Separation and determination of lanthanides, thorium and uranium using a dual gradient in reversed-phase liquid chromatography

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Abstract

Separation and determination of lanthanides, Th and U is of great relevance in different fields of science and technology. Reversed-phase high-performance liquid chromatography (RP-HPLC) using α-hydroxy isobutyric acid (α-HIBA) as an eluent on reversed-phase column modified to cation exchanger has been reported to achieve the separation. However, under those conditions, Th and U are eluted amongst lanthanides, making their quantification difficult due to overlapping with some of the lanthanides peaks. In this work, different chromatographic parameters (concentrations of eluent and ion interaction reagent, pH, etc.) were studied systematically to arrive at optimum chromatographic conditions. Using the dual (concentration and pH) gradient conditions, lanthanides, Th and U could be separated in 11 min by RP-HPLC with sequential elution of Th and U after the elution of all the lanthanides. The separation methodology was tested using SY-3 rock sample for the separation and determination of lanthanides, Th and U. The method allows an accurate determination of these elements in a single run using a single column. Also, the method is fast and cost-effective compared to the reported methods.
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1. Introduction

Determination of lanthanides, Th and U is important from the point of view of their technological applications especially in metallurgy, ceramic and nuclear industry [1–5]. Their determination in geological materials is helpful in mineral exploration program [6]. A knowledge of geochemistry of these elements is also necessary for understanding different geological processes such as chemical fractionation, terrestrial evolution, etc. [7,8]. For all these purposes, the development of analytical methodologies for the separation and determination of these elements becomes essential.

Concerning the measurement of lanthanides, Th and U, several analytical methods ranging from classical methods to modern instrumental analytical techniques are well documented [9]. High-performance liquid chromatography (HPLC) is one of the promising analytical techniques for multi-elemental separation and determination of different elements. Fast and high-efficiency separation of multi elements with reasonable precision, sensitive detection capability, low instrumentation and operating costs are some of the attractive features of this technique. As a result, several HPLC techniques have been reported in the past for determination of lanthanides and actinides in variety of samples relevant to geological, nuclear and mineral processing industries [10–14]. However, most of the reported methods suffered from the drawback due to the elution of U and Th along with some of the lanthanides [15–17]. Alternative approach included the use of two reversed-phase columns, one unmodified and other modified to cation exchanger, connected in series by column switching. The unmodified column retained U and Th, whereas lanthanides were separated on the modified column [10]. However, this needed a complicated experimental set-up with two HPLC pumps, columns and switching valve. The use of two columns for the separation of these elements leads to an increase in separation time and also in higher consumption of solvents/eluents used as mobile phase.

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This paper presents the details of the work carried out for optimization of chromatographic conditions to separate 14 lanthanides, Th and U in a single run. Under the optimized dual gradient conditions, lanthanides, Th and U are separated sequentially in 11 min, on a single column using one low-pressure quaternary gradient pump. The method has been verified by determining lanthanides, Th and U in a geological reference materials viz. SY-3 (syenite) rock sample.

2. Experimental

2.1. Instrumentation

The HPLC set-up consisted of a L-7100 (Merck Hitachi) low-pressure quaternary gradient pump, a Rheodyne sampling valve (Model 7725i) with 100 µL sample loop, a guard column (1 cm × 4.6 mm, Merck Chromolith column) and a monolith analytical column (10 cm × 4.6 mm, Merck Chromolith column), both containing C-18 reversed-phase material and a L-7450A (Merck Hitachi) 512 Diode Array Detector (DAD). The eluted components were monitored at a wavelength of 650 nm after a post-column reaction with a metallochromic Post-Column Reagent (PCR), which was added with a piston pump (Hurst, Princeton Ind.) into a low dead volume-mixing tee (Valco) via a pulse dampner (Model LP 21). The signal from the detector was processed by HSM 7000 software package and the chromatograms were monitored on a PC. The HPLC system was computer controlled through interface D-7000 (Merck Hitachi).

2.2. Reagents

Freshly deionised water (18.2 MΩ cm) purified with a Milli Q system (Gradient, Millipore) was used for all the dissolutions and dilutions. α-Hydroxy isobutyric acid (α-HIBA) from Fluka was used as eluent. Sodium n-octane sulfonate monohydrate (Sigma–Aldrich) was used as the ion interaction reagent (IIR). The oxides of lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Yb) and the nitrate salts of Th and U (as uranyl) were obtained from Indian Rare Earths Ltd., Alwaye, Kerala, India. Oxides of Ho, Er, Tm and Lu were obtained from Fluka with a chemical purity greater than 99.99%. SY-3 (Syenite) rock sample from Canadian Geological Survey was used for the method validation. High-purity reagents such as HCl, HNO_3, HF, NaOH, NH_4OH, etc. used during the sample treatment were obtained from Merck. Arsenazo(III) (Fluka) was used as the post column reagent.

The oxides of lanthanides were dissolved in nitric acid and evaporated to near dryness, and stock solutions were prepared in 2% HNO_3. The standardization of lanthanide solutions was done by titrating against standard EDTA solution in buffer solution of pH 5 using Arsenazo (III) as an indicator. Pyridine was added during the titration to get sharp end point. Th solution was also standardized by complexometric titration against standard EDTA solution at pH 3 using xylenol orange as indicator. U as uranyl was standardized by biamperometric method [18].

2.3. Procedure

All the experiments were conducted at room temperature (∼25 °C). Appropriate quantities of α-HIBA and sodium n-octane sulfonate were dissolved in water and made to 1 and 0.1 M, respectively. All the solutions were adjusted to the desired pH using high-purity NH_4OH and dil. HNO_3 and filtered through 0.45 µm Millipore membrane filters. The mobile phase was pumped through an RP C-18 monolith column using gradient HPLC pump until equilibrium condition was attained. The mixture of lanthanides, Th and U was injected using 100 µL loop and separated under the optimized dual gradient conditions on 4.6 mm × 10 cm monolith column. Throughout the experiment, flow rate of the mobile phase was maintained at 1 mL min^{-1}. The PCR solution [1.5 × 10^{-4} M Arsenazo(III) and 0.01 M urea in 0.1 M HNO_3] was delivered at a flow rate of 0.3 mL min^{-1}. After completing each run, the analytical column was re-equilibrated for 5 min with the initial chromatographic conditions for next run and the chromatographic peak area was used for quantification purpose.

2.4. Rock sample pre-treatment

SY-3 rock sample (∼100 mg accurately weighed) used for method validation was taken in a mixture of 3 mL of conc. HF and 4 mL and conc. HNO_3 and subjected to microwave digestion. The digestion of rock sample was carried out by stepwise program of different microwave powers (250, 450, 600 and 250 W) each for 5 min. The total time taken for the digestion of rock sample was less than half an hour. The digested sample was evaporated to dryness on a hot plate under infra-red lamp. This was further treated repeatedly (three times) with 5 mL of conc. HNO_3 to remove the excess of fluoride. The residue was taken in ∼20 mL of buffer of pH 8.5 (2 M NH_4NO_3 in NH_4OH) and was warmed to ensure complete precipitation. The precipitate was filtered using 0.45 µm membrane filter and washed with ∼40 mL of buffer solution of pH 7.5. The precipitate was further washed with 40 mL of 1 M NaOH solution and was transferred into a beaker and dissolved in conc. HNO_3. The contents of the beaker were evaporated to near dryness to remove HNO_3 and finally the residue was dissolved in 100 mL of water for HPLC separation.

3. Results and discussion

3.1. Separation mechanism of lanthanides, Th and U

In dynamically modified reversed-phase HPLC, IIR (n-octane sulfonate) is dynamically sorbed onto the hydrophobic surface of a reversed-phase column to provide a charged surface that can be used for ion exchange separation of

lanthanides [19,20]. However, U as uranyl ion and Th exhibit retention behaviour different from that of lanthanides. It has been shown that the α-HIBA complexes of U and Th can be retained on a reversed-phase column by hydrophobic adsorption mechanism [13]. At a given concentration of IIR, the reversed-phase column remains partly cation exchanger and hydrophobic. This could be exploited for the separation of lanthanides, Th and U on dynamically modified reversed-phase column by two different mechanisms.

3.2. Difficulties in determination of lanthanides by RP-HPLC

The separation of lanthanides, Th and U has been reported on the dynamically modified reversed-phase column [15,16]. With those chromatographic conditions, Th and U eluted amongst lanthanides and their peak shapes were found to be relatively broader than those of lanthanides (Fig. 1). This could cause the overlapping of two or more lanthanides with Th and U thus making their quantification difficult.

In natural samples of lanthanides, Th and U may be present along with transition elements. The use of Arsenazo(III), which is more specific for lanthanides, could detect the separated lanthanides selectively in presence of transition metal ions [17]. However, Th and U form complexes with Arsenazo(III) and their complexes absorb at the same wavelength as that of lanthanides complexes. Hence, the approach used for transition elements cannot be adopted to eliminate the interferences due to Th and U eluting between the different lanthanides. Using unmodified reversed-phase column, lanthanides eluted out as a group at the solvent front by α-HIBA while Th and U were well resolved. This approach has been reported for determination of Th and U in presence of lanthanides in various geological and mineral processing samples [12,14]. However, the determination of lanthanides in presence of Th and U or simultaneous determination of 14 lanthanides, Th and U by reversed-phase HPLC remained difficult.
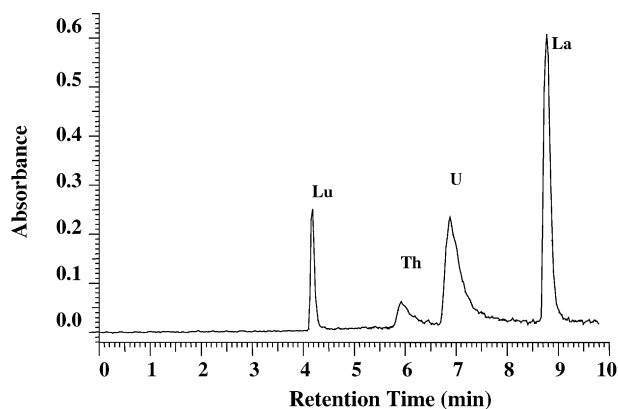
It was therefore necessary to search for the chromatographic conditions which can elute Th and U either before or after the separated lanthanides. Different chromatographic parameters such as IIR concentration, eluent concentration, and pH of eluent used in RP-HPLC were studied systematically using lanthanides (La and Lu), Th and U as discussed below.

3.3. Effect of concentration of IIR on retention of lanthanides, Th and U

In absence of IIR, the α-HIBA complexes of lanthanides showed no interaction with the hydrophobic reversed-phase column and eluted together as a group at the solvent front [12]. Due to the higher hydrophobicity of α-HIBA complexes of Th and U, they showed good retention on the reversed-phase column. With increase in IIR concentration, the hydrophobicity of this column decreases due to the sorption of IIR on the reversed-phase column. This resulted in decreasing the retention of Th and U. The increase in IIR concentration increases the ion exchange capacity of reversed-phase column thereby increasing the retention from Lu to La. However, even at higher IIR concentrations (>30 mM), when the reversed-phase stationary phase might be saturated with hydrophobic anions, Th and U continued to elute between Lu and La.

3.4. Effect of concentration of eluent on retention of lanthanides, Th and U

The influence of the concentration of α-HIBA on retention of lanthanides, Th and U dynamically modified reversed-phase columns is shown in Fig. 2. Increase in the concentration of α-HIBA, resulted in faster elution of lanthanides, Th and U from the modified column with no change in the pattern of separation. The effect of concentration of α-HIBA was studied at pH 4. Under this condition, α-HIBA is ∼63% ionized ($pK_a = 3.77$) [13]. With the increase in concentration of α-HIBA, the concentration of α-hydroxy isobutyrate ions

Fig. 1. Elution of Th and U amongst lanthanides, using the RP-HPLC. Chromatographic conditions: 0.07–0.5 M α-HIBA in 10 min and onwards at pH 4.0 and 3 mM sodium *n*-octane sulphonate using 10 cm C-18 column.
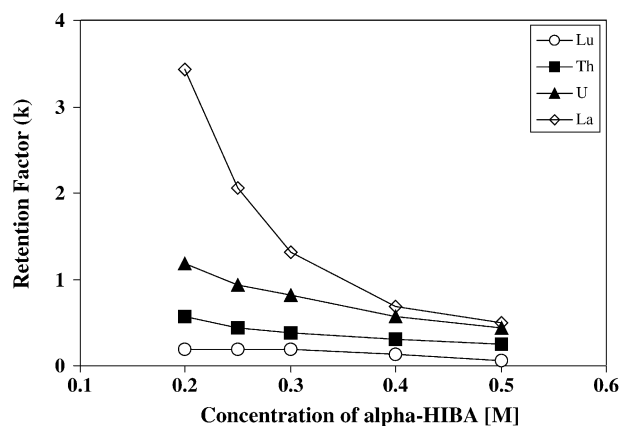

Fig. 2. Effect of concentration of α-HIBA of pH 4.0 on retention of lanthanides (Lu and La), Th and U on modified 10 cm C-18 column by 3 mM of sodium *n*-octane sulfonate.

increases in the mobile phase and this results in faster elution of lanthanides on the modified column. Also, the ∼37% unionized α-HIBA competes with the hydrophobic α-HIBA complexes of Th and U which leads to faster elution of Th and U at higher concentration of α-HIBA.

3.5. Effect of pH of mobile phase on retention of lanthanides, Th and U

The effect of pH of mobile phase on retention of lanthanides, Th and U was also studied on modified reversed-phase column (Fig. 3). At lower pH, higher fraction of unionized α-HIBA is responsible for the relatively faster elution of Th and U than lanthanides. However, under these conditions, Th and U are observed to elute among lanthanides because the retention of Lu is less affected by a change in the concentration as well as the pH of mobile phase. Due to increased ionisation of α-HIBA at higher pH, the concentration of unionized α-HIBA in the mobile phase decreases. This led to the faster elution of lanthanides from Lu to La and slower elution of Th and U. Above pH 5, Th and U showed higher retention factors compared to those for lanthanides and eluted after La.

3.6. Reversed-phase separation of lanthanides, Th and U

From the above studies, the pH of mobile phase was found to be a key parameter in the sequential separation of lanthanides, Th and U. It has been seen from Fig. 3 that at pH ≥ 5 of the mobile phase, Th and U are retained better than lanthanides on the dynamically modified reversed-phase column allowing the elution and separation of all lanthanides before Th and U. The concentration gradient of α-HIBA at pH 5.5 could resolve all the lanthanides on the reversed-phase column modified with 3 mM of sodium n-octane sulfonate. However, the peaks of Th and U were very broad, which limits their accurate quantification. Also for their complete elution, the chromatographic run-time increased from 10 min (for lanthanides) to 20 min (for lanthanides with Th and U).
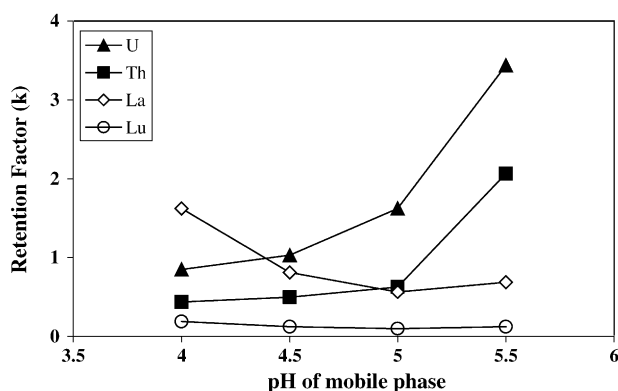

Fig. 3. Effect of pH of mobile phase on retention of lanthanides (Lu and La), Th and U on modified 10 cm C-18 column under isocratic condition: 0.25 M of α-HIBA and 3 mM of sodium n-octane sulfonate.
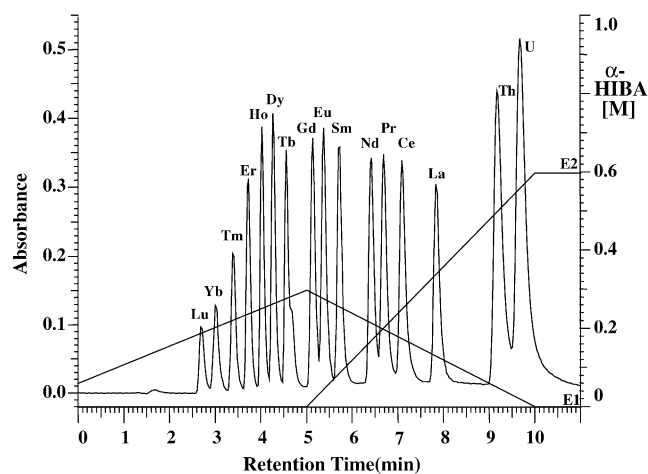

Fig. 4. Separation of 14 lanthanides, Th and U using the optimized dual (concentration and pH) gradients as given in Section 3.6. E1 is concentration of α-HIBA of pH 5.5 and E2 is concentration of α-HIBA of pH 2.0 used to show dual gradients.

The peaks of Th and U were improved by employing simultaneous gradient of decreasing pH of mobile phase along with the increasing concentration of α-HIBA. The use of a lower pH in the latter part of chromatographic run led to higher fraction of unionized α-HIBA which allowed faster elution of Th and U and also improved the peak shapes. Methanol can also be used for faster elution of Th and U from reversed-phase stationary phase as their α-HIBA complexes [13]. However, in this work, the use of low pH of α-HIBA is chosen to elute Th and U instead of methanol due to faster re-equilibration of analytical column under the pure aqueous conditions. The presence of methanol in the mobile phase causes faster removal of IIR from the surface of stationary phase and this may lead to a longer column re-equilibration time between two chromatographic runs. The IIR concentration was also increased stepwise from 3 to 10 mM in dual concentration gradient mode, which improved the resolution amongst the different lanthanides. However, the resolution between Th and U got degraded at higher concentrations of IIR in the mobile phase. At IIR concentration of 10 mM and above, both Th and U co-eluted after lanthanides, and hence, the IIR concentration was optimized to 6 mM. Under the optimised dual gradient conditions [α-HIBA of pH 5.5: 0.05–0.3 M in 0–5 min and 0.3–0 in 5–10 min and onwards; α-HIBA of pH 2.0: 0–0.6 M in 5–10 min and onwards], individual separation of 14 lanthanides, Th and U was successfully achieved in 11 minutes using 10 cm monolith column (Fig. 4).

3.7. Validation of the HPLC method for the separation and determination of lanthanides, Th and U using SY-3 (syenite) rock sample

The optimized RP-HPLC separation methodology for lanthanides, Th and U was demonstrated using SY-3 rock
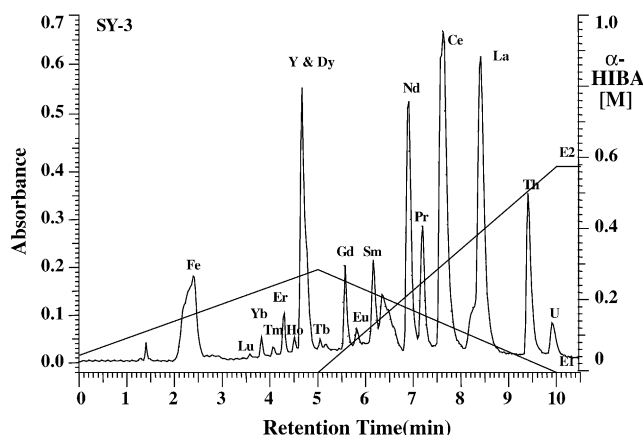
Fig. 5. Separation of lanthanides, Th and U in SY-3 (syenite) rock sample. E1 is concentration of α-HIBA of pH 5.5 and E2 is concentration of α-HIBA of pH 2.0 used to show dual gradients.

sample. The rock sample was treated as discussed in Section 2.4 and the lanthanides, Th and U were preconcentrated by co-precipitation with ferric hydroxide. Several co-precipitation methods have been documented using different carriers such Mg, Al, Fe, etc. [21–23] for lanthanides. Fe was chosen as carrier because it is one of the major constituents of rock samples, shows very less retention on RP-HPLC and elutes before Lu during the HPLC separation of lanthanides. One hundred microliters of the pre-treated rock sample solution was injected for HPLC separation of lanthanides, Th and U under the optimized gradient conditions. To avoid the merging of early eluting lanthanides such as Lu, Yb, Tm, etc. with Fe, gradient separation condition was slightly changed in the beginning to 0.05 M from the optimized 0.06 M. Fig. 5 shows the well-separated peaks of

lanthanides, Th and U in SY-3 rock sample. The carrier Fe eluted out at 2.4 min followed by the lanthanides from 3.5 min onwards. The quantification of lanthanides, Th and U was carried out using peak areas from the chromatograms. The results of their determination in SY-3 rock sample are given in Table 1. The determined values for most of the lanthanides, Th and U are in good agreement with the recommended values for the rock sample with accuracy and precision of 6%. Dy could not be determined in the rock sample due to its overlap with Y during the HPLC separation.

4. Conclusion

With the optimized chromatographic methodology, we could separate and quantify lanthanides, Th and U by RP-HPLC on a single column and with a simple experimental set up in a single chromatographic run using dual (concentration and pH) gradient conditions. The dual gradient elution can be achieved using a single quaternary low-pressure gradient pump. The pH gradient used during the separation improved the chromatographic peak shapes of Th and U eluting after lanthanides. The method was tested using SY-3 geological reference sample for lanthanides, Th and U. This resulted in interference-free determination of lanthanides, Th and U with precision and accuracy of 6%.

Table 1
Determination of lanthanides, Th and U in SY-3 rock sample by RP-HPLC

Elements	Recommended concentration (μg/g)	Determined concentration (μg/g[a])
La	1340	1360 ± 40
Ce	2230	2270 ± 30
Pr	223	221 ± 9
Nd	670	662 ± 24
Sm	109	102 ± 6
Eu	17	15 ± 1
Gd	105	102 ± 3
Tb	18	15 ± 2
Dy	118	ND
Ho	29.5	25 ± 2
Er	68	72 ± 4
Tm	11.6	9 ± 1
Yb	62	58 ± 3
Lu	7.9	9 ± 1
Th	1003	990 ± 20
U	650	640 ± 20

ND: not determined.

[a] Average and standard deviation from triplicate runs.

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