

## Study of the rare earth elements fractionation by solvent extraction: Use of HPLC as an analytical control technique

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### Abstract

The influence of the acidity and concentration of the rare earth elements (REE) in aqueous phase, the organic/aqueous phase ratio and the HCl concentration in stripping was estimated for the REE fractionation by solvent extraction. The assays were performed in batch tests by using 2-ethylhexylphosphonic acid, mono-2-ethylhexyl ester, diluted in isododecane ( $1 \text{ mol l}^{-1}$ ). The solution studied presented a REE concentration of  $16.54 \text{ g l}^{-1}$  (Nd 4.84%, Sm 61.36%, Eu 1.75%, and Gd 32.05%) in  $0.77 \text{ mol l}^{-1}$  hydrochloric medium. In order to control the analytical parameters (acidity and concentration of REE) in the aqueous solutions generated by the separation stages of the batch tests, a high-performance liquid chromatography (HPLC) technique was employed. The REE were separated from each other with  $\alpha$ -hydroxyisobutyric acid as eluent and *n*-octane sodium sulphonate as modifying agent, in a  $C_{18}$  reverse phase column. Eluted REE were monitored at 520 nm by a spectrophotometer after a post-column reaction with 4-(2-pyridylazo)resorcinol. Results are reported as extraction profiles and a chromatogram. For the studied parameters, it was found that, in lower acidity and concentration solutions, higher extraction percentages for the REE are obtained. In all assays, Gd and Eu were preferably extracted.

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### 1. Introduction

The study of rare earth elements (REE) fractionation by solvent extraction technique and their determination by high-performance liquid chromatography (HPLC) have been carried out in our laboratory [1,2].

The chemical properties of adjacent REE are very similar, thus making the separation of individual REE quite difficult. Different techniques for the separation of REE have been studied, varying from classical techniques, such as fractional crystallization and fractional precipitation, to more recent ones, such as ion-exchange and solvent extraction.

The solvent extraction technique has been proved very versatile and many studies have reported the use of this technique. In liquid–liquid extraction, different extractants have been researched. The most used ones, for REE separation, are the organophosphorus acids, with prominence of di-2-ethylhexyl phosphoric acid (D2EHPA), 2-

ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH(EHP)) and tri-*n*-butyl phosphate (TBP).

Peppard and co-workers [3–5] were among the first researchers to study the REE solutions fractionation by the solvent extraction technique, using organophosphorus acids as extractants. They found that the logarithm of the distribution ratio is a linear function of the REE ionic radii. They also observed that the distribution ratio increases with the atomic number, that is, with the decrease of the ionic radius, and is also favored by low acid concentrations in the aqueous phase.

Deqian et al. [6] compared the action of the extractants HEH(EHP) and D2EHPA, and found that the latter showed better extractability, although the former was advantageous, since an acid solution with lower concentration is enough for the REE stripping in organic phase and also, the absence of emulsion production, that sometimes occurs with the use of D2EHPA.

In the present paper, the determination of REE in aqueous solutions generated by solvent extraction process was investigated through a HPLC technique, with post-column reaction detection. This analytical technique can

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provide rapid and accurate results for the determination of all the REE [7], besides the selectivity and analysis of several elements simultaneously in a short time, when compared with conventional ion-exchange. In this technique, a modifier is added to the mobile phase, in the form of a hydrophobic ion, in order to create a charged surface on the reversed-phase column packing material. Metals in the sample are separated when they interact with the charged particles of the packing material. This method gave improved column efficiency for metal ions and greater flexibility in the choice of separation conditions.

## 2. Experimental

### 2.1. Extraction tests

The assays were performed at 25 °C in batch tests and were carried out in order to study the influence of some parameters in the solvent extraction. In order to study each parameter separately, the batch tests were divided into four blocks. In block 1, aqueous phase acidity was studied. In block 2, aqueous phase REE concentration was examined. In block 3, O/A phases ratio was studied. In block 4, stripping of the REE contained in the organic phase was examined with the use of HCl solutions.

For the organic phase, we used 2-ethylhexylphosphonic acid, mono-2-ethylhexyl ester, diluted in isododecane ( $1 \text{ mol l}^{-1}$ ).

The aqueous phase, contained in multi-element solutions with  $16.54 \text{ g l}^{-1}$  of REE (Nd 4.84%, Sm 61.36%, Eu 1.75%, and Gd 32.05%) in hydrochloric medium at  $0.77 \text{ mol l}^{-1}$ , was obtained from a semi-processed product from monazite sands, after a separation stage of the heavy fraction in the solvent extraction process.

The monazite sand processing, carried out by Nuclemon-Mineroquímica, was made with sodium hydroxide at high temperature. After filtration, we obtained a mixture of uranium, thorium and REE hydroxides. Then, a partial dissolution of the mixture of hydroxides with hydrochloric acid was made until a pH near 4 was reached. The thorium–uranium hydroxides were filtered and the REE were recovered as mixed chlorides [8].

The tests were performed in a single contact, by stirring the solution for 10 min with O/A phases ratio=1, using aqueous phase with REE concentration  $15.74 \text{ g l}^{-1}$  and pH 1.5, except in the blocks in which each parameter was separately evaluated. After each contact, the dispersion was left to rest during 20 min, for the phase separation to take place.

### 2.2. HPLC analysis

The analyses were performed in a liquid chromatograph (Waters), equipped with a linear gradient programmer, a load injection valve (Rheodyne 9125), a constant-flow

pump (Waters 625), a post-column reagent module (Waters RDM) and a programmable multiwavelength spectrophotometric detector (Waters 490). The output of the detector was linked to a Shimadzu CLASS LC-10 data system.

The samples containing the REE, obtained from the solvent extraction process, were filtered and diluted in a ratio range varying from 1/25 to 1/200, with water previously purified by a MilliQ system (Millipore). The resulting pH of the diluted samples was around 3.

Aliquots (10–100  $\mu\text{l}$ ) from the diluted REE samples were injected in a 4- $\mu\text{m}$  Nova-Pak  $\text{C}_{18}$   $3.9 \times 150 \text{ mm}$  column (Waters). The mobile phase used was  $\alpha$ -hydroxybutyric acid ( $\alpha$ -HIBA) and  $0.01 \text{ mol l}^{-1}$  *n*-octane sodium sulphonate (OS), as a column modifying agent, at pH 3.8 adjusted with NaOH. The concentration of the mobile phase was linearly programmed in binary gradient with 0.01 and  $0.40 \text{ mol l}^{-1}$  for 30 min, keeping constant the flow-rate of the mobile phase ( $1 \text{ ml min}^{-1}$ ).

The eluted REE were detected after a post-column reaction with  $0.05 \text{ mg l}^{-1}$  4-(2-pyridylazo)resorcinol (PAR), in  $2 \text{ mol l}^{-1}$  ammonium hydroxide and  $1 \text{ mol l}^{-1}$  acetic acid. The detection of the REE–PAR complexes in the effluent was monitored by a UV–Vis. detector at 520 nm, keeping the flow-rate of the post-reaction detection reagent solution at  $0.5 \text{ ml min}^{-1}$ .

The concentrations of the REE in the samples were calculated with the non-linear regression program in the LC-10 system. The analytical curves were generated by plotting the peak areas against known concentrations of the individual REE, covering the range expected for the samples.

## 3. Results and discussion

Fig. 1 shows the chromatogram of the aqueous solution under study. The REE concentration is proportional to the peak area, indicating the preponderancy of Gd and Sm elements in this solution.

From the distribution factors of the elements, defined as the distribution behavior of an element between immiscible aqueous and organic phases, the separation factors ( $\beta$ ) between two elements were calculated.

The influence of the aqueous phase acidity was observed for all the elements in the extraction process. The extraction percentage (% *E*) increases with the increase of pH (Fig. 2), with the better values occurring at pH 3.0. The calculated separation factors ( $\beta$ ) (Table 1), for all the pairs of elements, varied with the pH, and the highest  $\beta$  value was obtained for Sm/Nd, 9.2 at pH 1.5, while Gd/Eu showed minimum values when compared to the other element pairs. For the Gd/Sm pair,  $\beta$  showed low variation for the examined pH range, with the maximum value, 4.59, having been obtained for pH 1.5.

In Fig. 3, one can observe that the REE % *E* decreases

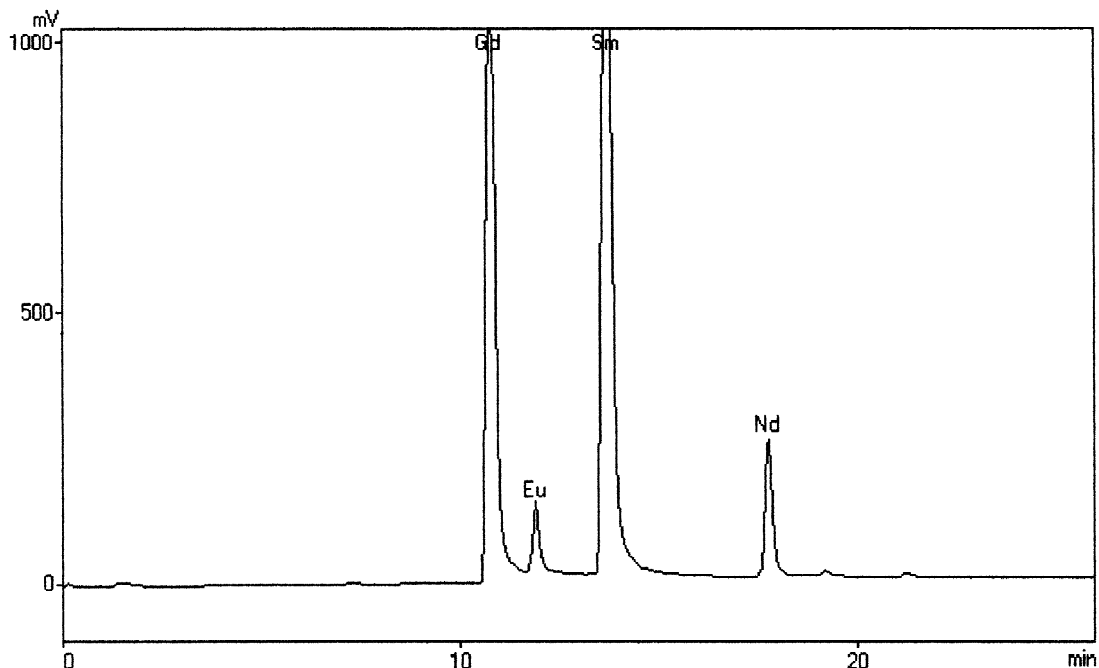


Fig. 1. Separation of REE in the sample studied. Experimental conditions: Waters Nova-Pak  $C_{18}$  column ( $150 \times 3.9$  mm I.D.); gradient separation at  $1 \text{ ml min}^{-1}$  from  $0.01$  to  $0.40 \text{ mol l}^{-1}$   $\alpha$ -HIBA at pH 3.8 over 30 min with 0.01 OS. Injection volume  $20 \mu\text{l}$ .

with the rising of REE concentration in aqueous phase. The  $\beta$  values (Table 1) showed strong variations with the variation of the REE concentration in aqueous phase, especially for the Sm/Nd pair, which also presented the higher  $\beta$  values. It was observed, for the Sm/Nd and Gd/Eu pairs, that the  $\beta$  values decrease with the increase of the REE concentration in aqueous phase, while for the Eu/Sm and Gd/Sm pairs an opposite behavior was observed, with the higher  $\beta$  values having been obtained for the higher examined REE concentration values.

In Fig. 4, one can notice that the %  $E$ , for all elements, increased with the rising of the O/A phase ratios. Nd and Sm showed the highest sensibility for the extraction

performance, as with the O/A ratio ranging from 4 to 1, the %  $E$  increased by a factor 4 for Nd and by a factor 2 for Sm. Eu and Gd showed lower sensibility, with no significant improvement of the %  $E$ . The  $\beta$  value (Table 1), for the Gd/Sm pair decreased with the rising of O/A ratio, indicating more efficient separation with O/A = 1 for this pair.

The REE in organic phase were removed (stripped) with hydrochloric acid solution. In Fig. 5, it can be observed that the elements showing the lower %  $E$  values, presented increased stripping rates, with higher percentage stripping (%  $S$ ) for Nd and Sm and lower %  $S$  for Eu and Gd, for the same examined concentration of the HCl solution. For

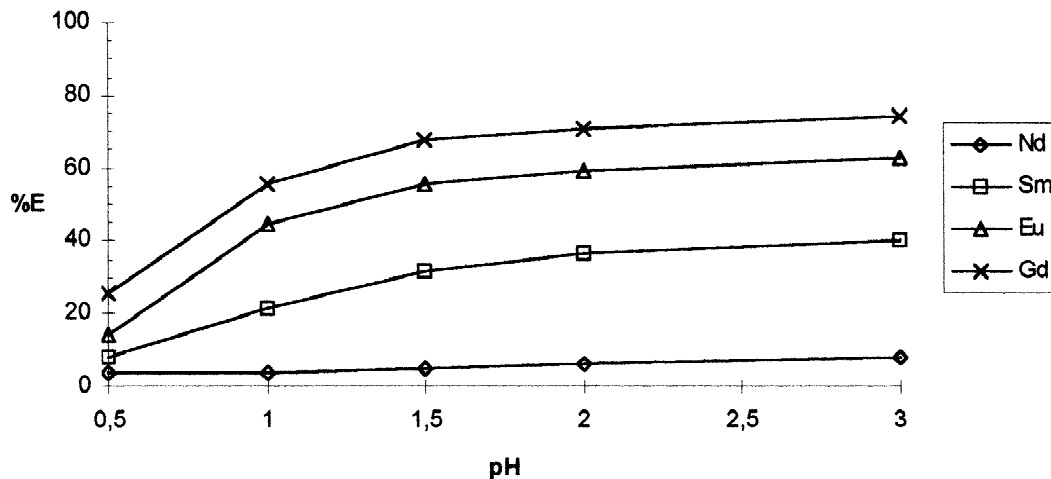


Fig. 2. Extraction percentage profile (%  $E$ ) versus aqueous phase pH.

Table 1  
Separation factors ( $\beta$ )

	Sm/Nd	Eu/Sm	Gd/Eu	Gd/Sm
Block 1: pH				
0.5	2.00	2.13	2.00	4.25
1.0	7.00	2.86	1.55	4.43
1.5	9.20	2.72	1.69	4.59
2.0	8.14	2.54	1.65	4.19
3.0	8.50	2.50	1.70	4.25
Block 2: [REE] ( $\text{g l}^{-1}$ )				
3.94	43.22	1.63	2.04	3.31
7.87	45.79	1.26	1.88	2.37
11.80	12.30	1.39	1.85	2.57
15.74	9.20	2.72	1.69	4.59
Block 3: O/A				
1	9.20	2.72	1.69	4.59
2	6.14	2.33	1.76	4.09
3	4.88	2.03	1.91	3.87
4	5.43	1.87	2.08	3.89

the HCl solutions with concentrations higher than  $1.0 \text{ mol l}^{-1}$ , all the elements are removed from the organic phase and for HCl solutions with  $0.5 \text{ mol l}^{-1}$  concentration, 96% of Sm and 70% of Gd are removed from the organic phase.

From the obtained results, the following trends were found: the %  $E$  increases along the lanthanidic series and it is more efficient when aqueous phases with low acidity, low REE concentration and higher O/A phase ratios are used. The REE %  $S$  in organic phase decreases along the lanthanidic series and is more efficient when more concentrated HCl solutions are used.

Given the obtained results, one can observe that the fractionation will occur between the elements Sm and Gd, and, among the examined conditions, those which presented maximum  $\beta$  values for the Gd/Sm and Eu/Sm pairs and lower  $\beta$  for the Gd/Eu pair and, therefore, favor the Sm/Gd separation, are: aqueous phase with  $15.74 \text{ g l}^{-1}$

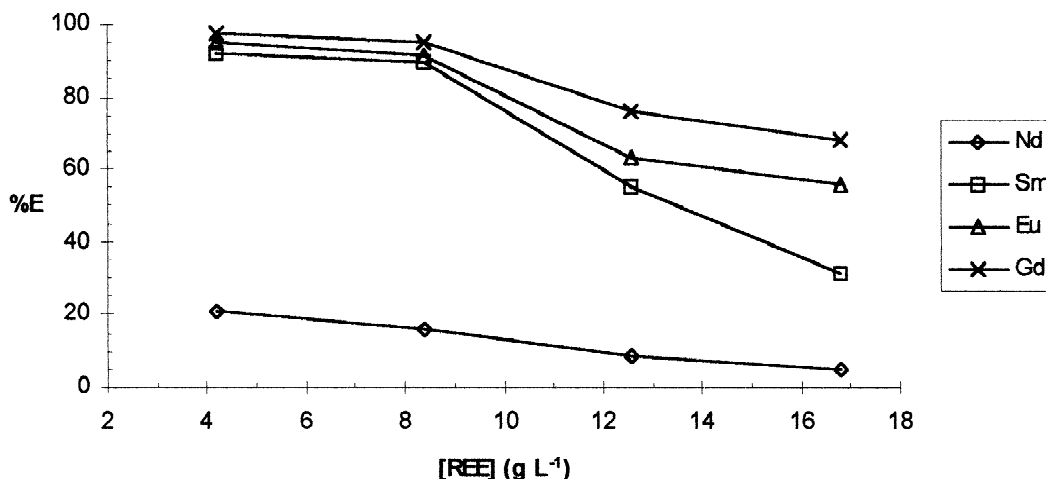


Fig. 3. Extraction percentage profile (%  $E$ ) versus REE concentration in aqueous phase.

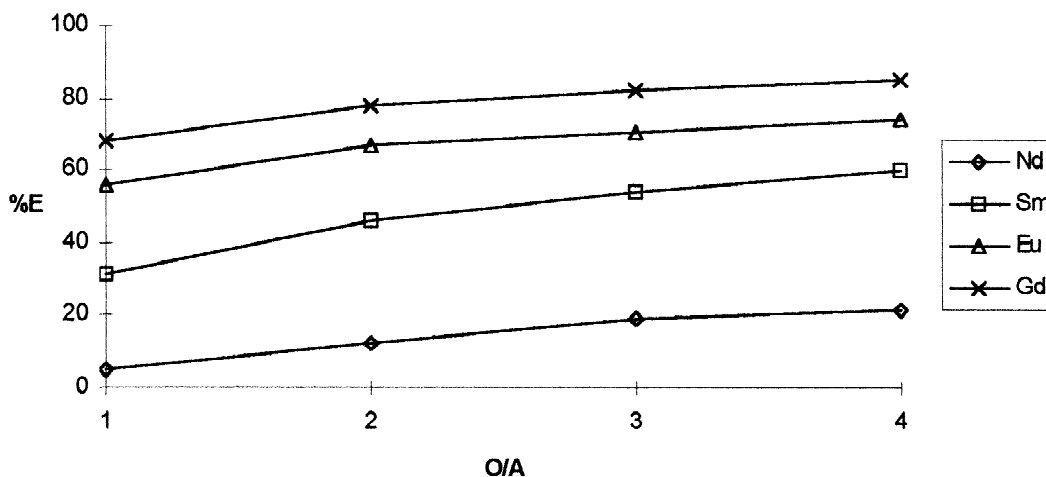


Fig. 4. Extraction percentage profile (%  $E$ ) versus organic and aqueous phases ratio (O/A).

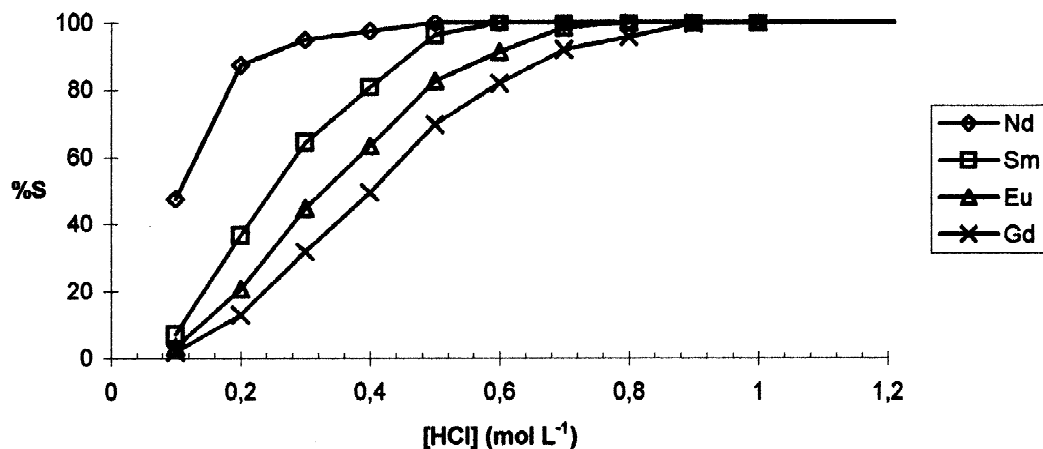


Fig. 5. Stripping percentage profile (%S) versus concentration of HCl solutions.

REE concentration, pH in the range 1–1.5 and O/A phase ratio in the range 1–2.

This study indicates that the proposed liquid chromatography method can be a good alternative to traditional methods, showing the applicability to the analytical control of REE fractionation process.

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