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Preconcentration and determination of rare-earth elements in iron-rich water samples by extraction chromatography and plasma source mass spectrometry (ICP-MS)

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Abstract

A 100-fold preconcentration procedure based on rare-earth elements (REEs) separation from water samples with an extraction chromatographic column has been developed. The separation of REEs from matrix elements (mainly Fe, alkaline and alkaline-earth elements) in water samples was performed loading the samples, previously acidified to pH 2.0 with HNO_3, in a 2 ml column preconditioned with 20 ml 0.01 M HNO_3. Subsequently, REEs were quantitatively eluted with 20 ml 7 M HNO_3. This solution was evaporated to dryness and the final residue was dissolved in 10 ml 2% HNO_3 containing 1 $\mu g\,l^{-1}$ of cesium used as internal standard. The solution was directly analysed by inductively coupled plasma mass spectrometry (ICP-MS), using ultrasonic nebulization, obtaining quantification limits ranging from 0.05 to 0.10 $ng\,l^{-1}$. The proposed method has been applied to granitic waters running through fracture fillings coated by iron and manganese oxy-hydroxides in the area of the Ratones (Cáceres, Spain) old uranium mine.

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Keywords: Rare-earth elements; Extraction chromatography; Waters; ICP-MS; Ultrasonic nebulization

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1. Introduction

For over 30 years, rare-earth elements (REEs) have been successfully used to interpret many geochemical processes, including the evolution of earth's mantle and crust, magma genesis, sedimentary petrology and ore genesis [1–3]. More recently, REEs have been used to identify hydrogeochemical [4–11] and in-stream [12] processes. In addition, the increase of industrial applications of REEs has led to enhanced releases of REEs to the environment [13]. Furthermore, these elements have been recognized to be chemical analogues of some fission products and actinides present in nuclear spent fuel and have been widely used in the performance assessment of radioactive waste repositories [14,15]. Thus, light REEs (LREEs) are analogues of Am, Cm and Pu(III) [16].

Elucidation of the geochemical behaviour of REEs in a weathering environment has been hindered by the very low aqueous concentrations, which generally are less than 1 $\mu g\,l^{-1}$ in surface and ground waters.

With the development of inductively coupled plasma mass spectrometry (ICP-MS) the determination of REE concentrations in water samples has become more routine. However, the detection of all the elements of this group in this type of samples usually requires a previous preconcentration step, since most of these elements are present in concentrations close to or below the detection limits of the analytical equipment. Without any preconcentration or separation step, detection limits for REEs are about 0.01–0.02 $\mu g\,l^{-1}$ with an uncertainty of approximately 5% [17,18]. Higher sensitivity is reached using more efficient sample introduction systems, such as ultrasonic nebulizers [19]. For the analysis of granitic waters, those detection limits are usually too high, since the retention of REEs by some mineral phases present in such areas reduces the content of

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these elements below 10 ng l^{-1}. For this purpose, several methods have been proposed and used for preconcentration of REEs, according to the nature of the samples. These methods include co-precipitation [20,21], solvent extraction [22], ion exchange chromatography [23–25] and solid-phase extraction [26,27]. Some of them require neutral or low acidic media and are not suitable for such samples that contain important amounts of iron, manganese and other transition metals due to precipitation of hydroxides or concomitant effects.

Solid–liquid extraction, technique that has been commonly known as extraction chromatography in radioanalytical chemistry [28], has been successfully used as less time consuming, very reproducible and low blank method for the analysis of some heavy metals and radionuclides in water samples. Recently, it has been applied to REE preconcentration, combined with ion exchange chromatography and other extraction chromatographic materials [29–31].

In this paper, a one-step extraction chromatographic procedure based on the use of a commercially available solid-phase extraction column (HDEHP, di(2-ethylhexyl) orthophosphoric acid supported on an hydrophobic substrate) is proposed for the preconcentration of REEs from iron-rich water samples. With this method, an enrichment factor of 100 or even higher can be easily obtained.

2. Experimental

2.1. Reagents

All reagents were of analytical grade quality supplied by Merck (Darmstadt, Germany). Water with a resistivity of 18 MΩ cm^{-1}, prepared using a Milli-Q system (Millipore, S.A., St. Quentin Yvelynes, France), was used throughout.

Table 1
Operating conditions of ICP-MS measurements

Incident power (W)	1300
Reflected power (W)	<5
Coolant gas flow rate (l min^{-1})	15
Auxiliary gas flow rate (l min^{-1})	1.2
Nebulizer gas flow rate (l min^{-1})	0.90
Sample uptake rate (l min^{-1})	1.0
USN heater temperature (°C)	130
USN cooler temperature (°C)	−3
Channels per a.m.u.	18
Scans	6
Passes per scan	8
Dwell time (ms)	16

Water and acids were further purified by sub-boiling distillation, using a PTFE still (Berghof, Einegen, Germany).

Working standard solutions for instrumental calibration were prepared by serial dilution of 1000 mg l^{-1} stock standard solutions (Alfa, Johnson Matthey, Karlsruhe, Germany) just before use.

Extraction chromatographic materials, Ln® Resin columns (100–150 μm particle size), were obtained from Eichrom Industries Inc. (Darien, IL, USA). This resin is based on the organophosphorous extracting agent HDEHP, di(2-ethylhexyl) orthophosphoric acid, dissolved in 0.1N nitric acid (0.3%, w/v) and supported on an inert polymeric substrate (40 wt%), Amberchrom CG-71 ms. These columns can be used only once due to the elimination of their extracting agent after the application of the preconcentration procedure.

All plasticware and glassware were soaked in 10% HNO_3 for at least 12 h before using and rinsed with sub-boiling water up to pH 6–7.

2.2. ICP-MS instrumentation

A quadrupole inductively coupled plasma mass spectrometer (Finnigan Mat SOLA, Bremen, Germany) coupled

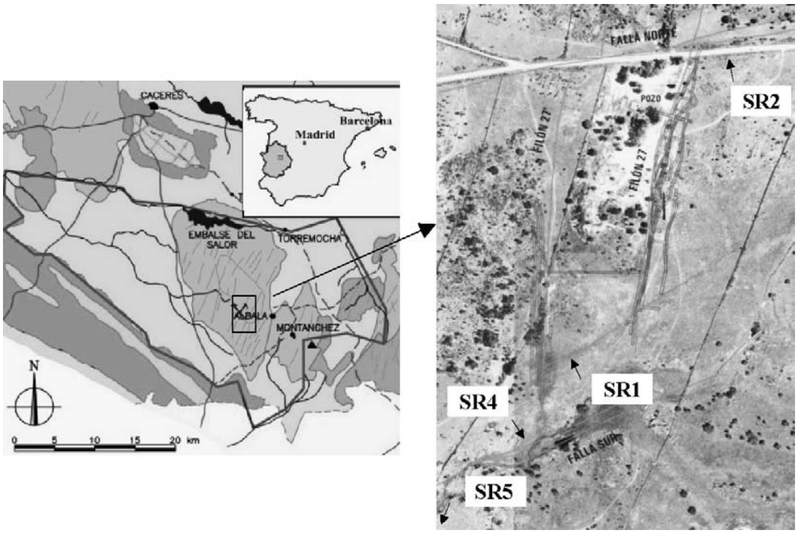

Fig. 1. Site map of Ratones mine and boreholes location.

Table 2
Characteristics of the studied boreholes

Borehole	Length/total depth (m)	Slope (°)	Stretch	Depth (m)
SR1	76.08/65.89	30	SR1-T1	50.11–76.08
SR2	79.19/74.41	20	SR2-T1	37.48–79.19
SR4	124.76/117.24	20	SR4-T3	0.0–36.98
SR5	500.88/500.88	0	SR5-T1	458.6–469.6
			SR5-T2	417.6–427.1
			SR5-T3	203.1–213.1
			SR5-T4	138.6–149.1
			SR5-T5	61.1–71.6

with a two-stages ultrasonic nebulizer (USN) U-6000 AT+ (CETAC Technologies Inc., Omaha, NE, USA) was used throughout. The sample was pumped to the USN via a Gilson Minipuls 3 (Villiers le Bel, France). External calibration, with cesium as internal standard, was used for the quantification of the rare-earth elements. Both plasma conditions and nebulizer parameters are summarized in Table 1.

2.3. Study site and description of the samples

The studied samples come from an old uranium mine (Ratones mine) located in the southern part of the Albalá Granitic Pluton (Cáceres, Spain). Two NNE–SSW subvertical quartz dykes were mined between 1955 and 1975, and the mine was finally restored in 1999. For this study, dykes were intersected by four boreholes (SR1, SR2, SR4 and SR5) between 65 and 500 m deep. Site map and boreholes description are given in Fig. 1 and Table 2, respectively.

Groundwater samples were collected from the bottom of several piezometers installed at different depths along the boreholes. Immediately after sampling the groundwaters were filtered using 0.45 μm filters and acidified to pH 2.0 with concentrated nitric acid, to avoid the precipitation of iron as $Fe(OH)_3$ and the possible co-precipitation of REEs.

The groundwaters in Ratones mine are poorly mineralized and have electric conductivities lower than $750\,\mu\text{S}\,\text{cm}^{-1}$. Their pH is close to neutral and the waters range from magnesium bicarbonate-type to magnesium sulphate-type in the intersection with the mineralized dykes, and finally to sodium bicarbonate-type, which is considered as the most evolved end member with the longest residence time (>16,000 years). Other physical and chemical characteristics of the groundwaters are shown in Table 3.

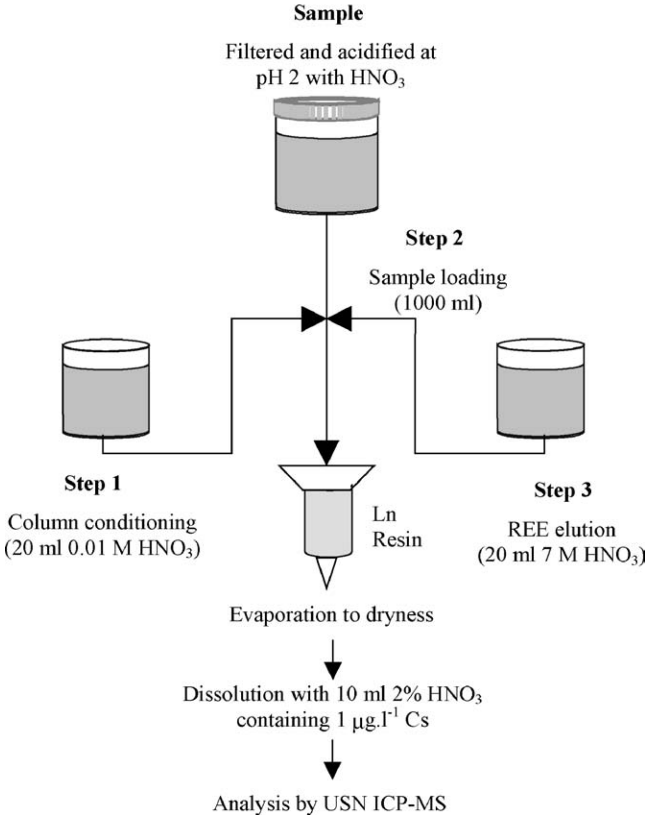

Fig. 2. Sample preconcentration scheme.

2.4. Sample preconcentration procedure

Fig. 2 shows the sample preconcentration general scheme. Columns were conditioned with 20 ml 0.01 M HNO_3 before use. Then 1000 ml of sample, previously adjusted to pH 2.0, were passed through the column with a constant flow rate of $1\,\text{ml}\,\text{min}^{-1}$. When the sample was completely loaded, rare-earth elements were eluted with 20 ml 7 M HNO_3 and collected in a PTFE vessel. The obtained solution was evaporated to dryness and the residue was dissolved in 10 ml 2% HNO_3 containing $1\,\mu\text{g}\,\text{l}^{-1}$ of Cs. This final solution was employed

Table 3
Main physical and chemical characteristics of groundwater samples in Ratones mine[a]

Stretch	pH[b]	Eh (mV)[b]	HCO_3^-	Cl^-	SO_4^{2-}	Ca	Mg	Na	K	Fe
SR1-T1	7.0	−200	243	7.9	41.7	35	26.3	21	2.8	16.1
SR2-T1	7.8	−190	64	5.4	13.7	3.3	5.9	21	1.1	0.63
SR4-T3	8.1	−310	178	7.8	170.3	36	34.3	43.7	2.2	15.8
SR5-T1	7.9	−300	314	18	1.6	7	5	110	2.9	0.09
SR5-T2	7.8	−280	321	26	8.9	7.2	7.2	115	2.8	0.13
SR5-T3	7.9	−280	273	13	2.1	9.3	6.9	88	2.4	0.06
SR5-T4	7.7	−130	186	11	9	16	9.9	39	3.7	<0.03
SR5-T5	7.1	−38	178	11	1.6	13	7.9	40	3.8	0.90

[a] Results are given in $\text{mg}\,\text{l}^{-1}$ unless indicated.
[b] In situ measured parameters.

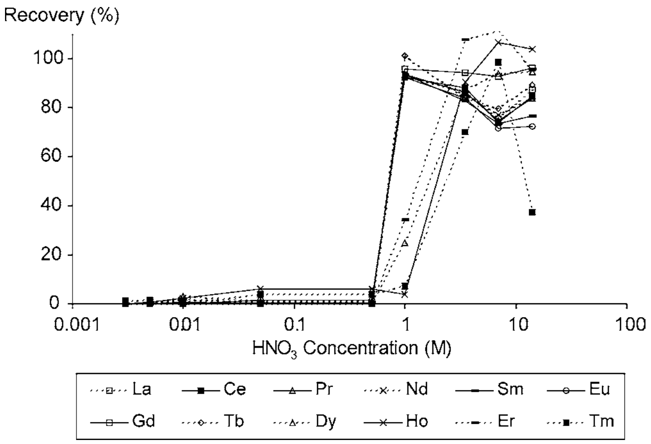

Fig. 3. Effect of acid concentration on total recovery.

to measure directly MREEs and HREEs (middle and heavy rare-earth elements, respectively), the less abundant REEs. For LREE analysis (light rare-earth elements), the most abundant REEs, the solution was diluted 10 times with a 1 μg l^{-1} Cs solution.

3. Results and discussion

3.1. Optimization of the chromatographic procedure

3.1.1. Effect of acid concentration

Extraction chromatography is strongly dependent of the pH of the solutions, due to the possibility of protonation of the organic ligands. This parameter is one of the most critical factors to take into account in the establishment of the experimental conditions of the method. In order to find the optimum pH conditions for the preconcentration and separation of the REEs, several assays were carried out varying the acid concentration from 0.003 to 14 M. Experiments were performed per triplicate with synthetic REE solutions containing 1 μg ml^{-1} of each REE and are summarized in Fig. 3. Uncertainty of the obtained recoveries was around 2%.

As it can be seen, a quantitative retention of the REEs is observed with acid concentrations below 0.01 M (pH 2). Therefore, these conditions were selected to load the water samples onto the Ln® Resin column.

The maximum recovery for all the studied elements was achieved with 7 M HNO_3, and a higher concentration of acid does not produce a significant enhancement on the efficiency of the process.

3.1.2. Effect of eluent flow rate

All the solutions were loaded in the columns using a Gilson peristaltic pump and PTFE tubbings. The bottom of the columns was also connected to the pump in order to keep a constant flow rate. The effect of this parameter on the adsorption and desorption mechanisms was also studied. The flow rate was varied from 1 to 5 ml min^{-1} and better results were obtained at low flow rates. A flow rate of 1 ml min^{-1} is recommended for both REE retention and elution steps.

3.2. Matrix effects on chromatographic separation

Matrix effects in the separation efficiency of the process were evaluated carrying out several experiments with mineral natural water of similar composition and characteristics to the studied groundwater samples, spiked with different concentrations of REEs.

Two hundred and fifty millilitres of commercial granitic mineral water (Fontvella®, Sant Hilari Sacalm, Gerona, Spain) were spiked with REEs, ranging from 5 to 5000 ng (for LREEs, the more abundant) and from 0.08 to 250 ng (for HREEs, the less abundant). The addition was carried out taking into account REE abundances in C1 chondrite [32].

The standard addition method presents a well-defined straight line for all the elements, as indicated in Table 4. These linear relations indicate the absence of relevant matrix effects of the main constituents of the samples, probably due to the high grade of selectivity this resin has for the REEs.

Table 4
Linear regression parameters for REE standard additions to Fontvella® mineral water

Element	Slope	Intercept	Correlation coefficient	Estimated content (ng l^{-1})
La	1.022 ± 0.018	9.2 ± 2.0	0.9994	8.9 ± 2.0
Ce	1.051 ± 0.020	17.5 ± 4.4	0.9993	16.4 ± 4.4
Pr	1.087 ± 0.018	1.73 ± 0.41	0.9994	1.57 ± 0.39
Nd	1.099 ± 0.016	8.3 ± 1.8	0.9996	7.5 ± 1.7
Sm	1.114 ± 0.012	1.86 ± 0.28	0.9998	1.66 ± 0.26
Eu	1.210 ± 0.018	0.57 ± 0.10	0.9996	0.468 ± 0.089
Gd	1.104 ± 0.020	1.15 ± 0.22	0.9994	1.03 ± 0.21
Tb	0.883 ± 0.081	0.56 ± 0.22	0.9917	0.59 ± 0.29
Dy	1.304 ± 0.018	0.65 ± 0.21	0.9996	0.49 ± 0.16
Ho	0.80 ± 0.13	0.44 ± 0.27	0.9740	0.44 ± 0.39
Er	0.995 ± 0.049	0.69 ± 0.20	0.9976	0.68 ± 0.23
Tm	0.951 ± 0.080	0.091 ± 0.055	0.9930	0.088 ± 0.063

Table 5
Lower and higher concentrations of the calibration solutions

Element	Lower concentration (ng ml^{-1})	Higher concentration (ng ml^{-1})
La	2.50	50.0
Ce	5.00	100.0
Pr	0.50	10.0
Nd	2.50	50.0
Sm	0.50	10.0
Eu	1.25	25.00
Gd	2.50	50.00
Tb	0.50	10.00
Dy	2.50	50.00
Ho	0.375	7.50
Er	0.75	15.00
Tm	0.125	2.50

3.3. Instrumental calibration

Due to the different range of expected concentrations for each rare-earth element, higher for LREEs and lower for HREEs, external calibration of the instrument was carried out taking into account C1 chondrite normalized concentrations. Thus, a set of five standard solutions has been prepared from 1000 mg l^{-1} monoelemental stock solutions, being the lower and higher contents of REEs as detailed in Table 5.

3.4. Analytical figures of merit

Instrumental quantification limits for each REE, using the above-mentioned instrumental calibration, are closely related to the abundance of the measured isotopes (see Table 6). Thus, for monoisotopic REEs, such as Pr, Tb, Ho and Tm, or those with a remarkable abundant isotope, such us La and Ce, the quantification limit was set to 5 ng l^{-1}. For those with a complex isotopic pattern, with several and low abundant isotopes, such as Nd, Sm, Gd, Dy and Er, the instrumental quantification limit was set to 10 ng l^{-1}.

Table 6
REE measured isotopes and its isotopic abundance [33]

Element	Measured isotopes (natural abundance %)
La	139 (99.91)
Ce	140 (88.45)
Pr	141 (100)
Nd	143 (12.18), 145 (8.3), 146 (17.19)
Sm	147 (15.0)
Eu	151 (47.8), 153 (52.2)
Gd	157 (15.65)
Tb	159 (100)
Dy	163 (24.9)
Ho	165 (100)
Er	166 (33.6)
Tm	169 (100)

Table 7
Reproducibility of the measurements

Element	Average (ng l^{-1})	S.D. (ng l^{-1})	R.S.D. (%)
La	18.7	1.3	6.9
Ce	24.2	1.1	4.6
Pr	9.8	0.53	5.4
Nd	31.7	2.7	8.6
Sm	9.6	1.2	13
Eu	1.90	0.19	10
Gd	6.63	0.51	7.7
Tb	1.01	0.18	18
Dy	15.0	1.2	7.7
Ho	6.20	0.86	14
Er	17.3	1.3	7.3
Tm	4.15	0.29	7.0

Considering a 100-fold preconcentration procedure (1000 ml of water sample were passed through the column and REEs were collected in 10 ml final volume at the end of the process), the quantification limits for the samples were 0.05 and 0.10 ng l^{-1} for monoisotopic and polyisotopic elements, respectively.

Six replicates of the commercial granitic mineral water were analysed in order to check the reproducibility of the procedure (Table 7). Relative standard deviations below 10% have been found for REE concentrations above 1.0 ng l^{-1}.

Table 8
Analysis of certified reference materials

Element	PPREE1		SCREE1	
	Certified value [34]	Obtained value	Certified value [34]	Obtained value
La	80.4/5.9	79.1 (2.3)	9.85/0.73	9.79 (0.46)
Ce	161/8	159.4 (5.6)	24.6/2.2	24.2 (1.3)
Pr	21.2/1.3	20.9 (1.9)	4.29/0.28	4.22 (0.19)
Nd	92.3/5.7	91.9 (5.3)	22.1/0.9	21.8 (0.4)
Sm	20.3/1.5	19.9 (2.1)	6.71/0.31	6.69 (0.21)
Eu	5.95/0.48	5.58 (0.47)	1.47/0.07	1.44 (0.05)
Gd	23.8/1.7	23.3 (2.6)	8.21/0.65	8.14 (0.31)
Tb	3.65/0.33	3.71 (0.41)	1.34/0.07	1.37 (0.06)
Dy	22.0/0.7	21.5 (0.3)	8.10/0.34	8.01 (0.24)
Ho	4.43/0.09	4.36 (0.07)	1.61/0.06	1.58 (0.06)
Er	11.9/0.4	11.7 (0.2)	4.35/0.21	4.25 (0.19)
Tm	1.48/0.05	1.42 (0.04)	0.582/0.023	0.59 (0.02)

Certified values are indicated as MPV (most probable value)/MAD (mean average deviation). All results are expressed in μg l^{-1}.

3.5. Validation of the analytical method

In order to check the accuracy of the obtained results after the application of the proposed method, four aliquots of 25 ml of two certified reference materials (PPREE1 and SCREE1, supplied by the U.S. Geological Survey, Denver, Colorado) were treated following the above-mentioned protocol. The high content of REEs in both reference materials and their limited volume made necessary to reduce the sample volume, without changing any other condition of the method.

Analytical results for both reference materials are detailed in Table 8, expressed as the average of the four replicates. Standard deviations of the replicates are indicated between parentheses.

A very good agreement is observed between recommended and obtained values, even taking into account the high concentration of REEs in these certified reference materials.

3.6. Application of the preconcentration scheme to groundwaters samples

Groundwaters in the surroundings of Ratones U-mine have a very low REE content, indicating the granitic nature of the site. Results of REE analysis are shown in Table 9. Due to the sample volume needed for each analysis (1 l) and the limited amount of sample obtained from the boreholes, replicates could not have been performed.

The plot of the REE content of the samples previously normalized to C1 chondrite values [32] displays an important LREE enrichment relative to HREEs and a positive Eu-anomaly for samples SR2-T1 and SR5-T2 (Fig. 4). Thulium is not included in the figure because its concentration was below the detection limit in most of the samples, and its representation could only give rise to wrong conclusions about possible anomalies.

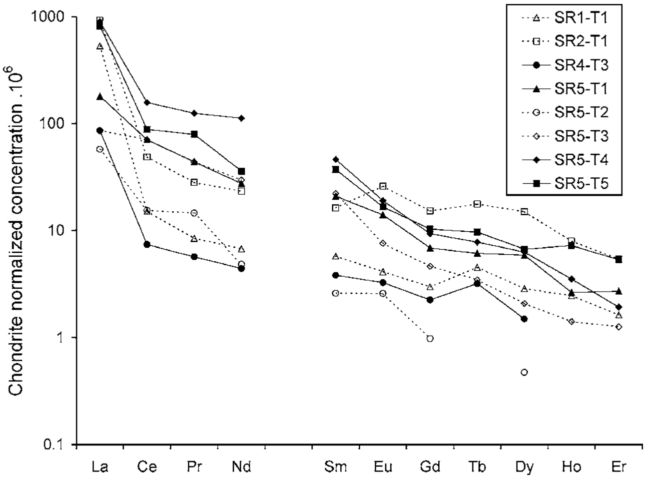

Fig. 4. Rare-earth element values for groundwater samples, normalized to C1 chondrite.

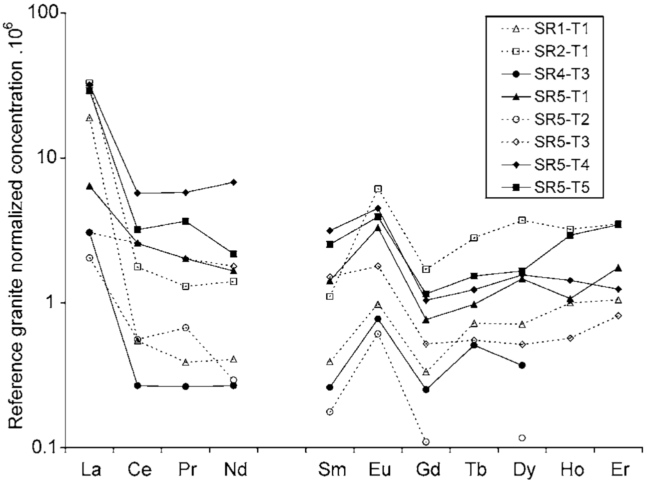

Fig. 5. Rare-earth element values for groundwater samples, normalized to reference granite (Perdices type).

However, if data are normalized to reference granite of the studied area (Perdices) [35], a more pronounced positive Eu-anomaly is observed for all the samples (Fig. 5). Although an enrichment of La is still detected, this is the only element that shows a different behaviour, excluding Eu, compared with the reference granite. The observed depletion for HREEs when the normalization is done with chondrite is not detected in this case. This fact can be explained by the presence of xenotime, which contains important amounts of HREEs, in

Table 9
Analytical results (in ng l^{-1}) for groundwater samples from Ratones mine (Spain)

Sample	SR1-T1	SR2-T1	SR4-T3	SR5-T1	SR5-T2	SR5-T3	SR5-T4	SR5-T5
La	130	225	21	44	14	21	220	200
Ce	9.6	31	4.7	45	9.8	45	100	56
Pr	0.81	2.7	0.55	4.2	1.4	4.2	12	7.6
Nd	3.2	11	2.1	13	2.3	14	53	17
Sm	0.89	2.5	0.59	3.2	0.40	3.4	7.1	5.7
Eu	0.24	1.5	0.19	0.81	0.15	0.44	1.1	0.96
Gd	0.61	3.1	0.46	1.4	0.20	0.95	1.9	2.1
Tb	0.17	0.66	0.12	0.23	<0.05	0.13	0.29	0.36
Dy	0.73	3.8	0.38	1.5	0.12	0.53	1.6	1.7
Ho	0.14	0.45	<0.05	0.15	<0.05	0.08	0.20	0.41
Er	0.27	0.91	<0.1	0.45	<0.1	0.21	0.32	0.89
Tm	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.08	0.26

the fracture fillings of the site [35]. However, the excess of La in these groundwater samples can only be explained by the high stability constants of lanthanum complexes with some inorganic anions present in the samples, mainly carbonates, due to the lower ionic radius of this element.

4. Conclusions

An easy method for separation of rare-earth elements from other constituents in iron-rich water samples has been developed and evaluated, obtaining preconcentration factors up to 100-fold.

The proposed method, based on the use of Ln® Eichrom columns, allows a direct treatment of water samples with high concentrations of transition metals (Fe, Mn, . . .), which can interfere in the separation and/or determination of REEs at sub-nanogram per litre levels. This procedure was performed under strong acid conditions for both sample loading and REE elution, avoiding the precipitation of such metals during the process.

The obtained results after the application of the method to certified reference materials indicate a very good accuracy, reliable reproducibility and quantification limits of few nanograms per litre. Furthermore, this procedure can be easily automated using a multiple-channels peristaltic pump, increasing the sample throughput of the analytical process.

The method has been applied to groundwater samples in the surroundings of an old U-mine (Ratones mine, Spain), providing REE profiles at different depths of the boreholes and valuable information about the behaviour of these elements in granitic sites. This information will be useful to better understand water–rock interactions.

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