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USE OF SEQUENTIAL COLUMNS IN ION EXCHANGE RARE EARTH SEPARATIONS

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ABSTRACT: The use of low graded ion exchange resin, combined with other of analytical grade, is described for Rare Earth (RE) separation by ion exchange. This method is less expensive, easily operated and almost efficient as the traditional separations with good graded resins.

KEY-WORDS: Rare earth; ion-exchange.

INTRODUCTION

Ion exchange is widely used in Rare Earth separation, and, since the first achievements, several improvements in the technique have been attempted. Resin, eluant and pH are some examples of the various parameters studied in those separations[1,4]. Very good conditions were achieved with the use of Dowex 50 X 4 resin, EDTA as eluant and Cu(II) or Zn(II) as the retaining ion[2]. In this method, two columns connected in series, and packed with the same resin (Dowex 50 X 4) are employed. The first column is loaded with the RE mixture, and the second with the retaining ion. In this paper it is described a modification of this method, using columns packed with different resins, the first being Amberlite IR-120 (20-50 mesh, commercial grade, 8% DVB) and the second with Dowex 50 X 4 (50-100 mesh). The results are compared with those previously obtained with either Dowex or Amberlite only in both columns. EDTA was used as eluant and Zn(II) as the retaining ion. Furthermore, the RE mixture is the same in all experiments compared.

EXPERIMENT

The starting material is a solution of Rare-Earth chloride from industrial Brazilian monazite treatment, and its composition is shown in Table 1. Most of the cerium was isolated from $RECl_3$ solution by oxidation with sodium hypochlorite solution. The final stock solution for all experiments here described showed 3% in Ce(III) content and was 0.386 M in RE. The low concentration of Ce(III) and the resulting increase in La(III) concentration improves the separation of the other RE first eluted[5,6].

Ion exchange. The experiments were run using two columns of 100 cm height by 2.5 i.d., connected in series, Zn(II) as the retaining ion, a 7.6 g/l solution of EDTA at pH 8.6 as eluent, and 400 ml of 0.368 M solution of $RECl_3$, corresponding to 25.2 g of RE oxides. The flow was kept at ~2 ml/cm^2. min. In one case (A), both columns were packed with Dowex. The first column loaded with RE and the second with Zn. In the other case (B), the first column was packed with Amberlite and loaded with RE, while the second column

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was packed with Dowex and loaded with Zn. In both cases the resins were initially in the ammonium form. The eluate treatment consisted of EDTA recovery; precipitation of RE as oxalates, which were burned. Individual RE content was analyzed spectrophotometrically[7] as $LnCl_3$ solution. Total RE content was determined gravimetrically[8] as oxide from oxalate precipitation and by EDTA complexometric titration with Xylenol Orange as indicator[9].

RESULTS AND DISCUSSION

Fig. 1 shows the chromatograms of experiments A and B in terms of RE oxides contents of the eluates. The total amount of recovered material is also given. Both figures show similar pattern of separation. La and Nd are separated with high purity and the remaining RE are enriched.

Table 2 shows that 25.16 g of RE oxides, corresponding to 99.8%, are recovered, and that 24.1 g, corresponding to 95.6% are enriched.

Table 3 shows that 25.0 g of RE oxides, corresponding to 99.2%, are recovered, and that 24.1 g, corresponding to 95.6 are enriched.

Since more than 99% of RE are recovered in both experiments, the M_i columns indicate also the RE composition of the stock solution.

The results indicate that recovery and enrichment are similar in both systems. However, M_f for each RE refers to the sum of weights in all enriched fractions, although having different RE contents.

La and Nd content in some fractions appeared to be equal to or greater than 90% and 99% as is seen in Table 4. This indicates that 87% of La is recovered with a purity 99% in experiment A, and 80% in experiment B, while 57% of Nd is recovered with purity 99% in experiment A and 52% in experiment B. If a purity 90% is chosen instead, the amount of recovered material with this purity becomes 91% and 87% of La in experiments A and B, respectively, and 82% and 66% of Nd in experiments A and B respectively. The remaining RE were just enriched to a content below 93%.

The results show that system B is almost as operative as system A and the separation is nearly dictated by the nature of the second column. This allows the use of the less expensive resin in the first column, as is described in this paper. Furthermore the flow in system B is easily kept constant.

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TABLE 1
Rare Earth distribuition in Brazilian Monazite, % as oxide

La	Ce	Pr	Nd	Sm	Gd	Y + RE
22.4	47.6	4.9	18.3	2.2	1.7	2.9

TABLE 2

Data from experiment A (Dowex 50 X-4 and Zn(II))

RE	M_i	$\%_i$	M_f	$\%_f$
Gd	0.739	2.9	0.739	100.0
Sm	0.981	3.9	0.981	100.0
Pr	1.902	7.7	1.845	97.0
Nd	8.100	32.2	7.726	95.4
Ce	0.766	3.0	0.766	100.0
La	11.911	47.3	11.288	94.8
Y + RE	0.761	3.0	0.761	100.0

M_i = Total weight of each RE recovered.
$\%_i$ = RE percentage relative to the total RE recovered.
M_f = Total weight of each RE in the enriched fractions.
$\%_f$ = Weight percentage of RE in the enriched fractions (relative to M_i).

TABLE 3

Data from experiment B (Amberlite IR-120 and Dowex 50 X-4 and Zn(II))

RE	M_i	$\%_i$	M_f	$\%_f$
Gd	0.757	3.0	0.757	100.0
Sm	1.062	4.2	1.062	100.0
Pr	8.078	32.3	7.753	96.0
Nd	1.880	7.6	1.831	97.4
Ce	0.758	3.0	0.758	100.0
La	11.708	46.8	11.164	95.3
Y + RE	0.766	3.1	0.766	100.0

M_i, $\%_i$, M_f and $\%_f$ as in Table 2.

TABLE 4

Comparative data of La(III) and Nd(III) enrichment in method A and B. From 25.2 g of RE_2O_3 eluted in each experiment

Experiment	La ≥ 90%	Nd ≥ 90%	La ≥ 99%	Nd ≥ 99%
A(g)	10.901	6.712	10.416	4.652
B(g)	10.30	5.344	9.350	4.248

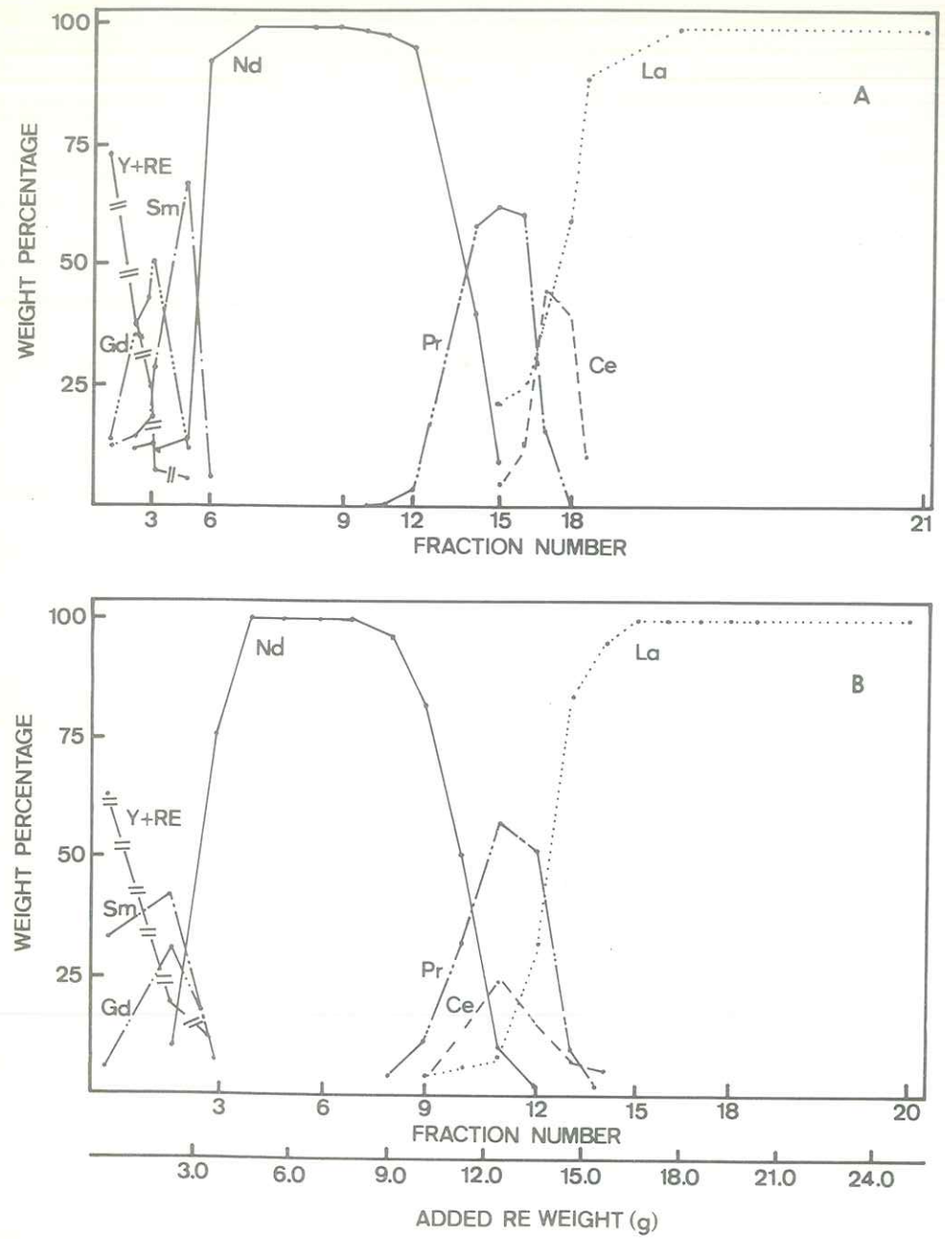

FIG. 1 — Eluate composition, elution of 25.2 g of RE oxides. A (Dowex 50 X-4 and Zn(II). B (Dowex 50 X-4, Amberlite IR-120 and Zn(II)).

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RESUMO: O uso de resinas de troca-iônica de grau laboratório, ou comercial, associado com outra de pureza analítica é descrito para a separação de Terras Raras (RE) por troca-iônica. Este método é mais econômico, mais facilmente operável e quase tão eficiente quanto os métodos tradicionais que utilizam apenas as resinas de maior pureza.

UNITERMOS: Terras raras; troca-iônica.

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