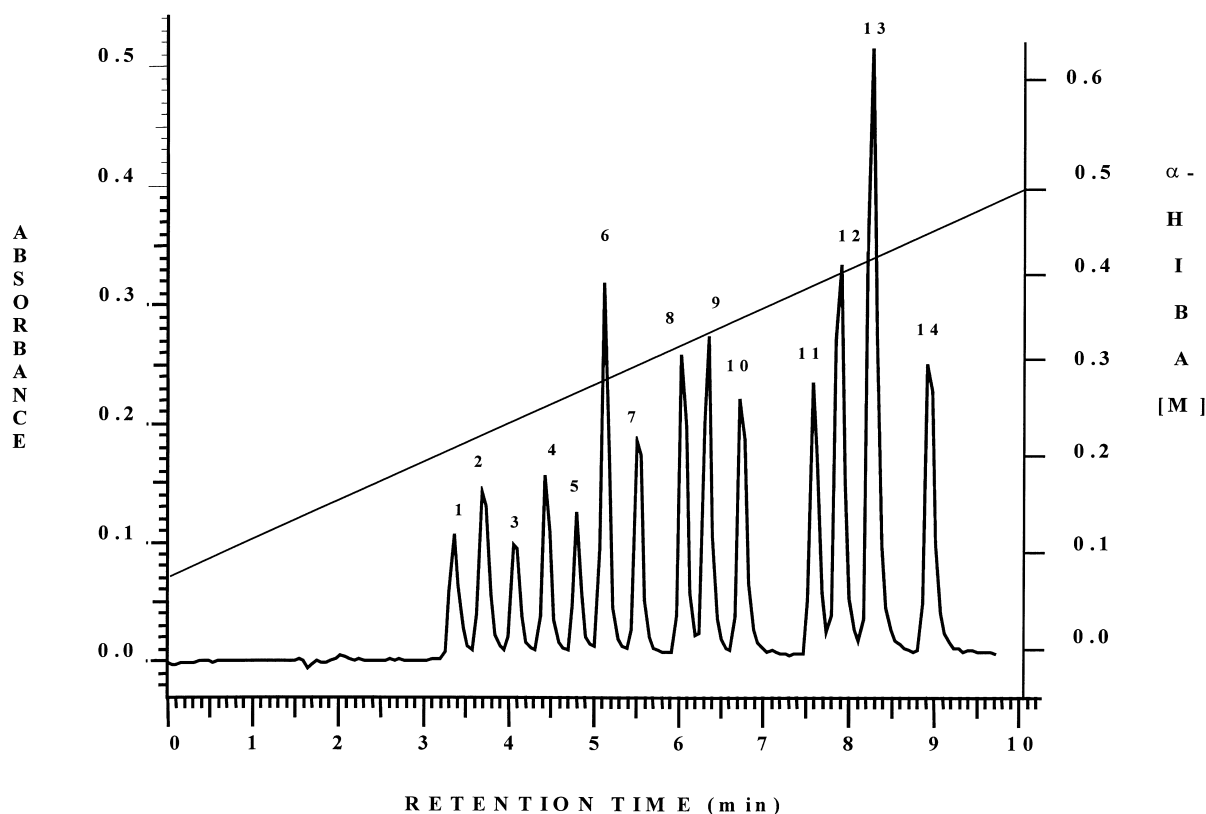
(1) Lu, (2) Yb, (3) Tm, (4) Er, (5) Ho, (6) Dy, (7) Tb, (8) Gd, (9) Eu, (10) Sm, (11) Nd, (12) Pr, (13) Ce, (14) La

Fig. 1. Gradient separation of lanthanides using lactic acid as an eluent. Mobile phase: 0.07 to 0.3 M lactic acid (pH 4.0) in 10 min; 0.003 M sodium *n*-octane sulphonate; flow-rate: 1 ml min⁻¹; temperature 25 °C; stationary phase: 4.6×150 mm, 5 μm C₁₈ RP column; post-column reagent: 1.5×10⁻⁴ M Arsenazo(III) in 0.01 M urea and 0.1 M HNO₃; flow-rate: 0.3 ml min⁻¹; monitoring wavelength: 645 nm.

matograms obtained for the separation of 14 lanthanides using the three different eluents viz. lactic acid, α-HIBA and α-H-α-MBA. As seen from Fig. 1, Sm, Eu and Gd are co-eluted, whereas Nd and Tb are seen as two well resolved peaks [13], in contrast to the fact that the log *K* values of Nd, Sm, Eu, Gd and Tb with lactate (Table 1, column II) are very close, expecting their co-elution. Similarly reported log *K* values are nearly identical (Table 1, column IV) for α-hydroxy-α-methylbutyrates of pairs (Ce, Pr; Eu, Gd; Tb, Dy; Er, Tm), but all the peaks are well resolved in their chromatographic separation (Fig. 3) using α-H-α-MBA as the eluent [20]. Hence, experiments were carried out to illustrate the exact behaviour of lanthanides with different eluents under the same chromatographic conditions for their better resolution.

Figs. 4–6 show the effect of mobile phase pH on

the elution pattern of a mixture consisting of La, Nd, Gd and Lu using the three eluents viz. lactic acid, α-HIBA and α-H-α-MBA, respectively. The effect was monitored using retention factor (*k*) which is defined as $k = (t_R - t_0)/t_0$ where *t*₀ and *t*_R denote the retention times of the non-retained peak and that of the element retained, respectively. A decrease in retention factor (*k*) for different lanthanides with increase in pH from 3.0 to 5.0 (in steps of 0.5 at a time) was observed in all three eluents. This is due to the change in elution efficiency of carboxylic acids with pH. The elution efficiency of the carboxylic acid depends on its strength, which in turn depends on its pH. The α-hydroxycarboxylic acids tested were all weak acids and undergo only partial ionisation and hence show poor eluting strength at low pH. However as the pH increases, the elution efficiency increases due to greater ionisation of the -COOH



(1) Lu, (2) Yb, (3) Tm, (4) Er, (5) Ho, (6) Dy, (7) Tb, (8) Gd, (9) Eu, (10) Sm, (11) Nd, (12) Pr, (13) Ce, (14) La

Fig. 2. Gradient separation of lanthanides using α -HIBA as eluent. Mobile phase: 0.07 to 0.50 M α -HIBA (pH 4.0) in 10 min; 0.003 M sodium *n*-octane sulphonate; flow-rate: 1 ml min⁻¹; temperature 25 °C; stationary phase: 4.6 × 150 mm, 5 μ m C₁₈ RP column; post-column reagent: 1.5 × 10⁻⁴ M Arsenazo(III) in 0.01 M urea and 0.1 M HNO₃; flow-rate: 0.3 ml min⁻¹; monitoring wavelength: 645 nm.

group. At low pH (3.0), the retention factors for different lanthanides differ significantly while at higher pH (5.0), these are quite close (Figs. 4–6). Hence pH 4.0, which gives adequate resolution in a shorter time, was selected as the optimum for comparative studies of the three eluting agents.

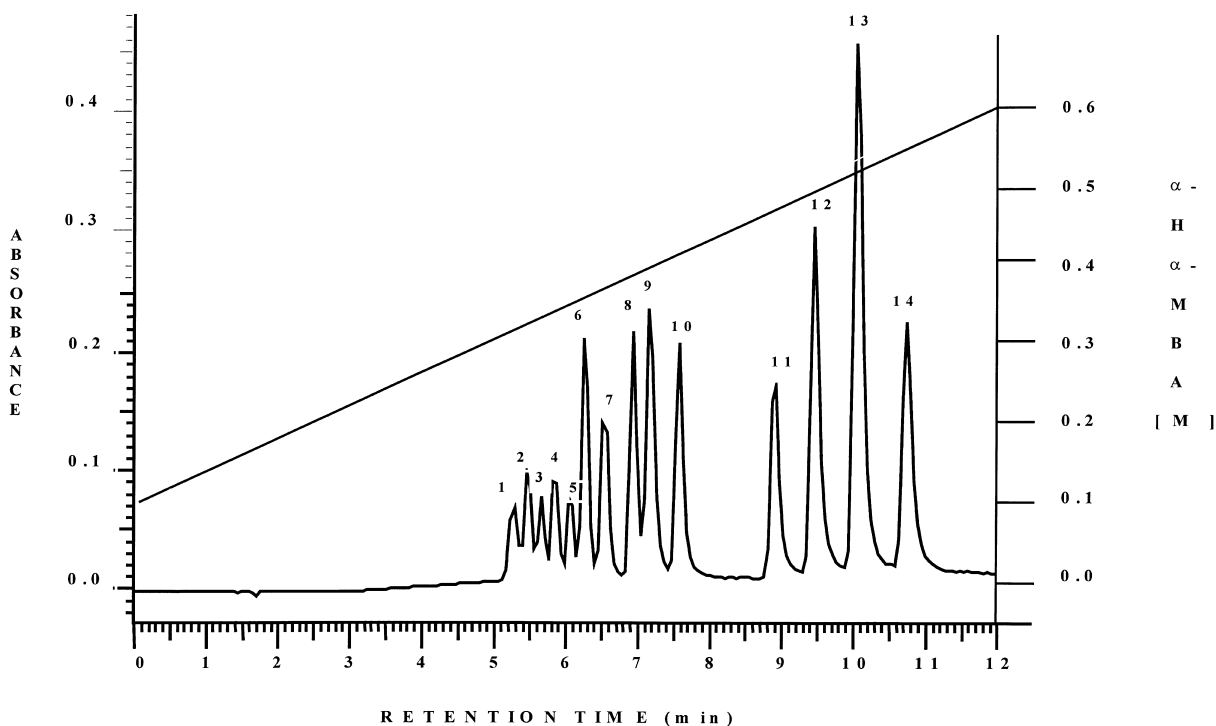
Previous workers have used a separation factor [10], i.e. ratio of retention factors, as a chromatographic parameter, which describes only the interaction of sample species in the chromatographic system. The data in Tables 2 and 3 show the comparison of resolution for heavier and lighter lanthanides using lactic acid, α -HIBA and α -H- α -MBA under identical chromatographic conditions. α -HIBA was found to be the best eluent for heavier lanthanides (Table 2). For lighter lanthanides

(LREE), an increase in resolution was observed from lactic acid to α -H- α -MBA (Table 3). We preferred to use the resolution term for comparative study of three eluents for lanthanides because it expresses the extent of base line separation between two adjacent lanthanides peaks. It was evaluated using formula:

$$R = 1.18 [(t_{R2} - t_{R1}) / (w_{1/2(1)} + w_{1/2(2)})]$$

where t_{R1} and t_{R2} are the retention time of two adjacent peaks 1 and 2, respectively, with their peak widths at half maximum height as $w_{1/2(1)}$ and $w_{1/2(2)}$, respectively.

It is evident from data shown in Table 3 that lactic acid cannot be used to separate Sm, Eu and Gd under the presently used experimental conditions. This is



(1) Lu, (2) Yb, (3) Tm, (4) Er, (5) Ho, (6) Dy, (7) Tb, (8) Gd, (9) Eu, (10) Sm, (11) Nd, (12) Pr, (13) Ce, (14) La

Fig. 3. Gradient separation of lanthanides using α -H- α -MBA as eluent. Mobile phase: 0.07 to 0.60 M α -H- α -MBA (pH 4.0) in 11 min; 0.003 M sodium *n*-octane sulphonate; flow-rate: 1 ml min⁻¹; temperature 25 °C; stationary phase: 4.6 × 150 mm, 5 μ m C₁₈ RP column; post-column reagent: 1.5 × 10⁻⁴ M Arsenazo(III) in 0.01 M urea and 0.1 M HNO₃; flow-rate: 0.3 ml min⁻¹; monitoring wavelength: 645 nm.

attributed to the nearly equal stability constants of Sm, Eu and Gd–lactate complexes [22]. Also the reproducibility in retention time for lanthanides was found to be poor (3 to 8%) using lactic acid as an eluent compared to that (within 1%) observed using α -HIBA and α -H- α -MBA. It is known that lactic acid easily reacts in concentrated solutions, forming a variety of esters. The esterified species get slowly hydrolysed producing a continuous change in complexing properties of the compound. This phenomenon explains the non-reproducibility in the lanthanide retention time from one injection to another using lactic acid [27].

It is clear from data given in Tables 2 and 3 that the resolution improves for a pair of adjacent lanthanides from Lu to La under isocratic conditions for all the three eluents. Hence, a linearly increasing concentration gradient of eluent was set to obtain separation of all the 14 lanthanides in a relatively

short time using the three different eluents and the chromatograms obtained are shown in Figs. 1–3. Distortions at the top of some of the chromatographic peaks in Figs. 1–3 and 7 are due to the noise generated by the short stroke piston pump used for delivering the post column reagent in the present work. The noise generated by the pump has a definite periodicity and shows up on those peak tops where this matches with the time at which the peak maximum appears. This can be avoided by using a Syringe Pump capable of delivering pulse-less flow. However, this Syringe pump was not accessible to us at the time of carrying out these studies. It may be noted that this addition of random noise at the peak top in no way degrades the resolution between adjacent lanthanides.

The above observations prompted us to combine the advantages of the two eluents viz. α -HIBA and α -H- α -MBA for effective separation of 14 lanth-

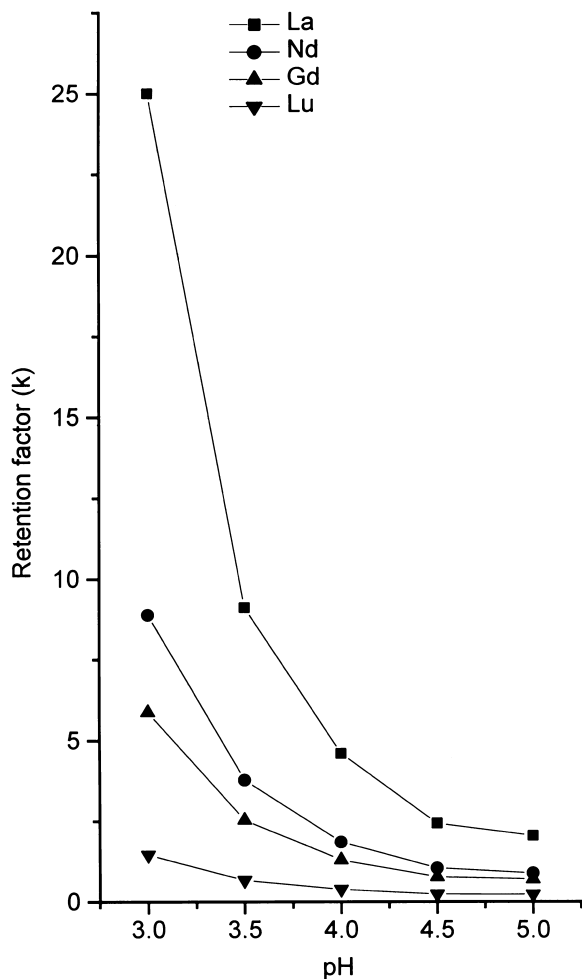


Fig. 4. Effect of pH of lactic acid on the elution pattern of lanthanides. Mobile phase: 0.25 M lactic acid; 0.003 M sodium *n*-octane sulphonate; flow-rate: 1 ml min⁻¹; temperature 25 °C; stationary phase: 4.6×150 mm, 5 μm C₁₈ RP column; post-column reagent: 1.5×10⁻⁴M Arsenazo(III) in 0.01 M urea and 0.1 M HNO₃; flow-rate: 0.3 ml min⁻¹; monitoring wavelength: 645 nm.

anides using RP–HPLC in gradient mode. α-HIBA, being better for the heavier lanthanide group, was used in the beginning followed by α-H-α-MBA, which is effective for the lighter lanthanide group. Table 4 presents comparative resolution data using the two eluents separately and by employing a mixture of eluents in gradient mode. It may be added that the real aim of the experiments performed in the

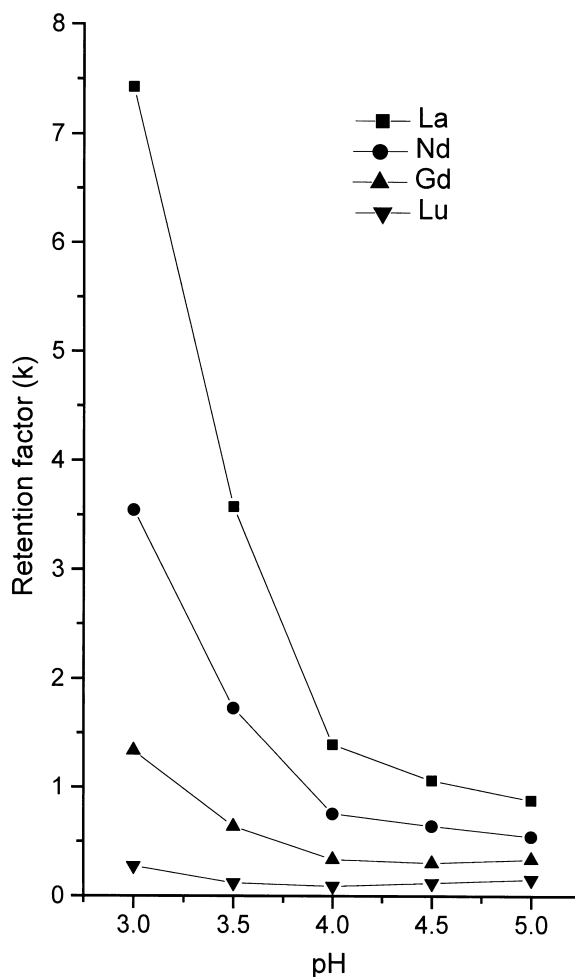


Fig. 5. Effect of pH of α-HIBA on the elution pattern of lanthanides. Mobile phase: 0.25 M α-HIBA; 0.003 M sodium *n*-octane sulphonate; flow-rate: 1 ml min⁻¹; temperature 25 °C; stationary phase: 4.6×150 mm, 5 μm C₁₈ RP column; post-column reagent: 1.5×10⁻⁴M Arsenazo(III) in 0.01 M urea and 0.1 M HNO₃; flow-rate: 0.3 ml min⁻¹; monitoring wavelength: 645 nm.

study was to achieve the best possible separation (resolution) between the adjacent lanthanides from the point of view of using HPLC for quantitative determination of lanthanides and also to use the fractions collected, after separation by HPLC, for subsequent isotopic analysis by mass spectrometry. Hence, the resolution values given in Table 4 for the 14 lanthanides refer to 13 pairs, each pair consisting of two adjacent lanthanides. The use of the cumula-

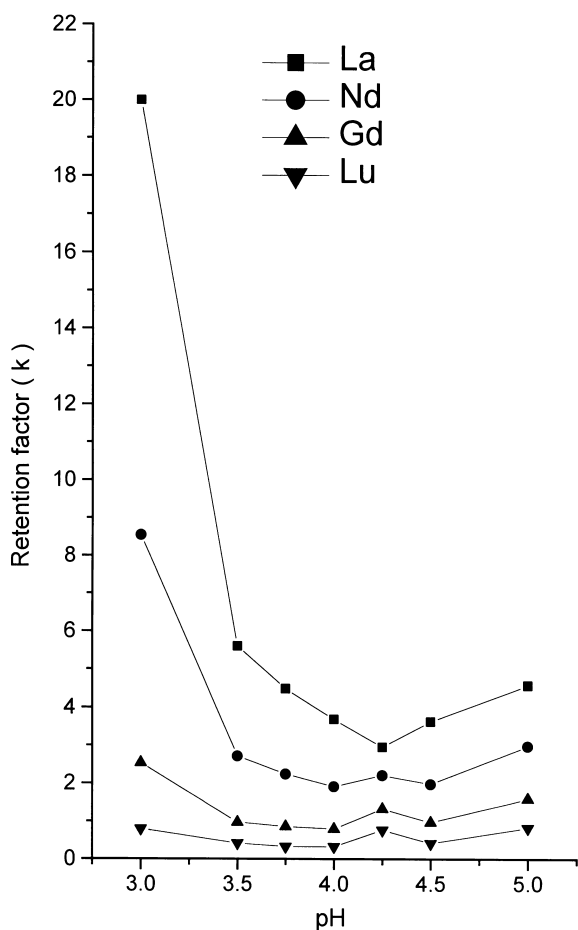


Fig. 6. Effect of pH of α -H- α -MBA on the elution pattern of lanthanides. Mobile phase: 0.25 M α -H- α -MBA; 0.003 M sodium *n*-octane sulphonate; flow-rate: 1 ml min⁻¹; temperature 25 °C; stationary phase: 4.6×150 mm, 5 μ m C₁₈ RP column; post-column reagent: 1.5×10⁻⁴ M Arsenazo(III) in 0.01 M urea and 0.1 M HNO₃; flow-rate: 0.3 ml min⁻¹; monitoring wavelength: 645 nm.

tive resolution function does not truly reflect this particular aspect, which is the main thrust of the present manuscript. However, we tried to calculate the average cumulative resolution function for the three complexing agents. The values obtained are 2.12, 1.83 and 2.48, respectively, for α -HIBA, α -H- α -MBA and (α -HIBA + α -H- α -MBA). The comparison of chromatograms, by visual inspection, can be misleading since the scales used for retention time (x -axis) is not the same in Figs. 1–3 and 7. The

Table 2

Resolution for heavy lanthanides pairs (Tb to Lu) using different eluents in RP-HPLC^a

Pairs of Lns	Lactic acid	α -HIBA	α -H- α -MBA
Lu–Yb	1.11	1.76	1.45
Yb–Tm	1.99	2.36	1.79
Tm–Er	2.04	2.82	2.03
Er–Ho	2.70	3.61	2.39
Ho–Dy	2.33	3.63	2.67
Dy–Tb	3.13	4.87	3.81

^a Chromatographic conditions: Mobile phase: 0.07 M eluent and 0.003 M sodium *n*-octane sulphonate at pH 4.0; flow-rate 1 ml min⁻¹; stationary phase: 4.6×150 mm, 5 μ m C₁₈ RP column; temperature 25 °C; post-column reagent: 1.5×10⁻⁴ M Arsenazo(III) and 0.01 M urea in 0.1 M nitric acid; flow-rate 0.3 ml min⁻¹; monitoring wavelength 645 nm.

scales have been varied to accommodate all the 14 peaks in a reasonable space in one page.

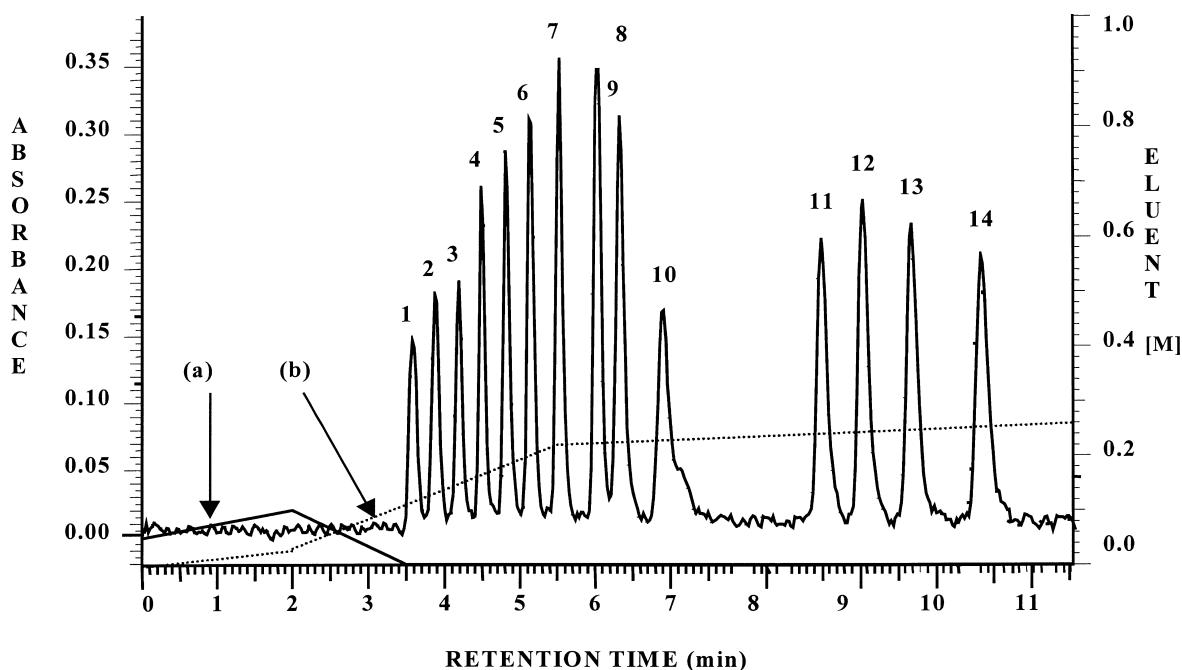
A number of studies were carried out to find the optimum composition of α -HIBA and α -H- α -MBA mixture. It was observed that an aggressive mixed gradient consisting of greater and longer use of α -HIBA was necessary to improve the resolution of heavy lanthanides by this mixed gradient. A number of experiments were conducted to optimise the early portion of the chromatogram (for heavier lanthanides) keeping in mind the greater and longer use of α -HIBA. The conditions finally arrived at consisted of using α -HIBA for a total period of 3.5 min (0.05 M to 0.10 M for 2 min, 0.10 M to 0 M from 2 min to 3.5 min).

Table 3

Resolution for light lanthanides pairs (La to Gd) using different eluents in RP-HPLC^a

Pairs of Lns	Lactic acid	α -HIBA	α -H- α -MBA
Gd–Eu	0	1.25	1.10
Eu–Sm	0	1.59	2.36
Sm–Nd	2.05	4.85	8.72
Nd–Pr	1.70	1.78	3.58
Pr–Ce	2.46	2.48	3.65
Ce–La	5.73	5.24	4.73

^a Chromatographic conditions: Mobile phase: 0.15 M eluent and 0.002 M sodium *n*-octane sulphonate at pH 4.0; flow-rate 1 ml min⁻¹; stationary phase: 4.6×150 mm, 5 μ m C₁₈ RP column; temperature 25 °C; post-column reagent: 1.5×10⁻⁴ M Arsenazo(III) and 0.01 M urea in 0.1 M nitric acid; flow-rate 0.3 ml min⁻¹; monitoring wavelength 645 nm.



(a) α -HIBA, (b) α -H- α -MBA

(1)Lu, (2)Yb, (3)Tm, (4)Er, (5)Ho, (6)Dy, (7)Tb, (8)Gd, (9)Eu, (10)Sm, (11)Nd, (12)Pr, (13)Ce, (14)La

Fig. 7. Separation of lanthanides using a gradient of two eluents. Mobile phase: α -HIBA: 0.05 to 0.10 *M* in 2 min, 0.10 to 0.0 *M* in 2.0 to 3.5 min; α -H- α -MBA: 0.0 to 0.03 *M* in 2 min, 0.03 to 0.22 *M* in 2.0 to 5.5 min, 0.22 to 0.28 *M* in 5.5 to 15 min; 0.003 *M* sodium *n*-octane sulphate; pH 4.0; flow-rate: 1 ml/min; temperature 25 °C; stationary phase: 4.6×150 mm, 5 μ m C₁₈ RP column; post-column reagent: 1.5×10^{-4} *M* Arsenazo (III) in 0.01 *M* urea and 0.1 *M* HNO₃; flow-rate: 0.3 ml/min; monitoring wavelength: 645 nm.

Fig. 7 shows the elution pattern of 14 lanthanides using the mixed gradients of two eluents i.e. α -HIBA and α -H- α -MBA. It is evident that all the 14 lanthanides can be nicely separated in 11 min using the two eluent system. Since we were mainly interested in lighter lanthanides for a specific purpose, the appearance of Y in the vicinity of Dy and Ho (well documented in the literature) was not considered. However, in our future studies, we will be including Y also as one of the components of the rare-earths.

We believe that the use of two eluents will further broaden the scope of HPLC for quantification of lanthanides with better reliability as well as help in minimising isobaric interferences during isotopic analysis of the separated fractions required for the various applications in nuclear technology and geological sciences.

4. Conclusions

From the comparative studies of three eluents, it is concluded that the longer alkyl group in the hydroxycarboxylic acids increases the resolution of lanthanides, in particular for lighter lanthanides. α -H- α -MBA is efficient for resolving lighter lanthanides like Nd from Ce and Sm, which is used in nuclear technology as a burn-up monitor and also in geochronology for age determination of rocks using a Sm–Nd couple.

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Table 4

Resolution for lanthanides using single and dual eluents in gradient mode^a

Pairs of Lns	α -HIBA*	α -H- α -MBA [†]	α -HIBA and α -H- α -MBA [‡]
Lu–Yb	1.40	0.65	1.42
Yb–Tm	1.62	1.38	1.80
Tm–Er	1.87	0.73	1.56
Er–Ho	2.08	0.99	1.72
Ho–Dy	1.89	0.95	2.12
Dy–Tb	1.99	1.26	2.36
Tb–Gd	2.66	1.98	3.01
Gd–Eu	1.57	1.04	1.04
Eu–Sm	1.82	1.91	2.30
Sm–Nd	4.36	5.86	7.22
Nd–Pr	1.64	2.23	2.13
Pr–Ce	1.79	2.32	2.44
Ce–La	2.91	2.47	3.16
	2.12	1.83	2.48

^a Chromatographic conditions: Mobile phase: *0.07 to 0.50 *M* α -HIBA in 10 min and 0.003 *M* sodium *n*-octane sulphonate at pH 4.0; [†]0.07 to 0.60 *M* α -H- α -MBA in 11 min and 0.003 *M* sodium *n*-octane sulphonate at pH 4.0; and [‡] α -HIBA: 0.05 to 0.10 *M* in 2 min, 0.10 to 0.0 *M* in 2.0 to 3.5 min; α -H- α -MBA: 0.0 to 0.03 *M* in 2 min, 0.03 to 0.22 *M* in 2.0 to 5.5 min, 0.22 to 0.28 *M* in 5.5 to 15 min and 0.003 *M* sodium *n*-octane sulphonate, pH 4.0; flow-rate 1 ml min⁻¹; stationary phase: 4.6 × 150 mm, 5 μ m C₁₈ RP column; temperature 25 °C; post-column reagent: 1.5 × 10⁻⁴ *M* Arsenazo(III) and 0.01 *M* urea in 0.1 *M* nitric acid; flow-rate 0.3 ml min⁻¹; monitoring wavelength 645 nm.

^b Average cumulative resolution function = mean of resolutions of lanthanide pairs.

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