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DETERMINATION OF TRACE AMOUNTS OF LANTHANIDES IN ROCKS AND MINERALS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Rare-earth elements have been determined by a high-performance liquid chromatographic procedure. The hydrochloric acid solution containing the rare-earth elements coming from the main separation of the whole group, contained in a rock sample and separated by a classical ion-exchange procedure, was eluted through a stainless-steel column packed with microparticulate silica, with bonded cation-exchange groups. Complete separation of individual lanthanides was achieved. A variable-wavelength detector was used following post-column complex formation with pyridylazoresorcinol. Results obtained on test solutions and on internal rock reference samples show good reproducibility and precision.

INTRODUCTION

The rare-earth elements (REE) may be considered the best representatives of trace elements with very similar physico-chemical properties, and are the most useful indicators of geochemical processes, because all have essentially the same chemical properties and display small, regular differences in mass and also in ionic radius (as a result of the lanthanide contraction). Since the compositional trend of the REE (or lanthanides) has been used by several authors¹⁻⁴ to investigate the evolution of igneous rocks and since the impact of REE abundance on the environment seems to become more and more important^{5,6}, an accurate determination of these elements is a very important step in analytical chemistry related to geochemical work.

Several techniques can be used in the analytical approach to such a problem. The majority of data in international standards on rocks and minerals, relating to REE content, have been obtained by radiometric techniques, such as instrumental and radiochemical neutron activation analysis⁷⁻⁹. However, these techniques are expensive and not readily available. In order to devise an alternative and widely applicable technique, we have studied atomic absorption spectrophotometry with electrothermal atomisation (ETA-AAS) of the lanthanides¹⁰⁻¹³, but ETA-AAS allows an accurate and sensitive determination for only the heavy REE. Recent research has stressed increased interest in high-performance liquid chromatography (HPLC), par-

ticularly as applied to inorganic analytical problems. One of the most interesting groups of metals investigated is the lanthanides, owing to the well-known difficulties in their analysis.

We have carried out a systematic study of lanthanide separation in order to apply HPLC procedures to their determination in natural or industrial samples. An improved application of HPLC to REE and transition-element (d-block) analyses has been carried out by Cassidy and Elchuk^{14,15} and Hwang *et al.*¹⁶. By a similar procedure we have previously^{17,18}, determined trace amounts of terbium and cerium in terbium, lanthanum-, and yttrium-doped oxide-sulphide phosphors.

The method is based on colorimetric detection of the lanthanide-PAR [4-(2-pyridylazo)resorcinol] monosodium salt, by formation of the dye after HPLC separation in a cation-exchange column and elution with DL-2-hydroxyisobutyric acid, buffered at pH 4.6 in a gradient elution mode. The whole group of lanthanides was previously separated on classical cation-exchange columns filled with strongly acidic sulphonated resin (Dowex 50W-X8) after acid solubilization of the rock samples¹⁹.

EXPERIMENTAL

Reagents

The following reagents were used: 40% hydrofluoric acid; 70% perchloric acid; 36% hydrochloric acid; 3 M hydrochloric acid in 25% ethanol solution; 4 M hydrochloric acid; borosilicate glass tube (180 m × 20 mm I.D.), packed with Dowex 50W X8 (acid form, 200–400 mesh) ion-exchange resin; 4-(2-pyridylazo)resorcinol monosodium salt, 0.050 mg/l, in 2 M ammonium hydroxide and 1 M ammonium acetate aqueous solution; DL-2-hydroxyisobutyric acid (HIBA), 0.03 and 0.07 M aqueous solutions buffered at pH 4.6 with sodium hydroxide; Partisil PXS 10/25 SCX (Whatman) cation-exchange stainless-steel HPLC column; REE standard solutions, obtained by dissolving pure oxides in mineral acids.

Apparatus

The following equipment was used: Perkin-Elmer 2 liquid chromatograph, equipped with a linear gradient programmer; Rheodyne M 7125 load injection valve (175- μ l loop); constant-flow peristaltic pump, Gilson Minipuls 2, used to transfer the PAR complexing solution; Perkin-Elmer LC 5 variable-wavelength spectrophotometric detector, equipped with Perkin-Elmer LC Autocontrol; Kipp & Zonen B5 strip-chart recorder; LDC 10 calculating integrator.

Procedure

Weigh out 1000.0 mg of finely powdered rock sample (120 mesh) in a PTFE dish. Moisten the powder with water to avoid spattering. Add 10 ml of 40% hydrofluoric acid and 10 ml of 70% perchloric acid, mixing with a platinum or PTFE rod. Allow to stand overnight in the fume-cupboard and then evaporate to dryness. Add 10 ml of each the two acids and evaporate to dryness again, then dilute to *ca.* 100 ml to give 0.6 M hydrochloric acid concentration. Pass this solution through a borosilicate glass tube (180 × 20 mm I.D.), filled with Dowex 50W X8 (acid form, 200–400 mesh) ion-exchange resin. Elute the matrix major and minor elements, which may interfere in the subsequent colorimetric PAR detection (sodium, potassium, calcium,

magnesium, iron, aluminium, titanium and some strontium), with 300 ml of 3 *M* hydrochloric acid in 25% ethanol solution. Elute the REE group (plus barium, scandium, yttrium, and the rest of the strontium) with 200–250 ml of 4 *M* hydrochloric acid. If necessary, evaporate this eluate to less than 50 ml in a PTFE beaker; then dilute to 50 ml in a standard flask. This last solution is injected into the HPLC system via a 175- μ l loop. A linear concentration gradient is started, from 0.03 *M* HIBA to 0.07 *M* HIBA (both buffered at pH 4.6 with sodium hydroxide) at 3%/min to the total solvents, at a constant the total flow-rate of 1.2 ml/min. The sample solutions are chromatographed on a stainless-steel cation-exchange column (Partisil PXS 12/25 SCX). The eluted metal ions are measured with a variable-wavelength detector (520 nm) after a post-column complexing reaction with PAR in a "T" cell by mixing the HIBA-REE eluate with PAR solution (from the peristaltic pump). The REE contents are calculated by the well-known calibration curve or standard addition method.

TABLE I

OCCURRENCE OF SOME MAJOR, MINOR, AND TRACE ELEMENTS IN SOME INTERNATIONAL REFERENCE ROCKS AND IN CALIBRATING SOLUTIONS

Values are given as percentages for the elements listed as their oxides, and in parts per million for the remainder.

<i>Element</i>	<i>GS-N granite</i>	<i>NIM-L hujavrite</i>	<i>Calibrating solution</i>
Al ₂ O ₃	14.69	13.64	15.00
Fe ₂ O ₃	3.73	9.96	5.00
MnO	0.06	0.77	0.50
MgO	2.32	0.28	1.00
CaO	2.54	3.22	2.00
Na ₂ O	3.76	8.57	5.00
K ₂ O	4.40	5.51	5.00
TiO ₂	0.69	0.48	0.50
F ₂ O ₅	0.27	0.06	0.10
Ba	1400	450	1000
Ce	140	240	100
Cr	55	10	50
Dy	1.5	3	5
Er	1.5	2	5
Eu	1.7	1.2	5
Gd	5	3	5
Ho	0.5	0.5	5
La	75	250	100
Lu	0.2	0.2	5
Nd	50	48	50
Ni	34	11	50
Pr	19	20	50
Sc	7	0.3	5
Sm	8.2	5	10
Sr	570	4600	1000
Tb	0.6	0.7	5
Tm	0.3	0.3	5
Y	19	22	50
Yb	1.7	3	5

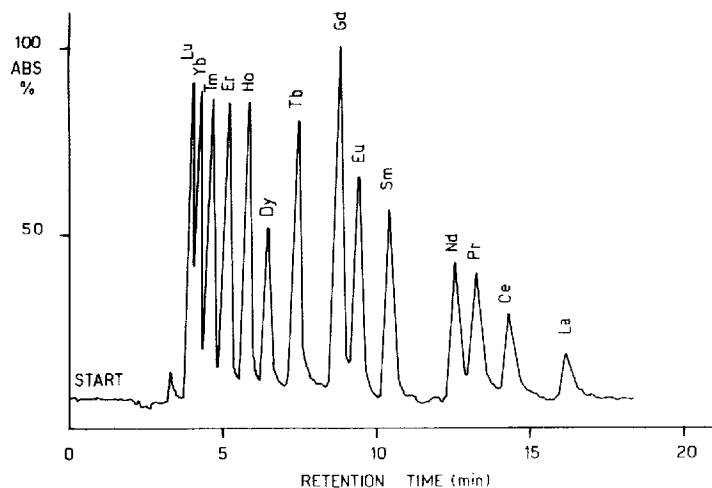


Fig. 1. HPLC chromatogram of the whole group of rare-earth elements in the standard solution, after ion-exchange separation.

RESULTS AND DISCUSSION

To evaluate the separations (both whole REE group and individual lanthanides) a calibration has been carried out by employing a "matrix" solution, containing major (sodium, potassium, calcium, magnesium, iron and aluminium), minor (titanium, barium, scandium, yttrium and strontium) and trace (REE) elements at the same ratio (between matrix and analysed element) occurring in natural samples^{20,21} (Table I). An aliquot of this solution was passed through the entire separation-

TABLE II

REE SENSITIVITY AND RECOVERY DATA FOR THE CALIBRATING SOLUTION

Element	Conc. taken (ppm)	Conc. found (ppm)	Recovery (%)	Sensitivity limit	
				ppm	ng
Ce	50	51	102	1.0	20
Dy	5	5	100	0.3	6
Er	5	4.8	96	0.3	6
Eu	5	4.9	98	0.4	8
Gd	5	5.1	102	0.3	6
Ho	5	4.7	94	0.3	6
La	100	99	99	1.0	20
Lu	5	4.7	94	0.5	10
Nd	50	50.5	101	0.5	10
Pr	50	50	100	1.0	20
Sm	10	9.9	99	0.3	6
Tb	5	5	100	0.15	3
Tm	5	4.8	96	0.2	4
Y	50	49.5	99	0.3	6
Yb	5	4.9	98	0.1	2

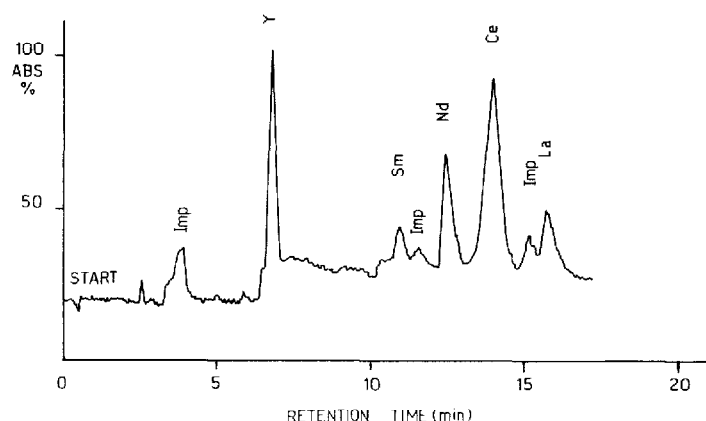


Fig. 2. HPLC chromatogram of the REE in rock NIM-L after acid treatment and ion-exchange chromatography.

HPLC-colorimetric procedure in order to test the proposed method. The chromatogram of the whole REE group is shown in Fig. 1.

Tests to evaluate the sensitivity and recovery of the proposed method have also been performed (Table II).

The suggested procedure has also been applied to the characterization of two international reference rock samples: NIM-L (lujavrite) of the National Institute of Metallurgy, Pretoria, South Africa, and STM-1 (syenite) of the U.S. Geological Survey, Reston, VA, U.S.A. The chromatogram obtained by our procedure is shown in Fig. 2. The results obtained are compared with literature values in Table III.

CONCLUSION

We believe that the proposed procedure shows adequate sensitivity and reproducibility for the determination of REE in most commonly studied silicate rocks. Moreover, such a determination appears to be faster and less expensive than those performed by other instrumental methods.

TABLE III

HPLC RESULTS OF SOME REE DETERMINATIONS IN STM-1 AND NIM-L INTERNATIONAL ROCK REFERENCE SAMPLES

Element	STM-1 (syenite)		NIM-L (lujavrite)	
	Found	Certified	Found	Certified
Ce	160.0 ± 10.7	146 ± 10	134 ± 3.4	232 ± 40
La	132 ± 20	146 ± 10	138 ± 4	228 ± 24
Nd	79 ± 8	78 ± 15	49 ± 20	48 ± 15
Pr	—	—	17 ± 8	21
Y	32 ± 2	45	13 ± 5	33 ± 21
Sm	42 ± 12	13 ± 2	—	—

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