

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 HNO₃, in a 2 ml column preconditioned with 20 ml 0.01 M HNO₃. Subsequently, REEs were quantitatively eluted with 20 ml 7 M HNO₃. This solution was evaporated to dryness and the final residue was dissolved in 10 ml 2% HNO₃ containing 1 μg 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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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 μg 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 μg 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 $18 \text{ M}\Omega \text{ cm}^{-1}$, prepared using a Milli-Q system (Millipore, S.A., St. Quentin Yvelines, France), was used throughout.

Table 1

Operating conditions of ICP-MS measurements

Incident power (W)	1300
Reflected power (W)	<5
Coolant gas flow rate (1 min^{-1})	15
Auxiliary gas flow rate (1 min^{-1})	1.2
Nebulizer gas flow rate (1 min^{-1})	0.90
Sample uptake rate (1 min^{-1})	1.0
USN heater temperature ($^{\circ}\text{C}$)	130
USN cooler temperature ($^{\circ}\text{C}$)	–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, Einingen, 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^{\circledR} Resin columns ($100\text{--}150 \mu\text{m}$ 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

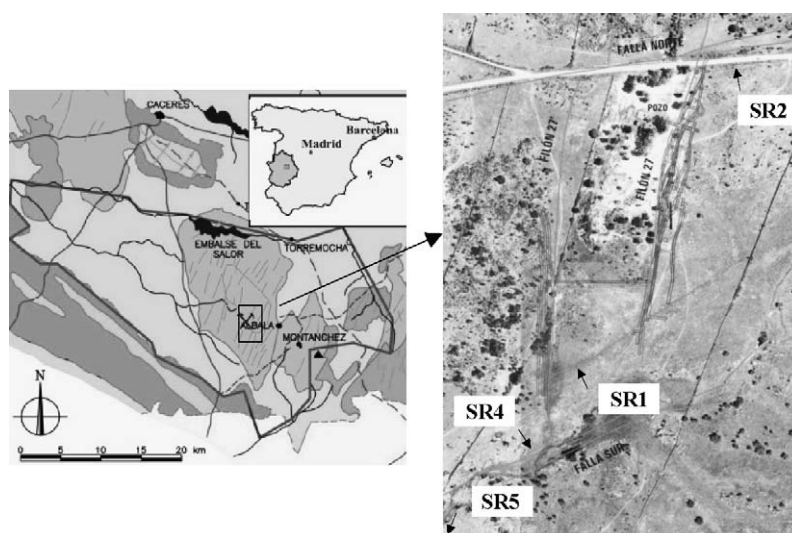


Fig. 1. Site map of Ratones mine and boreholes location.

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