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Improved capillary electrophoresis method for measuring rare-earth elements in synthetic geochemical standards

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Abstract

An improved capillary electrophoresis (CE) method for quantifying rare-earth elements (REEs) in synthetic geochemical standards was developed. Synthetic standard solutions were obtained from high purity metal oxides. The separation of REE total group (lanthanum to lutetium) was defined as a primary objective. Special attention was also focused on the optimized separation of europium (Eu) and gadolinium (Gd) because in earlier applications they presented overlapping problems. Their separation and quantitative determinations are essential for geological applications. For the rapid separation of REEs in synthetic geochemical standards, the temperature of the separation device was optimized. An analysis temperature of 15°C enabled both the rapid separation of REEs within 2 min and the overlapping problem of Eu–Gd to be resolved. The detection limits (<0.1 ng) and precision estimates (generally better than 5%) were found to be satisfactory for most geological applications. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The determination of the rare-earth elements [REEs; lanthanides (La–Lu) and yttrium (Y)] is identified as a fundamental geochemical research activity for inferring the origin of igneous, metamorphic and sedimentary rocks as well as for many other geological and planetary applications [1–4]. Although several methods have already been developed for the determination of the REEs, they are largely limited to the use of very expensive equipment, e.g. isotope dilution mass spectrometry, inductively coupled plasma mass spectrometry, inductively coupled plasma atomic emission spectrometry, neutron activation analysis, spark source mass spectrometry, X-

ray fluorescence, and secondary ion mass spectrometry [5–7]. Thus, a great need, especially in developing countries, still persists for investigating cheaper, faster and accurate methods, for which numerous separation techniques based on high-performance liquid chromatography (HPLC), ion chromatography (IC), capillary zone electrophoresis (CZE) and capillary electrophoresis (CE) have been developed [8–13].

A comparison study between IC and CE capabilities for the determination of inorganic ions was conducted by Haddad [13] who assessed both IC and CE techniques as a function of their separation efficiency, separation selectivity, analytical performance parameters, strengths and weaknesses among others. Haddad [13] established that these techniques are complementary rather than competitive, especially with respect to their separation selectivities and

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the type of applications to which they are most suited.

The HPLC and IC techniques have been applied for measuring a great variety of ionic and metallic elements (e.g. [8–13]). However, in the case of a complete chromatographic separation of the REEs, only some quantitative studies have been published [14–21]. These HPLC and IC studies have demonstrated that due to the large difference in ionic radii of REEs, the chromatographic separation of all REEs can be efficiently achieved under gradient elution conditions [14–20]. Isocratic chromatographic separation of REEs has not been developed satisfactorily and constitutes a challenge for the inorganic chromatographic science [21].

The first HPLC and IC applications for detecting REEs in geological samples was performed by Cassidy and Elchuck [14] and Mazzucotelli [16] who were partially successful in measuring a few elements of the REE group by HPLC procedures based on spectrometric detection systems. Cassidy [10] continued this difficult task through the development of an improved HPLC procedure capable of quantifying REEs in the nanogram (sub-mg/l concentration) range. This procedure was the subject of further research by Verma [18] who enhanced the HPLC method for the determination of 13 REEs in wide variety of rock and mineral samples using international geochemical reference materials. Such an improvement was achieved by a prior REE group separation from complex rock matrices and a gradient separation technique using 2-hydroxyisobutyric acid (HIBA) as eluent followed by a post-column reaction with 2,7-bis(*o*-arsenophenyl)azo-1,8 dihydroxynaphthalene-3,6-disulfonic acid (Arsenazo III).

Quantitative procedures based on the application of the CE technique for separating REEs have seldom been reported [22–24]. One of the first applications of CE for measuring REEs appeared in 1990 when Foret [22] developed a CZE procedure using an indirect UV absorbance detection system with a background electrolyte containing HIBA (as complexing counter-ion) and creatinine (as a UV absorbing co-ion). Although a nearly complete separation of fourteen REEs was achieved in less than 5 min (considerably less time than that usually required by HPLC or IC techniques; see Table 1), these experimental results were obtained for standard

solutions containing *similar* concentration levels (0.5 mM) for *all* lanthanides, implying all trace element ratios to be one which is not the case for geological materials. Another CE procedure was developed by Mao et al. [24] who achieved a simultaneous separation of 15 REEs (lanthanides and Y) within 10 min by means of a complex system based on a coupling of isotachopheresis (ITP) and CE techniques. This method seems to provide an optimized separation of all REEs, including the effective separation of Y from Dy without loss of the separation of Eu and Gd. However, its application to the analysis of REEs in real geochemical samples cannot be directly conducted since these experimental tests were again obtained with standard solutions having similar concentrations for all REEs (0.33 mM).

When samples with a more complex composition patterns or heterogeneous concentration levels (e.g. rock, mineral or hydrothermal fluid samples) need to be analyzed, problems in the separation of lanthanides should generally be expected (Fig. 1) [23]. Some of these problems could be related to overlapping of both Y–Dy and Eu–Gd peaks, or to a poor detection sensitivity of Tm, Yb, and Lu. The overlapping problems are usually attributed to small differences in the effective electrophoretic mobilities of lanthanide ions: $72.3 \cdot 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for La^{3+} to $67.0 \cdot 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for Lu^{3+} , with only slight differences between the neighbors [22]. Considering the inevitable presence of these interference and detection problems, most researchers usually omit Y and Eu from their REEs mixtures (e.g. see Fig. 2) or work with similar concentrations of Y, Tb, Dy, Sm, Eu or Gd and in fact, of all REEs [22–24]. Eu should not be neglected from a REE standard mixture since it is an extremely important element in the Earth Sciences, whereas Dy and Y are not too critical for such applications [1–4]. As an example, in volcanic rocks Y/Dy and Y/Tb ratios range from about 4 to 50 or more, and Sm/Eu and Gd/Eu ratios from about 1 to 20 or more [25]. It would probably be difficult to analyze such samples with the existing CE methods [22–24].

Within this context, additional laboratory work on CE technology for separating REEs and, in particular, for resolving the overlapping problem between Eu and Gd is still required. The aim of the present work is to provide an improved CE method

Table 1
Experimental characteristics of some HPLC, IC and CE developed procedures for separating REEs

Ref. ^a	Method	Detection system	Eu–Gd separation	Elapsed time (min)
[16]	HPLC	UV–Vis (520 nm) after PCR with PAR using a linear gradient eluent from 0.03M to 0.7M HIBA (pH 4.6)	Yes	<20
[17]	IC	UV–Vis (520 nm) after PCR with PAR using a gradient process with 100 mM oxalate, 100 mM diglycolic acid and distilled water	Yes	<20
[10]	HPLC	UV–Vis (658 nm) after PCR with Arsenazo III using a linear gradient eluent from 0.05M to 0.5M HIBA (pH 3.8)	Yes	<12
[22]	CZE	Indirect UV (220 nm) using 0.03 M creatinine–acetate and 0.004 M HIBA as background electrolyte	Yes	<5
[18]	HPLC	UV–Vis (658 nm) after PCR with Arsenazo III using a linear gradient eluent from 0.05 M to 0.5 M HIBA (pH 3.8)	Yes	<14
[13]	CE	Indirect UV (nm not reported) using 15 mM lactic acid and 10 mM 4-methylbenzylamine (pH 4.3) as background electrolyte	No	<4.6
[20]	IC	UV–Vis (520 nm) after PCR with PAR using a gradient eluent with oxalic acid diglycolic acid and distilled water	Yes	<35
[23]	CE	UV–Vis (654 nm) using 0.025 mM Arsenazo III in 15 mM citric acid and 20 mM Tris (pH 4.3) as background electrolyte	No	<7
[21]	IC	UV–Vis (658 nm) after PCR with Arsenazo III using 0.016M nitric acid with 0.5M potassium nitrate as eluent by an isocratic process (pH 3.8)	No	<70
[24]	ITP–CE	High frequency contactless conductivity detector combined with a separation unit of an ITP analyzer using 7.5 mM HIBA and 2.0 mM malonic acid as complexing agent (pH 4.8), a leading electrolyte of 20 mM ammonia water, an additive of 0.1% HPC and a terminating electrolyte of 20 mM carnitine hydrochloride	Yes	<10

^a Chronological order; PCR: post column reaction; PAR: 4-(2-pyridylazo)resorcinol.

that enables an optimized and rapid separation of all REEs in synthetic geochemical standards, with a special emphasis on the solution of the overlapping problem between Eu and Gd.

2. Experimental

2.1. Capillary electrophoresis instrumentation

A Quanta 4000 capillary electrophoresis instrument (Waters, Milford, MA, USA) equipped with a positive power supply and a variable-wavelength UV detection system at the *Museo Nacional de Ciencias Naturales* was used to generate all electropherograms. The applied voltage was +30 kV. The UV detection was set at a wavelength of 214 nm using a zinc lamp. CE instrument was interfaced to a data acquisition unit (Waters 820 Workstation) for collecting electropherographic data at 20 points per second (using Millennium 2000 software). The separations were carried out using a conventional fused-silica

capillary (36.5 cm length × 75 μm I.D.). Hydrostatic injection mode was used for elevating the sample at a constant height of 10 cm for 20 s. A temperature control system was employed for fixing the working capillary column temperature. The carrier electrolyte consisted of a mixture of 10 mM UVCat-1 Waters and 4 mM of HIBA (adjusted to a pH 4.4 with acetic acid). Instrument operating conditions are given as captions of the figures.

2.2. Chemical reagents

All chemical and standard solutions were prepared using deionized water (18 MΩ) produced from a Milli-Q water purification system (Millipore, Barcelona, Spain) and stored in polypropylene bottles. Stock aqueous solution of HIBA was prepared at a 100 mM concentration. This primary solution was then used for preparing a 4 mM HIBA working solution. All chemicals were of analytical reagent grade.

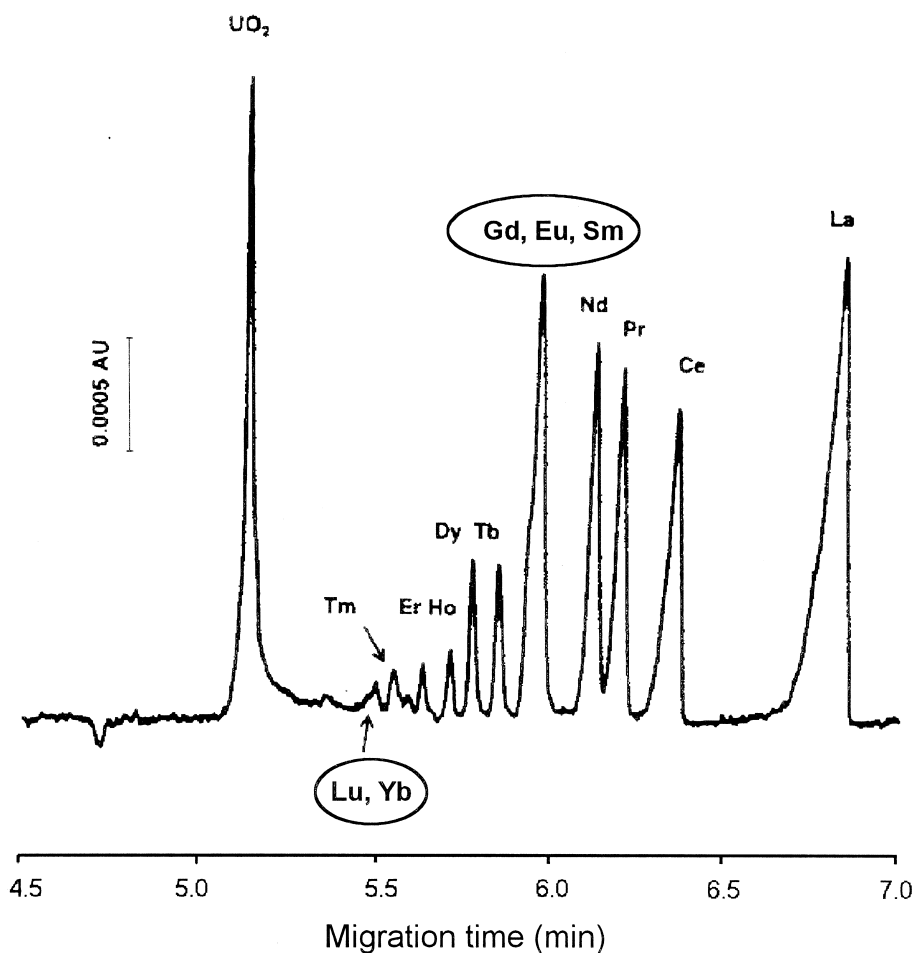


Fig. 1. Electropherogram of a typical separation pattern of 14 lanthanides. Background electrolyte 0.025 mM AIII in 15 mM citric acid and 20 mM Tris (pH 4.3); temperature, 25°C; separation voltage, -30 kV (30 μ A); injection of a standard solution containing 10 μ M of each metal [except 20 mM for Tm(III), Yb(III) and Lu(III)] in 10 mM HNO₃. For other operating conditions see the original literature source (modified after Macka et al. [23]).

2.3. Preparation of electrolytes

The concentration of the working electrolyte solution (WES) was selected on the basis of the experimental CE studies performed by Foret et al. [22] who suggested an optimum HIBA concentration of 4 mM for obtaining a good resolution of all REEs with times less than 5 min. On each working day the WES was prepared by a mixing process of a 10 mM UVCat-1 solution or electrolyte modifier (Waters) with a complexing agent solution of 4 mM of HIBA solution (FLUKA, Barcelona, Spain). The pH of the

electrolyte solution was then adjusted to 4.4 with diluted acetic acid and filtered through a 0.22 μ m membrane filter (Millipore, Barcelona, Spain) just prior to use.

2.4. REEs synthetic geochemical standards

Standard solutions containing 1000 mg/l of individual REEs prepared from high-purity metal oxides were used as stock solutions. The REE synthetic geochemical standards (SPV-1 and SPV-4)

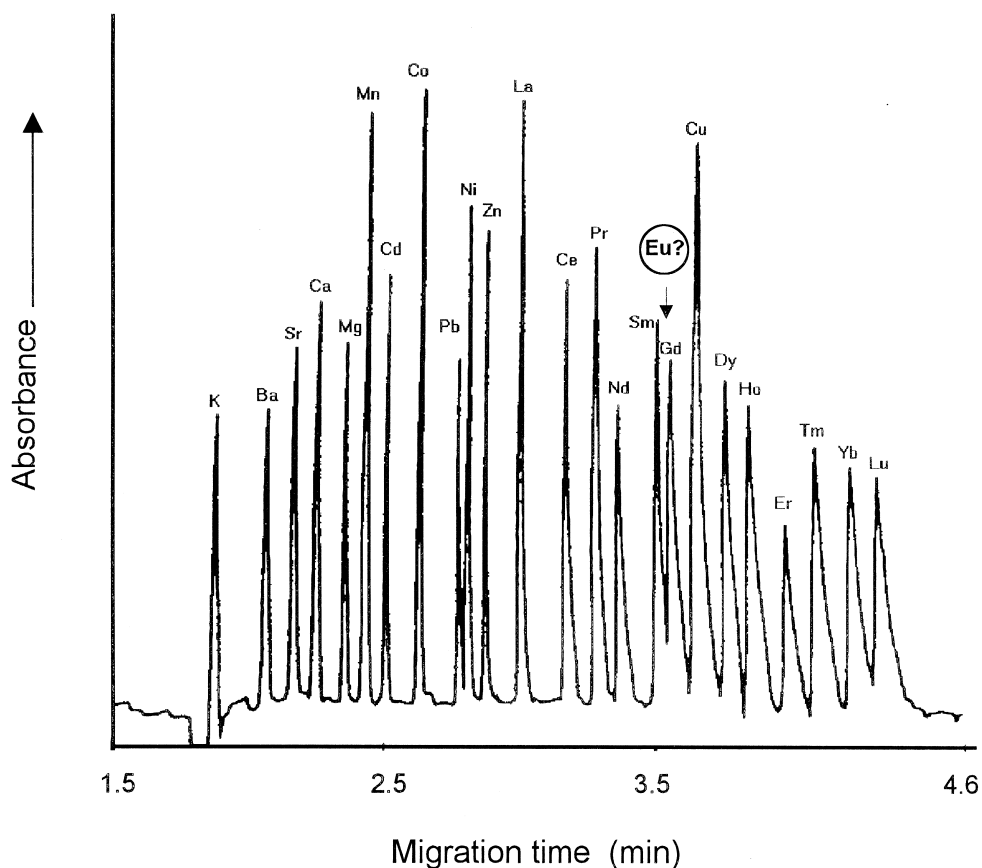


Fig. 2. Separation of cations and some lanthanide elements by co-EQF capillary electrophoresis with indirect spectrophotometric detection. The electrolyte was 15 mM lactic acid and 10 mM 4-methylbenzylamine at pH 4.3. Element identities are given in the peaks. Europium (Eu) was not included in the REE standard mixture. For other operating conditions see the original paper ([13]). Absorbance scale and REE concentrations were not reported in [13].

were prepared at the *Max-Planck Institut für Chemie*, Mainz, Germany, according to the relative abundance of each lanthanide in actual geological materials such as basalts, andesites, rhyolites, granites, etc. [18]. Table 2 presents the chemical composition pattern (in $\mu\text{g}/\text{ml}$) of these synthetic geochemical standards subsequently used for preparing the standard working solutions. Normally aliquots of 100 μl of this primary synthetic standard solution were evaporated and made up in 500 μl of Milli-Q water, and 20 μl of this working solution were injected into the instrument to obtain electropherograms. Thus, the actual quantities (in ng) of each lanthanide injected are also given in Table 2.

3. Results and discussion

3.1. Conditioning and operation of the CE instrument

Before initiating the capillary electrophoretic experimental tests, the equipment was set in operation for 20 min before conditioning by a flush with deionized water (10 min) and stabilizing by another flush period of 10 min with the working electrolyte solution. The CE equipment used the hydrostatic mode for injecting the sample into the capillary. This mode enabled a representative sample of a homogeneous mixture into the capillary to be introduced.

Table 2
Chemical composition pattern of the REE synthetic geochemical standards (SPV-1 and SPV-4)

REE	Chemical symbol	SPV-1 (µg/ml)	Quantity injected (ng)	SPV-4 (µg/ml)	Quantity injected (ng)
Lanthanum	La	34.627	138.508	78.525	314.100
Cerium	Ce	69.400	277.600	141.029	564.116
Praseodymium	Pr	10.784	43.136	14.531	58.124
Neodymium	Nd	42.334	169.336	69.945	279.780
Samarium	Sm	9.882	39.528	15.695	62.780
Europium	Eu	2.720	10.880	3.524	14.096
Gadolinium	Gd	10.251	41.004	11.144	44.576
Terbium	Tb	21.840	87.360	2.345	9.380
Dysprosium	Dy	10.669	42.676	7.267	29.068
Holmium	Ho	2.387	9.548	2.000	8.000
Erbium	Er	5.706	22.824	4.934	19.736
Thulium	Tm	1.084	4.336	0.756	3.024
Ytterbium	Yb	5.420	21.680	3.708	14.832
Lutetium	Lu	1.015	4.060	0.708	2.832

The capillary was immersed in the sample at a height of 10 cm above the running electrolyte level for 20 s. The capillary was then lowered into electrolyte for applying a voltage of +30 kV. Details on the instrument operation are given in the manufacturer's manual (Waters).

3.2. REE group separation

A complete and optimized separation of REEs in geological samples (rock, mineral or fluids) at trace levels (µg/g or ng/g) by CE techniques is a challenging analytical problem. An electropherogram originally published by Macka et al. [23] (Fig. 1) shows that an optimized separation of all 14 lanthanides involves a difficult analytical task since some elements of the REEs group exhibit a very low detection sensitivity due to their similar electrophoretic mobilities. A reverse order in the REE separation was obtained in less than 7 min by these authors. Overlapped peaks at ~5.5 min and ~6.0 min were also displayed in the same electropherogram. They are related to the co-migration processes of Lu–Tm and Gd–Eu–Sm, respectively (Fig. 1). The other eight elements (Er–Ho–Dy–Tb and Nd–Pr–Ce–La) were efficiently separated without problems.

Although the experimental results reported in Fig. 1 were not totally satisfactory, they constitute a good starting point for developing an improved CE method capable of an optimized separation of all the

lanthanide group. This work was performed in two experimental stages. In the first stage, electrolyte and operating conditions recommended by the related technical literature were directly employed for trying to separate all fourteen lanthanides contained in the synthetic geochemical standards [13,22].

Fig. 3 presents an electropherogram showing partial separation of the REEs. These separations were carried out in less than 2 min (~1.6 min), being a considerably reduced analysis time (see Table 1). La, Ce, Pr, Nd, Sm, Tb, Dy, and Er were baseline separated. They were readily identified because they exhibited an optimal peak shape. As expected, the electropherogram displays some detection problems related to: (i) the co-elution of Eu and Gd, (ii) a tailing problem in the Ho and Yb peaks, and (iii) a poor detection sensitivity of the Tm and Lu peaks. After the separation was performed, all REEs were detected by indirect photometry at a wavelength of 214 nm. At these conditions, the UV detection system showed a good linear response between the peak area and the REE concentration as well as between the peak height and the REE concentration. As can be observed in Fig. 3, the applied voltage attained an output signal of up to about +8 mV. All these CE tests were performed at the ambient temperature (25°C).

The second experimental stage was planned from consideration of the results obtained in the first stage. Two main aspects were carefully examined: (i) to

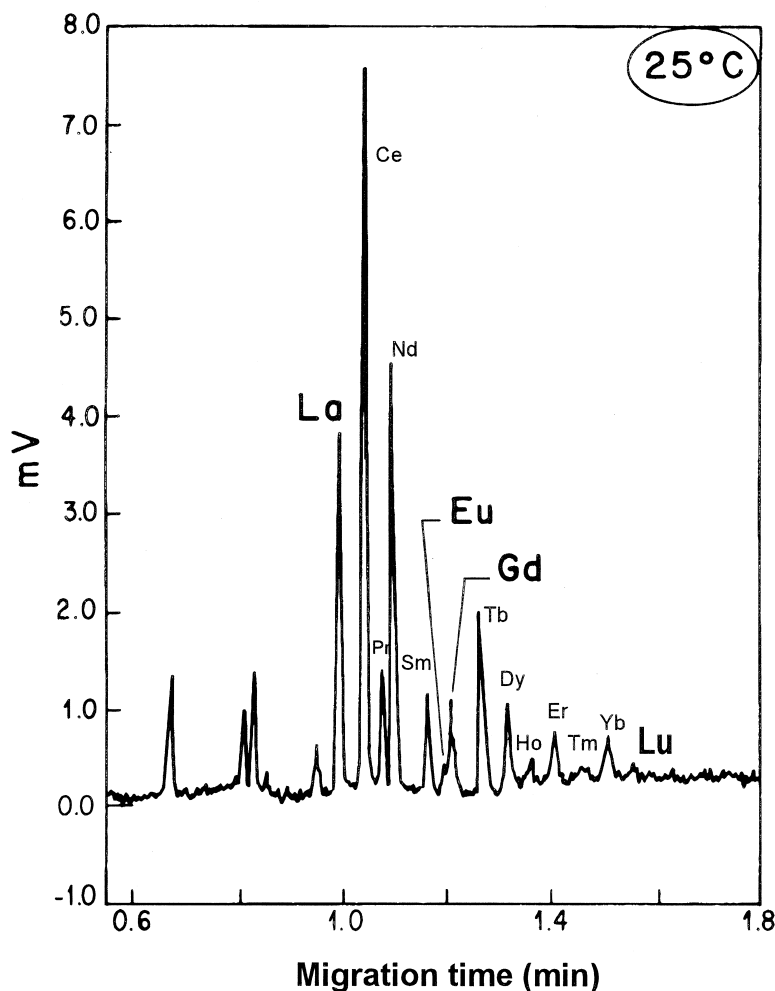


Fig. 3. Electropherogram of a typical separation pattern of 14 lanthanides. background electrolyte, 4 mM HIBA and 10 mM UVCat-1 (pH 4.4 with acetic acid); temperature, 25°C; separation voltage, +30 kV; injection of a SPV-1 standard solution. For other operating conditions see Section 2.1. Note Eu and Gd overlapping peaks in this electropherogram.

find out suitable CE experimental conditions for resolving the overlapped peaks corresponding to Eu and Gd, and (ii) to increase the detection sensitivity for measuring Tm and Lu at the concentration levels of the SPV-1 and SPV-4 standards.

3.3. Separation of Eu and Gd and enhanced detection of Tm and Lu

In these experimental tests, improvements in the separation efficiency of Eu and Gd were explored, by setting the capillary column temperature as an im-

portant operating parameter to be varied or modified. Capillary temperature has been identified as a highly effective parameter for enhancing both the speed and the separation efficiency of ions during a CE analysis [26,27]. Experimental work in CE for carrying out analyses at different temperatures of capillaries has generally been restricted because commercial CE instruments equipped to control the temperature either at temperatures below ambient or at temperatures above 70°C are not readily available [27]. However, some modifications in the instrument can be performed either for coupling a cooling system to

work with sub-ambient temperatures or for thermostating the capillary at higher temperatures.

At this experimental stage, the development of this new separation and detection method of REEs involved a systematic variation of the capillary temperature. The capillary column was run at three different temperatures: 15°C, 25°C and 35°C, which were achieved by using the temperature device commercially coupled to our CE instrument.

The temperature has a very important influence on the separation of Eu and Gd as well as on the CE reproducibility. Fig. 4 shows the electropherogram

obtained when the temperature of capillary was set at 35°C. At these thermal conditions, the separation of the REEs was carried out in less than 1 min. Even though, the analysis time was reduced in comparison with that obtained at 25°C, the overlapping problem between Eu and Gd was again exhibited. Likewise, a poor detection sensitivity in Tm and Lu was also observed.

Fig. 5 shows the electrophoretic results obtained when the capillary column temperature was set at 15°C. At these conditions, an excellent separation of the overlapped peaks (Eu and Gd) was obtained. The

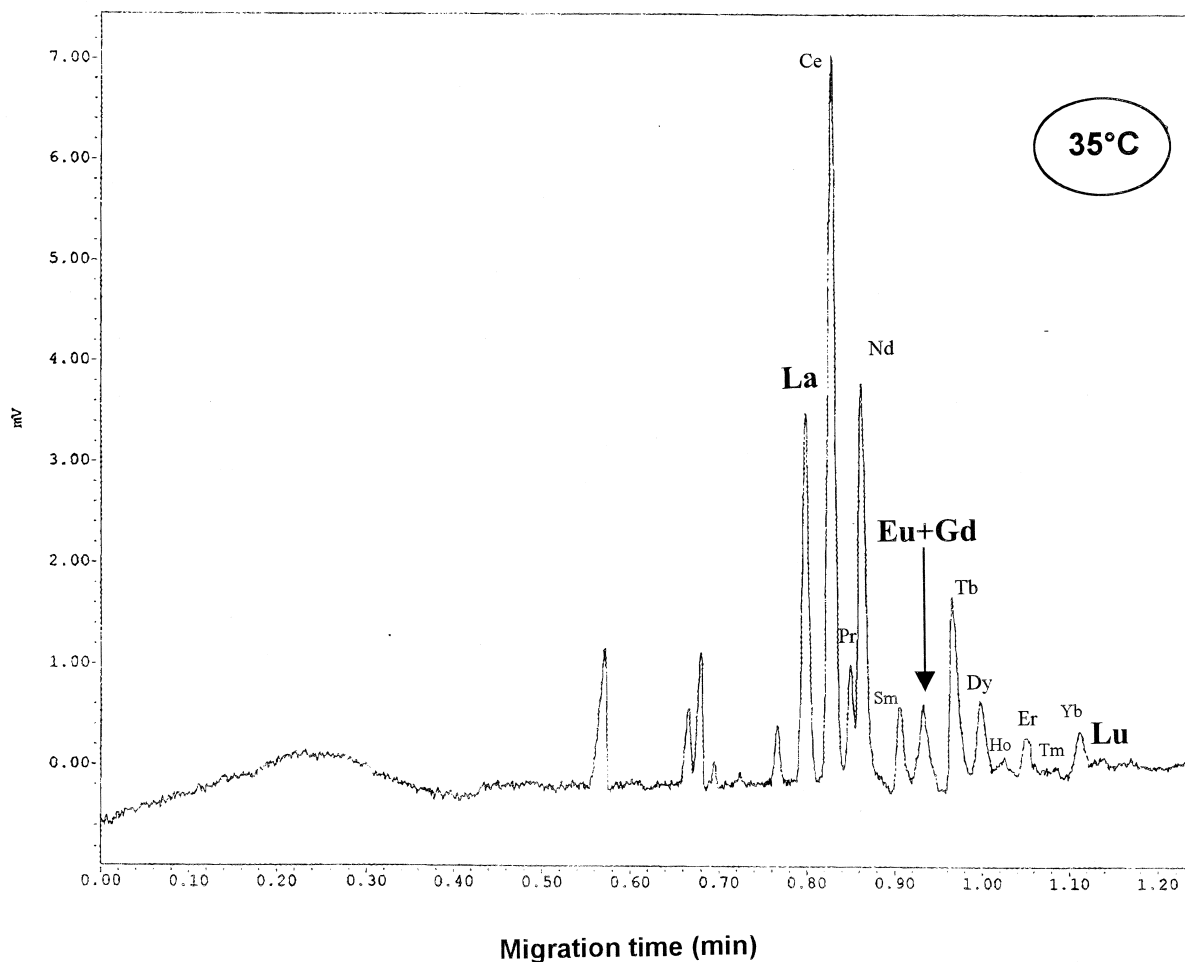


Fig. 4. Electropherogram of a typical separation pattern of 13 lanthanides. Background electrolyte, 4 mM HIBA and 10 mM UVCat-1 (pH 4.4 with acetic acid); temperature, 35°C; separation voltage, +30 kV; injection of a SPV-1 standard solution. For other operating conditions see Section 2.1. Note Eu and Gd overlapping peaks in this electropherogram.

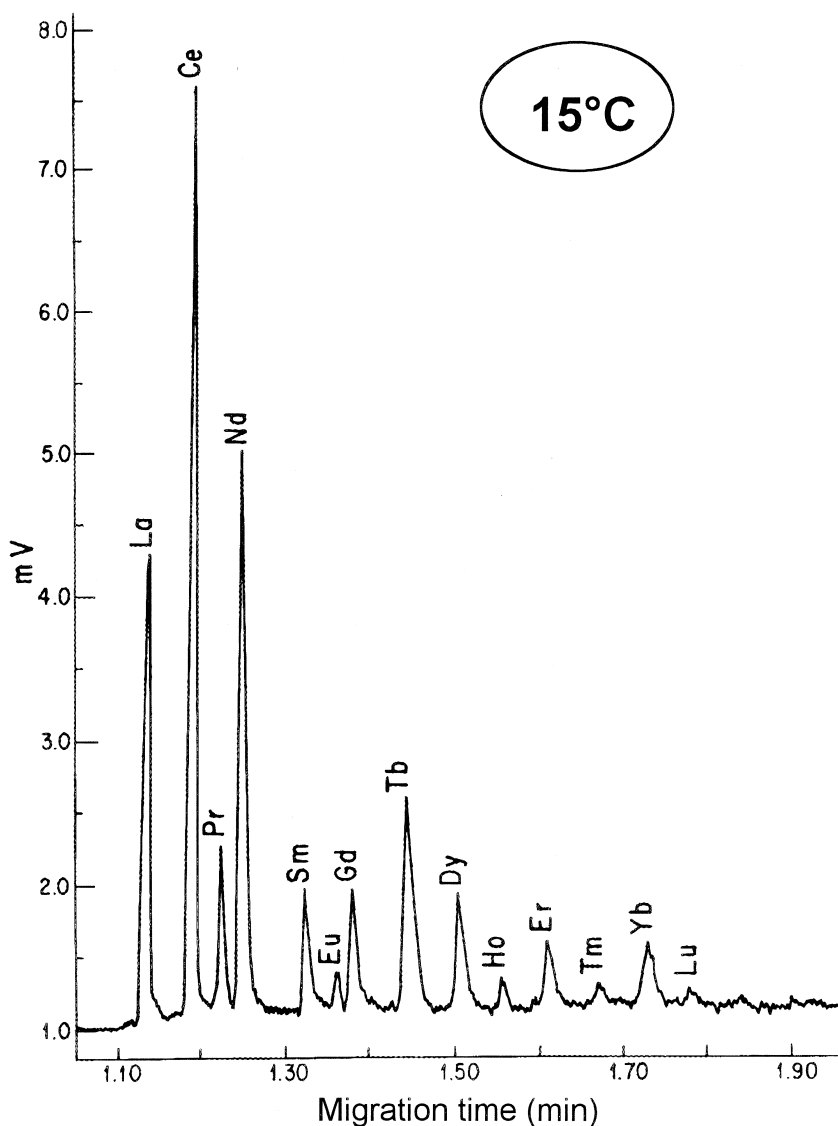


Fig. 5. Electropherogram of a typical separation pattern of 14 lanthanides. Background electrolyte, 4 mM HIBA and 10 mM UVCat-1 (pH 4.4 with acetic acid); temperature, 15°C; separation voltage, +30 kV; injection of SPV-1 standard solution. For other operating conditions see Section 2.1. Note Eu and Gd peaks are totally resolved in this electropherogram.

separation of lanthanides was carried out in less than 2 min (~1.8 min), a slightly longer period than that for the electropherogram at 25°C (~1.6 min). An efficient separation of Eu and Gd was probably achieved due to a temperature dependent reduction of electrophoretic mobilities of the ions. These results clearly show that a lower operating tempera-

ture of 15°C is most suited for a better determination of the REEs.

3.4. Precision tests

Reproducibility was evaluated by injecting six times the REEs synthetic geochemical standard

solutions. The operating conditions of the CE instrument are given as caption in Fig. 6. This figure shows a schematic diagram where the six electropherograms obtained during the reproducibility tests are compiled. An average relative standard deviation (RSD) of about 0.14% for the migration times was obtained. Peak area reproducibility (Table

3) ranged from 0.15 to 4.7% for all REEs, with the exception of Tm (9.3%). Similarly, peak height reproducibility varied from 0.17 to 3.9%, with the exception of Tm (5.4%) and Lu (7.5%). Because the natural concentration levels in geological materials are expected to be close to these synthetic standards, the reproducibility values obtained in this work are

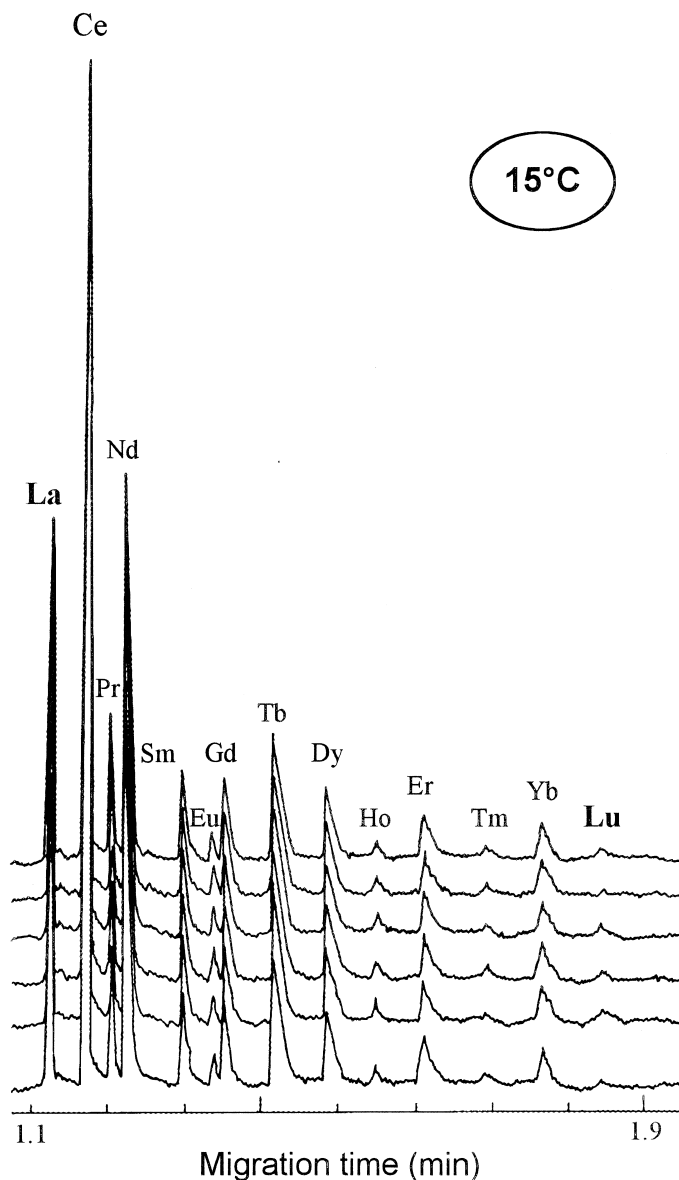


Fig. 6. Schematic diagram showing reproducibility results of six injections of standard solution SPV-1 at 15°C. Superposed electropherograms show all REEs to be well resolved. Operating conditions are summarized in Fig. 5. See Table 3 for more details.

Table 3
Reproducibility tests based on six injections of standard solution SPV-1

REE	Chemical symbol	Quantity Injected (ng)	Migration ^a Time (%)	Peak area ^a (%)	Peak height ^a (%)
Lanthanum	La	138.508	0.12	0.30	0.18
Cerium	Ce	277.600	0.15	0.15	0.21
Praseodymium	Pr	43.136	0.12	0.88	0.93
Neodymium	Nd	169.336	0.10	0.17	0.74
Samarium	Sm	39.528	0.07	1.77	1.20
<i>Europium</i>	<i>Eu</i>	<i>10.880</i>	<i>0.14</i>	<i>4.61</i>	<i>2.77</i>
<i>Gadolinium</i>	<i>Gd</i>	<i>41.004</i>	<i>0.06</i>	<i>2.63</i>	<i>2.81</i>
Terbium	Tb	87.360	0.10	2.64	1.61
Dysprosium	Dy	42.676	0.11	1.54	0.48
Holmium	Ho	9.548	0.09	3.23	3.93
Erbium	Er	22.824	0.14	1.30	1.38
Thulium	Tm	4.336	0.18	9.30	5.36
Ytterbium	Yb	21.680	0.24	2.12	1.52
Lutetium	Lu	4.060	0.30	4.73	7.48

^a The numbers refer to the relative standard deviation (RSD) values expressed in %.

representative of those expected for such applications. Finally, the estimated detection limits for the REEs (three times the background noise) are about 0.1 mV and the limits of quantification (five times the background noise) are around 0.2 mV. Two heavy REEs (Tm and Lu) in the synthetic standards are present at concentration levels close to the detection limits, which explains the larger errors obtained for these two elements during the reproducibility tests.

3.5. Calibration tests

The minimum linearity interval and the correlation coefficient for each REEs are shown in Table 4 for a four-point calibration. The linear relationship or response between peak area versus REEs sample concentration was confirmed for the fourteen elements. Such a relationship was rather good and sensitive for all REEs, except Tm and Lu present at significantly lower concentration levels (close to the detection limits for these elements) in the synthetic standards. For routine applications, the calibration curves for these two elements can be improved using standard solutions with higher concentrations of these lanthanides. Further, the final calibrations can be based on many more measurements (probably eight or more) of different standard solutions, intercalated between the analysis of the unknowns as was

done by Verma [18,19] for the determinations of the REEs by HPLC.

4. Conclusions

An alternative analytical CE method for determining the REE group in geological samples has been developed. The advantages of the present improved CE method over other similar CE separation techniques are: (i) an optimized separation of all REEs;

Table 4
Linearity of response for the individual REEs by CE (inferred from calibration curves with 4 data points)

REE	Chemical symbol	Quantity injected min.–max. (ng)	Correlation coefficients
Lanthanum	La	0–415.5	0.9994
Cerium	Ce	0–832.8	0.9998
Praseodymium	Pr	0–129.4	0.9998
Neodymium	Nd	0–508.0	0.9998
Samarium	Sm	0–118.5	0.9972
<i>Europium</i>	<i>Eu</i>	<i>0–32.6</i>	<i>0.9985</i>
<i>Gadolinium</i>	<i>Gd</i>	<i>0–123.0</i>	<i>0.9951</i>
Terbium	Tb	0–262.1	0.9994
Dysprosium	Dy	0–128.0	0.9969
Holmium	Ho	0–28.6	0.9946
Erbium	Er	0–68.5	0.9996
Thulium	Tm	0–13.0	0.8840
Ytterbium	Yb	0–65.0	0.9971
Lutetium	Lu	0–12.2	0.6561

(ii) an efficient resolution of the overlapping problem between Eu and Gd peaks; (iii) an enhancement in the detection limits; (iv) a significant reduction of the analysis time to less than 2 min; (v) linear calibration curves.

Thus, CE promises to become a valuable quantitative method (cheaper, accurate, and faster) for determining REEs at mg/l to $\mu\text{g/l}$ levels. It will constitute an excellent alternative method for geological applications, especially for developing countries.

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