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High-performance liquid chromatography determination of rare earth elements in solutions from solvent extraction process

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Abstract

Dynamic ion exchange has been used for rapid separation (15 min) and determination of rare earth elements (REE) in samples coming from semi-processed monazitic sand, after a heavy fraction separation by solvent extraction. In this study the hydrochloric acid solutions containing REE were injected into the mobile phase (α-hydroxyisobutiric acid) in the presence of hydrophobic ions on a C_{18} bonded silica reversed-phase column. The eluted REE were monitored by visible spectrophotometry at 535 nm after post-column reaction with pyridylazoresorcinol. The reversed-phase partition system is adequate to separate and detect all REE with good reproducibility. This method gave improved column efficiency for metal ions and greater flexibility in the choice of separation conditions. The results obtained in the present study showed good reproducibility and sensitivity and the method may be considered reliable enough to be used in routine quality control procedure. Comparison of the REE values obtained by high-performance liquid chromatography (HPLC) in this study with inductively coupled plasma atomic emission spectrometry (ICP–AES) values showed a good agreement for all elements.

Keywords: Liquid chromatography; Dynamic ion exchange; Rare earth elements; Solvent extraction process

1. Introduction

In general, different instrumental methods of analysis have been used for the determination of rare earth elements (REE) in various matrices [1]. Because of their similar chemical properties it is difficult to determine individual REE in mixtures by standard analytical methods.

Among many techniques, the most commonly reported are the neutron activation analysis (NAA) [2] and inductively coupled plasma atomic emission spectrometry (ICP–AES) [3,4]. These methods have limitations, like interference of different metal ions, high acidity of samples to be analyzed, high instrumental cost, etc.. ICP–MS is a relatively new technique, with high sensitivity, but it is expensive and in general tends to have poor reproducibility [5,6].

One of the main advantages of dynamic ion exchange chromatography is the greater flexibility with regard to separation conditions, resulting in superior resolution of REE [7–10].

Ion-exchange are dynamically formed when hydrophobic ions present in the mobile phase are absorbed on the hydrophobic surface of the column packing material to produce a charged double layer at the surface, where ion exchange can occur.

In this paper α-hydroxyisobutiric acid has been found to be an effective complexing agent coupled with post column reaction detection with 4-(2-pyridylazo)resorcinol, monosodium salt hydrate (PAR) for the dynamic ion exchange chromatography of REE in samples coming from semi-processed monazitic sand, after a heavy fraction separation by solvent extraction.

The aim of this paper is to demonstrate the application of the dynamic ion exchange in the analytical control of the rare earths fractionation process in a wide range of concentrations, and compare the REE values obtained by HPLC with ICP–AES values for the same samples.

2. Experimental

2.1. Reagents and materials

Stock solutions of REE were prepared by dissolving their pure oxides 99.99% (Johnson Mathey) in mineral acids. Eluents and sample solutions were prepared with distilled water that had been purified in a Milli-Q unit (Millipore) and filtered through a 0.2 µm membrane filter. The following reagents grade chemicals were used:

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4-(2-pyridylazo)resorcinol, monosodium salt hydrate (PAR), 0.05 mg/l in 2 M ammonium hydroxide and 1 M acetic acid; α-hydroxyisobutyric acid (α-HIBA), 0.07 and 0.4 M aqueous solutions buffered at pH 3.8 with ammonium hydroxide; 0.01 M sodium laurylsulphate (LS); Waters Nova-Pak C_{18} column (150×3.9 mm I.D.) and Waters C_{18} Guard-Pak (5.0×6.0 mm I.D.), housed in a Waters Guard-Pak (precolumn module).

2.2. HPLC apparatus

The liquid chromatograph used in this work was a 625 LC from Waters Associates, equipped with a linear gradient programmer, a Rheodyne 9125 load injection valve, a constant-flow peristaltic pump, a Waters 490 programmable multiwavelength spectrophotometric detector and a Waters RDM module (post-column reagent) used to transfer the PAR complexing solution. The output from the detector was recorded on a LC Workstation CLASS-LC10 Shimadzu.

2.3. Procedure

2.3.1. Solvent extraction process

The feed solution is the REE chloride, constituted of medium REE fraction after heavy fraction separation, from Brazilian monazite processing carried out by Nuclemon Mineroquímica, SP. This solution was prepared by adjusting the acidity, by addition of ammonium hydroxide, to pH 1.5 and showed as main constituents Sm (61%) and Gd (31%). The organic phase was the extractant 2-ethylhexyl phosphonic acid, mono-2-ethylhexyl ester, diluted to 1 M in isododecane.

The tests were carried out in continuous-circuit based on 4 extraction stages, 6 scrubbing stages and 4 stripping stages, using a micro-pilot unit of mixers–settlers. 0.5 and 2 M HCl solutions were used for the scrubbing and stripping sections, respectively. The phase ratios organic/ aqueous (O/A) were 1.2 for the extraction section, 2 for the scrubbing section and 3 for the stripping section.

The individual REE determinations in aqueous phases were accomplished by HPLC and an inductively coupled plasma atomic emission spectrometer (ICP–AES), Atoncomp, serial Ash-800.

2.3.2. HPLC procedure

Samples (10 to 100 μl) of the diluted REE fractions from the solvent extraction process were injected into the mobile-phase and α-HIBA concentration was then programmed linearly from 0.01 to 0.4 M several times. The sodium laurylsulphate concentration (0.01 M), the pH (3.8) and flow-rate (1 ml/min) were maintained at a constant level during the gradient program. The concentrations of REE in the samples were calculated with the non-linear regression program in the LC-10. The regression equation was generated with peak areas from several

Table 1
REE concentrations (g/l) in the solutions from solvent extraction process by HPLC and ICP–AES

REE	Feed solution flow 10 ml/min		Raffinate flow 25 ml/min		Strip liquor flow 10 ml/min	
	HPLC	ICP–AES	HPLC	ICP–AES	HPLC	ICP–AES
Pr	0.080	0.080	0.032	[a]	[a]	[a]
Nd	0.780	0.778	0.310	0.311	[a]	[a]
Sm	10.301	0.288	4.100	4.087	0.100	0.101
Eu	0.290	0.290	0.040	0.040	0.190	0.190
Gd	5.310	5.300	0.099	0.100	5.054	5.050
Tb	0.030	[a]	[a]	[a]	0.030	[a]

[a] Not detected.

standards covering the concentration range expected for the samples.

3. Results and discussion

To evaluate the separation and quantification of the REE, a calibration has been carried out by employing known standard REE mixtures. The REE concentrations were determined in the feed, raffinate and strip liquor solutions.

Table 1 lists the results for the three solutions and the comparison with ICP values. The typical chromatogram obtained for the feed solution, raffinate and strip liquor is shown in Fig. 1 Fig. 2 Fig. 3, respectively. The elution gradient used for the feed solution was programmed linearly from 0.01 to 0.4 M over 45 min. The same gradient was used for the raffinate and strip liquor solution over 30 min, as can be observed in Figs. 1 and 2.

These results demonstrate the total elution of individual REE. A comparison of the REE values, obtained by HPLC
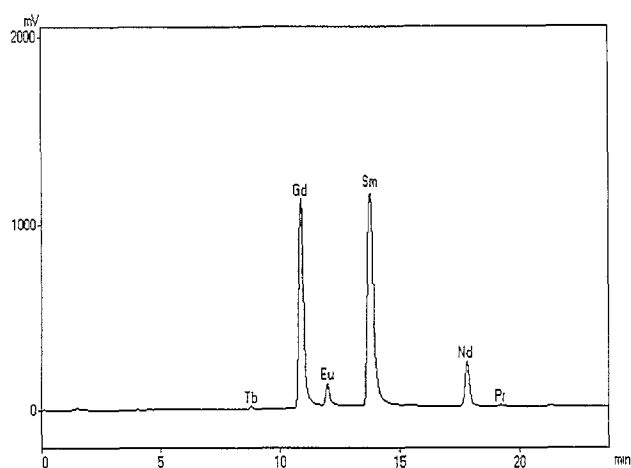

Fig. 1. Separation of rare earths in the solvent extraction process–feed solution. Experimental conditions: Waters Nova-Pak C_{18} column (150× 3.9 mm I.D.); gradient separation at 1 ml/min from 0.01 to 0.4 M α-HIBA at pH 3.8 over 45 min with 0.01 LS. Injection volume 20 μl.

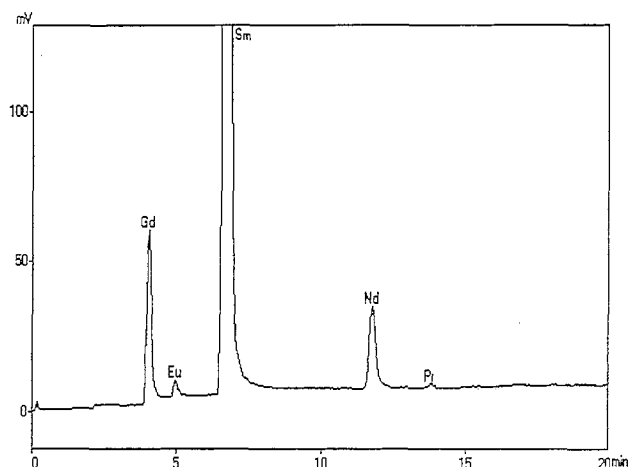Fig. 2. Separtion of rare earths in the solvent extraction process–rafinnate by gradient elution in 30 min. Experimental conditions as in Fig. 1. Injection volume 15 μl.

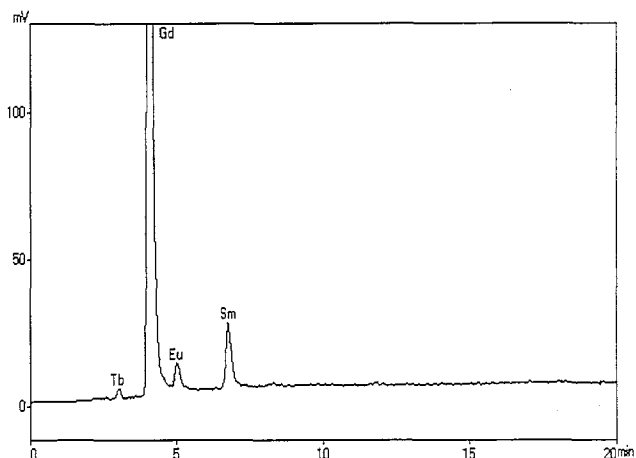in this study, with the ICP–AES showed agreement to within 1% for most of the elements.

Fig. 3. Separation of rare earths in the solvent extraction process–strip liquor by gradient elution in 30 min. Experimental conditions as in Fig. 1. Injection volume 10 μl.

The results obtained from the solvent extraction process were satisfactory, attaining the separation of the feed solution in a raffinate with about 90% Sm and a strip solution with 94% Gd. The proposed continuous-circuit configuration showed a high recovery yield, around 99% for Sm and 95% for Gd.

This study showed that HPLC is able to provide rapid and accurate analyses of REE which appear to be faster and less expensive than those performed by other instrumental methods.

Acknowledgments

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