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Short communication

Dynamic ion-exchange chromatography for the determination of lanthanides in rock standards

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Abstract

A high-performance liquid chromatographic procedure has been developed and tested for the determination of rare earth element (REE) concentrations in United States Geological Survey rock standards AGV-1, GSP-1 and G-2.

The procedure involved acid digestion of sample in PTFE pressure bombs, group separation of REEs, followed by elution of individual lanthanides using α-hydroxyisobutyric acid in the presence of hydrophobic ions on a C_{18} bonded silica reversed-phase column. The eluted REEs were monitored by visible spectrophotometry at 520 nm after post-column reaction with pyridylazoresorcinol. This reversed-phase partition system is suited to separate and detect all lanthanides elements in less than 20 min with good reproducibility.

Comparison of the results with literature values shows an agreement of $\pm 5\%$ for all elements. An internal standard deviation of $\pm 0.5\%$ was found for a single analysis, while triplicate analysis showed a standard deviation of 1–2%.

1. Introduction

The increasing utilization of the rare earth elements (REEs) and interest in their geological, nuclear and environmental roles [1,2] have enhanced the need for rapid, sensitive methods of determination.

Rare earth metals have been a difficult group of elements to separate individually due to their similar chemical properties. It is difficult to determine individual REEs in mixtures by standard analytical methods.

In general, REE determination in rock standards is carried out by instrumental and radiochemical neutron activation [3], mass spectrometry [4,5] and inductively coupled plasma [6]. In these techniques ion exchange using a complexing agent is generally employed. However this is time consuming with respect to elution and quantitation. Further, such a procedure requires large quantities of high-purity reagents and results in a high volume of acid wastes.

Studies have shown that dynamic ion exchange can be used for the high-performance liquid chromatographic (HPLC) separation and determination of metal ion in complex matrices [7–9].

In this technique a modifier is added to the mobile phase in the form of a hydrophobic ion to create a charged surface on the reversed-phase column packing material. Metals in the sample

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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.

The application of the dynamic ion exchangers for the determination of rare earths in United States Geological Survey (USGS) rocks standards in a wide range of concentrations, and the comparison with reference results, form the basis of this study.

2. Experimental

2.1. Reagents and materials

The reagents used for solutions and eluents were freshly prepared.

All solutions were prepared with distilled water that had been purified in a Milli-Q unit (Millipore). Eluents were filtered through 0.2-μm filters.

The following reagent-grade chemicals were used: 40% hydrofluoric acid; 70% perchloric acid; 37% hydrochloric acid; 65% nitric acid; 2 *M* hydrochloric acid; 8 *M* nitric acid; a quartz column of I.D. 0.8 cm containing 14 cm of Dowex 50W-X8 (200–400 mesh, 37–74 μm, hydrogen form); 4-(2-pyridylazo)resorcinol monosodium salt (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 octanesulfonate (OS); Waters Nova-Pak C_{18} column (150 × 3.9 mm I.D.); Waters C_{18} Guard-Pak (5.0 × 6.0 mm I.D.); housed in a Waters Guard-Pak (precolumn module); REE standard solutions, obtained by dissolving pure oxides (Johnson Matthey) in mineral acids.

2.2. HPLC apparatus

The liquid chromatograph used in this work was a 625 LC from Waters equipped with a linear gradient programmer, a Rheodyne 9125 load injection valve, a constant-flow peristaltic pump, a Waters 490 programmable multiwavelength spectrophotometric detector, a Waters RDM module (post-column reagent) used to transfer the PAR complexing solution and a Spectra-Physics 4400 computing integrator–recorder.

2.3. Procedure

Sample dissolution

REEs are generally concentrated in minor mineral phases resistant to acid digestion, which can be overcome by dissolution in PTFE pressure bombs [10]. We have replaced the decomposition technique, at ambient pressure, by high-pressure decomposition, because this procedure is less time consuming and permits by its higher reaction temperature a more effective decomposition. Samples of about 200 mg were digested in PTFE bombs with 8 ml of 40% hydrofluoric acid and 0.5 ml of 65% nitric acid at 160°C for 18 h. After the dissolution the acids were evaporated and a further dissolution and evaporation were done with 5 ml of 70% perchloric acid and 10 ml of 65% nitric acid in order to eliminate hydrofluoric acid and organic materials. Finally, the residue was dissolved in 2 *M* hydrochloric acid, the solution was evaporated and the residue was dissolved in 2 ml of 2 *M* hydrochloric acid for chemical separation.

Group separation of REEs [11,12]

A quartz column of I.D. 0.8 cm containing 14 cm of Dowex 50W-X8 cation-exchange resin was conditioned with 2 *M* hydrochloric acid. Sample dissolved in 2 ml of 2 *M* hydrochloric acid was passed through the column and the interfering matrix elements were eluted with 80 ml of 2 *M* hydrochloric acid. The column was subsequently neutralized with 7 ml of water and the REEs, as a group, were eluted with 40 ml of 8 *M* nitric acid. This REE fraction was evaporated to dryness, and dissolved in the mobile phase (2 ml) prior to injection into the HPLC system.

HPLC procedure

Samples (30 to 300 μl) of the REE fraction from the group separation were injected into the mobile phase and the α-HIBA concentration was

then programmed linearly from 0.07 to 0.4 *M* over 15 min. The OS concentration (0.01 *M*), the pH (3.8) and flow-rate (1 ml/min) were maintained constant during the gradient program. The eluted REEs were detected after a post-column reaction with PAR. These post-column reactant was added to the eluent in a PTFE mixing tee at 0.5 ml/min flow-rate, and the eluted metal ions were monitored by a programmable multiwavelength detector at 520 nm. The concentrations of the REEs in the samples were calculated with the non-linear regression program in the Spectra-Physics integrator. The regression equations were generated with peak areas from three standards covering the concentration range expected for the samples.

3. Results and discussion

The REE concentrations were determined on the USGS rock standards [13] andesite AGV-1, granodiorite GSP-1 and granite G-2. Many REE analyses have been reported for these samples in the literature [13–15] and the data of Gladney et al. [15] and Hooker et al. [16] are included in this study for comparison. The data of Gladney

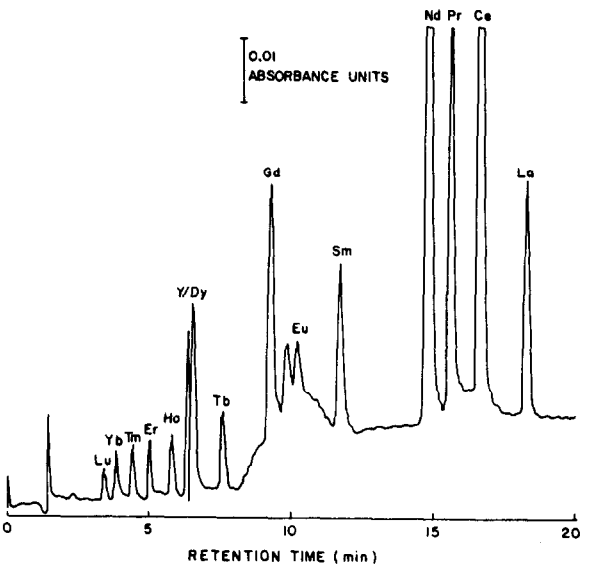

Fig. 1. Separation of rare earths in the standard solution SS2 by gradient elution. Experimental conditions: Waters Nova-Pak C_{18} column (150 × 3.9 mm I.D.); gradient separation at 1 ml/min from 0.07 to 0.4 *M* α-HIBA at pH 3.8 over 20 min with 0.01 *M* OS. Injection volume 100 μl.

are based on different techniques and these values are called "consensus" values.

To evaluate the separations a calibration has been carried out by employing known standard

Table 1
REE detection limit and analyses data for the calibration solutions

Element	SS1 (ppb)		SS2 (ppb)		SS3 (ppb)		Detection limit (ppb, w/w)
	Injected	Found	Injected	Found	Injected	Found	
La	179.22	180.57	399.32	399.44	1194.94	1200.19	1
Ce	71.38	71.33	869.61	833.68	2608.83	2618.06	1
Pr	47.16	46.72	158.58	159.18	475.74	477.64	1
Nd	70.54	69.50	300.74	300.92	902.74	902.88	1
Sm	15.61	15.58	34.78	34.49	104.34	104.74	1
Eu	4.93	5.44	9.15	9.16	27.45	27.66	1
Gd	18.00	17.96	40.11	43.45	120.33	120.34	1
Tb	4.69	4.49	10.46	10.93	31.38	31.39	1
Dy	18.59	19.31	20.71	19.81	62.13	62.15	1
Ho	5.05	4.81	9.38	9.62	28.14	27.87	1
Er	5.34	5.51	9.91	9.92	29.73	29.60	3
Tm	4.46	4.82	9.94	10.07	29.82	29.83	3
Yb	5.91	5.88	10.97	11.07	32.90	33.00	3
Lu	5.13	4.66	8.53	8.49	25.59	25.73	3
Y	20.00	20.74	19.74	19.81	59.22	59.91	1

Table 2
Results of REE abundances in USGS rock standard AGV-1

Element	REE (μg/g)		
	HPLC	Lit. [15]	Lit. [16]
La	36 ± 2	38 ± 3	38
Ce	69 ± 3	66 ± 6	68.7
Pr	6.7 ± 0.5	6.5 ± 0.9	–
Nd	35 ± 4	34 ± 5	32.1
Sm	5.4 ± 0.2	5.9 ± 0.5	5.83
Eu	1.57 ± 0.07	1.66 ± 0.11	1.54
Gd	5.17 ± 0.05	5.2 ± 0.6	4.76
Tb	0.66 ± 0.04	0.71 ± 0.11	–
Ho	0.71 ± 0.06	0.73 ± 0.08	–
Er	1.7 ± 0.1	1.61 ± 0.22	1.82
Yb	1.69 ± 0.04	1.67 ± 0.17	1.68

REE mixtures. The data of Table 1 list the results for three standards REEs (SS1, SS2 and SS3) mixture injected and the chromatogram for the SS2 is shown in Fig. 1. The results obtained demonstrate the total elution of individual REEs. The REE concentrations of USGS standards obtained in the present study are shown in Tables 2, 3 and 4.

The REE concentrations determined are the averages of three totally independent analyses involving separated dissolution, chemical separation and HPLC procedure. The internal relative standard deviation (R.S.D.) of the elemental values calculated for a single analysis was found

Table 3
Results of REE abundances in USGS rock standard GSP-1

Element	REE (μg/g)		
	HPLC	Lit. [15]	Lit. [16]
La	183 ± 11	183 ± 13	182
Ce	426 ± 15	406 ± 20	419
Pr	51.9 ± 0.3	51 ± 8	–
Nd	180 ± 3	190 ± 17	201
Sm	27.1 ± 0.2	26.8 ± 2.5	25.8
Eu	2.4 ± 0.1	2.36 ± 0.22	2.21
Gd	12.9 ± 0.3	13 ± 2	10.2
Tb	1.38 ± 0.04	1.36 ± 0.14	–
Ho	1.20 ± 0.06	1.2 ± 0.5	–
Er	2.4 ± 0.1	2.5 ± 0.4	2.11
Yb	1.74 ± 0.03	1.7 ± 0.4	1.5

Table 4
Results of REE abundances in USGS rock standard G-2

Element	REE (μg/g)		
	HPLC	Lit. [15]	Lit. [16]
La	96 ± 2	86 ± 5	97.7
Ce	161.2 ± 12	159 ± 11	160
Pr	19.2 ± 0.6	19 ± 2	–
Nd	50 ± 2	53 ± 8	54.8
Sm	7.1 ± 0.6	7.2 ± 0.6	7.27
Eu	1.4 ± 0.03	1.41 ± 0.12	1.34
Gd	4.14 ± 0.09	4.1 ± 0.8	3.97
Tb	0.38 ± 0.01	0.48 ± 0.07	–
Dy	1.8 ± 0.2	2.5 ± 0.5	2.11
Ho	0.37 ± 0.09	0.37 ± 0.02	–
Er	0.81 ± 0.07	1.2 ± 0.3	0.83
Yb	0.70 ± 0.06	0.78 ± 0.14	0.6
Y	10.9 ± 0.6	11.4 ± 2.3	–

to be in the order of 0.5%. The total R.S.D. based on triplicate analyses, was found to be in the range 1–2% for most of the elements.

Because of the appreciable overlap between the Dy and Y peaks in the sample G-2 it was not possible to obtain reliable peak areas for these elements. In the case of samples AGV-1 and GSP-1 it is not possible to separate the two elements (Dy and Y). For the three samples it was not possible to determine Lu and Tm because the concentrations of these elements was bellow the detection limit.

A comparison of the REE values obtained by HPLC in this study with the literature values [15,16] shows agreement to within 5% for most of the elements for GSP-1, AGV-1 and G-2.

A typical chromatogram obtained for a rock sample (AGV-1) after group REE separation is shown in Fig. 2.

5. Conclusions

The results showed that the method employed is efficient and has adequate sensitivity and reproducibility for the determination of REEs in complex matrices.

The use of α-HIBA as an eluting agent combined with dynamic ion exchangers for the sepa-

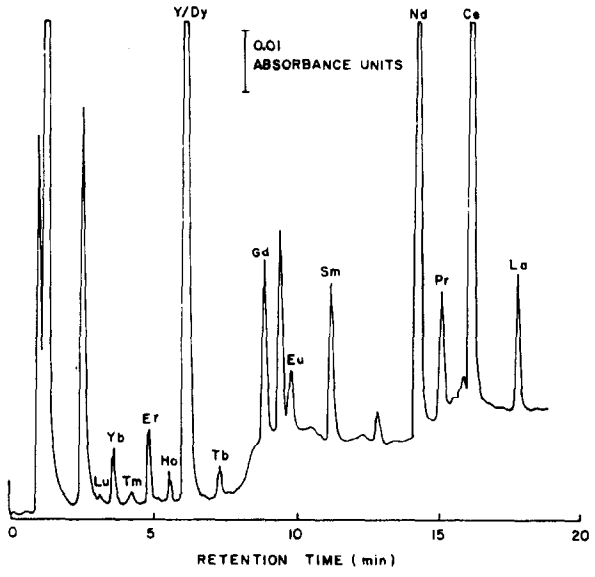

Fig. 2. Separation of rare earths in the rock solution AGV-1 by gradient elution. Experimental conditions as in Fig. 1.

ration of individual REEs have a number of advantages relative to conventional ion-exchange resins. Some of them are its high sensitivity, that little sample is required and multi-elements analyses can be carried out with a single injection.

HPLC has been shown to provide rapid and accurate methods for the analyses of REEs, as compared to the other techniques like isotope dilution mass spectrometry [4,16] and inductively coupled plasma mass spectrometry [17]. The major advantages of the technique are speed and low cost of analyses

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