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Separation of lanthanides and yttrium as anionic complexes by isocratic ion-interaction chromatography

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ABSTRACT

Rare earth elements in nitric acid solution can be individually separated by ion-interaction chromatography. The separation is achieved by isocratic elution with oxalic acid as the complexing agent in the eluent and tetra-*n*-butylammonium hydroxide as the ion-pairing reagent. The separated rare earth elements are measured spectrophotometrically after post-column reaction with Arsenazo III, and can be determined at levels $\geq$ 0.5 mg/l with a relative standard deviation of 0.01% for the individual rare earth elements at the 10 mg/l level. The order of elution is from lanthanum to lutetium, yttrium being eluted immediately after terbium.

INTRODUCTION

The determination of rare earth elements (REEs) is important in several industries such as in the nuclear power industry for the lanthanide fission products of irradiated fuels and in the mining industry for the determination of REEs in rock samples. The determination of REEs, particularly the individual members of the group, is a difficult and complex problem. Mintek has been involved for many years in the evaluation of analytical procedures, and in the development of sensitive and reliable methods such as the recently developed atomic emission spectrometric determination of REEs in minerals using a scanning monochromator system.

High-performance liquid chromatography (HPLC) followed by a post-column reaction was used for the separation and determination of REEs as early as 1972. In 1986, Cassidy *et al.* [1] and Barkley *et al.* [2] demonstrated that reversed-phase ion-interaction chromatography is a rapid and accurate method for the separation and determination of lanthanum in nuclear fuels and REEs in refining process streams. They employed a silica-based C_{18} reversed-phase column with hydroxyisobutyric acid (HIBA) as the complexing agent and octanesulphonate ($C_8SO_3^-$) as the ion-pairing reagent.

Because REEs have a positively charged trivalent state, they exist in a strongly hydrated state in solution. Organic chelating agents can replace part of the water of

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hydration, forming complexes that exhibit wide spreads between the formation constants. When complexes are formed with the positively charged trivalent REEs, the result is a net decrease in the charge of the REEs as the complex, with the largest decrease for the strongest complex [3]. The heavy REEs form strong complexes with a reduction in the positive charge. In ion-interaction chromatography, these complexes will be eluted first. Therefore, with HIBA and $C_8SO_3^-$, the order of elution was from lutetium to lanthanum. The separated REEs were measured spectrophotometrically after post-column reaction with Arsenazo III. A similar separation was achieved by Heberling *et al.* [3] with a pellicular latex-agglomerated resin-based ion exchanger, HIBA as the eluent and 4-(2-pyridylazo)resorcinol (PAR) as the chromogenic reagent in the post-column reaction. In this cation-exchange chromatographic separation, not only did the sensitivities of the lighter REEs, which were eluted last, decrease, but also these REEs were not completely resolved. In subsequent work that was based on the work of Cassidy *et al.* [1], the separation of the individual REEs, including the separation of yttrium from dysprosium, was achieved by ion-interaction chromatography [4]. The sensitivities for the REEs in that separation increased during the elution of lutetium to lanthanum, and the individual REEs were completely resolved.

When this order of elution is used to separate and determine trace amounts of REEs in the presence of large amounts of an individual REE, only the REEs heavier than the matrix REE can be separated and determined. All the REEs lighter than the matrix REE will be "swamped" by the relatively large amounts of the matrix REE. In order to separate and determine traces of REE on either side of an individual REE, the order of elution must be reversed, *i.e.*, lanthanum must be eluted first followed by the other REEs, with lutetium being eluted last. This can be achieved by the formation of anionic complexes of the REEs with suitable complexing agents such as citrates, tartrates and oxalates. Anionic complexes formed with the REEs and organic chelating agents exhibit a wide spread in the range of their formation constants. These anionic complexes of the individual REEs can be separated by anion exchange with an elution order from lanthanum to lutetium, a separation that was achieved by Heberling *et al.* [3] with a pellicular latex-agglomerated ion exchanger and gradient elution, using an eluent consisting of various amounts of oxalic and diglycolic acids. However, Heberling *et al.* did not achieve the resolution between ytterbium and lutetium. In addition, the sensitivity for the REEs increased from the minimum for the first REE eluted, lanthanum, to a maximum for dysprosium before decreasing again for ytterbrium.

The investigation described in this paper concentrated on the possible use of a silica-based C_{18} reversed-phase column for the anionic separation of individual REEs by ion-interaction chromatography with an elution order from lanthanum to lutetium so that better sensitivity could be obtained than that achieved by other investigations. Complete resolution between the fourteen individual REEs plus yttrium was also investigated.

EXPERIMENTAL

Apparatus and reagents

The chromatograph, which was assembled from Spectra-Physics components,

consisted of a pump (SP 8700 XR extended-range LC pump) and an injector fitted with a 50-μl sample loop. A photometric detector (SP 8773 XR) was fitted between the column and the computing integrator and was set at a wavelength of 658 nm and an absorbance range of 0.080. The chart speed and attenuation of the computing integrator (SP 4200) were set at 2.5 mm and 32, respectively. The column was a Supelcosil LC-18 (150 × 4.6 mm I.D., 5-μm particle size). An in-line filter containing a carbon-frit filter (0.5 μm) was placed immediately in front of the column to protect the column from particulate matter. The post-column reactor (PCR) was a modification of that used by Cassidy *et al.* [1]. It was made by the insertion of square-cut Teflon tubing (0.5 and 1.5 mm I.D. and O.D., respectively) into a bored-out Omnifit Teflon tee. A small plug of glass-wool was placed between the eluent inlet tube and the outlet tube to the detector. The PCR reagent reservoir was under a constant helium pressure, and this pressure forced the PCR reagent solution (Arsenazo III) into the PCR. The pressure was maintained with a regulator of 0–2 bar. The PCR solution passed along the outside of the eluent inlet tube, and then entered and mixed with the eluent within the plug of glass-wool. After mixing, the resulting solution flowed into the outlet tube to the detector.

All the solutions were prepared using freshly distilled water, and all the reagents were of analytical-reagent grade. Stock solutions (1 g/l) of the individual REEs were prepared by dissolution of their respective Specpure oxides. The oxides were ignited at 950°C for 3 h and then cooled in a desiccator. The appropriate amount of each oxide was dissolved in nitric acid (1:1) . The dissolution of cerium was completed by the addition of small amounts of sulphuric acid and hydrogen peroxide during the reaction. The acid concentration after the dissolution was controlled so that the concentration of nitric acid in each stock solution was 1%. Standard solutions of REEs in the concentration range 1–10 mg/l, either as the REE group or as the cerium and yttrium subgroups, were prepared by suitable dilution and mixing of the stock solutions.

The complexing reagent was oxalic acid. The ion-interaction reagent was a 0.1 *M* solution of tetra-*n*-butylammonium hydroxide (TBAOH), obtained from Merck (Darmstadt, F.R.G.). An aqueous solution containing the appropriate concentrations of oxalic acid and TBAOH was prepared, and the pH of the solution was adjusted to 4.6 with ammonia solution. The solution was then filtered through a Millipore Type HA filter with a pore size of 0.45 μm. After filtration, the pH value was checked and adjusted if necessary.

The post-column reagent was Arsenazo III ($1.5 \cdot 10^{-4}$ *M* solution in 1 *M* acetic acid), obtained from Fluka (Buchs, Switzerland). The reagent solution was also filtered through a 0.45-μm filter.

Chromatographic procedure

Flow-rates of 1.0 ml/min were selected for both the eluent and the Arsenazo III solutions, and the Supelcosil LC-18 column was equilibrated with an aqueous solution containing the required concentration of oxalic acid and TBAOH at pH 4.6 until a stable baseline was obtained. The sample was injected, and the individual REEs were separated by isocratic elution. The eluted REEs were monitored at 658 nm after they had undergone post-column reaction with Arsenazo III. A range of calibration standards for the required concentration levels were analysed, and calibration graphs

of peak height *versus* concentration were prepared for each of the separated REEs. The REEs in the sample were identified by their retention times, and their peak heights were compared with the calibration graphs. A detailed description of the procedure can be obtained from the authors.

RESULTS AND DISCUSSION

From preliminary work with citric, tartaric and oxalic acids, it appeared that oxalic acid was the most suitable complexing agent for the formation of anionic complexes with the REEs.

The concentration and the stability of an aqueous solution of Arsenazo III in 1 *M* acetic acid that was required for post-column reaction with the REEs was established in earlier work [4], and these conditions were used in this investigation. As stated previously [4], careful control of the purity of the reagents and eluents was found to be necessary to ensure good chromatograms and to reduce baseline noise to a minimum. To eliminate degradation of the column performance by bacterial action, all the water used was freshly distilled and reagents were freshly prepared and filtered through 0.45-μm carbon frit filters. In addition, an in-line filter containing a carbon frit (0.5 μm) was placed immediately before the column.

Separation by isocratic elution

In this investigation, the univariant method of optimization was used, each variable being optimized while the others were kept constant.

The concentrations of oxalic acid and the ion-interaction agent, TBAOH, in the eluent were varied until the amounts required for the separation of the individual REEs were found. Eluents containing small amounts of oxalic acid resulted in an incomplete formation of the anionic complexes, whereas eluents of relatively concentrated oxalic acid solutions reduced the retention times of the individual anionic complexes of the REEs. In both instances the REEs were not completely separated. The optimum concentration for both the oxalic acid and the TBAOH for the separation of the fourteen REEs was found to be 0.002 *M* (Fig. 1).

The pH of the eluent was varied between 3.5 and 6.0. The peak heights of the REEs were not affected by the pH of the eluent in this range and a pH value of 4.6 was chosen for further work.

Yttrium, which accompanies the REEs, is eluted under these conditions with the same retention time as terbium. It was found that concentrations of 0.0005 and 0.0025 *M* for oxalic acid and TBAOH, respectively, increased the retention times of all the REEs sufficiently to allow the determination of both yttrium and terbium. The time for elution of the REEs increased and the peaks became broader but, when an integrator was used to obtain either the peak height or the peak area for REE determination, the accuracy was not affected. Small variations in the concentration of TBAOH are critical in the separation of terbium an yttrium, and the required concentration for this separation must be strictly controlled. Fig. 2 shows the chromatogram obtained.

During the optimization of the physical parameters, maximum peak heights for all the REEs were obtained with flow-rates of 1.0 ml/min for both the eluent containing oxalic acid and TBAOH and the reagent solution of Arsenazo III (using a sample size of 100 μl).

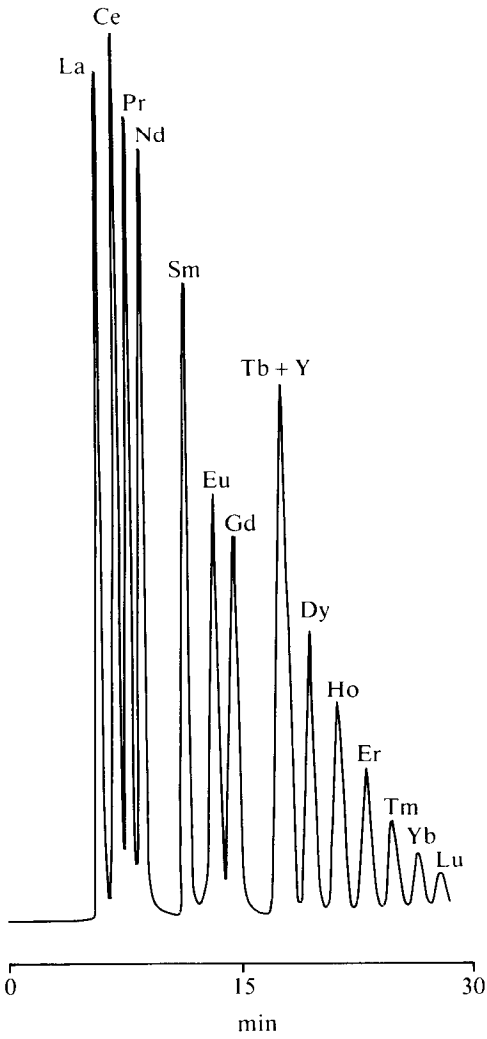

Fig. 1. Chromatogram showing the separation of the REEs. Conditions: oxalic acid, 0.002 *M*; pairing reagent, 0.002 *M* TBAOH; flow-rate of eluent and post-column reagent, 1 ml/min; pH of eluent, 4.6; sample volume, 50 μl; concentration of individual REEs, 10 mg/l; post-column reagent, $1.5 \cdot 10^{-4}$ *M* Arsenazo III plus 1 *M* acetic acid; spectrophotometer wavelength, 658 nm.

Order of elution

"Dynamic" ion exchangers are formed when hydrophobic ions (TBAOH), which are present in the mobile phase, are adsorbed on the hydrophobic surface of a reversed-phase column to produce a charged layer at the surface, where ion exchange can occur. The smallest ions, *i.e.*, the last and heaviest REEs in the series, form the strongest and most negatively charged complexes with oxalic acid. Therefore, when the REEs are separated by anion exchange, the elution order is from lanthanum to lutetium.

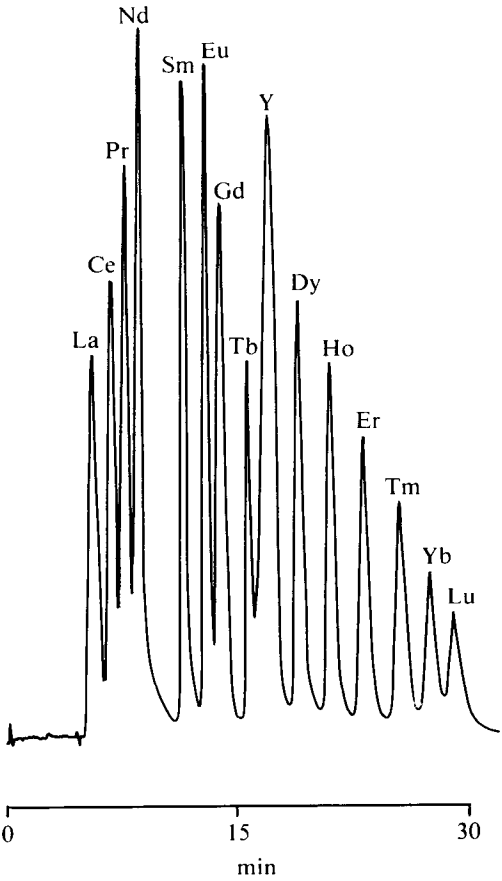

Fig. 2. Chromatogram showing the separation of yttrium from terbium. Conditions: oxalic acid, 0.0005 *M*; pairing reagent, 0.0025 *M* TBAOH; other conditons as in Fig. 1.

The separation of the REEs with this elution order from lanthanum to lutetium is applicable to the determination of trace amounts of REE impurities in a purified REE. The REEs lighter than the purified REE, particularly those adjacent to the individual purified REE, can be detected, identified and quantified. However, the REEs heavier than the individual purified REE could not be determined.

Interferences

Arsenazo III is specific for REEs, uranium and thorium [1]. Any transition metals that are present are not complexed by Arsenazo III under the conditions of the separation. As a result, they are eluted with, or just after, the void peak (about 2 min after injection) and do not interfere with the separation and determination of the REEs.

As most of the samples were in the form of dilute nitric acid solutions and traces of sulphuric acid were present in the standards from the dissolution of cerium, the effects of both nitric and sulphuric acids on the separation were investigated. It was

found that, as the acid concentrations increased, the retention times and the peak heights of the REEs decreased (Fig. 3). Solution of the REEs containing more than 0.05% acid resulted in a lack of resolution between the individual REEs and a reduction in their retention times. When the REE solutions containing 0.09 *M* sulphuric acid were neutralized with sodium hydroxide to pH 6, the retention times and peak heights of the REEs were not affected. Hence the acidity of the sample altered the formation constants of the anionic complexes and influenced the degree of complexation of the REEs. The acid anion had no affect on the separation at this level. To determine the possible effect of the acid anion at higher sulphate molarities, sodium sulphate was added to the REE solutions in the range 0.09–0.35 *M* with respect to the sulphate ion. Above 0.09 *M* of sulphate ion the peak heights decreased, whilst the retention times remained the same, indicating that above this level the sulphate anion acted as a competing ion causing displacement of the anionic complexes of REEs from the cationic sites of the ion-interaction reagent. Therefore, for optimum separation of the REEs the acidity and the acid anions must be controlled.

The small amounts of different hydroxides (lithium and sodium) and ammonia solution that were used for the adjustment of the pH of the eluent to the required level

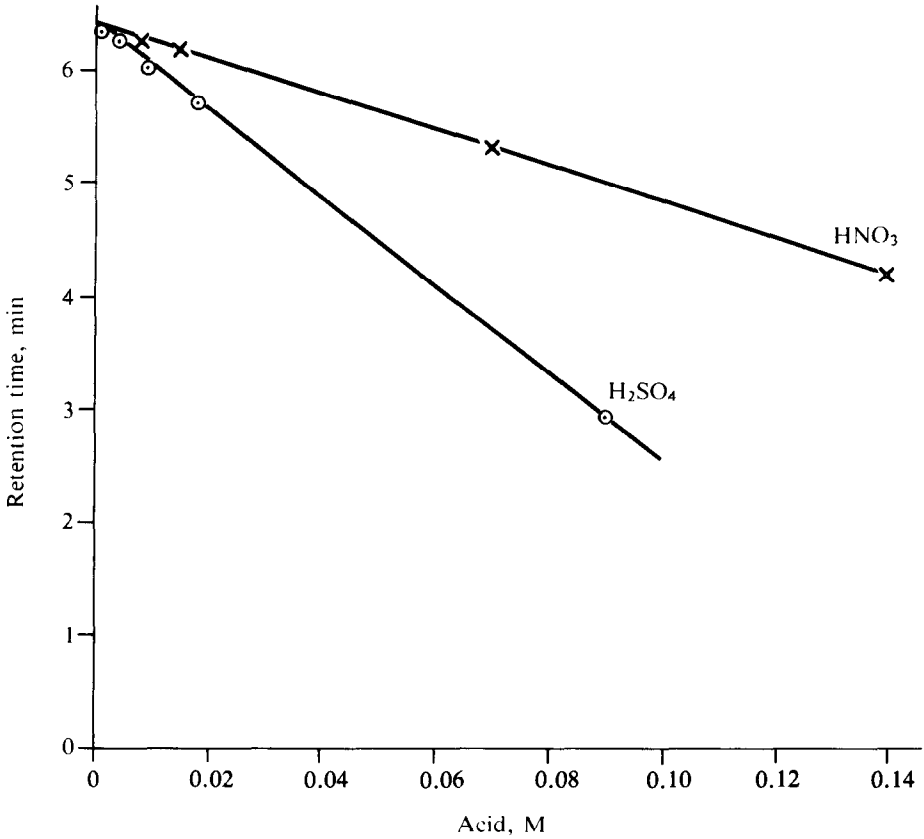

Fig. 3. Effect of acids on retention times. Conditions as in Fig. 1.

had no effect on the retention times or the peak heights. However, when large amounts of alkaline earth elements were present, the peaks obtained were broad, and there was a reduction in both the retention times and the resolution, indicating the effect of the reaction of alkaline earth cations with oxalate on the REE separation.

Sensitivity, precision and accuracy

The exact value of the detection limit of the REEs depends on the individual REEs, flow-rates of eluent and reagent, sample size and attenuation used. Any of these factors can be varied so that a particular analysis can be optimized. In the chromatograms for the separation of the REEs excluding yttrium (Fig. 1) and the separation of terbium from yttrium (Fig. 2), the attenuation remained constant throughout the elution of the REEs and the increasing insensitivity in the detection of the heavier REEs (terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium) is shown by the decreasing peak heights for these particular REEs. However, when the attenuation of the integrator was reduced between the elution of dysprosium and holmium, the sensitivity of the heavier REEs was increased. This increase in sensitivity depended on the attenuation that was used. Other factors that can affect the sensitivity are the background noise from pump pulsations and the purity of both oxalic acid and Arsenazo III. When necessary, the oxalic acid can be recrystallized. As stated previously, an important parameter is the quality of the water used in the preparation of the eluent and the reagent.

With careful control of the above factors individual REEs can be detected at a level of 0.01 mg/l with a limit of determination of 0.5 mg/l and higher. Table I gives the precision of the chromatographic separation and the subsequent detection with Arsenazo III at 658 nm.

TABLE I

PRECISION OF THE METHOD

Conditions as in Fig. 2.

Element	Relative standard deviation ($n = 10$)	
	10 mg/l REE	1 mg/l REE
La	0.0120	0.0816
Ce	0.0104	0.0698
Pr	0.0108	0.0509
Nd	0.0126	0.0549
Sm	0.0050	0.0628
Eu	0.0156	0.0333
Gd	0.0176	0.0634
Tb	0.0136	0.0513
Dy	0.0167	0.0478
Ho	0.0138	0.0523
Er	0.0184	0.0369
Tm	0.0174	0.0532
Yb	0.0165	0.0610
Lu	0.0120	0.0447
Y	0.0108	0.0654

TABLE II

COMPARATIVE DETERMINATIONS OF REE IN NITRIC ACID

All results are expressed as mg/l.

Element	Sample								
	FH 7701			FH 7702			FH 7703		
	C_1[a]	C_2[a]	AES[b]	C_1[a]	C_2[a]	AES[b]	C_1[a]	C_2[a]	AES[b]
La	<1	<0.5	<1	1.0	1.2	1.1	1.9	1.65	1.6
Ce	3190	3110	3270	975	951	1010	88	92	90
Nd	2.4	2.3	2.1	12	10	9.5	12	13	11
Sm	1.2	1.0	0.9	4.2	4.0	4.7	5.1	5.0	4.5
Eu	<1	<0.5	0.20	<1	0.6	0.79	1.4	1.3	1.1
Gd	<1	<0.5	<1	2.0	2.1	1.8	3.2	3.0	3.5

[a] C_1 and C_2 = chromatography.
[b] AES = atomic emission spectrometry.

TABLE III

COMPARATIVE DETERMINATIONS OF REE IN MINTEK REFERENCE MATERIALS

All results are expressed in mg/kg unless stated otherwise.

Element	Sample									
	66/69		50/71		30/70		18/69		49/71	
	C[a]	AES[b]	C[a]	AES[b]	C[a]	AES[b]	C[a]	AES[b]	C[a]	AES[b]
Y	n.a.[c]	1.38%	n.a.	0.67	n.a.	0.24%	n.a.	184	n.a.	39
La	9.90%	7.82%	3.72%	3.44%	1.38%	1.22%	0.31%	0.22%	495	515
Ce	16.06	16.2%	6.40%	7.09%	2.66%	2.54%	0.42%	0.37%	795	856
Pr	1.53%	1.62%	0.80%	0.77%	0.38%	0.27%	450	436	98	84
Nd	7.4%	6.52%	3.12%	2.97%	1.30%	1.11%	0.12%	0.11%	275	235
Sm	0.95%	1.02%	0.42%	0.38%	0.14%	0.16%	157	168	42	39
Eu	230	222	110	94	32	36	45	42	8	10
Gd	0.78%	0.82%	0.30%	0.32%	0.10%	0.13%	99	113	25	23
Tb	n.a.	702	n.a.	321	n.a.	146	n.a.	12	n.a.	4
Dy	0.30%	0.34%	0.14%	0.17%	702	686	35	51	n.d.[d]	10
Ho	423	445	240	244	72	78	n.d.	5	n.d.	3
Er	895	975	570	633	160	178	n.d.	9	n.d.	4
Tm	140	162	85	94	50	54	n.d.	3	n.d.	2
Yb	385	396	160	182	64	62	n.d.	9	n.d.	2
Lu	44	48	n.d.	11	n.d.	8	n.d.	1	n.d.	2

[a] C = chromatography.
[b] AES = atomic emission spectrometry.
[c] n.a. = Not analysed by chromatography.
[d] n.d. = Not detected.

The accuracy of the chromatographic separation and the subsequent determination of the individual REEs after post-column reaction with Arsenazo III was ascertained by a comparison of the results obtained by chromatography with those obtained by atomic emission spectrometry (AES). The samples included diluted nitric acid solutions obtained during the purification of individual REEs (Table II) and Mintek REE reference materials (Table III). The agreement between the two methods was generally good. However, lanthanum in sample 66/69 and some of the results in the milligrams per kilogram range in the other reference materials, such as erbium and thulium, were more scattered.

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