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Masterarbeit

Development of an analytical method for determination of rare earth elements in rock samples by HPIC-ICP-MS

erstellt am

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EIDESSTATTLICHE ERKLÄRUNG

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I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume.

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Dedicated to my parents and brother

Kurzfassung

Methodenentwicklung zur Bestimmung von Lanthaniden in geologischen Proben mittels HPIC-ICP-MS

Die Arbeit befasst sich mit der Optimierung einer analytischen Methode zur Feststellung der 14 natürlich auftretenden Lanthanide in geologischen Proben. Die vorgeschlagene Methode beruht auf einer Sinterung mit Natriumperoxid (Na_2O_2) nach Zusetzung einer Thulium Spikelösung. Weiters wird die Kationenaustauschtrennung der Lanthanide von den Matrixelementen sowie die Bestimmung einzelner Seltener Erden unter Verwendung eines gekoppelten HPIC-ICP-MS behandelt.

Zur Trennung der Seltenen Erden sowie Entfernung von Matrixelementen kam das Dowex 50W-X8 Kationenaustauschharz zum Einsatz. Die Lanthanide wurden separiert, um spektrale Interferenzen der polyatomaren Ionen (speziell BaO^+) bei der ICP-MS Messung zu verhindern und die Signalunterdrückung zu minimieren. Die effizienteste Trennung konnte mit Hilfe einer sauren Elution erreicht werden, wobei die Matrixelemente durch eine Lösung aus 2 mol l^{-1} HNO_3 und einer geringen Menge Oxalsäure und die Lanthanide mit 6 mol l^{-1} HNO_3. entfernt wurden.

Weiters wurde die Trennung und quantitative Bestimmung von Seltenen Erden mittels Hochleistungsionenchromatographie (HPIC) unter Einsatz von Oxal- und Diglykolsäure als mobile Phasen, geprüft. Dabei wurde der Einfluss von unterschiedlichen Gradientenmethoden auf deren Rückhaltevermögen und der daraus schließenden Effizienz der Trennung untersucht. Dazu wurde die IonPac® CS5A (2 x 250 mm) Ionenaustauschsäule verwendet, wobei die optimale Gradientenmethode eine Trennung und Bestimmung der 14 natürlich auftretenden Seltenen Erden in weniger als 17 Minuten ermöglicht.

Die Gültigkeit der hier vorgeschlagenen Methode wurde durch zwei bekannte Referenzproben, BIR-1 and BRP-1 überprüft. Dabei konnte eine generell gute Übereinstimmung mit publizierten und zertifizierten Werten festgestellt werden.

Messungen der Proben OU-1, OPC-1, OKUM und MUH-1 zeigten zufriedenstellende Ergebnisse mit einer Standardabweichung von 0,2 bis maximal 9% nach durchgeführter Rohdatenkorrektur mittels Thulium. Die Messungen des Referenzmaterials sowie der Proben unter Verwendung der vorgeschlagenen Methode lieferten gleichmäßige normalisierte Lanthanid Kurven.

Diese Arbeit bildet die Basis für weitere Konzentrationsuntersuchungen von Lanthaniden. In Kombination mit Isotopenverdünnung Massenspektrometrie (ID-MS) kann die geringste Messabweichung aller derzeit verfügbaren analytischen Methoden erreicht werden.

Abstract

Development of an analytical method for determination of rare earth elements in rock samples by HPIC-ICP-MS

The present study describes the optimization of an analytical procedure for the determination of 14 rare earth elements (REE) in geological samples. The proposed method involves sodium peroxide (Na_2O_2) sintering of sample material after addition of a Tm spike, the cation exchange separation of the REE from matrix elements, and the determination of individual REE by means of HPIC-ICP-MS coupling system.

The Dowex 50W-X8 cation exchange resin is used for the study of the REE group separation and the elimination of matrix elements. The REE are separated from the bulk matrix in order to avoid the spectral interference from polyatomic ions (in particular BaO^+) in the determination by ICP-MS and to minimize signal suppression. The most efficient separation consisted in a nitric acid media gradient elution, where the matrix elements are removed using 2 mol l^{-1} HNO_3 containing a small amount of oxalic acid and the REE are eluted using 6 mol l^{-1} HNO_3.

Furthermore, High Performance Ion Chromatography (HPIC), using oxalic acid and diglycolic acid as mobile phase, was investigated for the separation and the quantitative determination of rare earth elements (REE). In this matter, the influence of different gradient elution on the retention and hence the separation efficiency of the individual REE was studied. The separation was carried out using an IonPac® CS5A (2 x 250 mm) analytical column. The optimum gradient elution enables the separation and determination of the 14 naturally occurring REE in less than 17 minutes.

The validity of the proposed analytical procedure is assessed by analysis of two well characterized Reference Materials, BIR-1 and BRP-1. REE concentration data obtained for these reference materials are generally in good agreement with published and certified values.

Satisfactory results were obtained in the analysis of samples (OU-1, OPC-1, OKUM and MUH-1), including materials with low REE abundances. Relative standard deviation (RSD) ranging from 0,2 to less than 9% were obtained after raw data correction using Tm. Smooth REE normalized pattern were obtained for all the reference materials and samples analyzed by the proposed analytical procedure.

This work is the basis for further REE concentration studies. In combination with isotope dilution mass spectrometry (ID-MS), the lowest measurement uncertainties of all currently available analytical procedures can be achieved.

Resumen

Desarrollo de un método analítico para la determinación de tierras raras en muestras geológicas mediante HPIC-ICP-MS

El presente trabajo describe la optimización de un método analítico para la determinación de tierras raras (lantano, La, a lutecio, Lu) en muestras geológicas. El método desarrollado abarca desde disolución de la muestra mediante sinterizado con peróxido de sodio (Na_2O_2) previa adición de una solución estándar de tulio (Tm), hasta la determinación de los analítos utilizando un sistema de Cromatografía Líquida de Intercambio Iónico (HPIC) acoplado a un detector ICP-MS.

La solución de la muestra se sometió a un proceso de intercambio catiónico con el fin de eliminar la matriz y reducir las interferencias causadas por iones poliatómicos (en especial BaO^+) antes de la determinación mediante HPIC-ICP-MS. La resina Dowex 50W-X8 fue utilizada como fase estacionaria en esta separación cromatográfica. Una óptima separación de las tierras raras respecto a los elementos de matriz fue obtenida utilizando una elución en gradiente de ácido nítrico. Así, los elementos de matriz fueron eluídos con una solución de 2 mol l^{-1} HNO_3 que contenía cierta cantidad de ácido oxálico, y las tierras raras con una solución de 6 mol l^{-1} HNO_3.

La separación entre elementos de La a Lu se llevó a cabo mediante HPIC. Para esto se optimizó la separación cromatográfica que utiliza la columna de intercambio iónico IonPac® CS5A (2 x 250 mm) como fase estacionaria y una mezcla de ácido oxálico y ácido diglicólico como fase móvil. El gradiente de elución óptimo encontrado permite la separación y determinación de los14 elementos de tierras raras en menos de 17 minutos.

La validación del método analítico desarrollado se llevó a cabo a través de la determinación de la concentración de tierras raras en dos materiales de referencia, BIR-1 y BRP-1. Los valores obtenidos en las mediciones realizadas coinciden en gran magnitud con los valores publicados y certificados de estos dos materiales.

Adicionalmente se analizaron cuatro muestras geológicas (OU-1, OPC-1, OKUM y MUH-1). Los valores de desviación estándar relativa en las mediciones variaron entre 0,2 y 9%, luego de la corrección respecto a la concentración de Tm en la muestra. Las curvas normalizadas de tierras raras trazadas con las concentraciones halladas mostraron en todos los casos un patrón regular.

El procedimiento analítico propuesto representa la base de futuros estudios en combinación con la metodología de dilución isotópica (ID-MS). Entre todos los procedimientos analíticos actualmente disponibles para la determinación de tierras raras, ID-MS representa aquella con la menor incertidumbre en los resultados.

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1 Introduction

1.1 Problem Identification

The rare earth elements (REE) play an important role in various fields. They have been widely used in geochemistry, since the knowledge of their distribution in rocks and minerals is essential for the characterization of many geological processes [1]. Moreover, the determination of REE contents in food plants and products has shown great importance as they serve as tool for the identification of the geographic origin of food. [2]

However, due to their very similar chemical properties and their low concentration levels in most geological materials; the chemical analysis of the rare earth elements has been recognized as a complex analytical task. Complications arising from the preparation of representative samples, the low concentrations of these elements in most samples and the presence of various matrix elements pose crucial drawbacks in their accurate determination.

Several methods of analysis have been used for the determination of rare earth elements in geological samples. These methods include neutron activation (NAA), isotope dilution mass spectrometry (IDMS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission mass spectrometry (ICP-AES), and high performance liquid chromatography (HPLC) [3]. Each of them has advantages and disadvantages that will be discussed later in this work. In this regard, the on-line coupling of the HPLC and ICP-MS techniques poses a good option when determining individual REE. However, the chromatographic methods still confront some difficulties when achieving efficient separation of some REE [4]. Nevertheless, a number of investigations using different stationary phases, mobile phases and elution conditions have been reported; which indicates the interest in this methodology and assure future developments.

In general, the success of the applied analytical method is accompanied by appropriate chemical pretreatment and REE group separation, preconcentration or matrix simplification techniques. In that respect, several studies concerning ion exchange chromatographic methods for the determination of REE in geological materials have been reported. [5]

The present work presents the development of a method which combines the advantages of the chromatographic techniques with the good performance of an ICP-MS for the determination of individual rare earth elements in geological samples. The analytical procedure should be applicable on a routine basis and should confer additional confidence on the data. In addition, this analytical method would serve as a basis for the studies on the concentration of rare earth elements in pumpkin seed oil.

1.2 Goals and Targets

The present work aims to:

1. Develop a simple and effective procedure for selective group separation and preconcentration of the REE in geological samples by cation exchange chromatography for their subsequent analysis by ICP-MS.
2. Improve the chromatographic separation of individual REE using a sulfonated function group resin.
3. Propose the experimental design for coupling a liquid chromatography system with an inductively coupled plasma mass spectrometry (ICP-MS) detector, in order to develop an on-line method for individual determination of REE in geological samples, where a simultaneous isotope dilution step could be added for their accurate quantification.
4. Assess the validation of the proposed procedure by analysis of certified and well characterized reference materials.

2 General Information on Rare Earth Elements

2.1 Occurrence and Abundance

The group of rare earth elements (REE) comprises 15 elements, lanthanum to lutetium (atomic numbers 57-71), which have similar physical and chemical properties. These elements are also known in geochemistry as lanthanides and they are found in any natural occurrence (minerals and rocks) as associated groups rather than individually or as a combination of a few of them.

Despite their name, the REE are relatively abundant in the Earth's crust, especially when compared to more familiar elements such as Pb, Au and Ag. Discovered minable concentrations are, however, less common than for most other ores. In most minerals, they are dispersed as minor or trace constituents. Major and usually essential contents occur in over 70 minerals, whereas the most economically important are bastnäsite ($REE(CO_3)F$), monazite ($REE,Th(PO_4)$) and loparite ($(REE,Na,Ca)(Ti,Nb)O_3$). [6]

Bastnäsite deposits in China and the United States represent the largest percentage of the world's rare earth economic resources (see Figure 1). The second largest segment comprises monazite deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand, and the United States. [7]

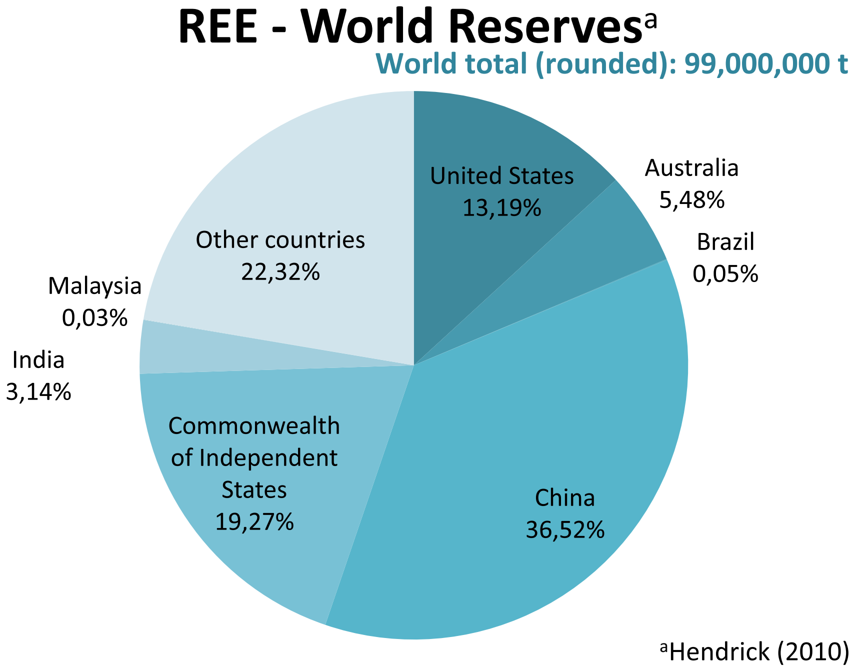


Figure 1. World's rare earth elements reserves

2.2 General Chemical and Geochemical Properties of the REE

The rare earth elements occupy a single position (of lanthanum, La) in the basic part of the Periodic Table; the other fourteen are shown separately as a group. They are frequently divided into two sub-groups: those with lower atomic numbers and masses, La to Eu, being referred to as the light rare earth elements (LREE); and those from Gd to Lu (higher atomic numbers and masses), known as the heavy rare earth elements (HREE). However, they are occasionally divided into three groups, e.g. LREE (La-Sm), middle rare earth elements or MREE (Eu-Dy), and HREE (Ho-Lu).

2.2.1 Oxidation states and ionic radius

The REE are members of Group IIIA in the periodic table and have very similar chemical and physical properties, as they all form stable 3+ ions of similar size. As shown in Figure 2, one significant feature of these elements is that, their trivalent ions exhibit a gradual decrease in ionic radius with increasing atomic number, from 1,14 Å for La^{+3} to 0,85 Å for $Lu^{+3.}$, as a result of their electronic configurations (see Table 1). This feature is known as the lanthanide contraction and occurs due to the imperfect shielding of one electron by another in the same 4*f* inner sub-shell, so that the effective nuclear charge acting on each 4*f* electron increases with increasing atomic number, causing thereby a reduction in the size of the 4*f* sub-shell. [8]

Yttrium (Y, atomic number 39), also a member of Group IIIA, shows comparable chemical properties as result of the size of its ionic radius and its electronic configuration, which links it with the heavier REE with which it is invariably associated in minerals and rocks. In many geochemical processes Y behaves similarly to Ho because of their trivalent oxidation states have nearly identical ionic radius.

The REE are strongly electropositive and so most of their chemistry is characteristic of ionic bonding, with a neglected covalent contribution. As mentioned above, all the REE show a constant valency of three in their chemistry and geochemistry. However, Ce can occur tetravalent under oxidizing conditions and valency of +2 may be shown by Eu in natural systems. The existence of these states can be explained partly on the basis of the enhanced stability of their electronic configurations. [6]

Despite their similarities in their chemistry and geochemistry, the steady decrease in ionic radius and the occurrence of oxidations states different to +3, for Eu and Ce, can cause the lanthanides to be fractionated relative to one another by a variety of petrological and mineralogical processes. The wide variety of types and sizes of the cation coordination polyhedral in minerals provides the means for this chemical fractionation, which has important consequences in geochemistry. [1]

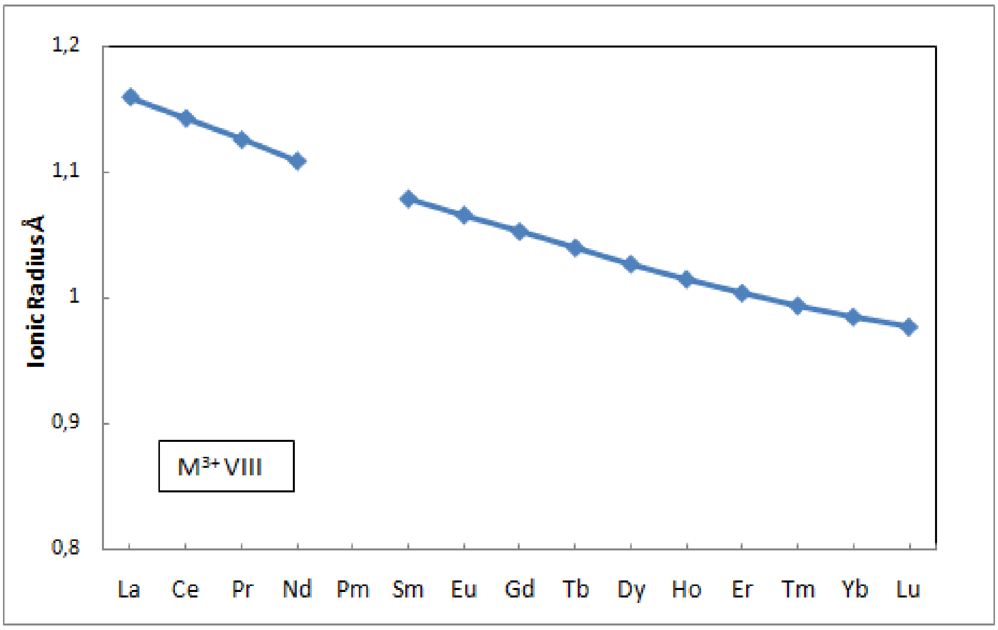


Figure 2. Ionic radius vs. atomic number, for trivalent REE in eight-fold coordination (Henderson, 1984)

Table 1. The rare earth elements and their electronic configurations

Atomic Number	**Symbol**	**Element**	**Atomic mass**[a]	**Electronic Configuration**
57	La	Lanthanum	138,91	$[Xe]5d^1 6s^2$
58	Ce	Cerium	140,12	$[Xe]4f^1 5d^1 6s^2$
59	Pr	Praseodymium	140,91	$[Xe]4f^3 6s^2$
60	Nd	Neodymium	144,24	$[Xe]4f^4 6s^2$
61	Pm	Promethium	(145)	$[Xe]4f^5 6s^2$
62	Sm	Samarium	150,4	$[Xe]4f^6 6s^2$
63	Eu	Europium	151,96	$[Xe]4f^7 6s^2$
64	Gd	Gadolinium	157,25	$[Xe]4f^7 5d^1 6s^2$
65	Tb	Terbium	158,93	$[Xe]4f^9 6s^2$
66	Dy	Dysprosium	162,50	$[Xe]4f^{10} 6s^2$
67	Ho	Holmium	164,93	$[Xe]4f^{11} 6s^2$
68	Er	Erbium	167,26	$[Xe]4f^{12} 6s^2$
69	Tm	Thulium	168,93	$[Xe]4f^{13} 6s^2$
70	Yb	Ytterbium	173,04	$[Xe]4f^{14} 6s^2$
71	Lu	Lutetium	174,97	$[Xe]4f^{14} 5d^1 6s^2$

[Xe]: configuration of xenon: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$

[a] Based on data in Henderson (1984).

Note that Promethium, best known as an artificial element, is practically absent in natural materials because it has no stable or long-lived isotope.

2.3 Data Presentation

2.3.1 Chondrite normalized diagrams

The rare earth elements are subject to the so called Oddo Harkins “even-odd” effect, in which the cosmic and terrestrial abundances of even atomic-numbered elements are greater than those of adjacent odd atomic-numbered elements.

Thus, if absolute abundances of REE in natural materials are plotted versus atomic number, this effect leads to a saw-tooth pattern that can make it difficult to distinguish the effects of chemical and physical fractionation processes (see Figure 3a). This alternation pattern arises from variations in the stability of a nucleus being dependent on whether the neutron number (N) and the proton number (Z) are odd or even. Those nuclei with both N and Z even exhibit an enhanced stability while those with both N and Z odd are the least stable. [6]

In order to remove the rhythmic alternation, the data are usually normalized by dividing absolute REE concentrations in natural samples by those in a chosen natural reference material and it is presented graphical as shown in Figure 3b. The plot is usually given as the logarithm of the normalized concentrations versus atomic number.

A variety of normalizing values for the REE can be found in the literature, but concentrations of these elements in chondritic meteorites are the most commonly used, as they are thought to represent relatively unfractionated samples of solar system material. Other frequently employed reference materials include sedimentary “average rocks” (e.g. North American Shale Composite or NASC and Post Archean Average Australian Shale or PAAS) or those abundances estimated for the Earth’s crust. Furthermore, in order to evaluate fractionation processes in a natural system, it is also common to normalize REE abundances of a system, relative to the REE concentrations of a reference material which is part of the system under investigation. For example, it may be appropriate to normalize the REE contents of natural waters to those of their parent sediments.

Normalized values for individual REE are denoted REE_N (e.g. La_N or Ce_N), as well as REE_{CN}, for those chondrite normalized (e.g. Eu_{CN}).

As it can be seen in Figure 3b, the LREE, relative to chondrites, are more abundant than are the HREE for this sample. In general, relative abundance values of the REE follow the general trend of decreasing abundance with increasing atomic number. In many cases, the position for any REE is placed away from the smooth trend defined by the others on a chondrite-normalized plot. This anomaly may appear as positive if the concentration of this REE_{CN} is greater than the chondrite-normalized abundances of its immediate neighbors, or negative if lower (as seen for Eu in Figure 3b). These anomalies are frequently reported for Eu and Ce as a result of the existence of divalent and tetravalent ions, respectively, in natural systems.

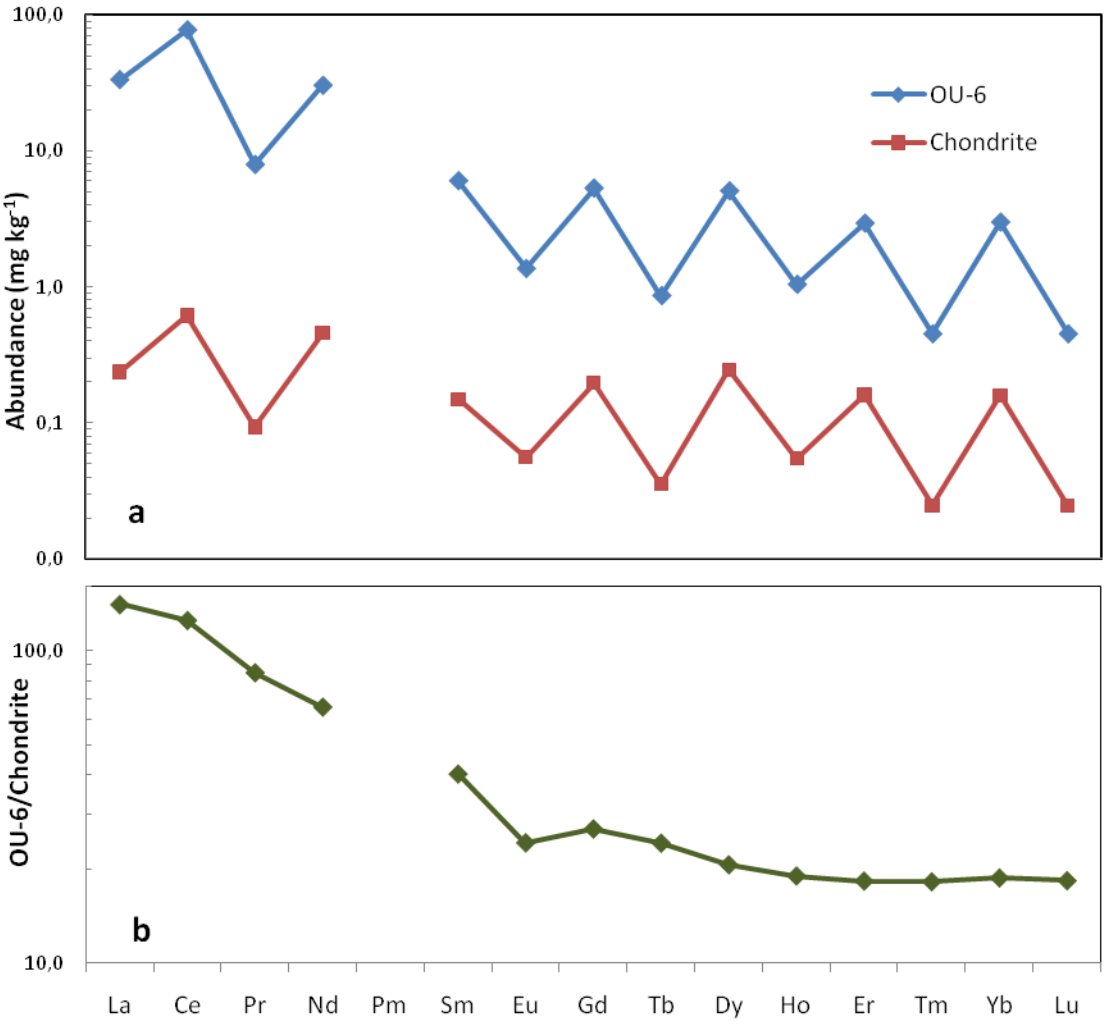


Figure 3. Graphical representation of the rare earth elements in natural samples.

(a) Actual abundances of the REE in a Certified Reference Material, OU-1 (Penrhyn Slate) [9], and in ordinary chondrites by Wasson and Kallemeyn (1988). (b) Chondrite-normalized abundances of the REE in NASC. The values plotted in (a) were used to construct this graphic.

Unfortunately, there is a considerable variation in the reported REE concentrations of chondritic meteorites, which has lead to a wide variety of normalizing values in the literature [10]. Thus far, the adoption of only one agreed set of chondrite-normalizing concentrations has not occurred. Table 2 shows some commonly used REE concentration values for preparing chondrite-normalized plots.

Table 2. The REE composition of commonly used chondritic meteorites.

	Chondrites						
	Wakita et al. (1971)[a]	Masuda et al. (1973)[a]	Nakamura (1974)[a]	Evensen et al. (1978)[a]	Boynton (1984)[a]	Wasson & Kallemeyn (1988)[b]	McDonough & Sun (1995)[a]
REE	Concentration values in µg/g (ppm)						
La	0.34	0.378	0.329	0.2446	0.310	0.236	0.237
Ce	0.91	0.976	0.865	0.6379	0.808	0.616	0.613
Pr	0.121	-	-	0.09637	0.122	0.0929	0.0928
Nd	0.64	0.716	0.630	0.4738	0.600	0.457	0.457
Sm	0.195	0.230	0.203	0.1540	0.195	0.149	0.148
Eu	0.073	0.0866	0.0770	0.05802	0.0735	0.056	0.0563
Gd	0.26	0.311	0.276	0.2043	0.259	0.197	0.199
Tb	0.047	-	-	0.03745	0.0474	0.0355	0.0361
Dy	0.30	0.390	0.343	0.2541	0.322	0.245	0.246
Ho	0.078	-	-	0.05670	0.0718	0.0547	0.0546
Er	0.20	0.255	0.225	0.1660	0.210	0.160	0.160
Tm	0.032	-	-	0.02561	0.0324	0.0247	0.0247
Yb	0.22	0.249	0.220	0.1651	0.209	0.159	0.161
Lu	0.034	0.0387	0.0339	0.02539	0.0322	0.0245	0.0246

[a] Data from Korotev (2009) [10]

[b] Wasson and Kallemeyn (1988) [11]

2.4 Importance of the Rare Earth Elements

The rare earth elements have become important from both scientific and technological points of view.

The scientific significance of the REE relies on the realization that their behavior and observed degree of fractionation in a rock or mineral can be essential for understanding geochemical and petrogenetic processes.

The application of REE abundances to petrogenetic problems has centered on the study of their distribution patterns and the radioactive decay scheme of some of their isotopes. The first helps to evaluate the nature and source of rocks and minerals; since the REE mobilization during processes of magma and rock formation can be predicted regarding their geochemical properties (ionic radius, ionic charge and nature of bonding in geologic systems) [6]. The second provides a tool to determine the ages of rocks and minerals. Components of this approach are the decays of ^{138}La to ^{138}Ce, ^{147}Sm to ^{143}Nd, and ^{176}Lu to ^{176}Hf (atomic number 72) [1].

Their importance have additionally grown due to the current use of analytical methods which are capable to generate wide data sets on several trace elements at a short time, and hence allow geochemist to consider the REE abundances when performing petrogenetic studies, even when the elements occur at very low concentrations.

Furthermore, the REE are of economic interest because the REE have many important conventional and high-technology applications. Mixtures of the REE have traditionally been used in catalysis (petroleum cracking, catalytic converters), ceramics, alloys, glass polishing and coloring compounds. However, individual REE are increasingly being used in high-technology applications such as high-strength permanent magnets (used in automobiles, computers, etc.), cathode-ray tubes, fiber-optic cables, refrigeration and rechargeable batteries. [12]

3 Analytical Procedure

Developments in analytical chemistry have facilitated the routine determination of individual REE in several geological materials, even when these are present at very low concentrations and despite the fact that they have very similar chemical properties.

The most important analytical methods applied so far include: neuron activation analysis (NAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), isotope dilution mass spectrometry (IDMS) high performance liquid chromatography (HPLC) and ion chromatography (HPIC), and to a minor extent X-ray fluorescence spectrometry (XRF). Each of them has its advantages, disadvantages and limitations, with regard to its ability to determine the individual REE effectively, instrumental detection limits and the difficulties of operation and sample preparation.

Both variants of NAA: instrumental activation analysis, INAA, as well as radiochemical activation analysis, RNAA, offer high sensitivity and are capable of the simultaneous determination of many trace elements even at part per billion (ppb) levels. NAA has the advantage of being a non destructive technique. The fact that the sample does not have to be put into solution provides relative freedom from analytical blanks. However, difficulties may be encountered in the determination of Pr, Er, Dy, Gd and Ho, due to the weak emission of gamma rays or the unsuitable half-life of their isotopes. Main drawbacks of NAA are the high cost (requires access to a nuclear reactor and long cooling times prior to the determination) and safety requirements to handle radioactive materials. [6] [13] [14]

The ICP-AES and ICP-MS techniques have shown significant contribution in the determination of REE in geological materials with very good specificity, precision and accuracy, high sensitivity and wide dynamic range. On the other hand, spectrometric determinations of REE in geological matrices are characterized by several limitations such as high instrumental detection limits relative to the low REE concentration in most samples; and high levels of chemical or spectral interferences, as a result of high concentrations of matrix elements (e.g. Al, Ba, Ca Fe, Mg, Mn, Na, etc.) and other minor trace elements. Consequently, the determination of REE by ICP-AES requires prior separation of these elements from the matrix and their preconcentration for accurate results. ICP-MS has lower detection limits and the spectra obtained are fairly simple, with far less spectral interference than those in ICP-AES. For that reason, most of the REE can be directly determined in a wide range of rocks types. However, significant isobaric, background and matrix induced interferences do arise and must be taken into account. [15]

Isotope dilution mass spectrometry is a method of proven high accuracy, for which the sources of systematic error are normally understood and controlled. For this reason, IDMS is internationally accepted as a definitive method [16]. Nevertheless, there is also a small possibility for analysis of REE without previous separation and concentration by this technique, due to the detectability of the analytes and unwanted matrix effects.

The separation of individual members of the REE group employing both, HPLC and HPIC, techniques have proved to be satisfactory, and have also been applied for their quantification using online detection systems (i.e. UV–Vis, ICP-AES and ICP-MS). The selectivity, low amount of sample needed and simultaneous analysis of several elements in a relative short time are some advantages of these techniques. However, chemical dissolution of the sample is required, as well as the previous separation of REE from most of the major rock components to prevent overloading and precipitation of interfering elements in the column [4] [17].

The present work is based on the application of an on-line HPIC/ICP-MS coupling system as suitable method for the determination of REE in geological samples. In order to provide a better understanding of this approach, the following sections present the necessary steps prior separation and quantification by HPIC/ICP-MS (i.e. decomposition and preconcentration of samples); as well as the important features of both, HPIC and ICP-MS, techniques concerning their use on the determination of REE.

3.1 Sample Preparation

The rock or mineral must be placed in solution prior to analysis by HPIC and ICP-MS. This pre-treatment should be followed by a REE group separation or matrix simplification technique to remove matrix elements that coelute with the REE during chromatographic separation and cause interferences in the REE determination.

3.1.1 Sample Decomposition Procedures

The complete dissolution of geological samples has proven to be difficult due to the presence of resistant accessory minerals (e.g. garnet and zircon). The choice of the decomposition method mainly depends upon the mineralogical characteristics of the rock sample, the nature of the elements to be determined, precision and accuracy requirements, technical capability of personnel, time constraints, and the instrument used for estimation. [18]

Balaram et al. (1995) compare three different decomposition methods (i.e. open acid digestion, closed vessel digestion and fusion dissolution method) for the determination of REE in anorthosites and other rock samples by ICP-MS. These three methods showed comparable accuracies. Additionally, precisions better than 6%RSD were obtained for most elements measured [18] . The procedures description and observations are summarized below.

The open acid digestion, was performed mixing the sample with a mixture of HF, HNO_3 and $HClO_4$ in an open system (i.e. PTFE beakers), and kept overnight for digestion, followed by evaporation of the mixture to almost dryness at the next day. The constant addition of acid mixture during the evaporation step at 200 °C was necessary to achieve a satisfactory recovery of elements such a Cr, Ni, Zr, Ta, and Nd. It was reported, that sometimes elements such as Fe, Pb, etc. were picked up from the environment during sample preparation, and hence high procedure blank values were obtained by this method.

In the closed vessel digestion, the sample was mixed with an acid mixture containing HNO_3, HF and HCl (3:6:1) in a PTFE pressure decomposition vessel. After sealing the vessel, this was placed in an electric oven at 110°C for 12 h. This procedure yielded very low blank values and was found very effective for samples having high chromium content.

For fusion dissolution, the sample was mixed with lithium metaborate in a graphite crucible and fused at 1000 °C for 5 min. After cooling, the melt was completely dissolved with an HNO_3 acid solution. The fusion results were very good for elements such as Cr, Zr, Hf and showed a very good agreement with the certified values. This procedure showed high blank values, and it was observed the loss of some volatile elements (e.g. Zn, Cs) due to the high fusion temperature. Furthermore, the associated increase in the total dissolved solids caused a reduction of the signal when measuring by ICP-MS.

As mentioned above, the results obtained by the three procedures were in agreement with certified values. The methods based on fusion or sintering pose a good option when choosing an adequate decomposition procedure, due to the fact that the REE are often associated with high chemical resistant minerals, such as garnet and zircon. The complete decomposition of these two minerals is necessary, because they strongly fractionate Sm from Nd, and Lu from Hf [19]. In that matter, the use of Na_2O_2 or Na_2CO_3sintering has been found to be one of the best ways of achieving complete dissolution in the determination of REE by ICP-MS [15] [18] [20]. However, these techniques add high amount of salt to the sample solution, which lowers the sensitivity of analytical techniques (i.e. ICP-MS), due to the salt deposition on the cones and their subsequent clogging.

Microwave digestion has been also employed in the acid dissolution of geological samples and it poses an option for sample preparation. [21] [22] [23]

3.2 Pre-concentration and Group Separation of Rare Earth Elements

The concentration of the REE in geological samples is typically low in comparison with the high abundance of other elements present in the matrix solution. For these reasons, matrix separation procedures and pre-concentration techniques including coprecipitation [24], solvent extraction [25] and ion exchange using cation [26] and anion [27] exchange resins have been used prior to analysis of sample solutions.

Among all the available techniques, ion exchange chromatography affords a simple separation method if determinations are to be made by ICP-AES, ICP-MS, mass spectrometry by isotope dilution, or neutron activation using a radiochemical separation. [5]. The principles and practical application of this technique to the separation of REE are highlighted in the following section.

3.2.1 Ion exchange chromatography

Exchange chromatography refers to the reversible exchange of species between a solid phase and a mobile phase. In the individual case of ion exchange, the species to be exchanged are ions. The resin that serves as solid or “stationary” phase is normally packed into a suitable glass tube, the “column”, and the sample solution poured onto the top of this column. The sample is then “eluted” by washing its components through the column using a suitable solvent. The species are separated one from another due to differences in their affinity towards the resin. The higher the affinity, the larger the volume of eluent required to wash it out of the exchange column [5]. Figure 4 illustrates the idealized exchange procedure when separating two different analytes.

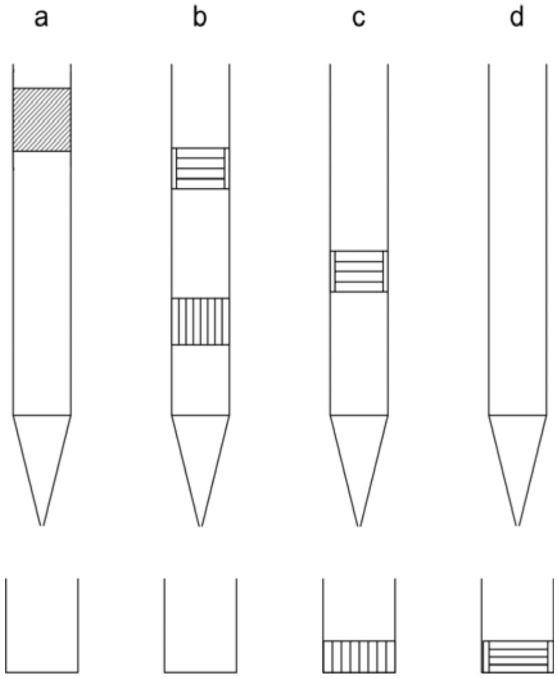


Figure 4. Ion exchange separation technique. (a) A solution containing two different species is loaded onto the column. (b) The sample is eluted with the first aliquot of eluent and separated in two fractions. (c) After the first analyte has been completely eluted, the second analyte is desorbed from the resin with the second aliquot of solvent until complete elution is achieved (d)

Ion exchange separation procedures, cation as well as anion exchange, have been used in the determination of rare earth elements for the following reasons:

i) To concentrate the rare earth elements from a large to a small sample volume to allow a concentration level above the determination limit of the analytical technique used for their quantification.

ii) To remove matrix elements which cause interferences in the determination and preclude a reliable analysis.

iii) To reduce the total dissolved solid content in solutions prepared by fusion or sintering techniques.

3.2.1.1 Separation of REE by cation exchange

Cation exchange has been widely used for the group separation of REE. Commonly used strong cation exchange resins include Dowex AG 50W-X8 (200-400 mesh) [28], Dowex AG 50W-X12 [29], Bio Rad AG 50-X8 (100-200 mesh) [5], Ostion LGKS 0800, sulfonated polystyrene and bonded-phase silica. [17]

This separation technique makes use of three factors in achieving selectivity: the differences in oxidation state; the radius of the trivalent REE ions; and the formation constants for complexes formed between REE ions and additives in the mobile or stationary phase.

The technique involves the separation of the rare earth elements as a group. The strong affinity of the free hydrated REE ions allows them to remain strongly bound to the resin while other species (including transition metals, and alkali and alkaline earth elements) are washed through the column and separated. The hydronium ion (H_3O^+) competes strongly for the chelating sites on the resin and hence mineral acids are effective eluents.

The cation exchange separation of REE has been carried out in glass columns containing varied amounts of resin slurry and using mostly hydrochloric acid and/or nitric acid solutions as eluents. In general, the separation procedure follows the scheme described below:

i) The resin is preconditioned by passing certain amount of HCl or HNO_3 acid solution,
ii) The sample solution is loaded onto the column.
iii) The sample is eluted using gradient elution technique.
iv) The column is washed for re-use by eluting HCl or HNO_3 solutions.

A gradient elution technique refers to the use of successive aliquots of eluents. Typically the concentration or acid strength (for acids) of the eluent is increased with every aliquot, in order to decrease the affinity of the analytes for the resin and promote their desorption. In this regard, the trivalent REE ions show high affinity for cation exchangers and cannot be eluted from the stationary phase in the absence of relative high concentrated acid solutions (e.g. 3-6 mol l^{-1} HCl and 2-8 mol l^{-1} HNO_3) or adequate complexing agents. [17]

A comparison study of the separation of REE using nitric and hydrochloric acid as eluents is presented in Potts (1992). The same cation exchange resin, Bio Rad AG 50-X8 100-200 mesh, is used in both separation tests. Here it is found that the elution using nitric acid eliminates effectively Al, Ba, Be, Ca, K, Mg, Mn, Na, Sr, Ti, U, V; but, a large quantity of Fe and some Zr remain in the REE fraction. On the other hand, by using the hydrochloric acid elution, the complete elution of Al, Be, Fe, K, Mg, Mn, Na, Ti, U, V is achieved; however, significant concentrations of Ca, Sr, Zr, and all Ba are carried over in the REE fraction. Such observations should be taken into account when choosing an adequate separation procedure.

The main drawbacks concerning the separation of rare earth elements by cation exchange are the long time required for the percolation of the gravity-operated columns and the large volume required to elute all the analytes of concern. Most chromatographic columns are 10-20 cm length and 1-2 cm i.d., filled with ~20 g cationic resin (100-200 or 200-400 mesh). Here the eluents flow at approximately 1 ml min^{-1}, and complete separation is only achieved after several hours of work. In addition, the use of such large volume of eluents may cause a contamination blank, which impedes the accurate determination of the rare earth elements. This has led to the development of ion exchange micro-columns and complex chromatographic systems. [30] [31]

3.2.1.2 Separation of REE by anion exchange

Separation of rare earth elements by anion exchange chromatography have been mostly performed using commercially available strong anion exchange resins, such a Dowex 1-X8 [32], Dowex 2-X8 (200-400 mesh) [33], Dowex 1-X4 [34], MCI GEL CA (08S, 08B, 06Y) and Amberlite CG 400 (200-400 mesh) [17]; and mixed solvent elution (e.g. nitric acid-glacial acetic acid, nitric acid-methanol) [17].

The separation is accomplished because negatively charged REE ions are formed when dissolved in nitric acid mixtures containing excess methanol or glaciar acetic acid (presumably REE-methoxy, $REE(OCH_3)_x^{(x-3)}$; and REE-acetate, $REE(OOCCH_3)_x^{(x-3)}$, respectively). This technique has been used not only with the aim to remove matrix elements which seem to show no anion exchange (i.e. Al, Fe, K, Mg, Mn, Na and Sc), but also to split the rare earth elements into fractions. [5] [17]

Anion exchange has not been as popular as cation exchange for REE separation due to the poor column performance and low REE recoveries. It has been mostly applied in the determination of rare earth elements by isotope dilution.

3.3 High Performance Liquid and Ion Chromatography

Of all the separation techniques such as chromatography, coprecipitation and liquid-liquid extraction, only high performance liquid chromatography (HPLC) and ion chromatography (HPIC) are capable of separating individual rare earths elements.

The separation of different species by HPLC and HPIC is based on the same chromatographic principles explained in the previous section, with the difference that here the analytes interact between a stationary and mobile phases in a high-pressure system. This allows shorter time of analysis, the use of packing material with smaller particle size and the consequent high degree of resolution.

Both HPLC and HPIC techniques have been also applied for the quantification of REE using online detector systems.

3.3.1 Instrumentation

The HPLC or HPIC system basically consists of five main parts:

i) a mobile-phase supply system,
ii) a sample injection system,
iii) a separation system,
iv) a detection system, and
v) an interface and data processing system.

The basic set-up of a HPLC or HPIC contains a simple isocratic mobile-phase system (i.e. only one eluent is introduced to the system). The use of two or more eluents is possible when two or more pumps are involved in the mobile-phase supply system for mixing the eluents (see Figure 5). In this case, the delivery system can be operated in a gradient elution mode (i.e. the composition of the mobile phase could vary continuously).

The sample is injected into the analytical column either manually, using a syringe, or automatically, using an electro-pneumatic valve with a sample loop or an autosampler.

The separation process takes place on the chromatographic column according to the HPLC or HPIC mechanism. In both cases, the mobile phase (degasified eluent) flows through the analytical column which acts as a carrier for the sample solution. High performance ion chromatography is a form of liquid chromatography. The difference between HPLC and HPIC is the packing material of the column. In contrast to HPLC, where a hydrophobic ion present in the eluent (known as column modifier) is adsorbed onto the surface of a hydrophobic resin to provide a charged surface for the ion exchange separation, high performance ion chromatography uses conventional ion exchange columns whereby functional groups on the resin exchange with the ions of interest. [35]

The detection system could contain one or more on-line detectors. The detector should be able to monitor column effluents and provide a stable base line, low noise-level, high sensitivity, high reproducibility and response to all analytes of interest. Commonly used on-line detectors for REE determination include UV-Vis spectrometers, ICP-AES and ICP-MS. [4]

For the UV-Vis detection method, the mobile phase and the REE are introduced into a post-column reaction module after leaving the analytical column. There they are mixed with an appropriately post-column reagent and the rare earth elements are then detected by measuring the absorbance of the complex formed with the post-column reagent [36]. Arsenaso III and 4-(2-pyridylazo)-resorcinol monosodium salt (PAR) have been the most widely used post-column reagents. In both cases, the REE are detected photometrically as color complexes, at a wavelength of 650 nm and 520 nm respectively.

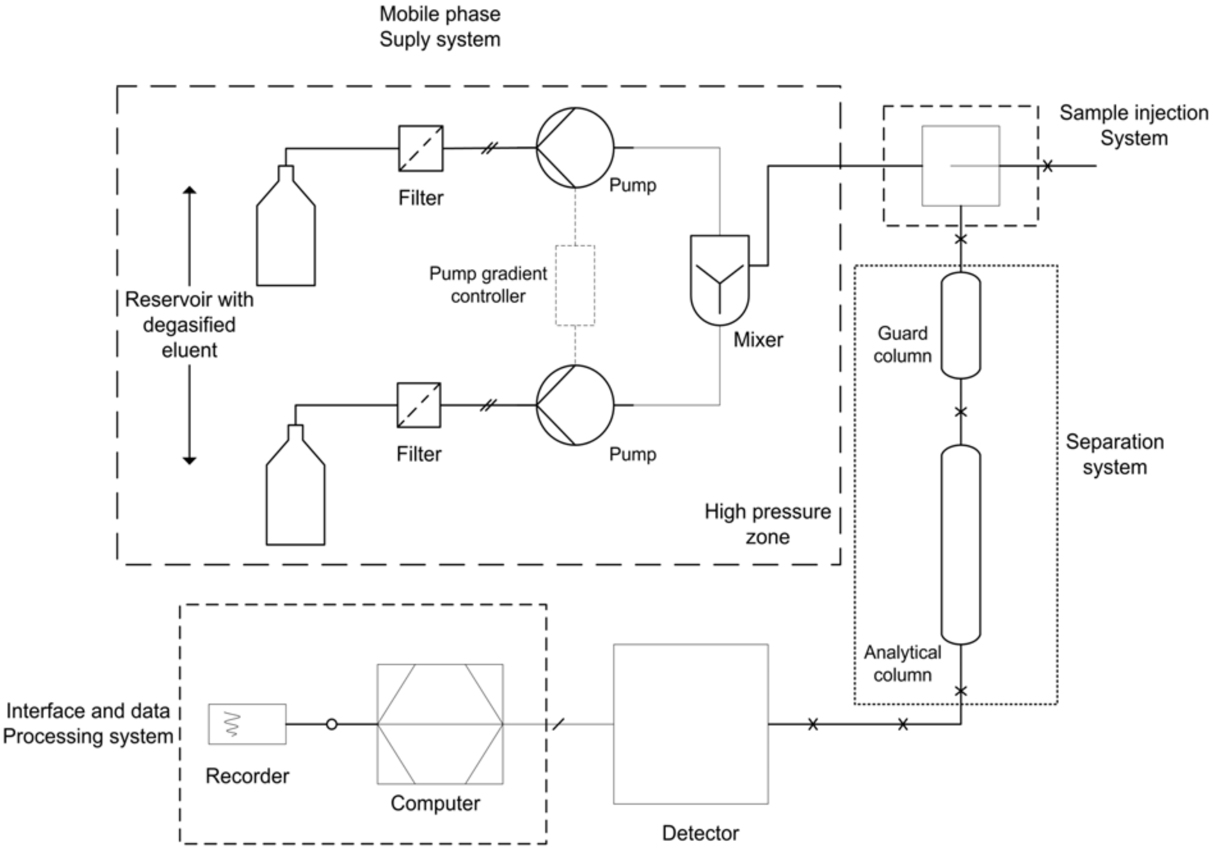


Figure 5. Schematic diagram of a typical HPLC or HPIC set-up with two eluents.

By detection chromatographic peaks with ICP-MS, it is possible to determine much lower concentrations than with photometric detection. ICP-MS currently represents the most sensitive detector and it is especially suited for on-line coupling of liquid chromatographic methods, since the liquid that elutes from the HPLC or HPIC system can be directly introduced into the torch of the ICP-MS.

The detector system is connected to a personal computer equipped with specialized chromatographic software. The software provides chromatographic information such as retention times, and peak height or peak areas.

3.3.2 Stationary and Mobile Phases

The aim of the chromatographic technique is to achieve the best possible separation, for which all the single chromatographic conditions should be optimized.

The rare earth elements cannot be separated easily from each other as trivalent cations by conventional cation exchange because their ionic properties are too similar. However, it has been shown that certain organic chelating agents, contained in the mobile phase, can replace part of the REE water hydration, forming complexes that enable ready separation of the individual REE by conventional cation or anion exchange processes.

Verma et al. (2007) have published a complete review covering important developments on HPLC and HPIC techniques for the determination of REE. The two LC methodologies mostly used for REE determination are:

i) reversed-phase high performance liquid chromatography (RP-HPLC) using a C-18 column type and hydroxyisobutyric acid (HIBA) as mobile phase [37] [38] [39]. Rare earth elements form singly positive charged complexes with HIBA that lower the affinity of the lanthanide for the resin. The degree of complexation increases with increasing atomic number, thus the REE which form the most stable complexes with HIBA, such Lu, will elute first. Lanthanides such as La, which forms a weaker complex with HIBA, elute later.

   The complete separation of the 14 REE in synthetic standards using this separation methodology has been reported. The separation was achieved in less than 15 min using a gradient elution of HIBA. [40]

ii) HPIC using a IonPac CS5 column and a complex mixture of pyridine-2,6-dicarboxilic acid (PDCA), oxalic acid and diglycolic acid as mobile phase. The use of stronger complexing agents, such as oxalic acid, results in the formation of anionic REE-complexes. Under these conditions, the REE can be separated by anion exchange. PDCA is used as eluent chelator when transition metals (e.g. Fe) are present. The transition metals form stable monovalent or divalent anionic complexes with PDCA, while the rare earth elements form stable trivalent anionic complexes with it. The resulting ionic charge differences permit the separation of REE from transition metals prior separation of individual rare earth elements.

   By using this scheme, the separation of 12 REE in a wide variety of rock types has been reported. Here, the separation was achieved in less than 20 min. [35].

The two mentioned separation methodologies are by no means the only available separation techniques for the determination of rare earth elements. They are however, the most widely study and represent the currently the most efficient separation schemes.

3.4 Inductively Coupled Plasma Mass Spectrometry

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is an analytical technique for the determination of trace, minor and major elements. This technique allows the measurement of a wide range of elements in a single multi-element acquisition; it accepts almost any sample type and also provides isotopic information. Due to these reasons, it has been widely accepted as a useful tool by researchers, including those involved in geological matters. [15]

A commercial ICP-MS instrument consists of the following main components:

i) a sample introduction system,

ii) a plasma torch,

iii) an interface/vacuum system, and

iv) a mass analyzer and detector

In the typical configuration, ICP-MS implies the combination of an argon plasma source with a quadrupole mass analyzer. Figure 6 illustrates the distinct parts of a typical ICP-MS. The mode of operation and function of each part are outlined in the following section.

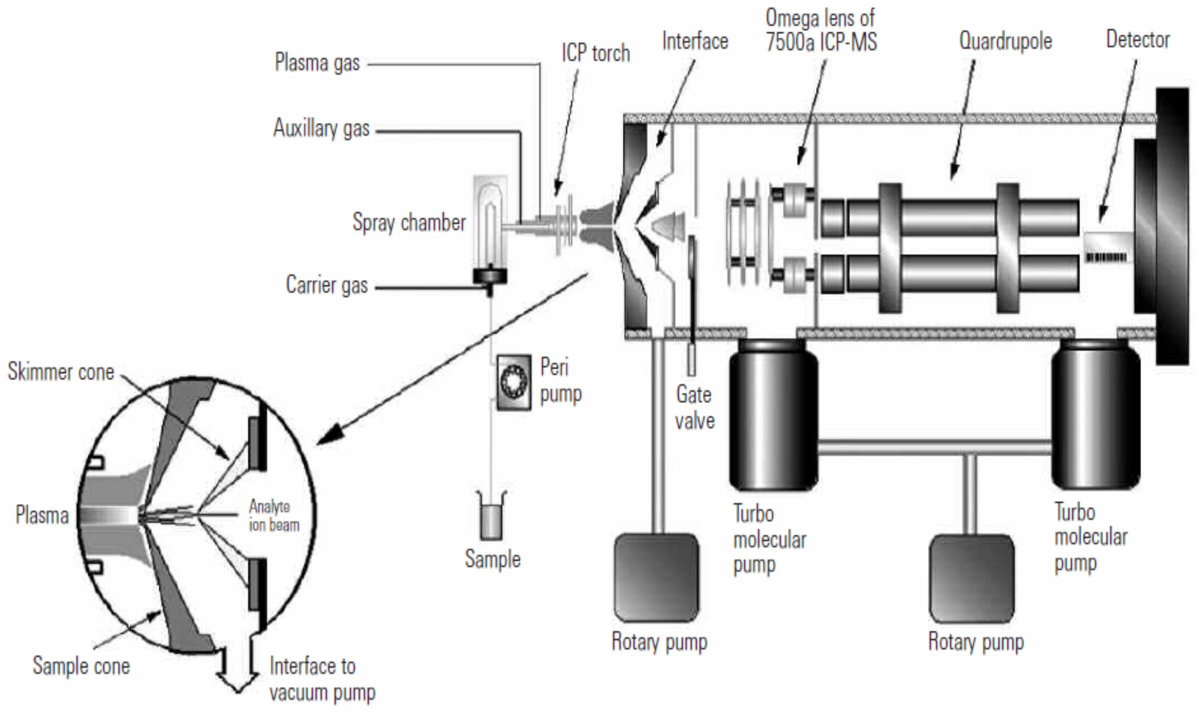


Figure 6. Schematic diagram of an Agilent 7500 Series ICP-MS instrument. Agilent Technologies (2005).

3.4.1 Fundamentals of ICP-MS

The sample is typically introduced into the ICP-MS in liquid form by pumping it into the sample introduction system, which consist of a nebulizer and spray chamber. It emerges as a fine aerosol (with particles less than 10 µm diameter), which is eventually swept into the central channel of the argon plasma.

The plasma source operates at very high temperature. It is generated in a stream of argon contained in a quartz tube or “torch”. The torch is located in the center of a cooled copper coil and operates at atmospheric pressure.

As the aerosol droplets travel through the different heating zones of the plasma torch, they are dried, vaporized, atomized, and ionized. During this time, the sample is transformed from liquid aerosol into a gas. When it finally arrives at the analytical zone of the plasma, at approximately 7500K, it exists as positively charged ions.

The ions produced in the plasma are extracted into the vacuum system through the interface consisting of two metal plates or “cones” (sample and skimmer cones) with small central orifices. The ions are separated from the photons and residual neutral material by means of electrostatic lenses as they pass through the vacuum system.

Finally, the positively charge ions reach the chamber where the mass spectrometer (MS) and detector are housed. There, the quadrupole mass analyzer separates the ions according to their mass to charge ratio (m/z). Taking into account that the plasma produces almost exclusively single-charged ions, the m/z is equal to the mass of the ion. The electron multiplier detects, counts and stores the total signal for each mass (m/z), and creates a fairly simple mass spectrum.

The produced spectrum provides a simple representation of the sample, where the position of the peak in the spectrum refers to the nature of the element (isotope) and the height of the peak corresponds to its concentration. Thus, quantitative analysis is possible by comparing the mass peaks to those generated by calibration standards under equal experimental conditions. [15] [41]

3.4.2 Analysis of REE

The isotopes of all the REE, from the mass range of 139 to 179 a.m.u., can be determined by ICP-MS. The combination of high sensitivity with the relatively simple spectra has made ICP-MS more attractive than other techniques for the determination of these elements in rock samples. For that reason, several studies on the determination of REE in geological samples by ICP-MS have been published. [20] [21] [23] [42]

3.4.2.1 Spectral interferences

Spectroscopy interferences are probably the most significant class of interferences in ICP-MS. They are caused by atomic or molecular ions that have the same mass to charge ratio (m/z) as the analytes of interest. Such interferences are mainly caused by polyatomic ions that are formed from precursors having numerous sources, such as the sample matrix, reagents used for preparation, plasma gases, and entrained atmospheric gases. [43]

The main drawbacks associated with the determination of REE by ICP-MS arise from the spectral interference of the LREE with the HREE. The REE which are subject to oxygen may easily form oxides (MO^+) and hydroxides (MOH^+). These species occur 16 a.m.u. or 16+1 a.m.u above the parent ion and present a potential analytical problem for LREE since they overlap with some of the low abundance HREE. [44]

Furthermore, the neighbor element barium (normally present at higher concentrations than REE in nature) can form polyatomic ions BaO^+ and $BaOH^+$ which interfere with the analysis of some REE. Table 3 shows potential spectroscopic interferences reported in the literature for the determination of REE by ICP-MS. [43] [45]

To overcome spectral interferences, a number of measures including algebraic correction [28], internal standardization [21], isotope-dilution [16], the standard addition method, the application of matrix matching reference materials for calibration, among others, are employed to obtain accurate REE data when precision is aimed.

The algebraic correction scheme is one approach to correct for the oxide and hydroxide overlap interference. The major advantage is the simplicity of its application, possible without any additional laboratory work. However, the mathematical correction to avoid the interference of barium on europium is prone to large errors, due to the low stability of barium oxide, and negative results are sometimes obtained when the ratio of Ba/Eu is high [28] [46]. Considering the last, the separation of Ba from the analyte system prior REE determination by ICP-MS would be of great significance, especially due to the polyatomic interferences on Eu, which is important to describe the REE pattern in most geological materials (Eu anomaly).

Table 3. Possible spectroscopic interferences on the REE in their determination by ICP-MS

Lanthanide	**Mass**	**Abundance**	**Interference**
La	139	99,9	^{123}TeO, ^{123}SbO
Ce	140	88,5	^{124}TeO, ^{124}SbO
Pr	141	100	^{125}TeO
Nd	146	17,2	^{98}Ru^{16}O$_3$, ^{130}Ba^{16}O
	150	5,64	^{102}Ru^{16}O$_3$, ^{134}Ba^{16}O, ^{150}Sm
Sm	147	15,0	^{99}Ru^{16}O$_3$, ^{130}Ba^{16}OH
	152	26,7	^{104}Ru^{16}O$_3$, ^{136}Ba^{16}O, ^{136}Ce^{16}O, ^{135}Ba^{16}OH, ^{152}Gd
	154	22,7	^{138}Ba^{16}O, ^{138}La^{16}O, ^{138}Ce^{16}O, ^{137}Ba^{16}OH, ^{154}Gd
Eu	151	47,8	^{135}Ba^{16}O, ^{134}Ba^{16}OH
	153	52,2	^{137}Ba^{16}O, ^{136}Ba^{16}OH
Gd	155	14,8	^{139}La^{16}O
	156	20,5	^{140}Ce^{16}O, ^{139}La^{16}OH, ^{156}Dy
	157	15,7	^{138}B^{19}F, ^{141}Pr^{16}O^{+}, ^{140}Ce^{16}OH
	160	21,9	^{144}Nd^{16}O, ^{144}Sm^{16}O, ^{160}Dy
Tb	159	100	^{143}Nd^{16}O, ^{142}Ce^{16}OH, ^{142}Nd^{16}OH
Dy	161	18,9	^{145}Nd^{16}O, ^{144}Nd^{16}OH, ^{144}Sm^{16}OH
	162	25,5	^{146}Nd^{16}O, ^{145}Nd^{16}OH
	163	24,9	^{147}Sm^{16}O^{+}, ^{146}Nd^{16}OH
Ho	165	100	^{149}Sm^{16}O, ^{148}Nd^{16}OH, ^{148}Sm^{16}OH
Er	166	33,6	^{160}Nd^{16}O, ^{150}Sm^{16}O, ^{149}Sm^{16}OH
	167	22,9	^{151}Eu^{16}O^{+}, ^{150}Nd^{16}OH, ^{150}Sm^{16}OH
	168	26,8	^{152}Sm^{16}O, ^{152}Gd^{16}O, ^{151}Eu^{16}OH
Tm	169	100	^{153}Eu^{16}O, ^{152}Sm^{16}OH, ^{152}Gd^{16}OH
Yb	171	14,3	^{155}Gd^{16}O, ^{154}Sm^{16}OH, ^{154}Gd^{16}OH
	172	21,9	^{156}Gd^{16}O
	173	16,1	^{157}Gd^{16}O
	174	31,8	^{158}Gd^{16}O, ^{158}Dy^{16}O, ^{157}Gd^{16}OH, ^{174}Hf
Lu	175	97,4	^{159}Tb^{16}O, ^{158}Gd^{16}OH

3.4.3 Coupling of ICP-MS to a chromatographic system

The combination of chromatographic techniques with ICP-MS represents currently a growing area of study. This coupling system has been used in order to overcome the isobaric interferences mentioned in the previous section. [31] [36] [47] [48] [49]

However, the varying compositions of the eluents used as mobile phase for the chromatographic separation could influence the ionization efficiency in the plasma and the exact external calibration of chromatograms, hindering therefore the quantitative determination by ICP-MS.

Heumann et al. (1998) describe the on-line coupling of chromatographic methods with inductively coupled plasma mass spectrometry, where a simultaneous isotope dilution step is added for accurate quantification of chromatographic peaks. The advantage of applying the isotope dilution technique is that the quantification by the ID analysis is based on the measurement of isotope ratios and not on the absolute intensity of the ions. Thus, 100% recoveries of REE are not essential as samples are spiked prior to separation, and so the drawbacks of this on-line coupling are overcome. [16] [50]

It is expected that the technique of ID will be used in our laboratory more extensively together with HPIC-ICP-MS systems due to the exceptional precision and accuracy of their combined approach.

4 Experimental

4.1 Materials and Reagents

All reagents used in the preparation of samples were of analytical grade. Sodium peroxide (purity 95%, Alfa Aesar), and HCl (fuming 37% v/v, sub-boiled) were used for sample dissolution. The nitric acid solutions were prepared from concentrated HNO_3 (65% v/v, sub-boiled).

Rare earth elements standard solutions were prepared by diluting a multi-element ICP-MS standard solution (Inorganic Ventures, Ontario, Canada) with 1 % v/v HNO_3.Thulium standard solutions were made by serial dilutions of 1000 µg ml^{-1} single element stock solution (Inorganic Ventures, Ontario, Canada) in a final medium of 1 % v/v HNO_3. All the dissolutions were prepared using deionized water (18 $M\Omega cm^{-1}$), purified by a Milli-Q Plus ultrapure water system, Millipore Corporation.

Separation of the sample matrix was performed using Bio-Rad® borosilicate glass columns filled with Dowex 50W-X8 cation exchange resin with a particle size between 200 and 400 mesh.

Oxalic acid and diglycolic acid were reagents of analytical grade. The solution of diglycolic acid was pre-cleaned by passing it through a Dowex 50W-X8 cation exchange column, in order to reduce the high background signal of this eluent. Both eluents were placed in ultrasonic bath for degassing prior to use.

4.2 Instrumentation

Individual REE were separated using a Dionex chromatographic system (Dionex Corporation, Sunnyvale, California, U.S.A.) equipped with a Dionex GS50 gradient pump, an IonPac® CG5A (2 x 50 mm) guard column and an IonPac® CS5A (2 x 250 mm) analytical column.

Detection was by means of an Agilent 7500 Series ICP-MS (Agilent Technologies). Chromatographic data were collected in a personal computer and analyzed using Agilent 7500 Series ICP-MS Plasma Chromatographic Software.

4.3 Geological Reference Materials

The determination of the REE concentrations in reference materials is used to monitor the quality and accuracy of ICP-MS measurements in the present work [51]. The reference materials BIR-1 (Icelandic Basalt) [52], and BRP-1 (Basalt Ribeirão Preto) [53] were chosen to evaluate the effectiveness of the proposed analytical methodology due to their different REE concentration range.

4.4 Samples

The rock samples OU-10 (Longmyndian greywacke, Geo*PT*24), OPC-1 (Portland Cement Geo*PT*26), OKUM (Komatiitic Basalt) and MUH-1 (Harzburgite) were analyzed in different steps of the proposed methodology (i.e. cation exchange separation, determination by HPLC-ICP-MS and/or determination by HPLC-ICP-MS after Tm addition).

4.5 Sample Preparation

All the samples and reference materials analyzed in the present study were prepared using the procedure indicated below.

About 100 mg of powdered sample material were weighted together with 0,6 g fine grained Na_2O_2 in a carbon crucible. The crucibles were taken into a muffle furnace at 480 °C for 0,5 h for sample sintering. After the crucibles were cooled, water was added carefully and the resulting solution was centrifuged to separate the undissolved material. The supernatant was collected in a volumetric flask and the solid material was dissolved using 3 ml HCl 3 mol l^{-1}. The crucibles were rinsed with 2 ml of concentrated HCl and the solution formed was added to the volumetric flask together with the dissolved material and diluted to 100 ml with MilliQ water [20].

4.6 Ion Exchange Chromatographic Group Separation

The cation exchange chromatography with a sulfonated polystyrene resin, Dowex 50W-X8 for the separation of rare earth elements from unwanted matrix elements was studied. The resin was chosen because it is well known to provide an effective REE separation, and also because the involved eluents are inorganic acids, which make the final solution suitable for ICP-MS analysis.

Previous studies using the same resin show that after elution with increasing concentrations of HCl, elements such as Ba, Ca, Sr and Zr remain in the REE-fraction [26] [5]. Using HNO_3 as eluent, Ba, Ca and Sr are efficiently desorbed from the resin prior to the elution of REE, but Fe and part of Zr are retained and elute together with the REE group [5]. Several studies consider the use of both acid in a sequential elution to minimize the number of non-REE constituents and their concentrations in the final solution [28] [54] [55] [56] [57] .

In the present work, two main separation schemes were studied in order to remove the matrix elements from the samples and preconcentrate the rare earth elements: the HNO_3/HCl sequential elution and the separation using a nitric acid media. The main characteristic of each separation scheme is explained later in this work.

At the beginning of the experiments, the resin slurry was placed in a borosilicate glass column and converted in its H^+ form by equilibration with an acid media. All the experiments were carried out using the geochemical reference material BRP-1 as sample. The elution profiles of Ba, Fe, and the REE were studied by collecting 5 ml (Ba and Fe fractions) and 2,5 ml (REE fraction) aliquots of the eluents from the beginning of the elution steps.

The collected fraction were diluted to 10 ml with water and analyzed by ICP-MS. Indium and rhenium were used as internal standards. Geochemical reference samples of a similar matrix were used for calibration. The ICP-MS operating parameters are shown in Table 4.

The use of a set of columns packed with 2-5 ml of resin was chosen to perform the separation tests, instead of only one column filled with big amounts of the resin, in order to reduce the elution time per sample (see Figure 7).

The optimization of the complete process was pursued by changing the diameter of the glass columns, the amount of resin employed, the volume of the analyzed sample and the volume of the involved eluents.

Table 4. ICP-MS operating parameters and conditions

ICP-MS instrument	Agilent 7500 Series
Instrument power	1500 W
Nebulizer	PFA microconcentric
Sample cone	Nickel
Skimmer cone	Nickel
Carrier gas flow rate	1 l min^{-1}
Makeup gas flow rate	0,1 l min^{-1}
Sample uptake rate	approx. 0,2 ml min^{-1}

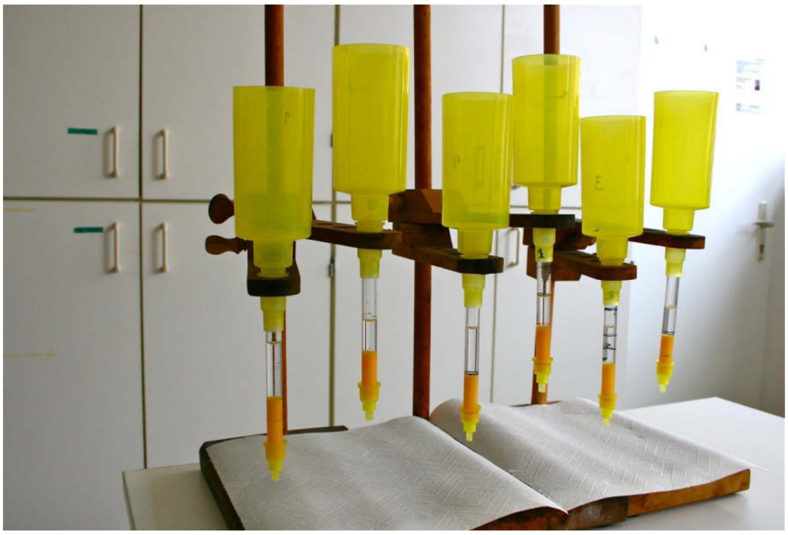


Figure 7. Battery of columns filled with Dowex 50W-X8 used for the cation exchange separation procedures.

4.6.1 HCl/HNO_3 sequential elution

For these experiments, the cation exchange column was conditioned with 2 mol l^{-1} HCl. Afterwards, the sample was loaded onto the resin column and Fe and other unwanted matrix elements were eluted with 2 mol l^{-1} HCl. The column was rinsed with water to minimize the concentration of HCl. Afterwards, Ba and other alkaline earth elements were eluted using 2 mol l^{-1} HNO_3. Finally, the REE were eluted with 6 mol l^{-1} HNO_3, followed by 8 mol l^{-1} HNO_3. Table 5 summarizes all the procedures performed following this scheme.

Table 5. HCl/HNO_3 sequential elution procedures tested for separation and preconcentration of rare earth elements

		Chromatographic Separation Procedure			
		1	**2**	**3**	**4**
Column (length x diameter)		10 cm x 10 mm	10 cm x 10 mm	10 cm x 10 mm	10 cm x 10 mm
Amount of resin (ml)		3	5	5	5
Column equilibration		20 ml 2 mol l^{-1} HCl	20 ml 2 mol l^{-1} HCl	20 ml 2 mol l^{-1} HCl	20 ml 2 mol l^{-1} HCl containing 0,5 mol l^{-1} oxalic acid
Sample volume (ml)		5	5	5	5
Elution Gradient **Step**	1	40 ml 2 mol l^{-1} HCl	20 ml 2 mol l^{-1} HCl	15 ml 2 mol l^{-1} HCl	20 ml 2 mol l^{-1} HCl containing 0,5 mol l^{-1} oxalic acid
	2	5 ml H_2O	10 ml 4 mol l^{-1} HCl	10 ml H_2O	10 ml H_2O
	3	40 ml 2 mol l^{-1} HNO_3	10 ml H_2O	15 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	50 ml 2 mol l^{-1} HNO_3
	4	30 ml 6 mol l^{-1} HNO_3	50 ml 2 mol l^{-1} HNO_3	35 ml 2 mol l^{-1} HNO_3	20 ml 6 mol l^{-1} HNO_3
	5	--	30 ml 6 mol l^{-1} HNO_3	20 ml 8 mol l^{-1} HNO_3	10 ml 8 mol l^{-1} HNO_3

4.6.2 Nitric acid media

In this study, the cation exchange column was first conditioned with 2 mol l^{-1} HNO_3 containing oxalic acid. After the sample solution was passed through the column, Fe and other transition metals were eluted using 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} or 0,7 mol l^{-1} oxalic acid. Afterwards, 2 mol l^{-1} HNO_3 was loaded onto the column, whereby the alkaline earth elements are washed off prior to elution of the REE. The REE and Y are eluted using 6 mol l^{-1} HNO_3 and 8 mol l^{-1} HNO_3. Table 6 show details about the separation procedures that were evaluated regarding this separation schemes.

Table 6. Nitric acid media procedures tested for separation and preconcentration of rare earth elements

		Chromatographic Separation Procedure							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Column (length x diameter)		10 cm x 10 mm	10 cm x 10 mm	10 cm x 10 mm	10 cm x 10 mm	10 cm x 10 mm	10 cm x 10 mm	10 cm x 10 mm	10 cm x 10 mm
Amount of resin (ml)		5	5	3	3	3	3	3	3
Column equilibration		20 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	20 ml 2 mol l^{-1} HNO_3 containing 0,7 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,7 mol l^{-1} oxalic acid	25 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	25 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	25 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	25 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid
Sample volume (ml)		5	5	1	1	1	1	10	20
Step Elution gradient	**1**	20 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	20 ml 2 mol l^{-1} HNO_3 containing 0,7 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,7 mol l^{-1} oxalic acid	10 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	10 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	10 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	10 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid
	2	30 ml 2 mol l^{-1} HNO_3	40 ml 2 mol l^{-1} HNO_3	25 ml 2 mol l^{-1} HNO_3	25 ml 2 mol l^{-1} HNO_3	30 ml 2 mol l^{-1} HNO_3	30 ml 2 mol l^{-1} HNO_3	30 ml 2 mol l^{-1} HNO_3	30 ml 2 mol l^{-1} HNO_3
	3	30 ml 6 mol l^{-1} HNO_3	20 ml 6 mol l^{-1} HNO_3	20 ml 6 mol l^{-1} HNO_3	20 ml 6 mol l^{-1} HNO_3	20 ml 6 mol l^{-1} HNO_3	20 ml 6 mol l^{-1} HNO_3	20 ml 6 mol l^{-1} HNO_3	20 ml 6 mol l^{-1} HNO_3
	4	20 ml 8 mol l^{-1} HNO_3	10 ml 8 mol l^{-1} HNO_3	10 ml 8 mol l^{-1} HNO_3	10 ml 8 mol l^{-1} HNO_3	10 ml 8 mol l^{-1} HNO_3	5 ml 8 mol l^{-1} HNO_3	10 ml 8 mol l^{-1} HNO_3	5 ml 8 mol l^{-1} HNO_3

Table 5. Nitric acid media procedures tested for separation and preconcentration of rare earth elements (cont.)

		Chromatographic Separation Procedure							
		9	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Column (length x diameter)		10 cm x 10 mm	10 cm x 10 mm	10 cm x 5 mm	10 cm x 5 mm	10 cm x 5 mm	10 cm x 5 mm	10 cm x 5 mm	10 cm x 5 mm
Amount of resin (ml)		2	2	2	2	2	2	2	2
Column equilibration		25 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	25 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid
Sample volume (ml)		10	10	1	1	1	5	5	10
Elution gradient	**Step** **1**	10 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	7 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	12 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	12,5 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	15 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	10 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid	10 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid
	2	30 ml 2 mol l^{-1} HNO_3	18 ml 2 mol l^{-1} HNO_3	20 ml 2 mol l^{-1} HNO_3	12 ml 2 mol l^{-1} HNO_3	15 ml 2 mol l^{-1} HNO_3	15 ml 2 mol l^{-1} HNO_3	15 ml 2 mol l^{-1} HNO_3	15 ml 2 mol l^{-1} HNO_3
	3	20 ml 6 mol l^{-1} HNO_3	20 ml 6 mol l^{-1} HNO_3	20 ml 6 mol l^{-1} HNO_3	10 ml 6 mol l^{-1} HNO_3	12,5 ml 6 mol l^{-1} HNO_3	20 ml 6 mol l^{-1} HNO_3	15 ml 6 mol l^{-1} HNO_3	15 ml 6 mol l^{-1} HNO_3
	4	10 ml 8 mol l^{-1} HNO_3	5 ml 8 mol l^{-1} HNO_3	10 ml 8 mol l^{-1} HNO_3	5 ml 8 mol l^{-1} HNO_3	5 ml 8 mol l^{-1} HNO_3	5 ml 8 mol l^{-1} HNO_3	5 ml 8 mol l^{-1} HNO_3	5 ml 8 mol l^{-1} HNO_3

4.6.3 Detection Limits

The determination of detection limits provides a useful mechanism for evaluating the analytical method and its applicability compared to other methods. The detection limits are matrix, instruments, method and analyte specific. For this reason, it is important to carefully control the variables that may cause a detection limit to be high, such as blank contamination. [58]

Two detection limits were determined in the present work using the procedural blanks obtained during the sample preparation and matrix separation:

The Limit of Detection (LOD) is commonly defined as the lowest concentration level of an analyte, which gives an instrumental signal significantly different from a blank or background signal. It is given as the mean concentration of the blank measurements (x_i) plus 3 times the standard deviation (s) of a blank.

The limit of quantitation (LQD) or limit of determination is the lowest concentration at which the analyte can be reliably detected. Quantitation is generally agreed to begin at a concentration equal to 10 standard deviations of the blank. The LQD is determined then by the equation $LQD = x_i + 10s$. [58]

4.7 Separation and Determination of Individual Rare Earth Elements by HPLC-ICP-MS

The separation and determination of rare earth elements by a coupled HPIC-ICP-MS system using a IonPac® CS5A exchange column, preceded by a smaller IonPac® CG5A guard column has been studied.

The analytical column CS5A contains both cation and anion exchange sites, providing so a heterogeneous system for the separation of the rare earth elements. Bruzzoniti et al. (1996) explain the separation mechanism on the CS5A column at the presence of oxalic and diglycolic acid by means of the high stability constants of this ligands with the REE, which allows the formation of $(REE)L_3^{3-}$ species. Using oxalic acid as complexing agent, the LREE are separated by anion exchange and eluted from the column, while the HREE remain fixed as cations in the ion exchange sites of the resin. The use of diglycolic acid, a stronger ligand, will assist the formation of HREE complexes and their subsequent separation by anion exchange. [59]

The HPIC method developed in this study is based on the technique of Dionex (1991), which describes the REE separation using the CS5A column and a mixture of oxalic acid, diglycolic acid and deionized water as mobile phase [60]. However, several modifications were made in order to optimize the separation and the detection with ICP-MS.

Figure 8 shows the basic chromatographic system used in all the optimization experiments.

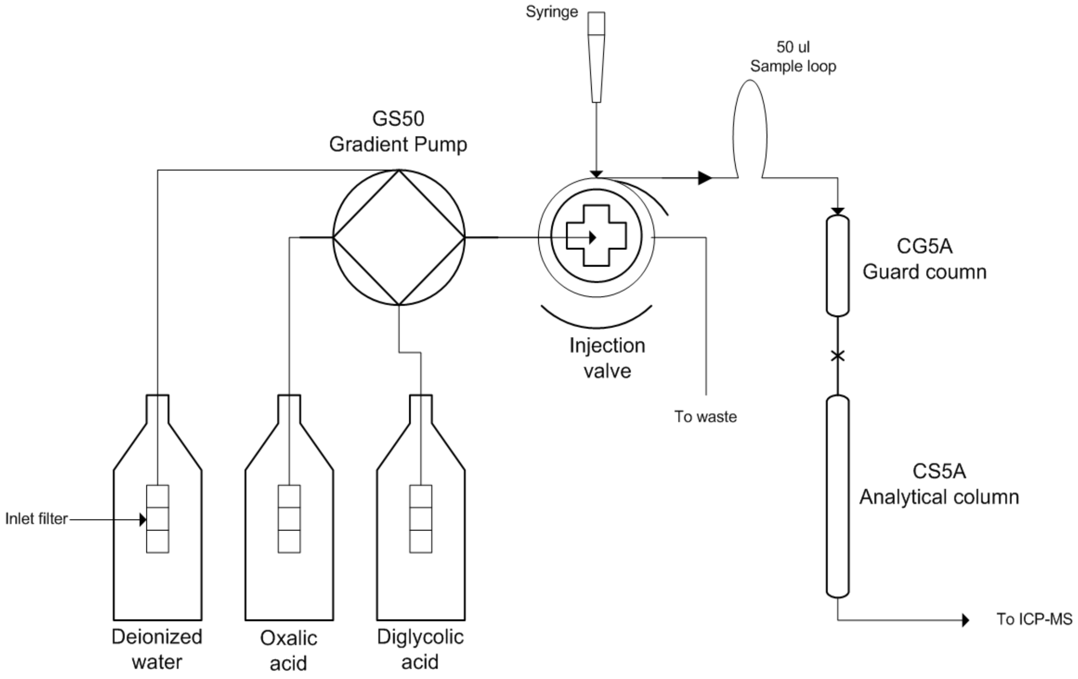


Figure 8. Schematic HPIC system used for this work.

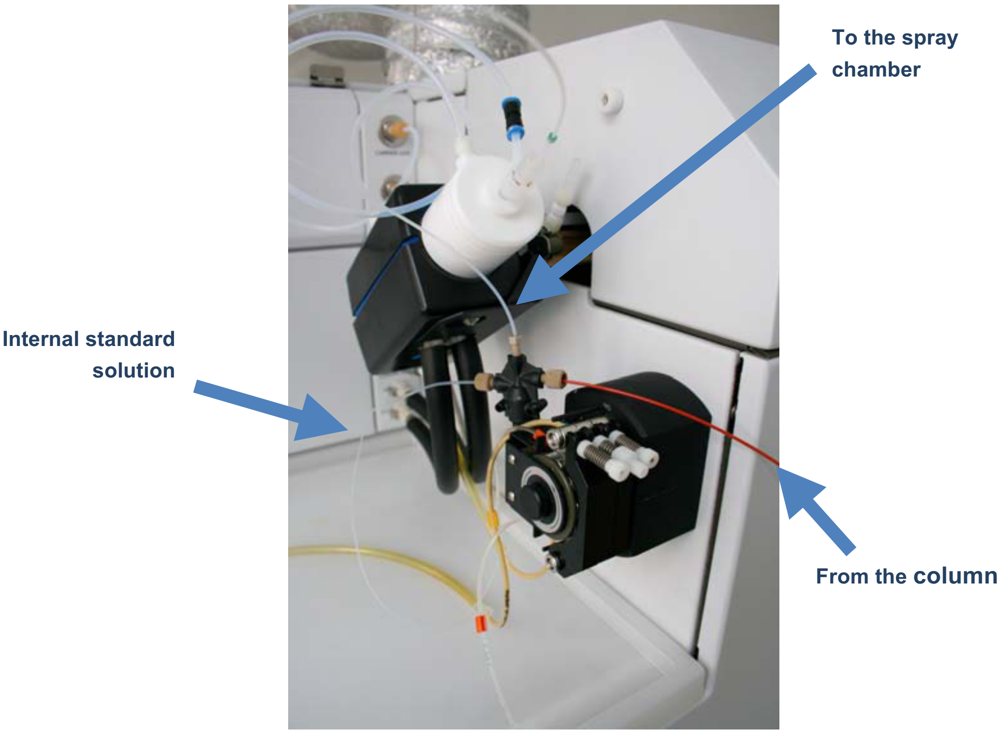


Figure 9. Post-column detection system. A two inlet device is used to mix the eluent flow with a standard solution before nebulization into the ICP-MS to correct for drift in sensitivity.

Numerous experiments were conducted in order to find the best separation conditions for the rare earth elements. A REE synthetic solution was used as sample to perform the optimization tests. The sample solution was injected into a 50 µl sample loop and introduced into the eluent stream via injection valve. Following separation, the eluent was mixed with a 50 ng ml^{-1} In and Re solution for internal standardization and directed to the ICP-MS spray chamber for detection. The internal standard solution was pumped constantly into the analytical stream via peristaltic pump at a rate of 0,1 ml min^{-1} (see Figure 9). The HPIC-ICP-MS operating conditions are given in Table 7.

Table 7. Analytical conditions for the analysis of rare earth elements by HPIC-ICP-MS

HPIC:	
Guard column	IonPac® CG5A
Analytcal column	IonPac® CS5A
Eluent 1	Deionized water
Eluent 2	0,1 mol l^{-1} Oxalic acid, pH 4,8
Eluent 3	0,1 mol l^{-1} Diglycolic acid, pH 4,8
Flow rate	0,3 – 0,4 ml min^{-1}
Sample loop volume	50 µl
ICP-MS	Agilent 7500 Series

4.7.1 Separation procedure optimization

The optimization was basically performed for the mobile phase. The gradient program described in Dionex TN23 (1991) was chosen as starting point for the optimization.

The modifications made to this method include the use of an ammonia solution for pH adjustment, instead of lithium hydroxide which may cause problems in ICP-MS analysis due to the salt loading. Another major modification was the elimination of the post column reaction step, since it was found to be unnecessary when using ICP-MS as detector. Figure 10 shows the chromatogram obtained at the starting point of the optimization experiments. Here the chromatographic peaks for Y, La, Ce, Pr, and Nd are plotted using a secondary y-axis for better visualization.

The gradient was reset to the initial separation conditions and hold for 10 min between each chromatographic run in order to equilibrate the column.

The optimization procedure focused on:

i) achieving complete separation of Yb from Lu,

ii) increasing the separation efficiency of the elements from La to Nd, and

iii) reducing the total time required for the separation and elution of all the REE.

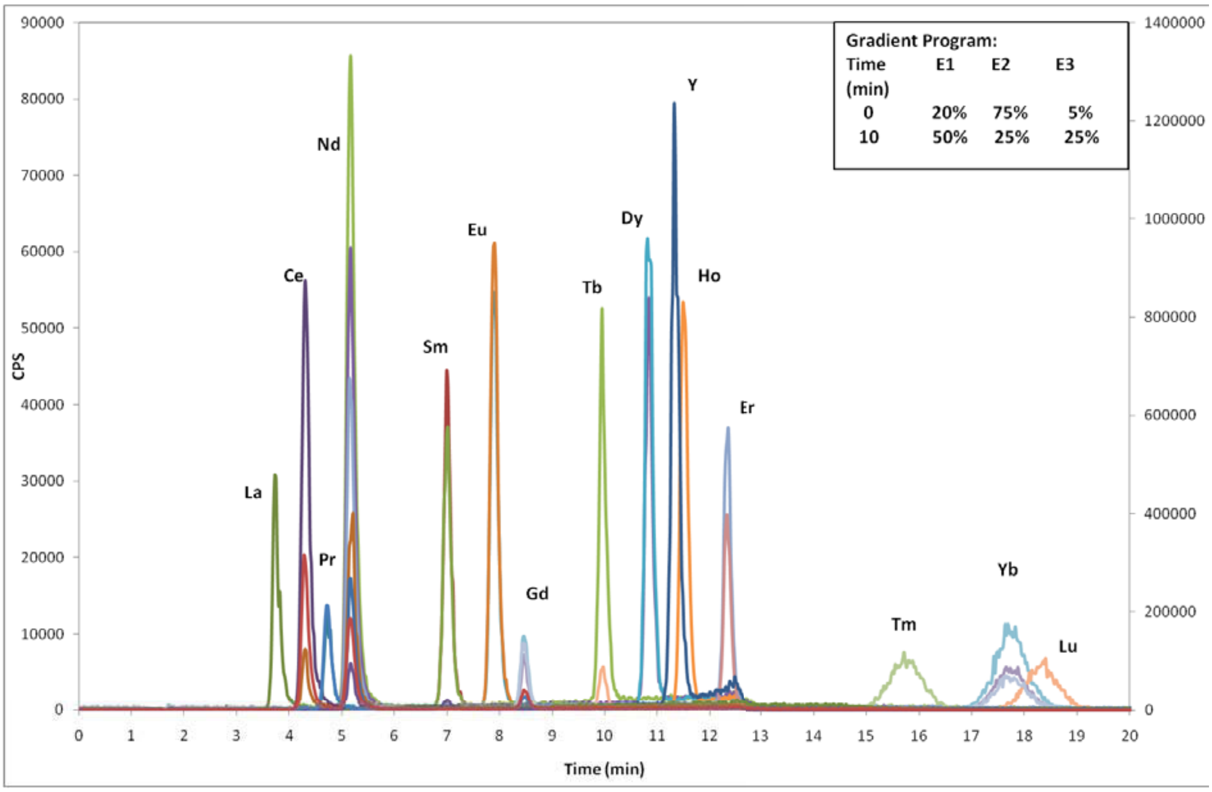


Figure 10. Chromatogram of a REE synthetic sample solution obtained at the beginning of the optimization process. The analytical conditions are listed in Table 7. The gradient program was taken from Dionex (1991). The pH value of E2 and E3 was adjusted to 4,8 with 4 mol l^{-1} ammonia solution.

4.7.2 Isobaric mass interferences

The chromatographic separation of REE prior determination by ICP-MS eliminates all possible interfering overlaps, including those caused by isobaric (REE$^+$) and polyatomic (REEO$^+$ and REEOH$^+$) species, which affect the ICP-MS measurement. For example, CeO, PrO and NdO are well separated from the corresponding Gd isotopes of 16 a.m.u. higher, as can be observed in Figure 11.

Cerium isotope ^{142}Ce is also well separated from ^{142}Nd (see mass 142 in Figure 11). That means that the concentration or isotope ratios can be measured directly on the corresponding peaks without interferences from other rare earth elements.

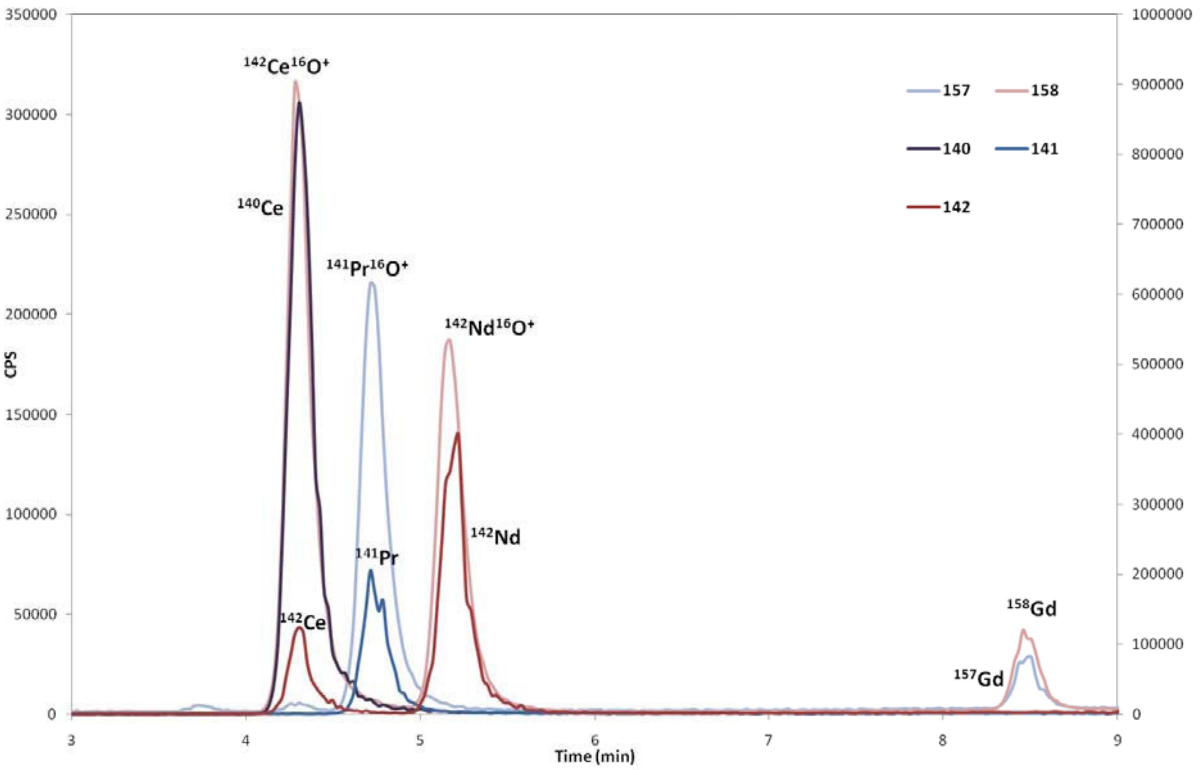


Figure 11. Chromatogram of Ce, Pr, Nd and Gd. The interferences from polyatomic and isobaric species are overcome by the chromatographic separation. The masses 140, 141 and 142 are plotted using a secondary y-axis.

4.7.3 Method Standardization

Once the optimum conditions for cation exchange, as well as for HPIC separation, were established, data on REE concentration in geological reference materials (BIR-1 and BRP-1) and samples (OU-1, OPC-1 and OKUM) were obtained and compared with reference values to assess the validation parameters of the proposed methodology.

4.7.4 Standard Addition

Experiments which consider the approach presented in Barrat, et al. (1996), were additionally performed in order to overcome the errors introduced by sample losses during the sample handling and chromatography, and to improve the quantification of the REE in samples with low concentration levels of these elements.

The work from Barrat, et al. (1996) describes a method based in the addition of a known amount of thulium (Tm) to the sample, which can be used in routine analysis of geological samples. [61].

The Tm addition has been applied under the assumption that the positive Tm anomaly in the REE pattern of a sample cause by the addition of a small amount of Tm can be used to monitor the losses during the analytical process by comparing the measured concentration of thulium in the sample with the concentration obtained by interpolation of the correspondent Tm abundance using the Er and Yb abundances in chondrites. The principles of the quantification of REE in a sample spiked with Tm were described in Barrat, et al. (1996) and are presented below.

First, the thulium concentration of the sample with no spike contribution (C_{Tm}^{*}) is calculated by interpolation of the concentrations of erbium and ytterbium the sample solution, C_{Er} and C_{Yb} (in µg g^{-1}), respectively; using the chondritic abundances as follows:

$$C_{Tm}^{*} = 0{,}02561\ ((C_{Er}/0{,}166).(C_{Yb}/0{,}1651)^{1/2}$$

The abundance of a rare earth element in a sample, [X] (in µg g^{-1}), can be obtained according to:

$$[X] = (M_{Tm}\ .\ C_x)/((M\ .\ (C_{Tm} - C_{Tm}^{*}))$$

Where M is the mass of sample spiked with Tm (in g); M_{Tm}, the amount of Tm added (in g); and C_x, the measured concentration for X (in µg g^{-1}) in the sample solution.

This calculation is valid only if the HREE abundances of the sample follow a normal REE pattern, which means the absence of Yb anomaly, feature that has been observed in some extraterrestrial minerals.

5 Results and Discussion

5.1 Cation Exchange Separation Elution Curves

The percentage amounts of eluted elements were plotted versus the eluted volume. The elution profiles of the REE, together with those of Fe and Ba for all the separation procedures tested are shown in Appendix A-1. In each case gradient elutions were used (as indicated on the diagrams).

The elution curves showed in this section were chosen to be representative of all the elution patterns which achieved good separation results, and are used to compare all the factors tested by the optimization of the cation exchange group separation of REE using a Dowex 50W-X8 resin.

The total time required for each separation procedure varied from 2 to 4 hours, depending on the amount of resin, sample and eluents employed, and on the internal diameter of the column. A reduction in the flow rate was always observed when a higher acid concentration was used (i.e. 4 mol l^{-1} HCl, 6 mol l^{-1} and 8 mol l^{-1} HNO_3), because of dehydration and consequent compaction of the resin.

5.1.1 HCl/HNO_3 sequential elution

The elution curves obtained for this separation scheme indicates that Fe and Ba are completely washed off the column by elution with 2 mol l^{-1} HCl and 2 mol l^{-1} HNO_3, respectively.

Figure 12 shows the chromatographic separation of eight REE from Fe and Ba using HCl/HNO_3 sequential elution. On these conditions a large fraction of Fe elutes with the addition of 15 ml of 2 mol l^{-1} HCl. Water is added to avoid mixing HCl and HNO_3 which may cause the increase in acid strength and the subsequent desorption of the REE from the resin. The elution of Ba begins after the addition of the first 20 ml of 2 mol l^{-1} HNO_3, finishing this process after the total addition of 50 ml of 2 mol l^{-1} HNO_3. Oxalic acid was added to the first 15 ml of 2 mol l^{-1} HNO_3 to assure complete elution of Fe. The REE elution starts when 8 mol l^{-1} HNO_3 is added.

In order to decrease the volume of eluent needed to separate Fe, 2 mol l^{-1} HCl containing oxalic acid was employed. As showed in Figure 13, Fe is completely removed with the first 15 ml of this eluent. On the other hand, 50 ml of 2 mol l^{-1} HNO_3 are still needed to complete barium elution. Effective desorption of REE with 6 mol l^{-1} HNO_3 is achieved as well as with 8 mol l^{-1} HNO_3. Therefore, the use of 6 mol l^{-1} HNO_3 is preferred for the elution of REE, because it represents a reduction in the amount of reagents needed.

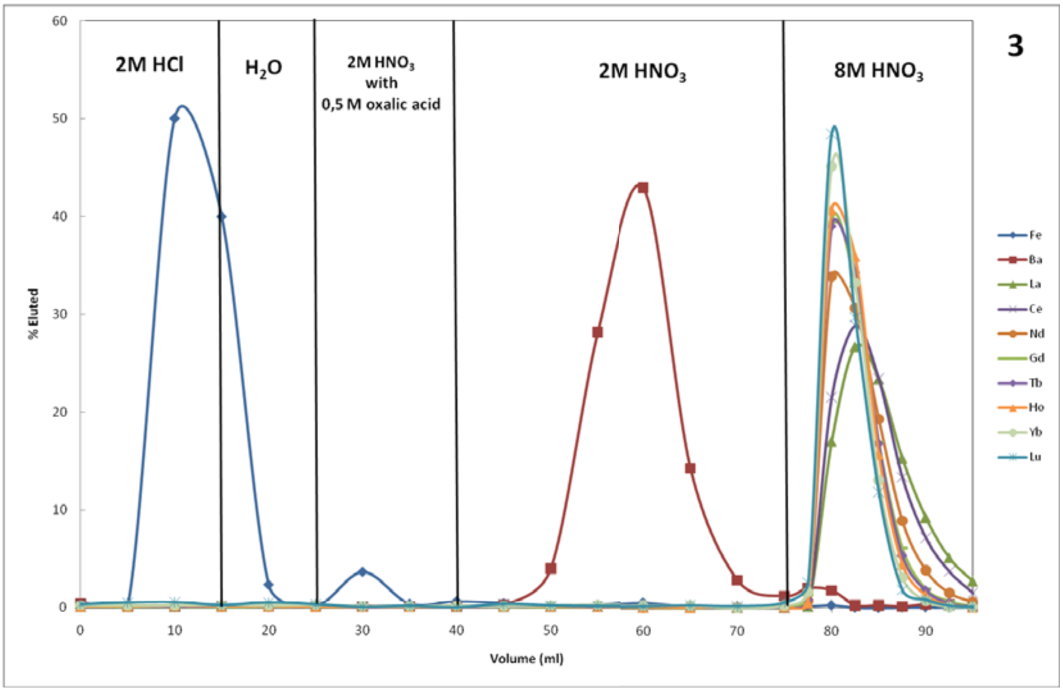


Figure 12. Amount of eluted elements (%) vs. elution volume with 2 mol l^{-1} HCl, 2 mol l^{-1} HNO_3 and 8 mol l^{-1} HNO_3. Five milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 5 ml Dowex 50W-X8

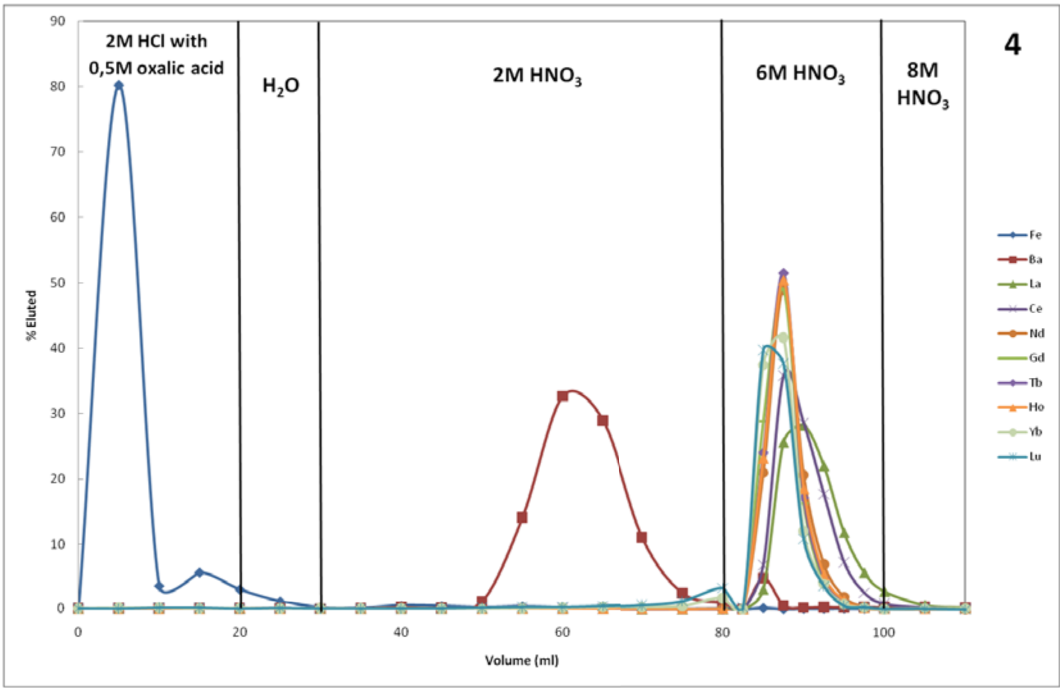


Figure 13. Amount of eluted elements (%) vs. elution volume with 2 mol l^{-1} HCl containing 0,5 mol l^{-1} oxalic acid, followed by 2 mol l^{-1}, 6 mol l^{-1} and 8 mol l^{-1} HNO_3. Five milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 5 ml Dowex 50W-X8

The volume of 2 mol l^{-1} HCl used to elute Fe has to be carefully chosen considering the amount of resin and volume of sample employed. This is because the elution of larger volumes of 2 mol l^{-1} HCl could cause the removal of small portions of the heavy rare earth elements together with the Fe fraction. Due to the same reasons higher concentrations of hydrochloric acid, as well as volumes of water lower than 10 ml, are not recommended (see Appendix A-1).

In general, it was observed that the use of 10 ml or more of water leads to inactivation of the resin. Thus, the elution of Ba begins after addition of 20ml of 2 mol l^{-1} HNO_3 and the complete separation of REE from Ba is not possible without elution of a total volume of 50 ml or more of 2 mol l^{-1} HNO_3.

5.1.2 Nitric acid media

As shown in Figure 14, an efficient separation of REE from Fe and Ba can be achieved using a nitric acid gradient elution. The separation of Fe is aided by the addition of oxalic acid as complexing agent in the first 2 mol l^{-1} HNO_3 elution fraction. The total volume of eluents needed for the separation process has been reduced to 70-80 ml comparing to 100-110 ml needed for separation by HCl/HNO_3 sequential elution. For this reason, the nitric acid media separation scheme was chosen for further experiments, concerning different amounts of resin, sample volume and column diameter.

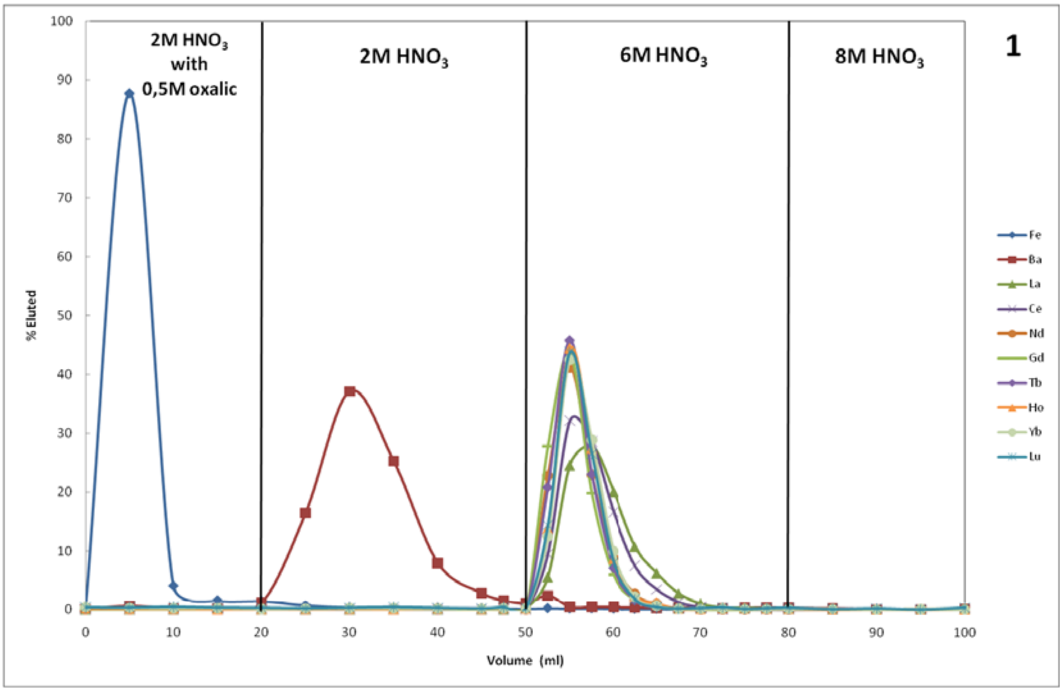


Figure 14. Amount of eluted elements (%) vs. elution volume with 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid; followed by 2 mol l^{-1}, 6 mol l^{-1} and 8 mol l^{-1} HNO_3. Five milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 5 ml Dowex 50W-X8.

Further tests were carried out using a glass column of 10 cm length x 10 mm i.d., packed with 3 ml cation exchange resin. The elution curves for this procedures showed that efficient separation can be achieved using a total volume of 70 ml of eluents (i.e. 10 ml 2 mol l^{-1} HNO_3 with 0,5 mol l^{-1} oxalic acid, 30 ml 2 mol l^{-1} HNO_3, 20 ml 6 mol l^{-1} HNO_3 and 10 ml 8 mol l^{-1} HNO_3).

The efficiency of this elution gradient was tested by varying the amount of sample. Volumes of 1, 5, 10 and 20 ml sample were tested. In each case, an effective REE separation from the studied matrix elements was achieved. Figure 15 shows the elution pattern of the nitric acid gradient elution for 20 ml sample solution using 3 ml cation exchange resin.

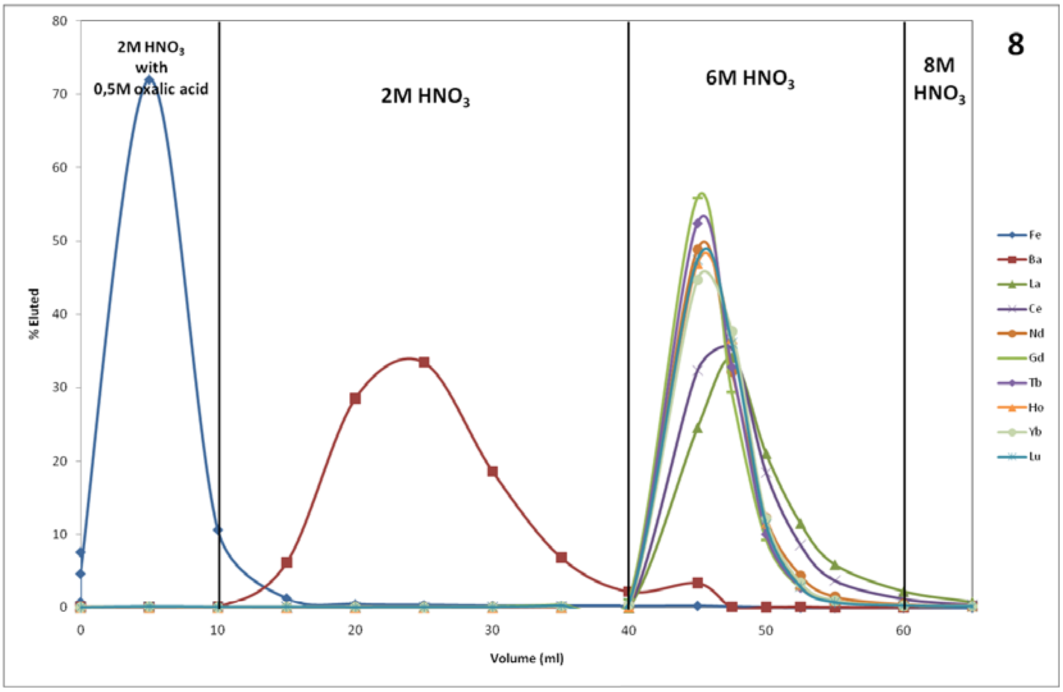


Figure 15. Amount of eluted elements (%) vs. elution volume with 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid; followed by 2 mol l^{-1}, 6 mol l^{-1} and 8 mol l^{-1} HNO_3. Twenty milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 3 ml Dowex 50W-X8.

The chromatographic separation of REE with 10 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid, 30 ml 2 mol l^{-1} HNO_3, 20 ml 6 mol l^{-1} HNO_3 and 10 ml 8 mol l^{-1} HNO_3 using 2 ml cation exchange resin packed in a 10 cm length x 10 mm i.d glass column was also studied. The decrease in the amount of resin from 3 to 2 ml lead to elution of part of the REE with 2 mol l^{-1} HNO_3 and consequently a quantitative recovery of REE cannot be achieved. In order to avoid early desorption of REE, the volume of 2 mol l^{-1} HNO_3 used was decreased from 30 to 20 ml. As a consequence, the barium elution has not been completed when the REE elution starts and the effective separation from Ba was not possible (see Appendix A-1 for more details on the elution curves obtained).

The effective separation of the REE from Fe and Ba using 2 ml of cation exchange resin was successfully achieved when the inter diameter of the column was reduced 10 from to 5 mm. In this case, the reduction of amount of resin leads to a reduction of the total volume of eluents needed for the efficient separation as shown in Figure 16, On the other hand, the elution flow rate was decreased due to the lower diameter of the column, increasing in this way the time needed for the separation.

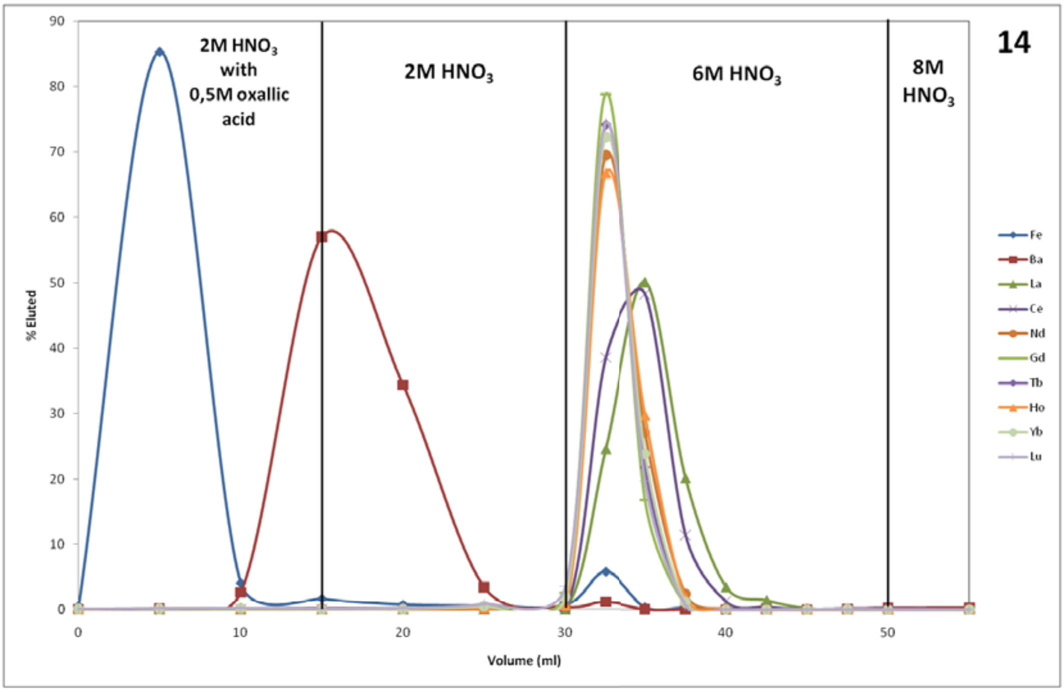


Figure 16. Amount of eluted elements (%) vs. elution volume with 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid, followed by 2 mol l^{-1}, 6 mol l^{-1} and 8 mol l^{-1} HNO_3. Ten milliliter of sample solution were passed through a 10 cm length x 5 mm i.d. glass column packed with 2 ml Dowex 50W-X8.

The best conditions for separation of matrix elements by means of Dowex cation exchanger, including total time required for elution, amount of eluents and separation efficiency were encountered by using 3 ml of resin packed in a glass column.

The procedure finally adopted was as follows: The cation exchange column is first conditioned with 25 ml 0,5 mol l^{-1} oxalic acid in 2 mol l^{-1} HNO_3. After equilibration, the sample solution is passed through the column. Afterwards, Fe and other transition metals are eluted using 10 ml 2 mol l^{-1} HNO_3 containing 0,5 mol l^{-1} oxalic acid. Then, 30 ml of 2 mol l^{-1} HNO_3 are loaded onto the column, whereby the alkaline earth elements are washed off prior to elution of the REE. These two fractions containing the major matrix elements are discarded. The

REE and Y are eluted using 25 ml 6 mol l^{-1} HNO_3 and the column is washed further with 15 ml 8 mol l^{-1} HNO_3.

The elution step using 8 mol l^{-1} HNO_3 is not necessary for the separation since complete REE elution is reached with 6 mol l^{-1} HNO_3, but the step is maintained in order to assure quantitative desorption of all the REE and cleaning of the column.

The REE fractions, 6 mol l^{-1} and 8 mol l^{-1} HNO_3 fractions, are collected in a PTFE beaker and evaporated to dryness on a hot plate. The residue containing the REE is brought into solution with 1% v/v HNO_3 for further analysis.

5.1.3 Blank values and detection limits

The blank is one of the most important measures in trace analysis, since the quantity and standard deviation of the blank are necessary to calculate the detection limits of any measurement process. [62]

The procedural blanks of the propose methodology were determined using the blank solutions coming from the sample preparation procedure as samples.

As can be seen in Table 8, the use of analytical grade reagents and sub-boiled grade acids guarantee low procedural blank values. The detection (LOD) and determination (LQD) limits were calculated as specified in Section 4.6.3 and are shown in the same table.

Table 8. Procedure blanks and limits of detection.

REE	**Mean**[a] (*n* = 7)	**s**	**RSD**	**LOD** [b]	**LQD** [c]
	mg kg^{-1}		%	mg kg^{-1}	mg kg^{-11}
La	0,010	0,0059	59,3	0,027	0,069
Ce	0,0082	0,0043	53,1	0,021	0,052
Pr	0,00070	0,00045	64.8	0,0020	0,0052
Nd	0,0025	0,0019	77,5	0,0085	0,022
Sm	0,00040	0,00022	54,9	0,0011	0,0026
Eu	0,00018	0,00016	86,7	0,00065	0,0018
Gd	0,00039	0,00020	51,6	0,0010	0,0024
Tb	0,00033	0,00029	88,1	0,0012	0,0032
Dy	0,00044	0,00027	60,9	0,0013	0,0031
Ho	0,00017	0,000092	53,2	0,00045	0,0011
Er	0,00023	0,00011	48,1	0,00057	0,00135
Tm	0,000029	0,000010	35,1	0,000059	0,00012
Yb	0,00047	0,00031	66,6	0,0014	0,0036
Lu	0,000035	0,000015	44,9	0,000081	0,00019

[a] Results based on *n* injections

5.1.4 Recovery and separation factors

The recovery of the REE using the proposed cation exchange procedure, as well as the separation factors of Fe and Ba, for three soil reference samples (BRP-1, BIR-1 and OKUM) are listed in Table 10 to Table 11. Iron is reported as oxide; while the Ba and the REE are reported in terms of elemental abundances.

The separation factors of Ba and Fe are more than 98%, which indicates that these elements are efficiently removed by the proposed cation exchange separation. The recovery of the rare earth elements is generally higher than 90% for every soil sample. Europium and samarium show the lowest recovery values, while lanthanum and Cerium show the highest values. The last is a sign of small contamination which could be easily corrected by using procedural blanks.

Table 9. The separation factors of Ba, Fe, and recoveries for REE in BIR-1

BIR-1					
		Before separation [a]	After separation [a]	Separation factor	REE recovery
		(n=3)	*(n=3)*	%	%
Fe_2O_3	% m/m	11,5	0,046	100	
Ba	mg kg^{-1}	6,19	n.d.	100	
Y	mg kg^{-1}	16,0	15,0		94
La	mg kg^{-1}	0,568	0,759		134
Ce	mg kg^{-1}	1,70	2,11		124
Pr	mg kg^{-1}	0,395	0,381		96
Nd	mg kg^{-1}	2,39	2,40		100
Sm	mg kg^{-1}	1,09	1,01		92
Eu	mg kg^{-1}	0,507	0,469		92
Gd	mg kg^{-1}	1,81	1,70		94
Tb	mg kg^{-1}	0,354	0,335		95
Dy	mg kg^{-1}	2,56	2,43		95
Ho	mg kg^{-1}	0,571	0,547		96
Er	mg kg^{-1}	1,70	1,60		94
Yb	mg kg^{-1}	1,64	1,59		97
Lu	mg kg^{-1}	0,245	0,230		94

[a] The mean values are based on the replicate sample preparation (n = number of measurements).
n.d. = not detected

Table 10. The separation factors of Ba, Fe, and recoveries for REE in BRP-1

BRP-1					
		Before separation [a]	After separation [a]	Separation factor	REE recovery
		(n=3)	*(n=3)*	%	%
Fe_2O_3	% m/m	15,8	0,043	100	
Ba	mg kg^{-1}	579	13,9	98	
Y	mg kg^{-1}	45,4	41,8		92
La	mg kg^{-1}	39,5	43,9		111
Ce	mg kg^{-1}	92,7	94,1		101
Pr	mg kg^{-1}	12,9	12,0		93
Nd	mg kg^{-1}	52,5	50,8		97
Sm	mg kg^{-1}	11,1	10,2		92
Eu	mg kg^{-1}	3,41	3,05		89
Gd	mg kg^{-1}	10,6	9,75		92
Tb	mg kg^{-1}	1,53	1,42		93
Dy	mg kg^{-1}	8,66	8,05		93
Ho	mg kg^{-1}	1,60	1,51		94
Er	mg kg^{-1}	4,27	3,94		92
Yb	mg kg^{-1}	3,51	3,35		95
Lu	mg kg^{-1}	0,501	0,462		92

[a] The mean values are based on the replicate sample preparation (n = number of measurements)

Table 11. The separation factors of Ba, Fe, and recoveries for REE in OKUM

OKUM					
		Before separation [a]	After separation [a]	Separation factor	REE recovery
		(n=4)	*(n=4)*	%	%
Fe_2O_3	% m/m	11,8	0,030	100	
Ba	mg kg^{-1}	2,62	n.d.	100	
Y	mg kg^{-1}	9,82	8,94		91
La	mg kg^{-1}	0,421	0,498		118
Ce	mg kg^{-1}	1,14	1,17		102
Pr	mg kg^{-1}	0,250	0,240		96
Nd	mg kg^{-1}	1,51	1,46		97
Sm	mg kg^{-1}	0,722	0,635		88
Eu	mg kg^{-1}	0,300	0,265		88
Gd	mg kg^{-1}	1,16	1,05		90
Tb	mg kg^{-1}	0,226	0,212		94
Dy	mg kg^{-1}	1,60	1,50		94
Ho	mg kg^{-1}	0,354	0,333		94
Er	mg kg^{-1}	1,03	0,97		94
Tm	mg kg^{-1}	0,156	0,147		95
Yb	mg kg^{-1}	1,00	0,951		95
Lu	mg kg^{-1}	0,151	0,138		91

[a] The mean values are based on the replicate sample preparation (n = number of measurements).
n.d. = not detected

The concentration values of the REE, obtained after the cation exchange separation, are compared with reference values to demonstrate the validity of the proposed methodology (see Table 12). Reference values for BRP-1 and BIR-1 are certified and preferred values, respectively [51]. Update compilation [63] of REE contents for OKUM were used to compare the values obtained in this study.

Table 12. Results (mg kg^{-1}) of REE in BRP-1, BIR-1 and OKUM after cation exchange with any further chromatographic separation step.

Element	**BRP-1**		**BIR-1**		**OKUM**	
	Mean [a] (RSD %)	Ref. value (RSD %) [51]	Mean [a] (RSD %)	Ref. value (RSD %) [51]	Mean [b] (RSD %)	Ref. value [63]
La	43,87 (0,5)	42,6 (2,3)	0,76 (0,7)	0,615 (3,4)	0,50 (14,7)	0,413
Ce	94,07 (0,3)	93,3 (1,3)	2,11 (0,2)	1,92 (4,2)	1,17 (9,7)	1,294
Pr	12,05 (0,8)	12,3 (1,6)	0,38 (0,2)	0,37 (5,4)	0,24 (2,6)	0,237
Nd	50,78 (1,0)	51,9 (1,7)	2,40 (1,5)	2,38 (0,4)	1,46 (4,3)	1,505
Sm	10,24 (0,3)	11,2 (1,8)	1,01 (1,5)	1,12 (1,8)	0,64 (4,1)	0,711
Eu	3,05 (1,1)	3,4 (2,3)	0,47 (1,2)	0,53	0,26 (4,2)	0,30
Gd	9,75 (0,7)	10,4 (2,9)	1,70 (0,7)	1,87 (2,1)	1,05 (2,2)	1,147
Tb	1,42 (0,8)	1,5 (3,3)	0,33 (1,3)	0,36 (8,3)	0,21 (1,3)	0,224
Dy	8,05 (0,5)	8,5 (3,5)	2,43 (0,8)	2,51	1,50 (0,5)	1,61
Ho	1,51 (0,2)	1,6 (3,7)	0,55 (0,9)	0,56 (8,9)	0,33 (0,5)	0,351
Er	3,94 (0,3)	4,2 (2,4)	1,60 (0,6)	1,66	0,97 (0,7)	1,042
Yb	3,35 (0,8)	3,5 (2,6)	1,59 (1,1)	1,65	0,95 (0,4)	1,009
Lu	0,46 (1,2)	0,5 (4,0)	0,23 (1,2)	0,25 (8,0)	0,14 (0,5)	0,148

[a] The average value of three replicate samples.

[b] The average value of four replicate samples

As can be seen in Table 12, the measured values are in good agreement with the reference values, indicating good accuracy of the results. In the case of the soil reference samples BRP-1 and BIR-1, the intermediate precisions of measured values (RSD %) are less than 2% for all the REE. The precision calculated for the rare earth elements in OKUM is less than 2% RSD. for the HREE and better than 15% for LREE and MREE.

5.2 HPIC-ICP-MS Chromatographic Data Analysis

5.2.1 Separation of La, Ce, Pr and Nd

First of all, it has been observed that by using opposing linear gradients of oxalic acid and diglycolic acid from the beginning of the elution, the peaks of the elements from La to Nd are not well separated from each other, even when the amount of oxalic acid is reduced. As shown in Figure 17, the separation efficiency is slightly improved when the amount of diglycolic acid is set to 0% at the beginning of the elution gradient.

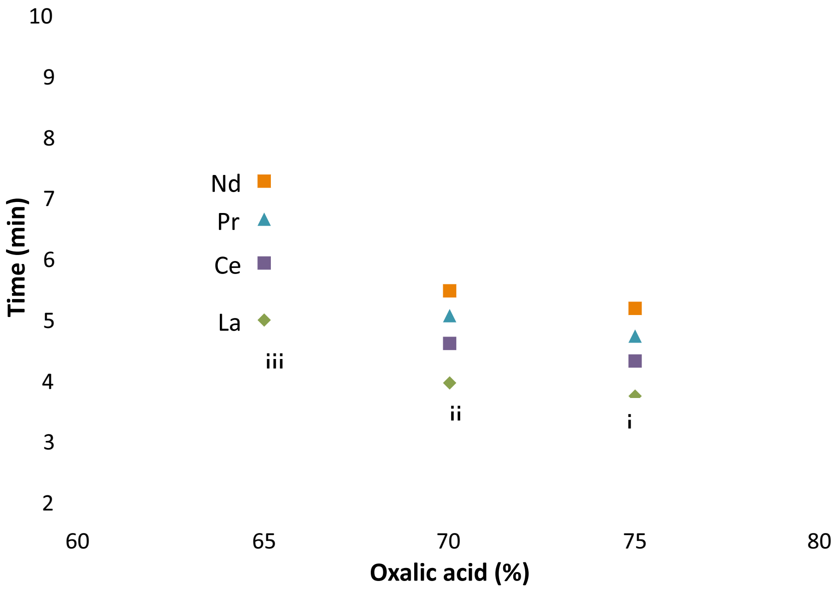


Figure 17. Effect of the concentration of the eluent mixture on the retention time of La, Ce, Pr and Nd. The gradient elution run as follows: (i) 10 min from 5 to 25% diglycolic acid and from 75 to 25% oxalic acid; (ii) 10 min from 5 to 25% diglycolic acid and from 70 to 25% oxalic acid; and (iii) 12 min from 0 to 30% diglycolic acid and from 65 to 20% oxalic acid.

Considering the observed retention times, it was decided to test the elution of the elements from La to Nd using a constant concentration of oxalic acid and no diglycolic acid. Figure 18 illustrated the results of these tests. It can be observed that the separation efficiency increases by reducing the amount of oxalic acid in the eluent stream.

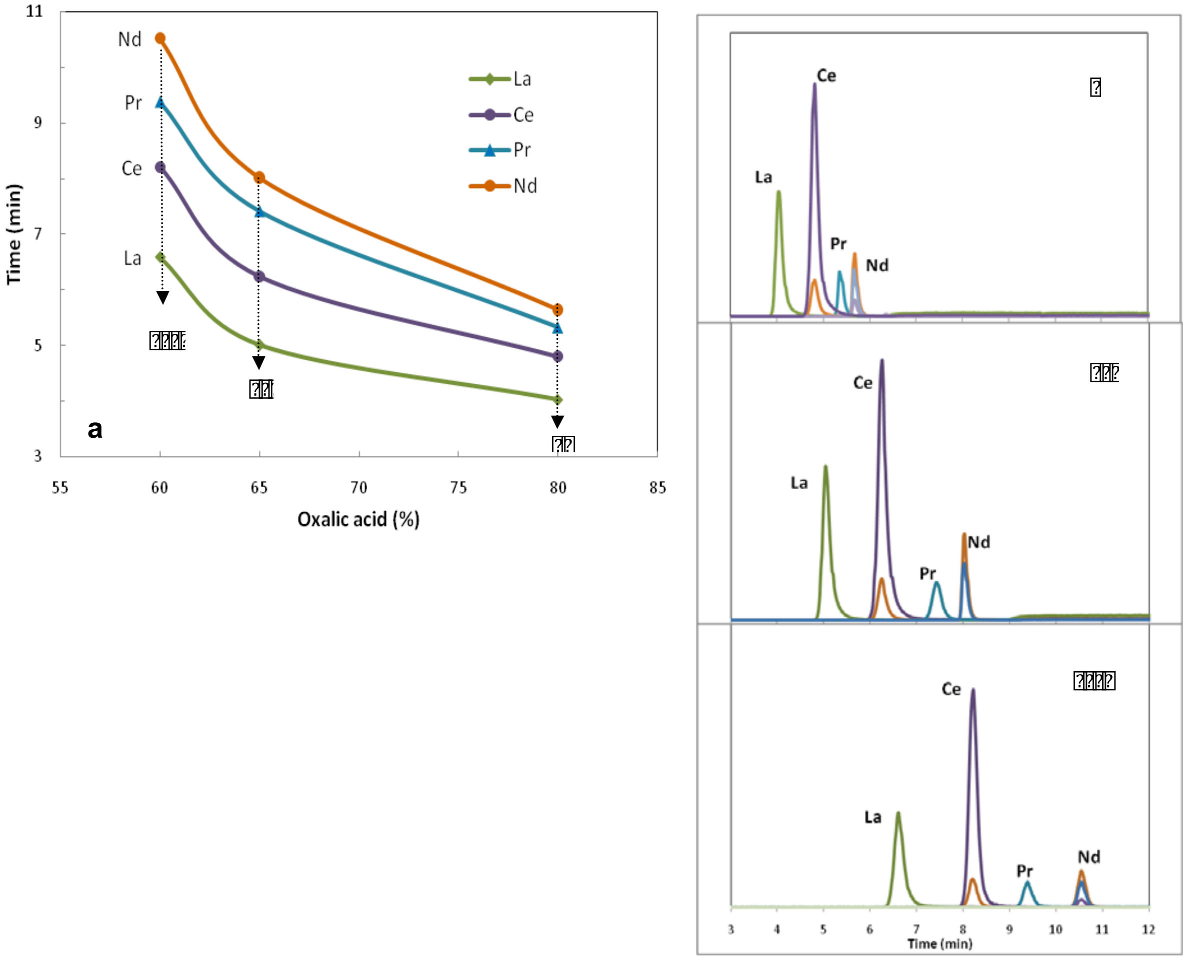


Figure 18. (a) Retention times of La, Ce, Pr and Nd as a function of the amount of oxalic acid in the eluent mixture (diglycolic acid 0%, pH 4,8). (b) Chromatograms of the REE from La to Nd under constant elution conditions given in (a).

Owing to the good separation and the low peak-tailing obtained by eluting La, Ce, Pr and Nd with 60% oxalic acid and 40% deionized water in the eluent mixture, the run of 5 min under these constant conditions has been chosen for the separation of these elements. By using this elution step, the total time of analysis has been increased in approximately 5 min.

5.2.2 Separation of elements from Sm to Lu

As seen in the previous section, achieving the efficient separation of the elements from La to Nd has implied an increase in the retention times of these elements, and consequently a rise in the total time of analysis required for the separation of all REE. For that reason, the use of a gradient elution as next step in the elution program is necessary to achieve a separation of the elements from Sm to Lu within an acceptable time frame.

In the present study, several linear gradient programs were tested in order to find the optimum separation conditions for the elements from Sm to Lu, and to reduce their retention times. The most representative chromatograms and their corresponding gradient programs are shown below in this section. The chromatographic peaks for Y, La, Ce, Pr, and Nd are plotted using a secondary y-axis. To see all the chromatograms obtained during the optimization process, please refer to Appendix A-2.

Figure 19 illustrates a REE chromatogram obtained during the second step of the optimization process. As can be observed, the lanthanides from Sm to Lu are subject to opposing oxalic acid and diglycolic acid gradient elution. It is clear that with exception of Yb and Lu, the individual REE peaks are fairly well separated. Nevertheless, there is a big gap in retention times between Nd and Sm due the absence of Pm in natural samples, which needs to be reduced in order to decrease the total time of analysis.

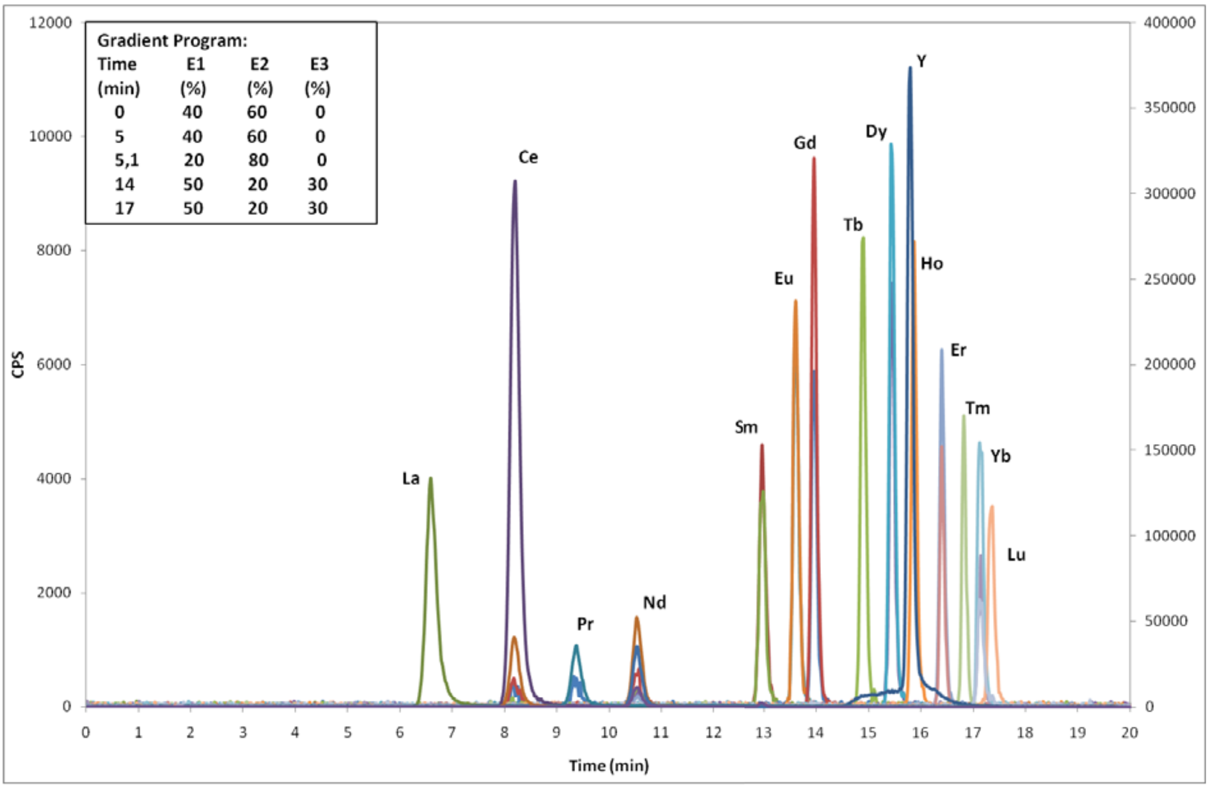
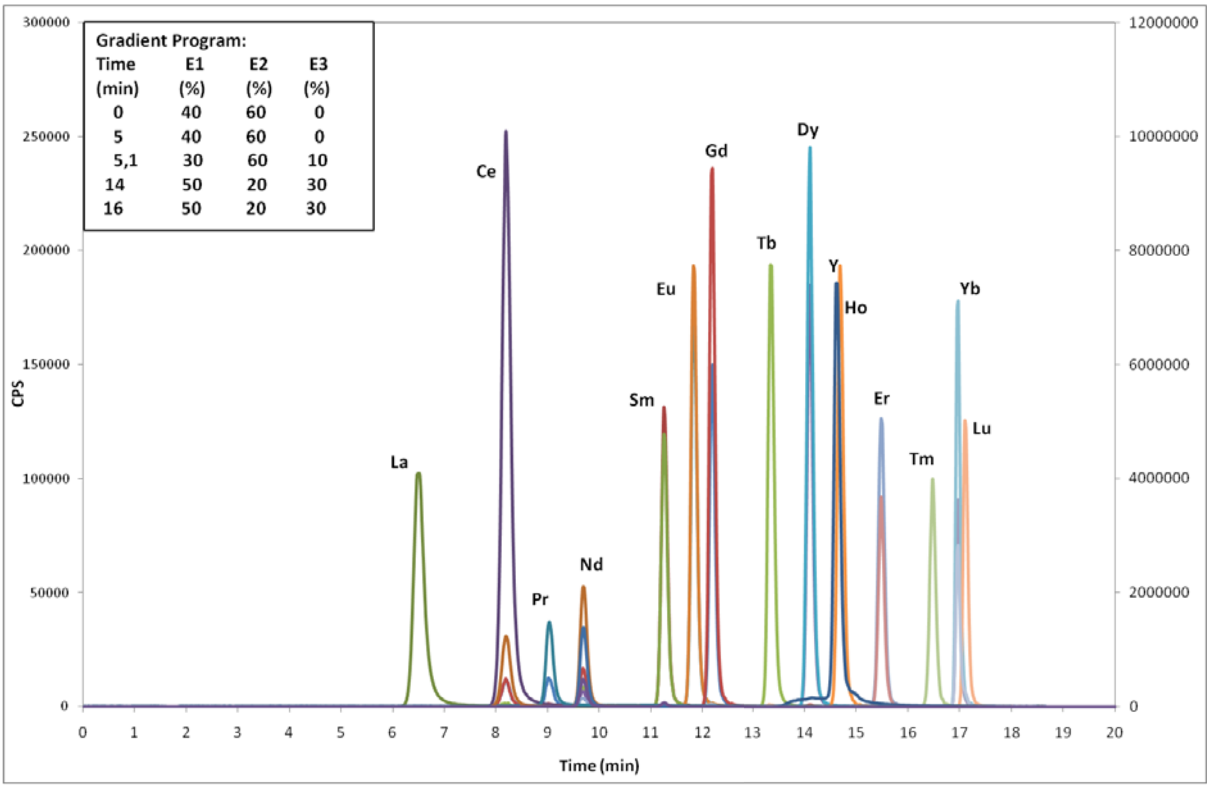


Figure 19. Chromatogram obtained during the optimization process. Yb and Lu are not well resolved from each other.

The retention times of the elements from Pr to Tm are reduced by increasing the concentration of diglycolic acid in the gradient elution, as seen in Figure 20. However, Yb and Lu remain overlapped.



Gradient Program:

Time (min)	E1 (%)	E2 (%)	E3 (%)
0	40	60	0
5	40	60	0
5,1	30	60	10
14	50	20	30
16	50	20	30

Figure 20. Chromatogram obtained during the optimization process. The gap between the LREE peaks and the peaks of the other REE has been reduced by increasing the concentration of diglycolic acid in the gradient elution step. Yb and Lu are not well resolved from each other.

Despite the numerous elution gradients tested in this optimization step, a good separation of Yb from Lu was not achieved, neither increasing nor decreasing the concentration of oxalic acid and diglycolic acid in the eluent mixture. Therefore, changes in eluent pH and eluent flow rate were additionally tested in order to study their influence in the separation of these two elements.

The pH of the eluents oxalic acid and diglycolic acid was adjusted to 4,3 with a 4 mol l^{-1} ammonia solution. Details on the chromatogram obtained can be found in Appendix A-2. It was observed that, as the pH of the eluents decreased, the retention times also decreased. Thus, the separation efficiency was significantly reduced. These results agree with the study described by Bruzzoniti et al. (1996). The variation in eluent pH was no further studied. The pH value of 4,8 was selected here as the optimum pH for the separation of the REE.

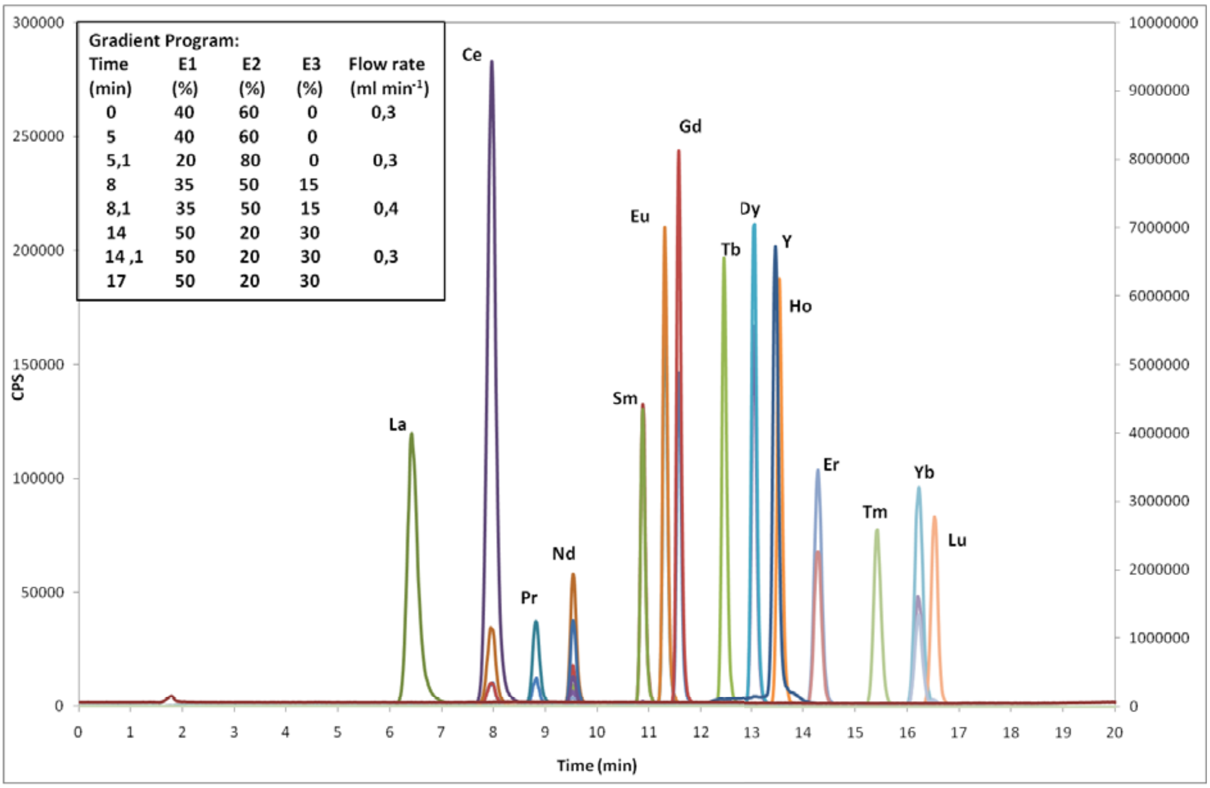
Flow rates of 2 and 4 ml min^{-1} were tested at different time points of the gradient elution program (see Appendix A-2). The optimum separation of all the rare earth elements was achieved by changing the eluent flow rate and gradient program as follows:

Table 13. Gradient program used for the complete separation of REE.

Time (min)	E1 (%)	E2 (%)	E3 (%)	Flow rate (ml min^{-1})
0	40	60	0	0,3
5	40	60	0	
5,1	20	80	0	0,3
8	35	50	15	
8,1	35	50	15	0,4
14	50	20	30	
14,1	50	20	30	0,3
17	50	20	30	

For eluent descriptions, see Table 7.

Figure 21 illustrates the chromatogram showing the separation of the 14 REE after optimization. As can be seen, a very good separation is achieved using the proposed procedure (Table 13) within 17 minutes. The separation of Ho from Y is possible through the ICP-MS system, which can discriminate masses and identified each element signal individually.



Gradient Program:

Time (min)	E1 (%)	E2 (%)	E3 (%)	Flow rate (ml min^{-1})
0	40	60	0	0,3
5	40	60	0	
5,1	20	80	0	0,3
8	35	50	15	
8,1	35	50	15	0,4
14	50	20	30	
14 ,1	50	20	30	0,3
17	50	20	30	

Figure 21. Chromatogram obtained under optimum separation conditions. The 14 REE are well separated from each other. The total elution time has been reduced to less than 17 minutes.

5.2.3 Calibration Curves

The linear calibration curves, passing through the origin, were obtained for all the REE using a number of synthetic solutions prepared in HNO_3 media (1% v/v) from a commercially available lanthanide standard mixture solution for ICP-MS analysis. These solutions were analyzed by HPIC-ICP-MS using the proposed elution gradient before sample analysis.

Due to the significant variation in the peak height observed occasionally during chromatographic analysis, peak area was chosen as giving more consistent and reproducible measurements of concentration than peak height. Figures 22 to 24 show the typical calibration curves for the REE obtained using synthetic standard solutions. As can be seen good linearity was obtained between concentration and peak area.

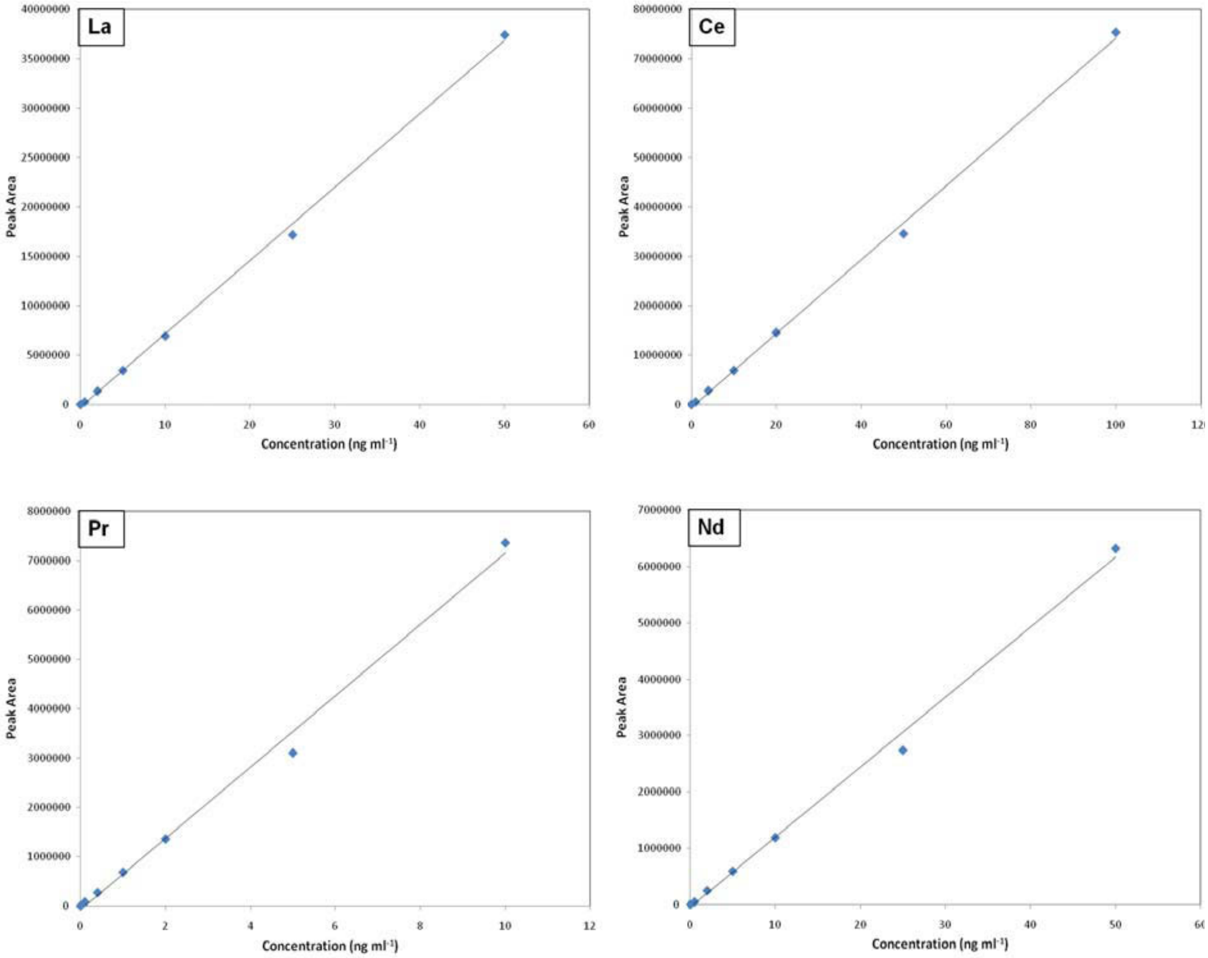


Figure 22. Typical calibration curves for La, Ce, Pr and Nd by HPIC-ICP-MS showing a measure of peak area vs. concentration.

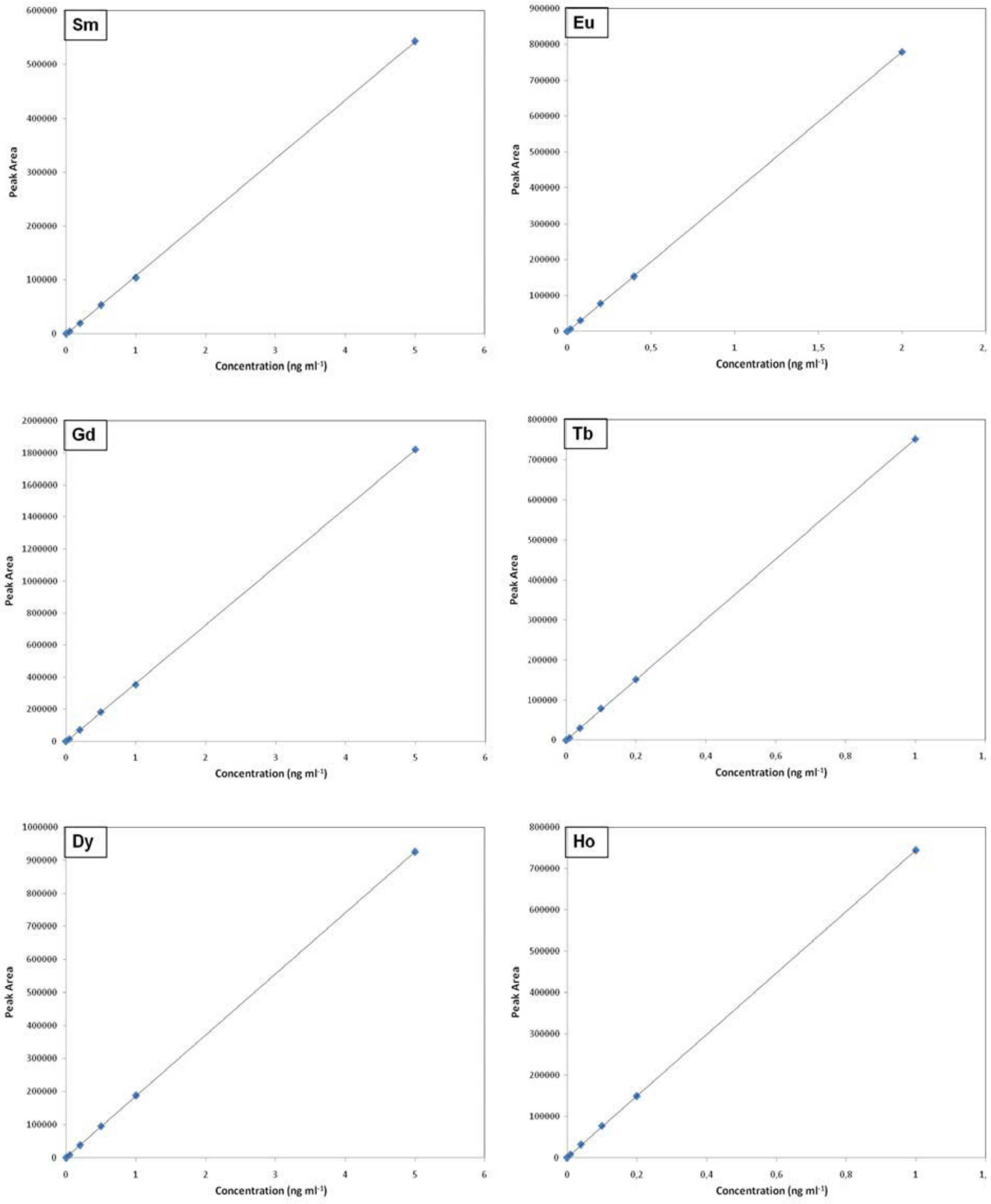


Figure 23. Typical calibration curves for Sm, Eu, Gd, Tb, Dy and Ho by HPIC-ICP-MS showing a measure of peak area vs. concentration.

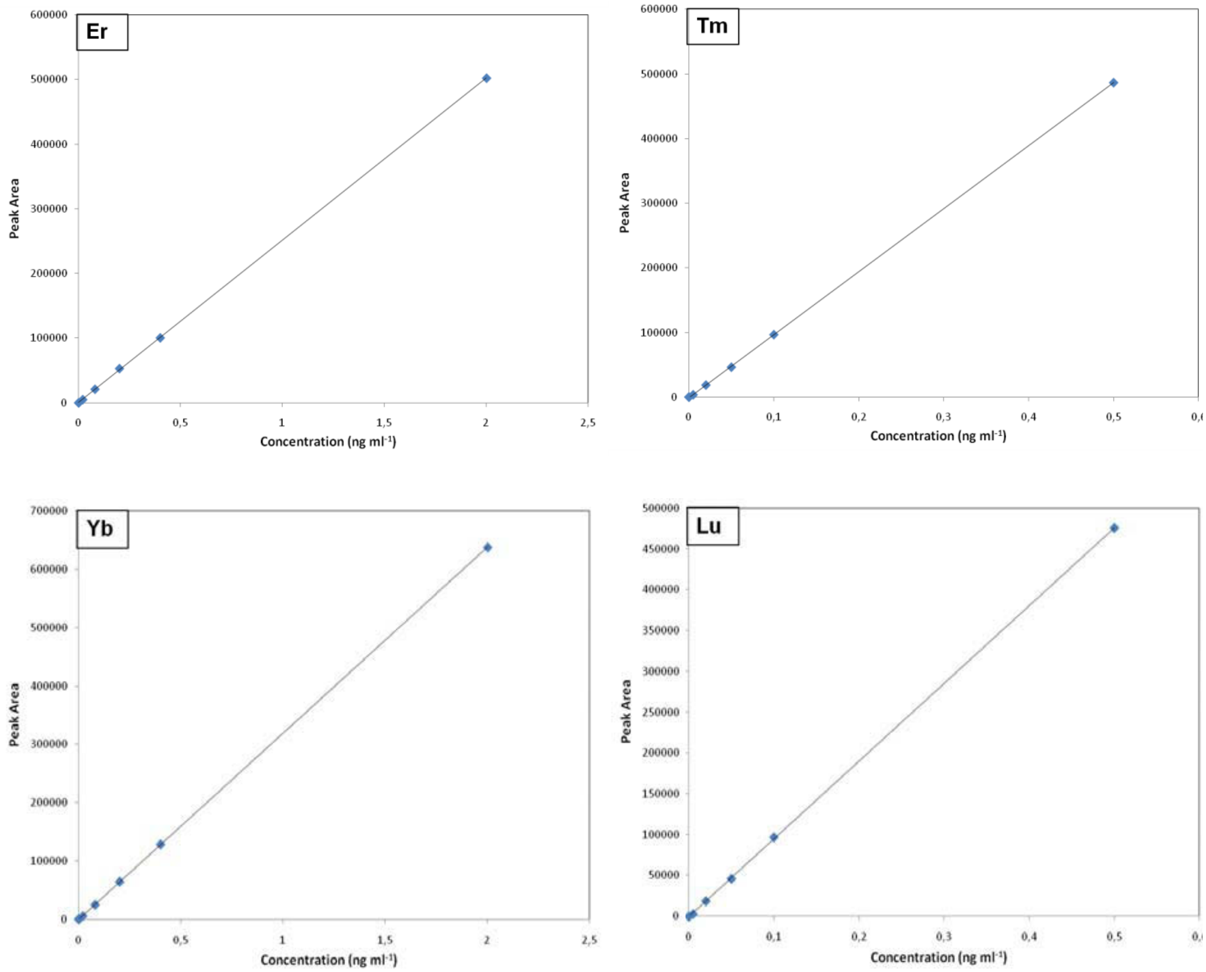


Figure 24. Typical calibration curves for Er Tm, Yb and Lu by HPIC-ICP-MS showing a measure of peak area vs. concentration.

The use of a REE standard mixture solution to obtain the calibration curves for all the 14 rare earth elements has the disadvantage that when a variety of samples are analyzed, which include samples with strong HREE enrichment (i.e. OKUM) and those with LREE enrichment (i.e. BRP-1), the REE abundances for all the samples cannot be determined with the same precision by using a calibration curve with only a few points. Thus, the analysis of more REE standard dissolutions is necessary to cover the wide range of REE concentration in different rock samples, which requires longer time of analysis.

5.2.4 Precision and accuracy

The REE concentration values obtained for two geological reference materials (BIR-1 and BRP-1) after analysis by the proposed methodology (including sample preparation and preconcentration procedures) are reported.

Blank solutions processed in the same way as all the samples analyzed were injected at the beginning of the sample run to check the baseline and to obtain the blank chromatograms. The HPIC injection loop was rinsed with approx. 1 ml 1% v/v HNO_3 before each sample injection to avoid contamination from the previous sample.

The cation exchange separation procedure adopted (see Section 5.1.2) allows the concentration to be changed (diluted or concentrated) in order to maintain the REE amounts in the sample solution within the calibration range and above the determination limit of the method.

The concentration values for each REE were calculated using calibration curves as those found in the previous section. Data on peak areas were first corrected for instrumental drift and then for procedural blank. Results for the reference materials are detailed in Table 14. Smooth REE-normalized patterns were obtained for both reference materials (see Figure 25 and Figure 26).

Table 14. Results (mg kg^{-1}) of REE for BIR-1 and BRP-1 by HPIC-ICP-MS

	BIR-1					**BRP-1**				
	Mean[a] (*n* =3)	±	s	RSD (%)	Ref. Value	Mean[a] (*n* =3)	±	s	RSD (%)	Ref. Value
La	0,65	±	0,21	31,6	0,62	42,64	±	1,32	3,1	42,6
Ce	2,17	±	0,40	18,2	1,92	97,86	±	3,15	3,2	93,3
Pr	0,39	±	0,05	11,6	0,37	12,33	±	0,13	1,0	12,3
Nd	2,52	±	0,26	10,5	2,38	51,01	±	2,14	4,2	51,9
Sm	1,02	±	0,09	9,3	1,12	9,01	±	1,24	13,7	11,2
Eu	0,49	±	0,05	10,3	0,53	2,66	±	0,40	14,9	3,42
Gd	1,87	±	0,23	12,5	1,87	9,08	±	0,89	9,8	10,4
Tb	0,38	±	0,04	9,8	0,36	1,40	±	0,10	6,9	1,52
Dy	2,93	±	0,31	10,6	2,51	8,38	±	0,51	6,1	8,50
Ho	0,63	±	0,05	8,3	0,56	1,59	±	0,08	5,0	1,62
Er	1,89	±	0,16	8,7	1,66	4,07	±	0,21	5,2	4,20
Tm	0,28	±	0,03	12,4	0,25	0,56	±	0,04	7,5	0,57
Yb	1,82	±	0,24	13,1	1,65	3,23	±	0,35	11,0	3,48
Lu	0,27	±	0,04	14,3	0,25	0,44	±	0,05	11,3	0,50

[a] Results based on *n* injections

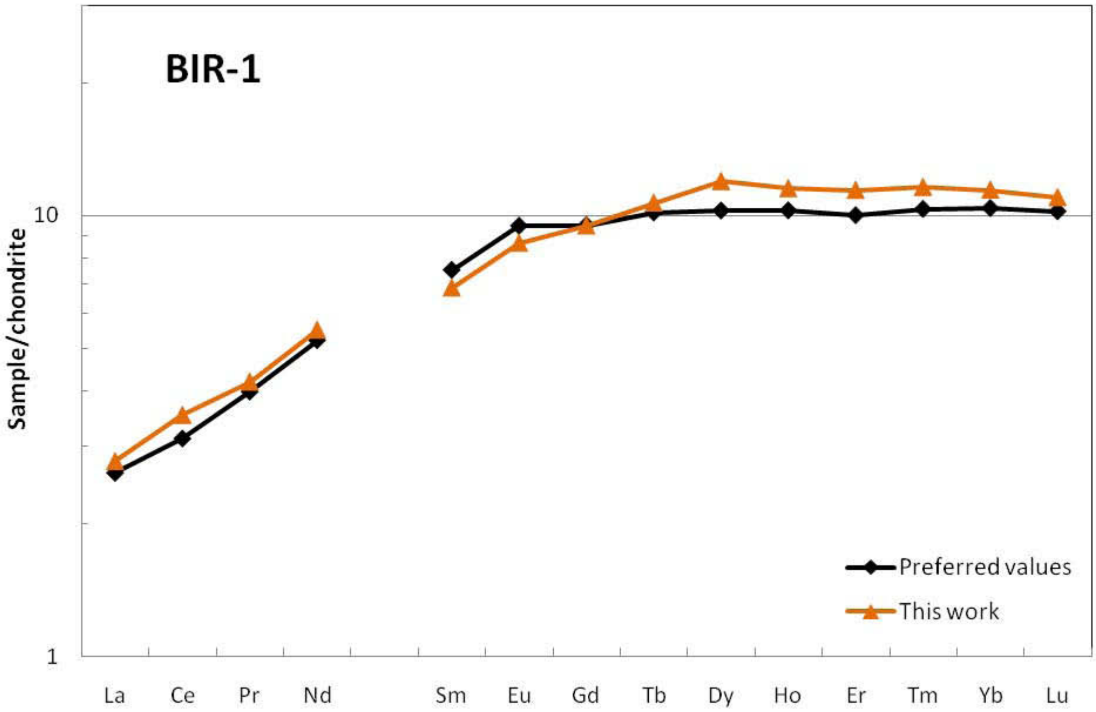


Figure 25. Chondrite-normalized REE pattern of BIR-1. Chondrite normalization values are taken from Wasson and Kellemeyn (1988).

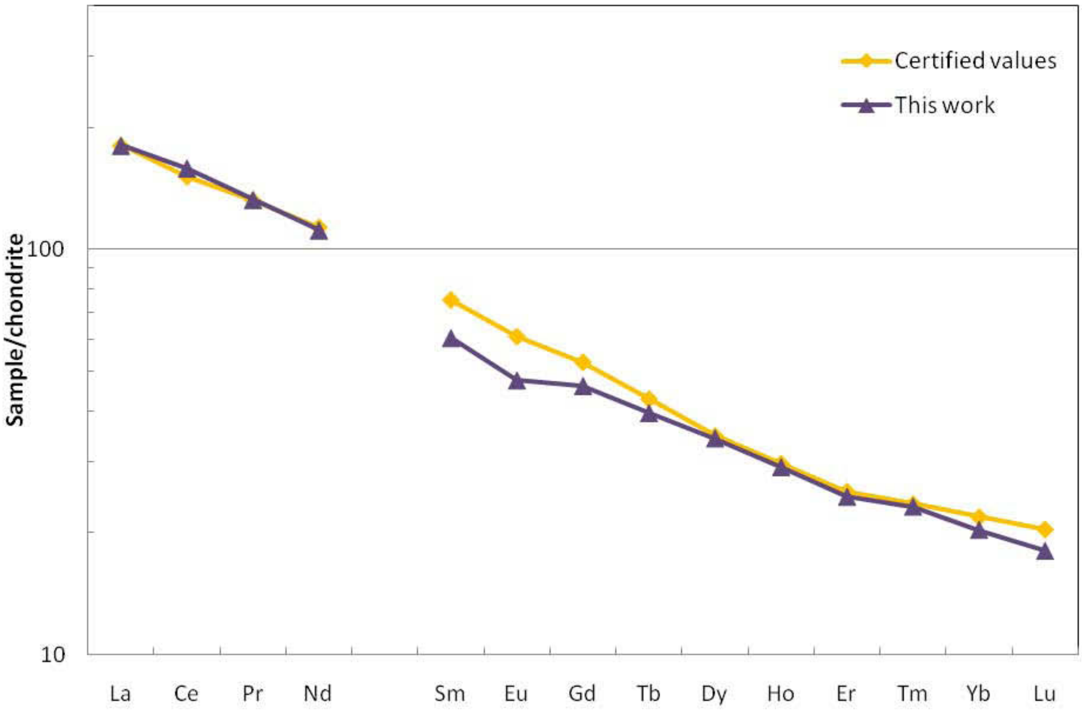


Figure 26. Chondrite-normalized REE pattern of BRP-1. Chondrite normalization values are taken from Wasson and Kellemeyn (1988).

Good agreement is observed between reference and most measured values. Based on the replicate analysis of samples, relative standard deviations (RSD) are better than 15% except where the concentrations of LREE are below 2,2 mg kg^{-1}. In general, the precision of the measured values was not found satisfactory for samples with low LREE abundances.

5.2.5 Sample Analysis

Three geological samples (OU-10, OPC-1 and OKUM) were analyzed by the proposed methodology (i.e. from sample preparation to determination by HPIC-ICP-MS). Peak areas were use for quantification of the analytes. The concentration values were calculated using calibration curves as those found in Section 5.2.3.

The obtained concentration values are listed in Table 15 and Table 16. The reference values for these samples are also listed in the respective table for comparison. [64]

The RSD of the measurements ranged from 0,4 to 13,3% for the REE in OU-10 and OPC-1. In the case of OKUM, the RSD values for the LREE are higher as desired, due to the low concentration of these elements in the sample, as well as reported for BIR-1. The chondrite-normalized pattern for the measured values in comparison with the reference values is shown in Figure 27. The pattern is smooth with exception to the value obtained for La, which is higher as expected probably due to contamination of the sample.

Table 15. Results (mg kg^{-1}) of REE for OU-10 and OPC-1 by HPIC-ICP-MS

	OU-10					**OPC-1**				
	Mean[a] (*n* =2)	±	s	RSD (%)	Ref. Value	Mean[a] (*n* =3)	±	s	RSD (%)	Ref. Value
La	17,85	±	0,40	2,2	18,80	24,81	±	2,20	8,9	23,10
Ce	39,24	±	2,25	5,7	38,00	46,39	±	5,81	12,5	42,94
Pr	5,05	±	0,58	11,5	4,70	6,52	±	0,69	10,7	6,22
Nd	18,44	±	0,84	4,5	18,70	26,04	±	2,06	7,9	23,60
Sm	2,88	±	0,15	5,3	3,90	5,55	±	0,48	8,6	4,39
Eu	0,68	±	0,01	2,2	1,00	1,20	±	0,14	11,7	0,98
Gd	3,08	±	0,30	9,8	3,70	4,58	±	0,32	7,1	3,63
Tb	0,56	±	0,06	10,4	0,61	0,59	±	0,06	10,3	0,51
Dy	3,63	±	0,19	5,3	3,65	3,36	±	0,36	10,6	2,79
Ho	0,76	±	0,05	6,6	0,75	0,66	±	0,09	13,2	0,54
Er	2,20	±	0,01	0,6	2,20	1,76	±	0,19	11,0	1,49
Tm	0,33	±	0,02	4,6	0,34	0,28	±	0,03	10,5	0,21
Yb	2,09	±	0,06	3,0	2,20	1,61	±	0,21	13,1	1,32
Lu	0,30	±	0,00	0,4	0,34	0,24	±	0,02	9,3	0,19

[a] Results based on *n* injections

Table 16. Results (mg kg^{-1}) of REE for OKUM by HPIC-ICP-MS (without Tm correction).

	OKUM				
	Mean[a] (*n* =3)	±	s	RSD (%)	Ref. Value
La	0,63	±	0,17	27,6	0,41
Ce	1,20	±	0,33	27,7	1,29
Pr	0,23	±	0,06	26,1	0,24
Nd	1,39	±	0,30	21,3	1,51
Sm	0,66	±	0,16	24,0	0,71
Eu	0,28	±	0,05	18,0	0,30
Gd	1,12	±	0,18	15,8	1,15
Tb	0,21	±	0,03	12,8	0,22
Dy	1,53	±	0,17	11,3	1,61
Ho	0,34	±	0,05	15,3	0,35
Er	1,04	±	0,16	15,1	1,04
Tm	0,16	±	0,02	10,2	0,15
Yb	0,97	±	0,10	10,3	1,01
Lu	0,14	±	0,01	9,2	0,15

[a] Results based on *n* injections

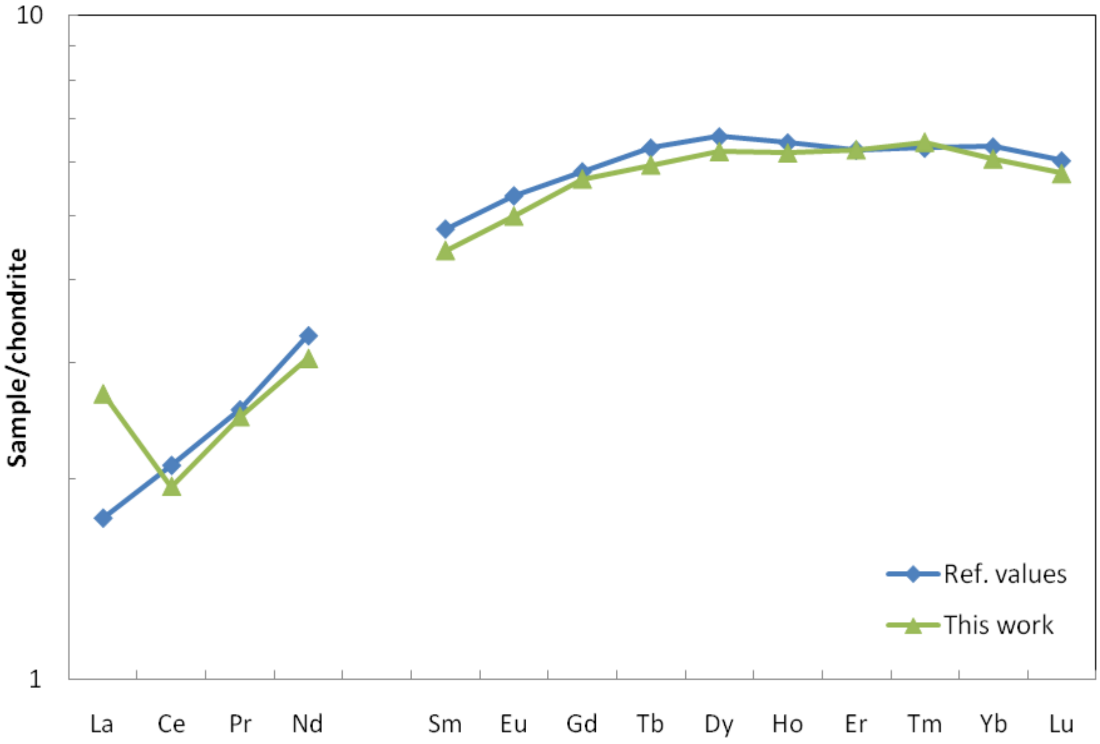


Figure 27. Chondrite-normalized REE pattern of OKUM. Chondrite normalization values are taken from Wasson and Kellemeyn (1988).

5.2.6 Tm Addition

The Tm standard addition was applied for analysis of two geological samples, OKUM and MUH-1, in order to improve the precision of the method for samples with low LREE abundances.

Sample material was spiked with a solution of pure Tm (50 ng of Tm for the equivalent of 20 mg of sample) and then processed as any other sample (i.e. alkaline fusion, cation exchange matrix separation and separation, and determination of individual REE by HPIC-ICP-MS).

Calibration curves were plotted using REE synthetic standard solutions and the data on REE concentration obtained for the samples were corrected as described in Section 4.7.4.

As shown in Table 17, the intermediate precision expressed as RSD% are better than 2% for the HREE and between 1,7 and 7,8% for the LREE and MREE. By comparing these results with the RSD values listed in Table 16 (for the same sample, but without Tm correction), it can be clearly observed that the precision was significantly improved (i.e. lower RSD values), which indicates the quality of the methodology and the importance of standard addition when precise quantification of the REE is aimed.

The chondrite-normalized pattern for the REE values obtained after Tm correction is shown in Figure 28. The smoothness of the pattern indicates that the data are reliable and its proximity to the reference values indicates the accuracy of the methodology.

Table 17. Results (mg kg^{-1}) of REE for OKUM after Tm addition.

	OKUM				
	Mean (*n* = 3)	±	s	RSD (%)	Ref. Value
La	0,42	±	0,03	6,2	0,41
Ce	1,41	±	0,11	7,8	1,29
Pr	0,24	±	0,01	3,3	0,24
Nd	1,44	±	0,02	1,7	1,51
Sm	0,66	±	0,02	2,9	0,71
Eu	0,29	±	0,02	6,0	0,30
Gd	1,14	±	0,04	3,6	1,15
Tb	0,21	±	0,00	1,9	0,22
Dy	1,59	±	0,02	1,5	1,61
Ho	0,34	±	0,00	0,9	0,35
Er	1,07	±	0,02	2,3	1,04
Tm	0,15	±	0,00	1,1	0,15
Yb	0,98	±	0,00	0,2	1,01
Lu	0,15	±	0,00	1,2	0,15

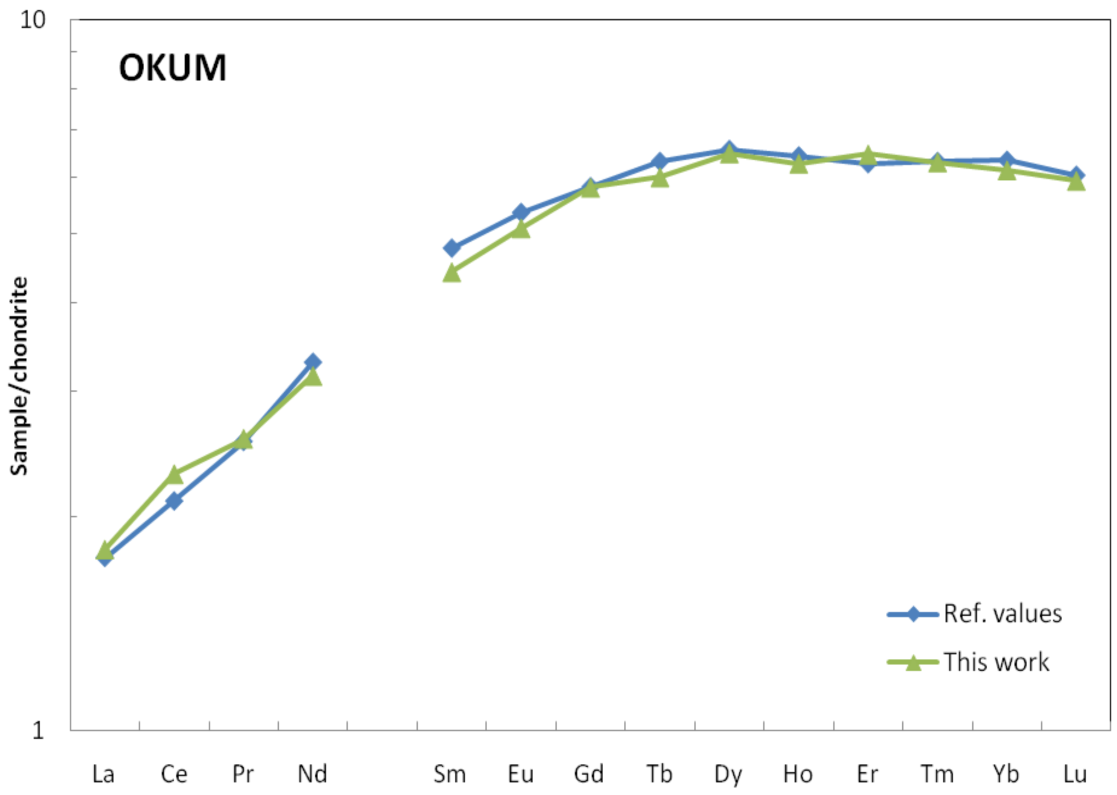


Figure 28. Chondrite-normalized REE pattern of OKUM after correction using Tm standard. Chondrite normalization values are taken from Wasson and Kellemeyn (1988).

The REE concentration values for the geological sample MUH-1 were measured and corrected with the presented scheme. The average values of four replicates are listed in Table 18. The reference values (compiled values) [63] are given in the same Table for comparison.

As can be seen (Table 18), the measured values are in good agreement with the compiled data. The RSD values of the measurements are better than 10% for all the REE despite their low concentrations, which proves the efficiency of the correction procedure. Figure 30 shows the REE normalized pattern for MUH-1. The smooth plot obtained, especially for the HREE, is a sign of reliable data.

An important observation in the application of this methodology is that the data correction was satisfactory only when the Tm used for quantifying REE abundances was added to the material sample before the sample preparation (i.e. alkaline fusion). It was found that, if the Tm standard is added to the sample solution after digestion, as recommended in Barrat et al. 1999, the Tm does not behave the same way as the other REE during sample separation.

Table 18. Results (mg kg^{-1}) of REE for MUH-1 after Tm addition.

	MUH-1 Mean (n = 4)	±	s	RSD (%)	Ref. Value
La	0,162	±	0,008	5,2	0,139
Ce	0,235	±	0,008	3,5	0,209
Pr	0,036	±	0,002	6,1	0,035
Nd	0,183	±	0,010	5,2	0,180
Sm	0,062	±	0,006	9,1	0,068
Eu	0,024	±	0,002	9,6	0,026
Gd	0,106	±	0,007	6,4	0,107
Tb	0,021	±	0,001	5,4	0,021
Dy	0,157	±	0,005	3,3	0,155
Ho	0,036	±	0,001	2,7	0,035
Er	0,112	±	0,004	4,0	0,108
Tm	0,017	±	0,001	3,7	0,017
Yb	0,120	±	0,004	3,4	0,117
Lu	0,019	±	0,001	3,6	0,019

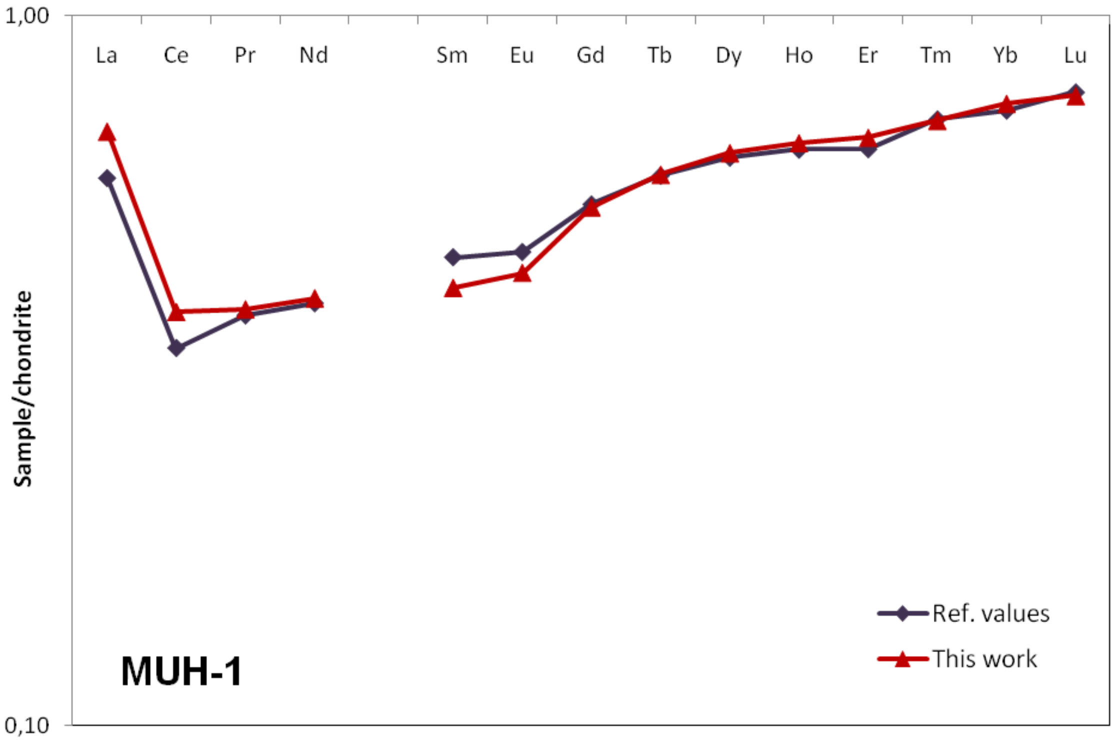


Figure 29. Chondrite-normalized REE pattern of MUH-1. Chondrite normalization values are taken from Wasson and Kellemeyn (1988).

6 Conclusion

The spectral interferences caused by matrix elements, especially barium, in inductively coupled plasma mass spectrometry are entirely eliminated by means of Dowex 50W-X8 cation exchange chromatography. The proposed elution scheme involves a gradient elution with a nitric acid media. Barium, Fe and, other alkaline earth elements and transition metals, are efficiently washed off the column with 2 mol l^{-1} HNO_3 containing certain amount of oxalic acid, while the REE are retained. The REE are then eluted with 6 mol l^{-1} HNO_3. Recoveries for REE range typically from 90 to 120%.

The complete chromatographic separation of individual rare earth elements was achieved using an IonPac® CS5A (2 x 250 mm) analytical column, and oxalic acid and diglycolic acid as eluents under gradient elution conditions. The complete separation is aided by the ICP-MS system. Using the propose HPIC scheme the full range of REE can be determined in less than 17 min.

The REE were quantified using peak areas. Calibration curves (concentration vs. peak area) were plotted using REE synthetic standard solutions. The REE concentration values obtained for all the analyzed geological materials were corrected for instrumental drift and procedural blank.

The validity of the proposed method is assessed by analysis of two reference materials, BIR-1 and BRP-1. A good agreement between measured values and reference values is found for most REE. Smooth chondrite normalized curves were obtained for all the analyzed reference materials and geological samples. The level of precision found in the experiments depends upon the concentration of a particular REE in the sample solution. Precisions better than 15% RSD were found for samples with high REE concentrations. Higher RSD values were obtained for samples with low REE concentrations (lower than 2,2 mg kg^{-1}), especially for the LREE.

An additional standard addition step was incorporated to the method in order to achieve more reliable results when analyzing samples with low REE abundances. The addition of a known amount of Tm to the sample solutions was used for correction of procedural errors. By using this methodology, precisions ranging from 0,2 to 9% RSD were obtained with comparable accuracies for two samples with low REE abundances. Smooth REE pattern were obtained for the two analyzed samples.

The data collected in the present work demonstrate that the proposed analytical procedure (which includes Tm addition) provides the required accuracy and precision for geochemical studies. This analytical procedure fulfills all the necessary requirements for the following analysis by isotope dilution. That is, the separation of the isotopes studied from the matrix elements which cause interferences in the analysis, and the complete separation of individual REE by HPLC.

7 Indices

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7.2 Abbreviations

°C	degree Celsius
Å	angstrom
a.m.u	atomic mass unit
cm	centimeter
CPS	counts per second
e.g.	*exempli gratia* (for example)
et al.	*et alii* (and others)
etc.	*et cetera* (and so forth)
g	gram
h	hour
HIBA	hydroxyisobutyric acid
HPIC	high performance ion chromatography
HPLC	high performance liquid chromatography
HREE	heavy rare earth elements
i.d.	internal diameter
i.e.	*id est* (that ist)
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ID	isotope dilution
ID-MS	isotope dilution mass spectrometry
INAA	neuron activation analysis
K	Kelvin
kg	kilogram
l	liter
LC	liquid chromatography
LOD	limit of detection
LQD	limit of quantification
LREE	light rare earth elements
m/z	mass to charge
mg	milligram
min	minute
ml	mililiter
mm	millimeter
MREE	middle rare earth elements
MS	mass spectrometer
N	neutron number
n.d.	not detected
NASC	North American Shale Composite

ng	nanogram
PAAS	Post Archean Average Australian Shale
PAR	4-(2-pyridylazo)-resorcinol monosodium salt
PDCA	pyridine-2,6-dicarboxilic acid
PFA	perfluoroalkoxy
ppb	part per billion
PTFE	polytetrafluoroethylene
REE	rare earth elements
RP-HPLC	reversed-phase high performance liquid chromatography
RSD	relative standard deviation
s	standard deviation
UV-Vis	Ultraviolet-visible
v/v	volume in volume
vs.	versus (against)
W	Watt
XRFS	x-ray fluorescence spectrometry
Z	proton number
µg	microgram
µl	microliter
µm	micrometer

7.3 Tables

7.4 Figures

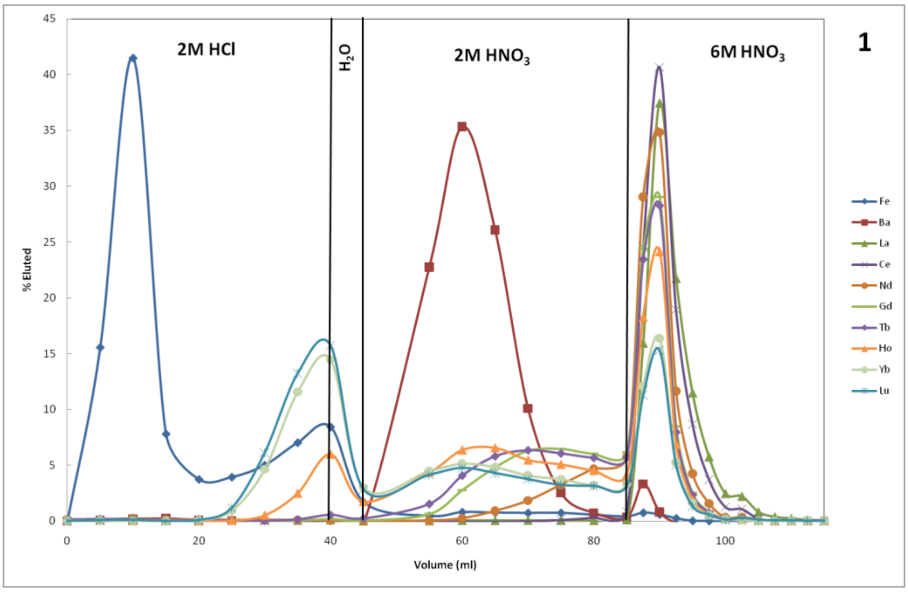
Appendix

A-1. Elution Curves

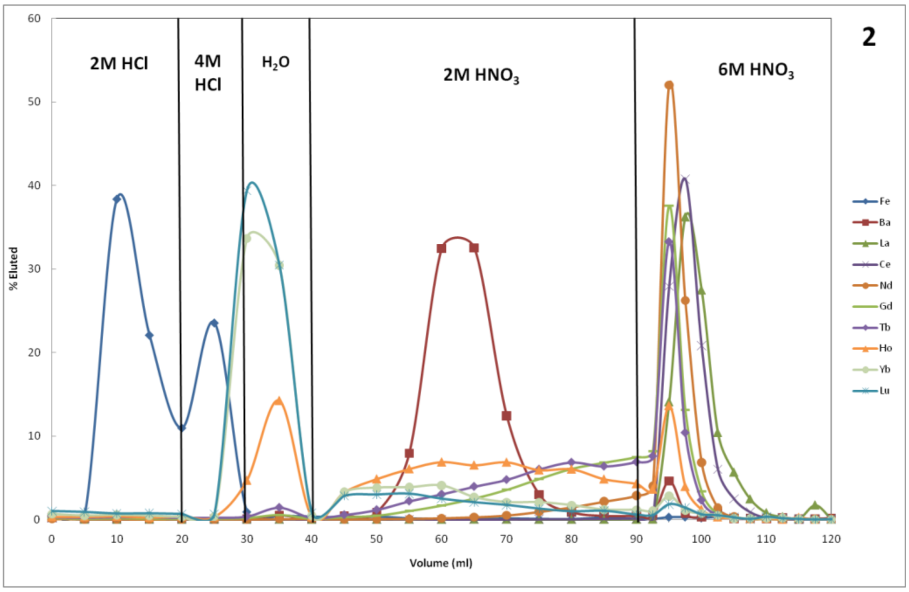
Data shows the percentage amounts of Fe, Ba and eight REE from the sample solution (an alkaline fusion of BRP-1) found in successive fractions eluted from the column.

HCl/HNO$_3$ sequential elution

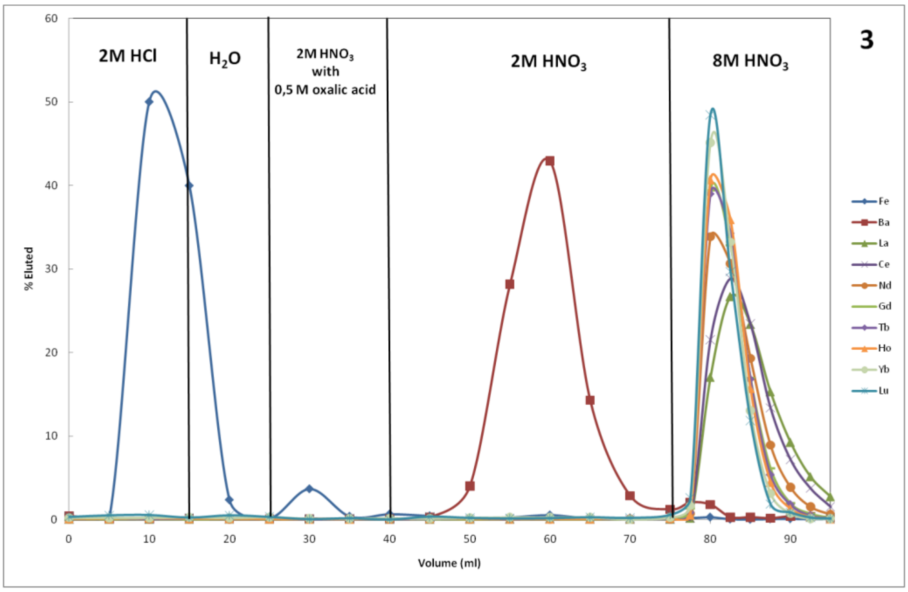
Procedure 1: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Five milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 3 ml Dowex 50W-X8.



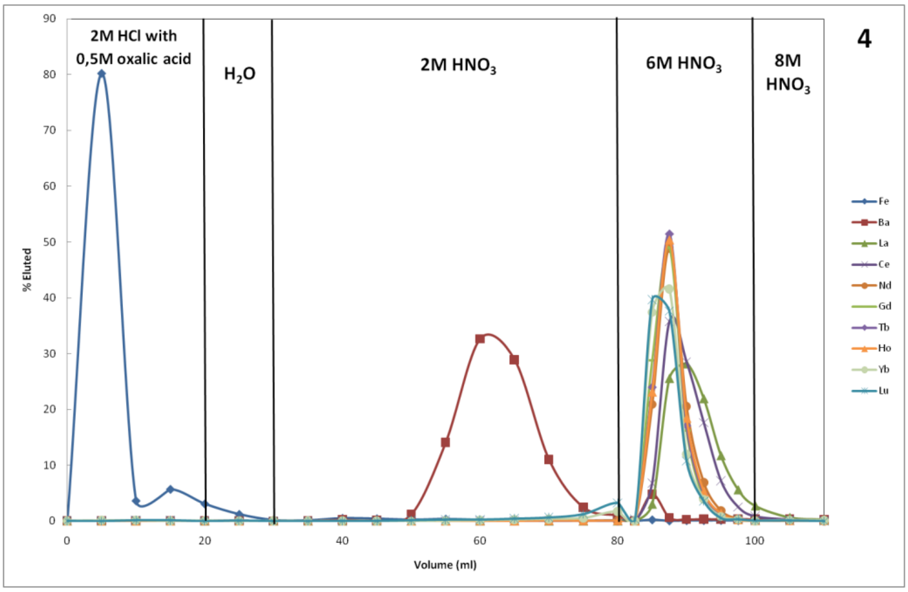
Procedure 2: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Five milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 5 ml Dowex 50W-X8.



Procedure 3: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Five milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 5 ml Dowex 50W-X8.

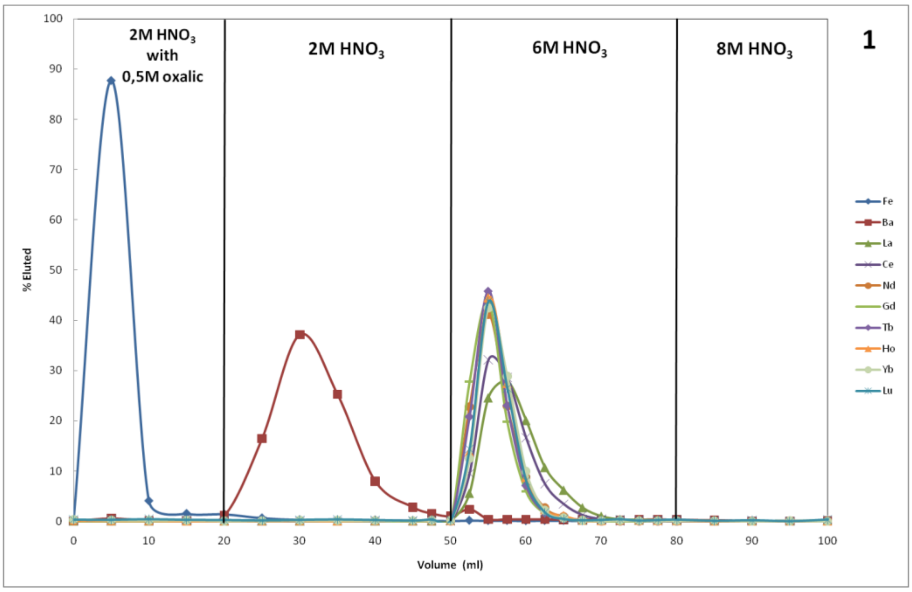


Procedure 4: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Five milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 5 ml Dowex 50W-X8.

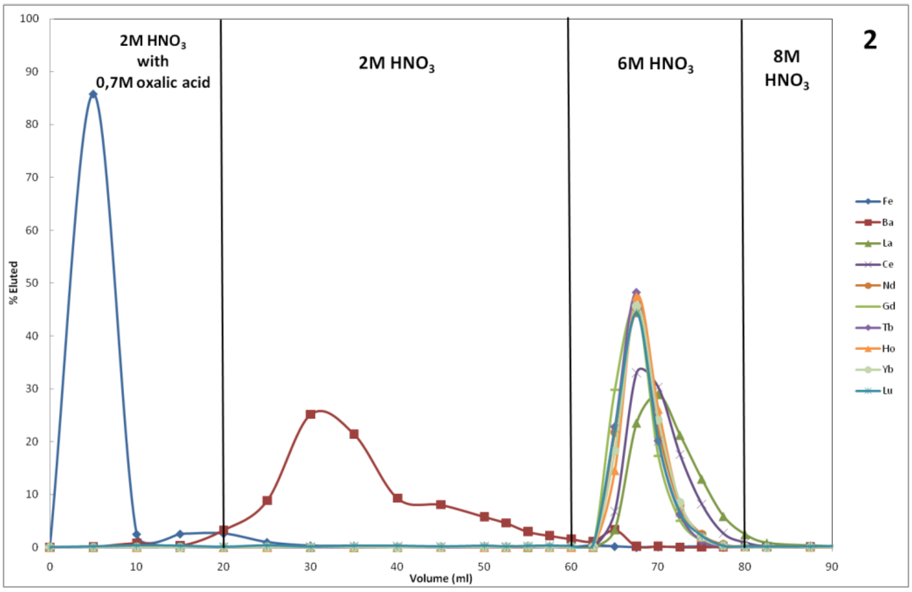


Nitric acid media

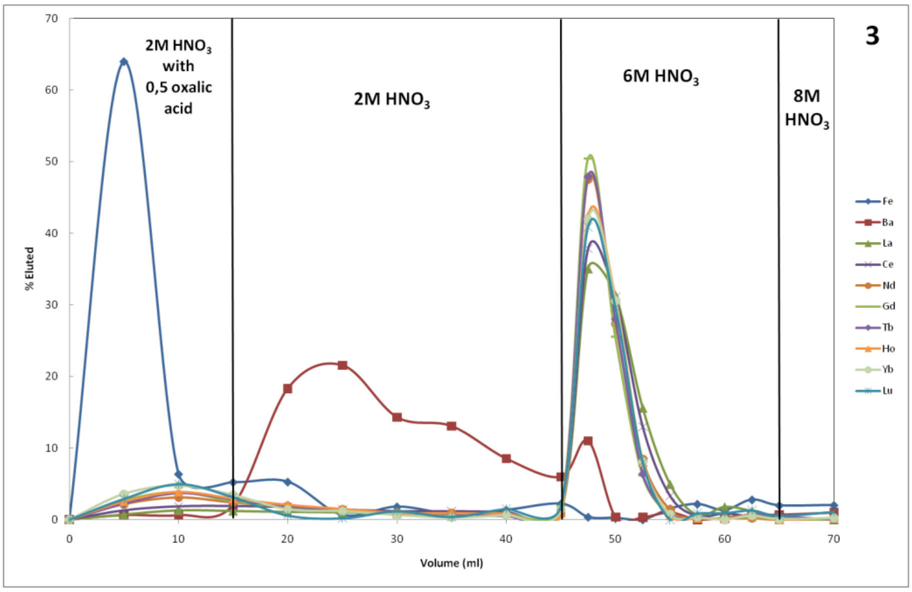
Procedure 1: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Five milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 5 ml Dowex 50W-X8.



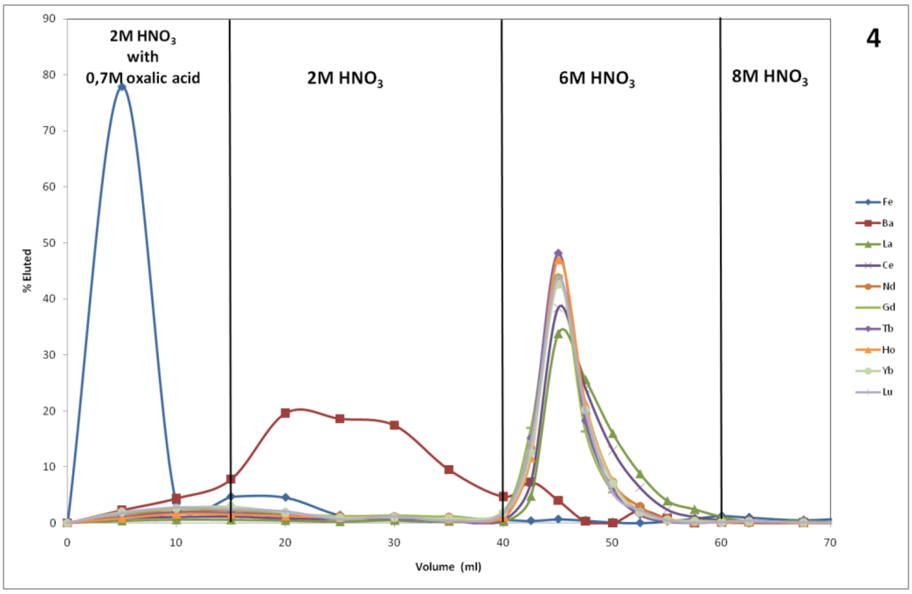
Procedure 2: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Five milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 5 ml Dowex 50W-X8.



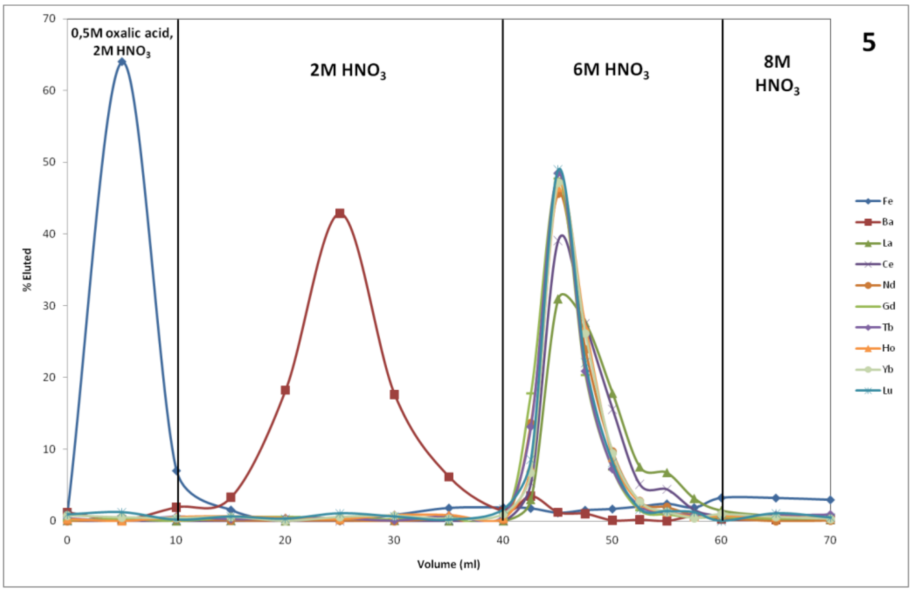
Procedure 3: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. One milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 3 ml Dowex 50W-X8.



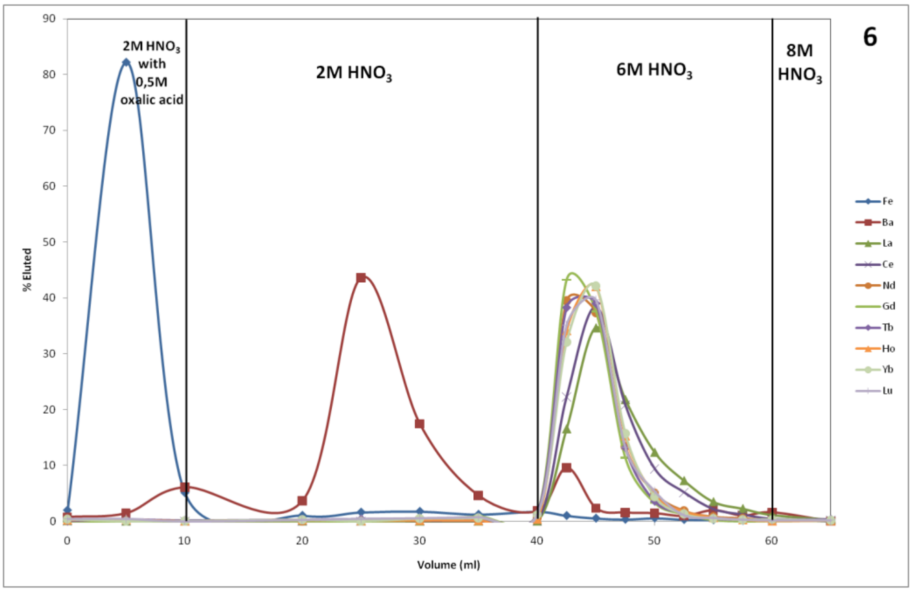
Procedure 4: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. One milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 3 ml Dowex 50W-X8.



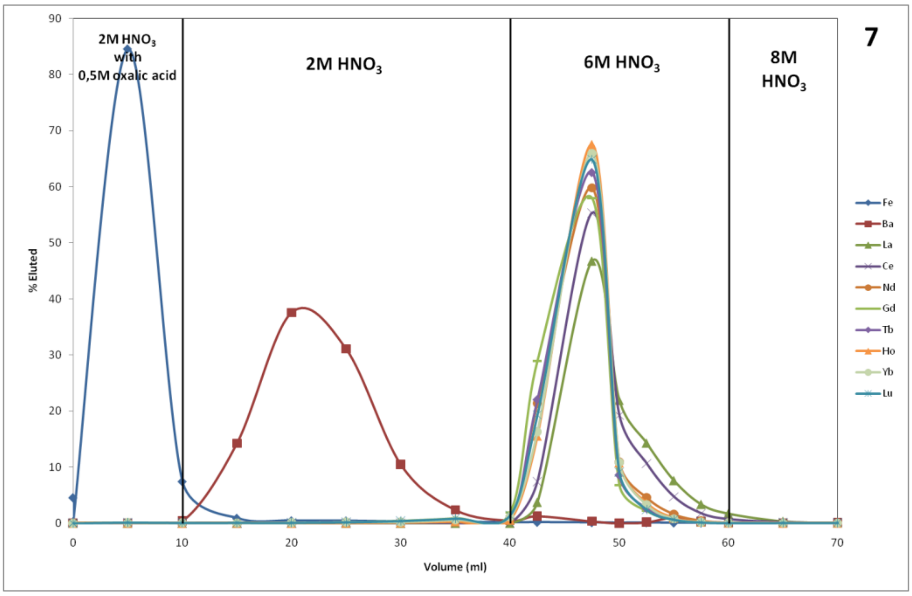
Procedure 5: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. One milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 3 ml Dowex 50W-X8.



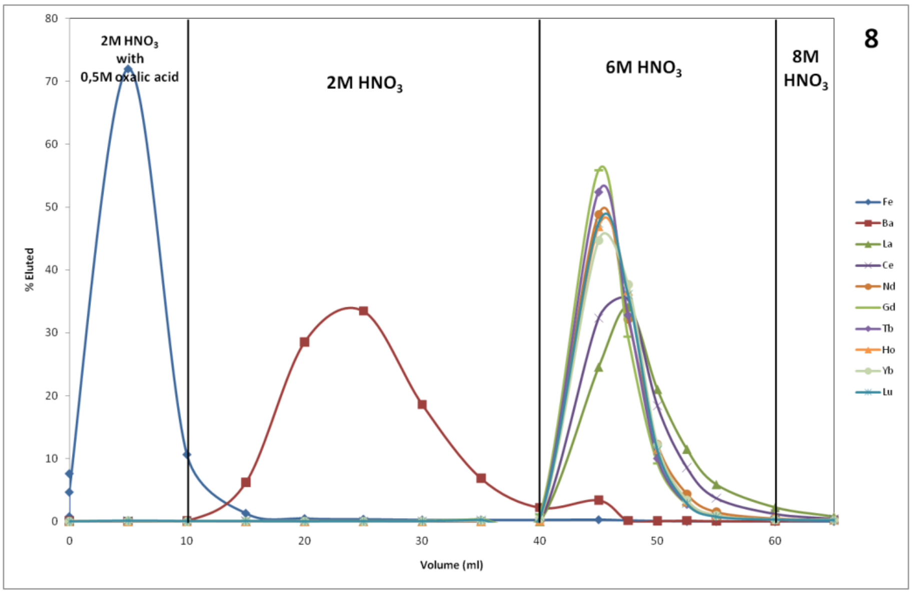
Procedure 6. Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. One milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 3 ml Dowex 50W-X8.



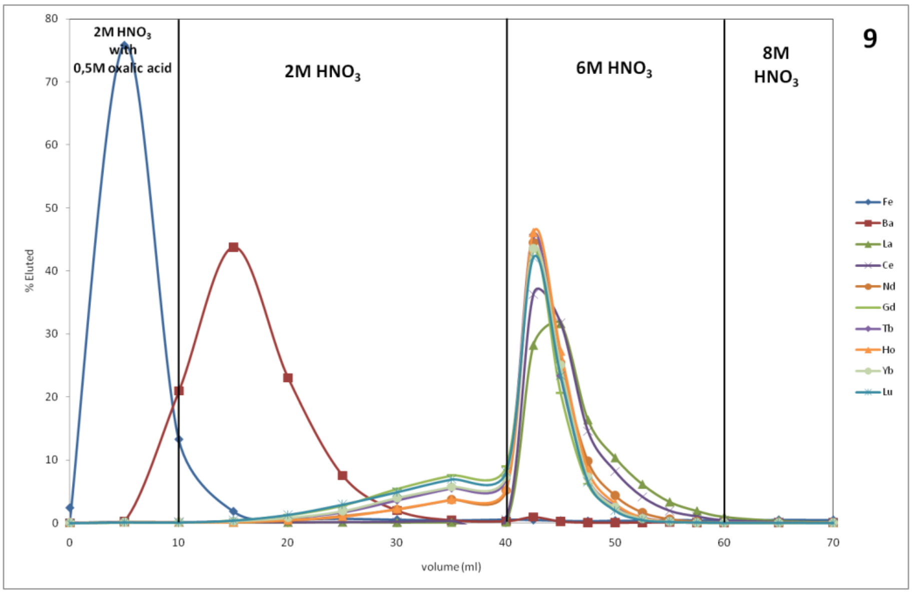
Procedure 7: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Ten milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 3 ml Dowex 50W-X8.



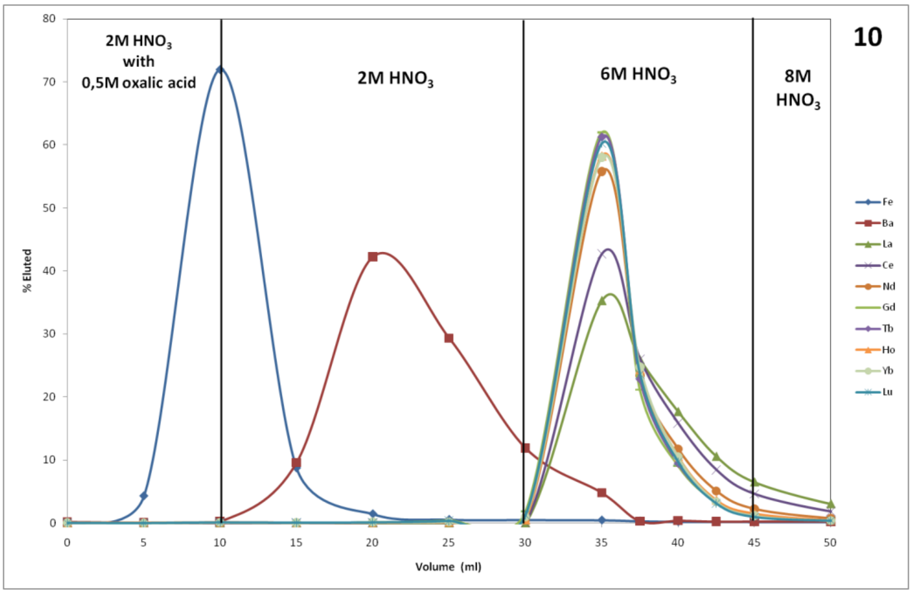
Procedure 8: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Twenty milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 3 ml Dowex 50W-X8.



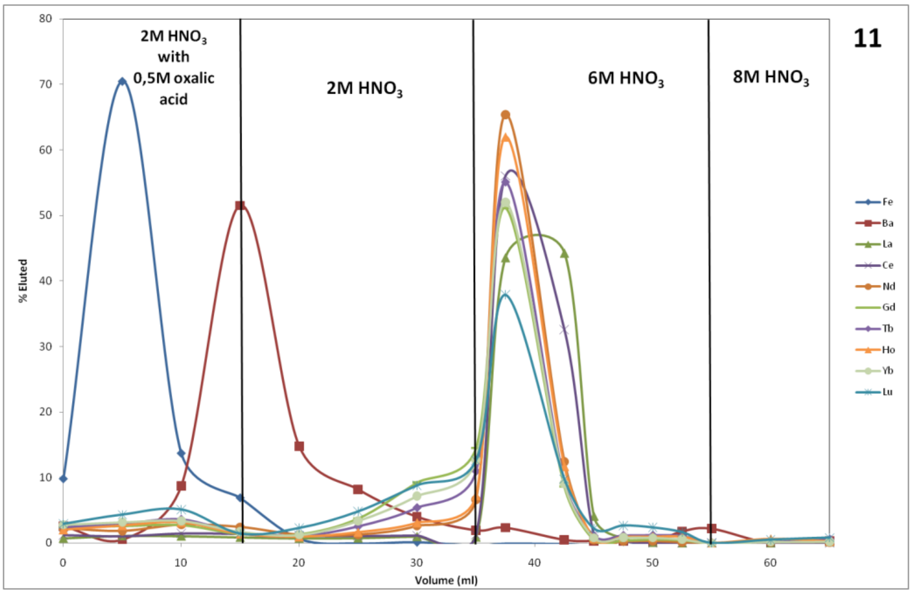
Procedure 9: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Ten milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 2 ml Dowex 50W-X8.



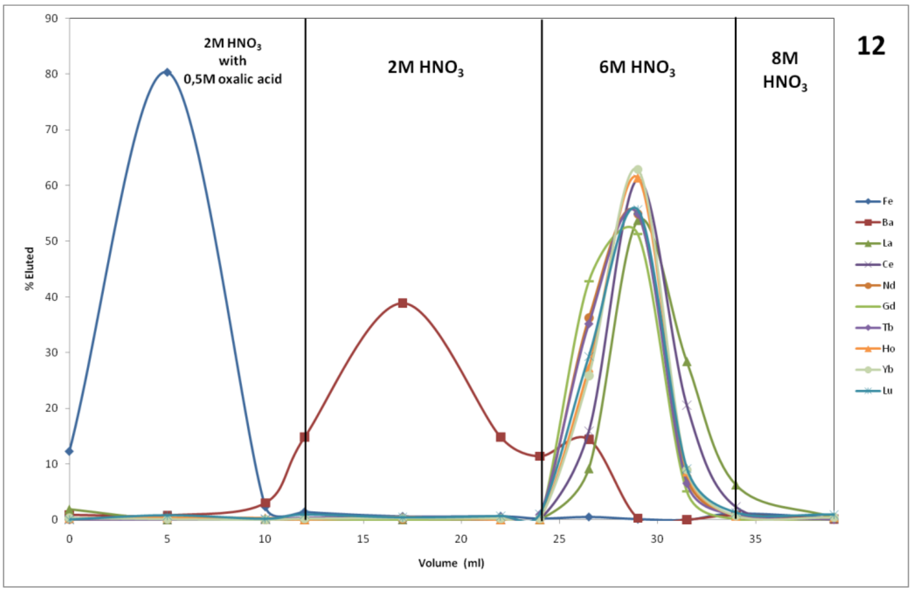
Procedure 10: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Ten milliliter of sample solution were passed through a 10 cm length x 10 mm i.d. glass column packed with 2 ml Dowex 50W-X8.



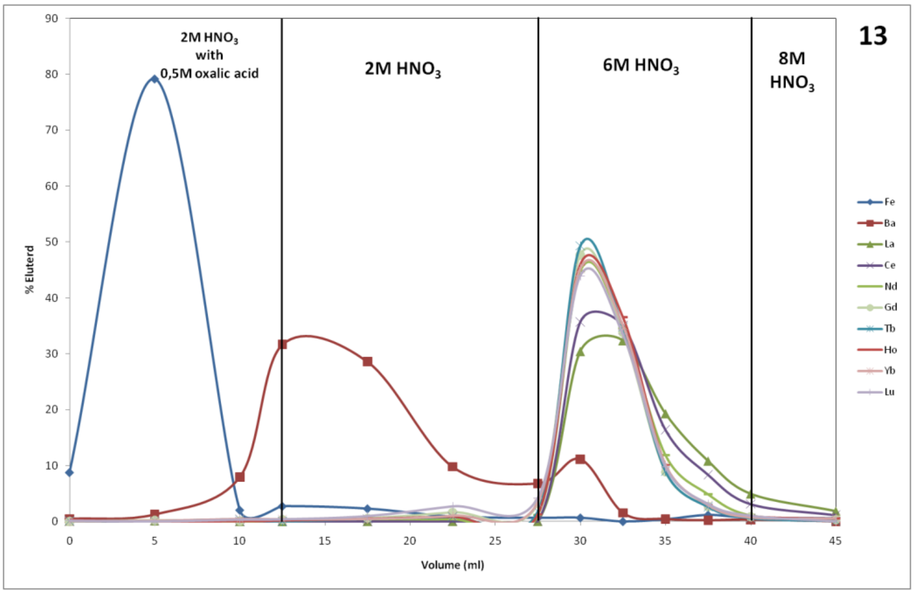
Procedure 11: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. One milliliter of sample solution were passed through a 10 cm length x 5 mm i.d. glass column packed with 2 ml Dowex 50W-X8.



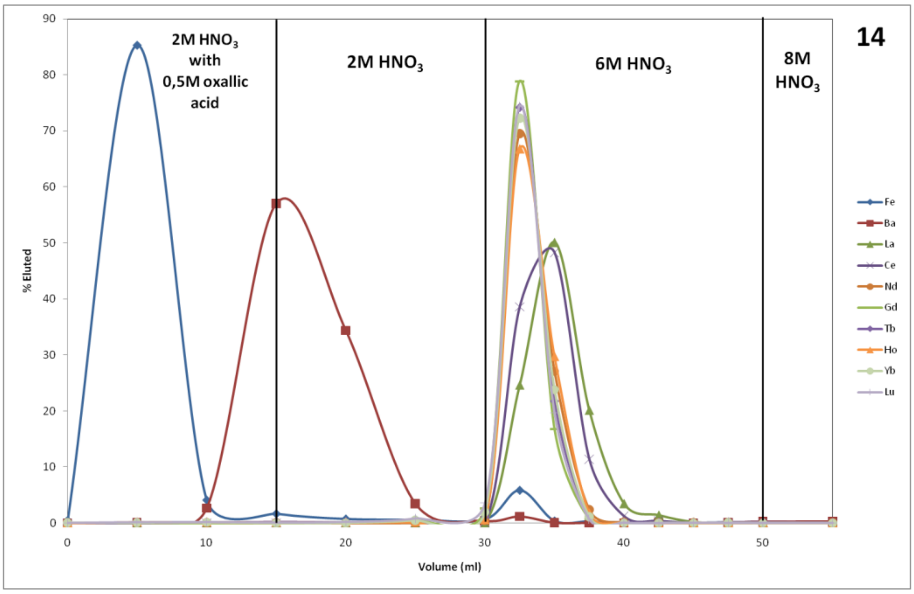
Procedure 12: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. One milliliter of sample solution were passed through a 10 cm length x 5 mm i.d. glass column packed with 2 ml Dowex 50W-X8.



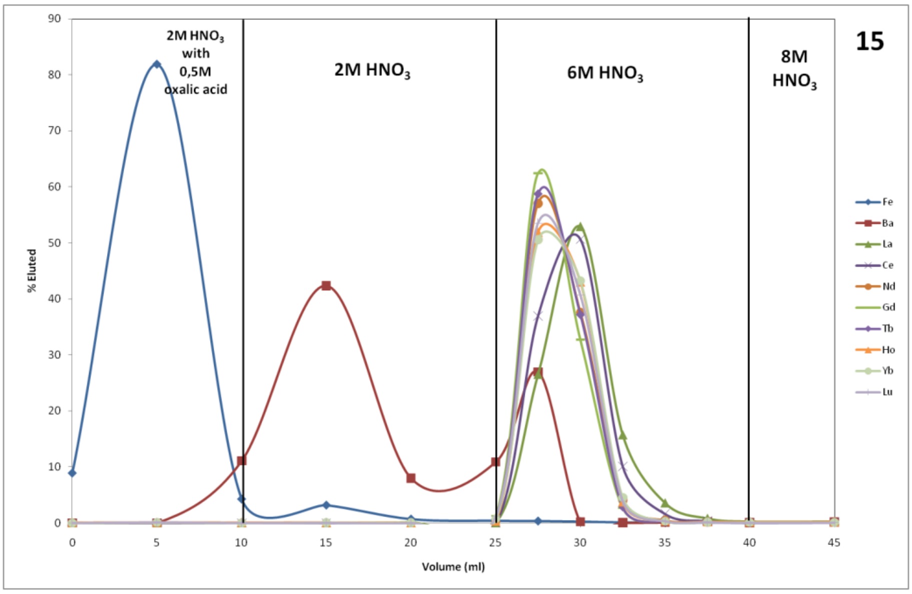
Procedure 13: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. One milliliter of sample solution were passed through a 10 cm length x 5 mm i.d. glass column packed with 2 ml Dowex 50W-X8.



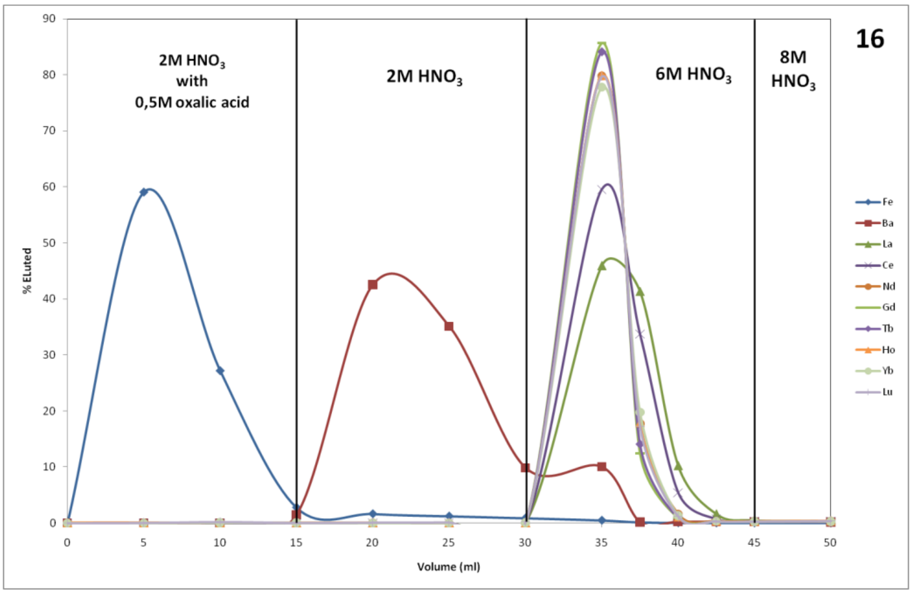
Procedure 14: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Five milliliter of sample solution were passed through a 10 cm length x 5 mm i.d. glass column packed with 2 ml Dowex 50W-X8.



Procedure15: Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Five milliliter of sample solution were passed through a 10 cm length x 5 mm i.d. glass column packed with 2 ml Dowex 50W-X8.



Procedure 16. Amount of eluted elements (%) vs. elution volume. The elution steps are shown in the graphic. Ten milliliter of sample solution were passed through a 10 cm length x 5 mm i.d. glass column packed with 2 ml Dowex 50W-X8.



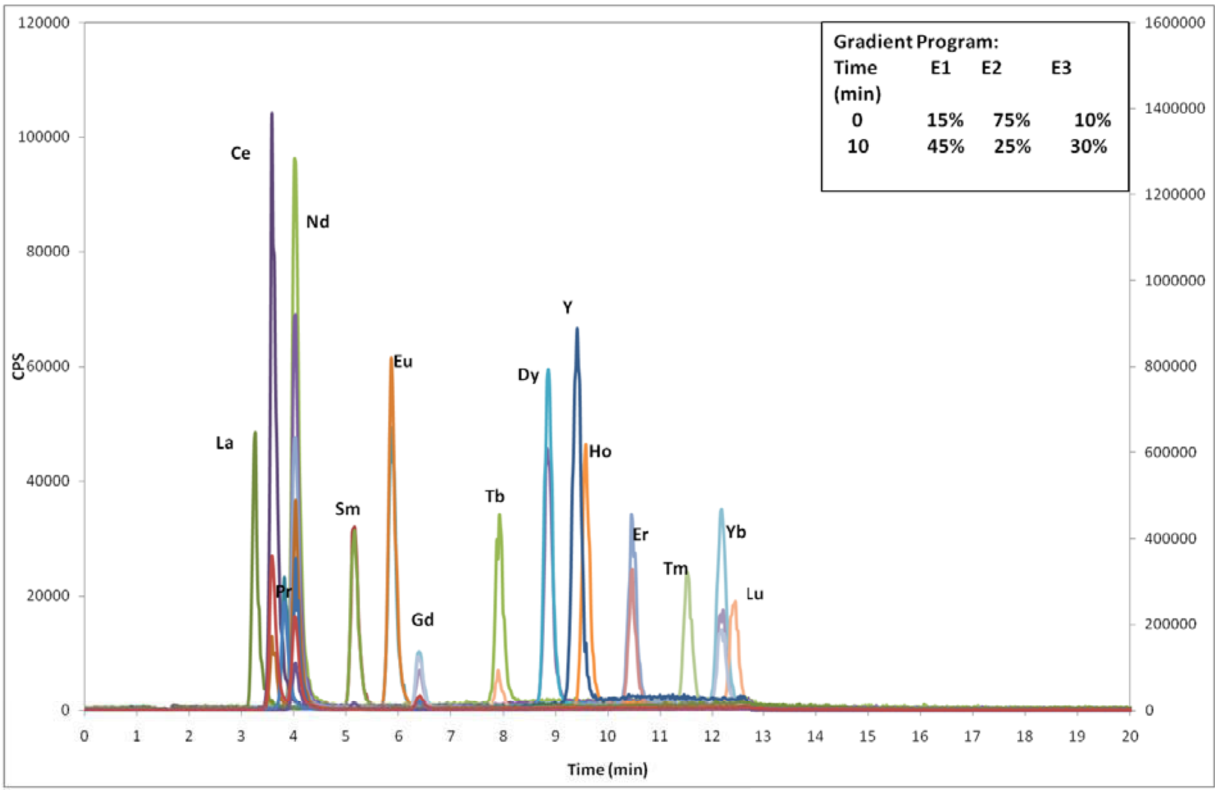
A-2. HPIC Chromatograms

This appendix includes the ion chromatograms obtained during the separation process optimization by HPIC, which were not shown in the text. The chromatographic peaks for Y, La, Ce, Pr, and Nd are plotted using a secondary y-axis for better visualization.

The elution programs are shown in the respective chromatogram. E1, E2 and E3 make reference to the eluents used as mobile phase, where:
E1 = deionized water,
E2 = 0,1 mol l^{-1} oxalic acid,
E3 = 0,1 mol l^{-1} diglycolic acid.

The pH of E2 and E3 was adjusted to 4,8, except where is specified.

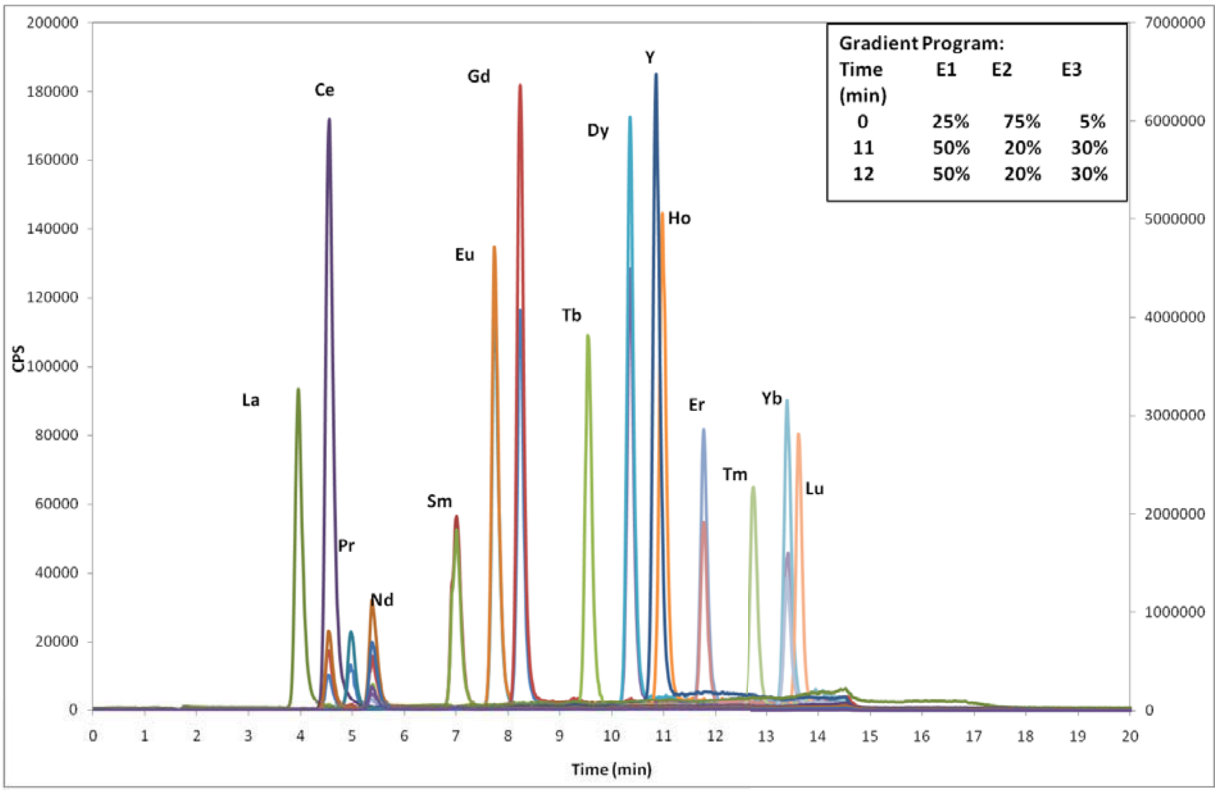
Chromatogram 1



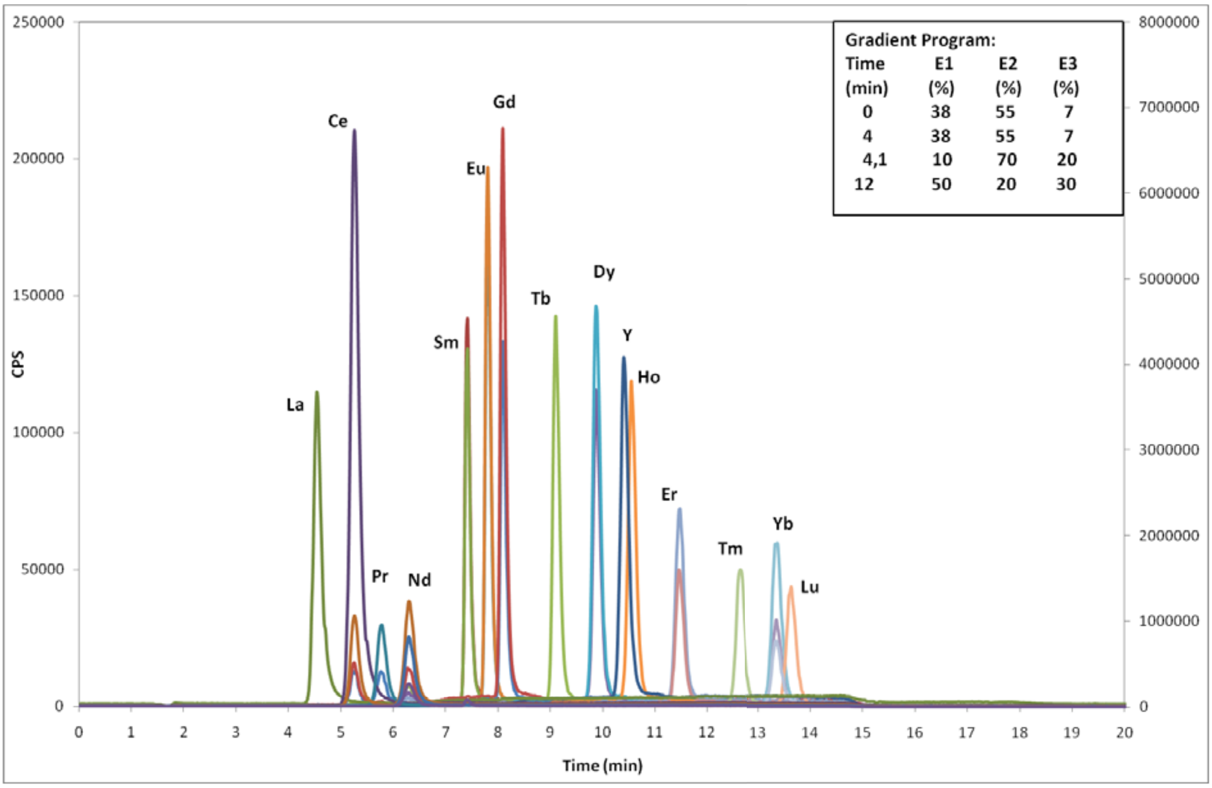
Gradient Program:

Time (min)	E1	E2	E3
0	15%	75%	10%
10	45%	25%	30%

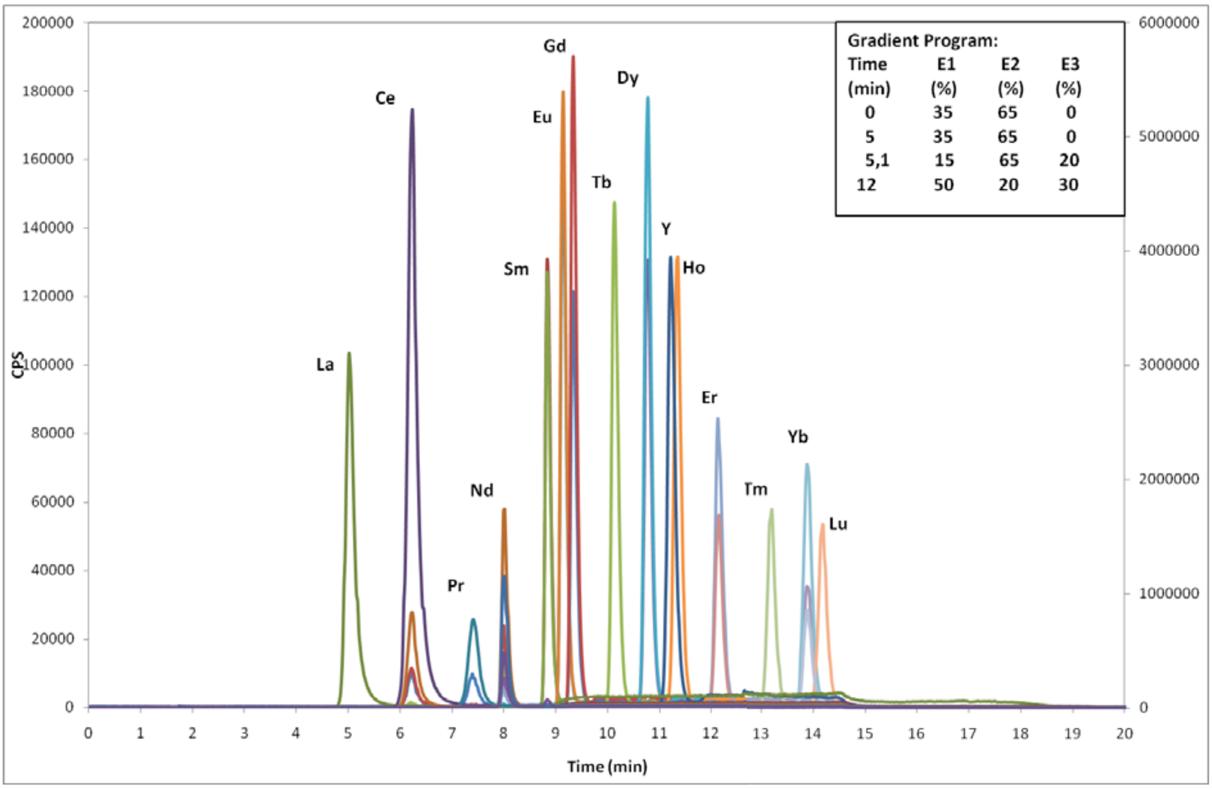
Chromatogram 2



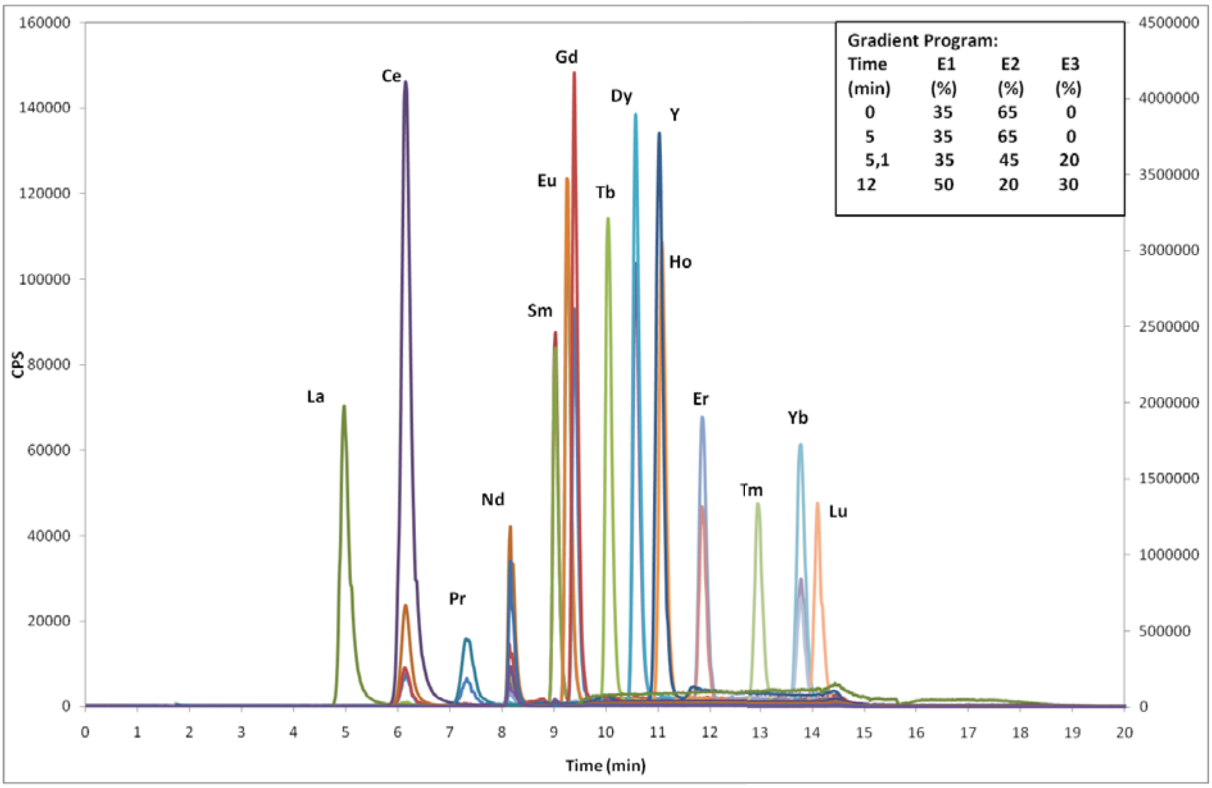
Chromatogram 3



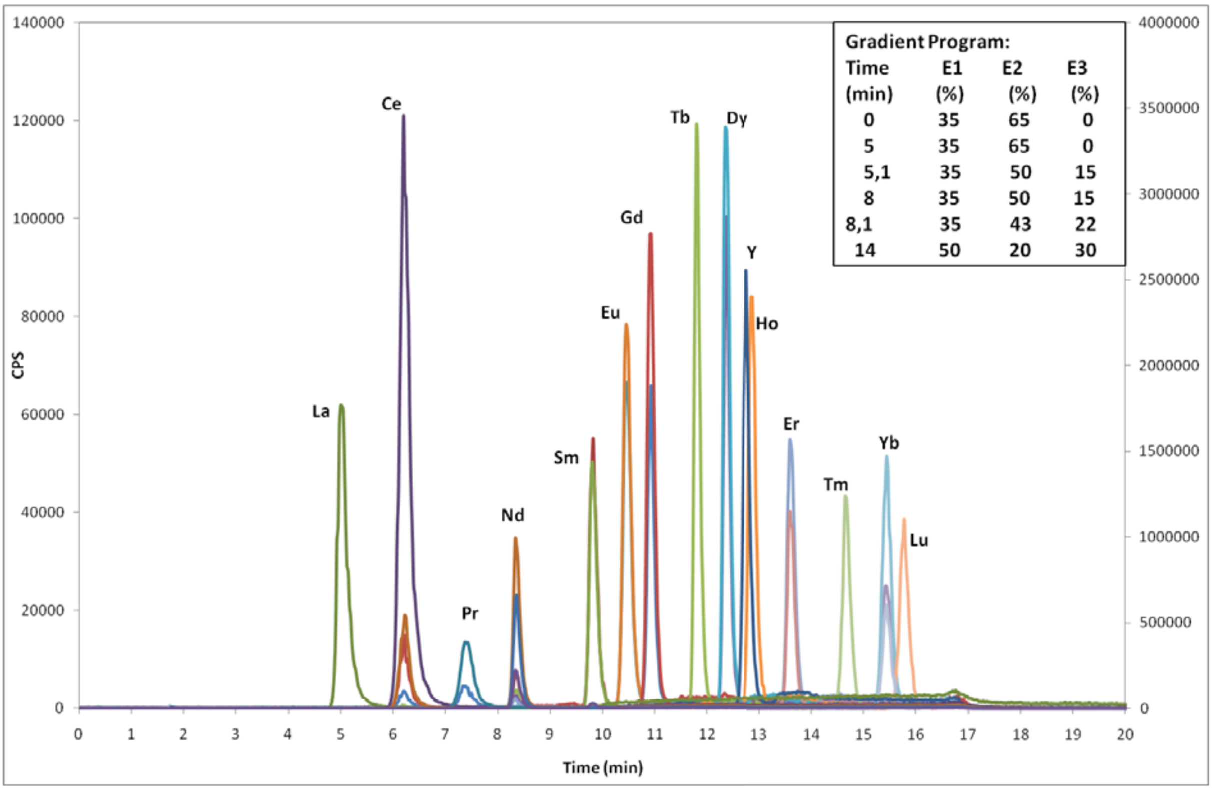
Chromatogram 4



Chromatogram 5



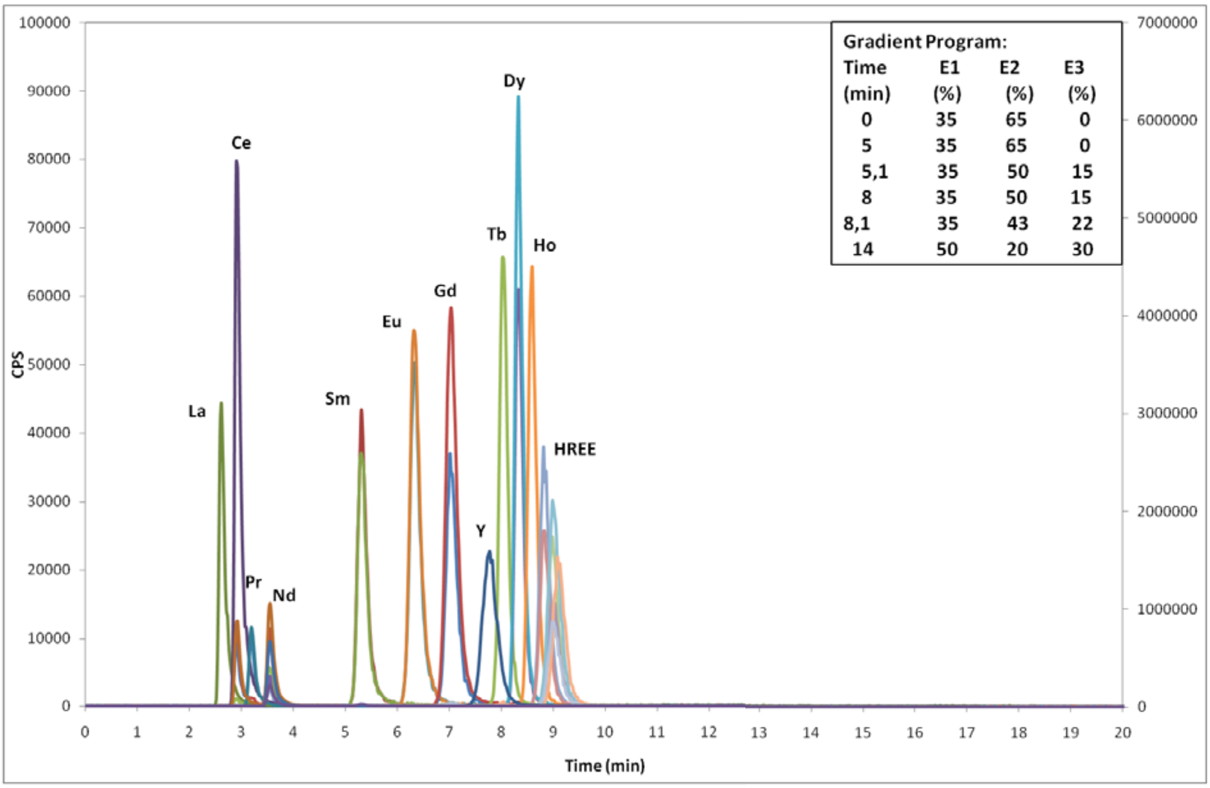
Chromatogram 6



Gradient Program:

Time (min)	E1 (%)	E2 (%)	E3 (%)
0	35	65	0
5	35	65	0
5,1	35	50	15
8	35	50	15
8,1	35	43	22
14	50	20	30

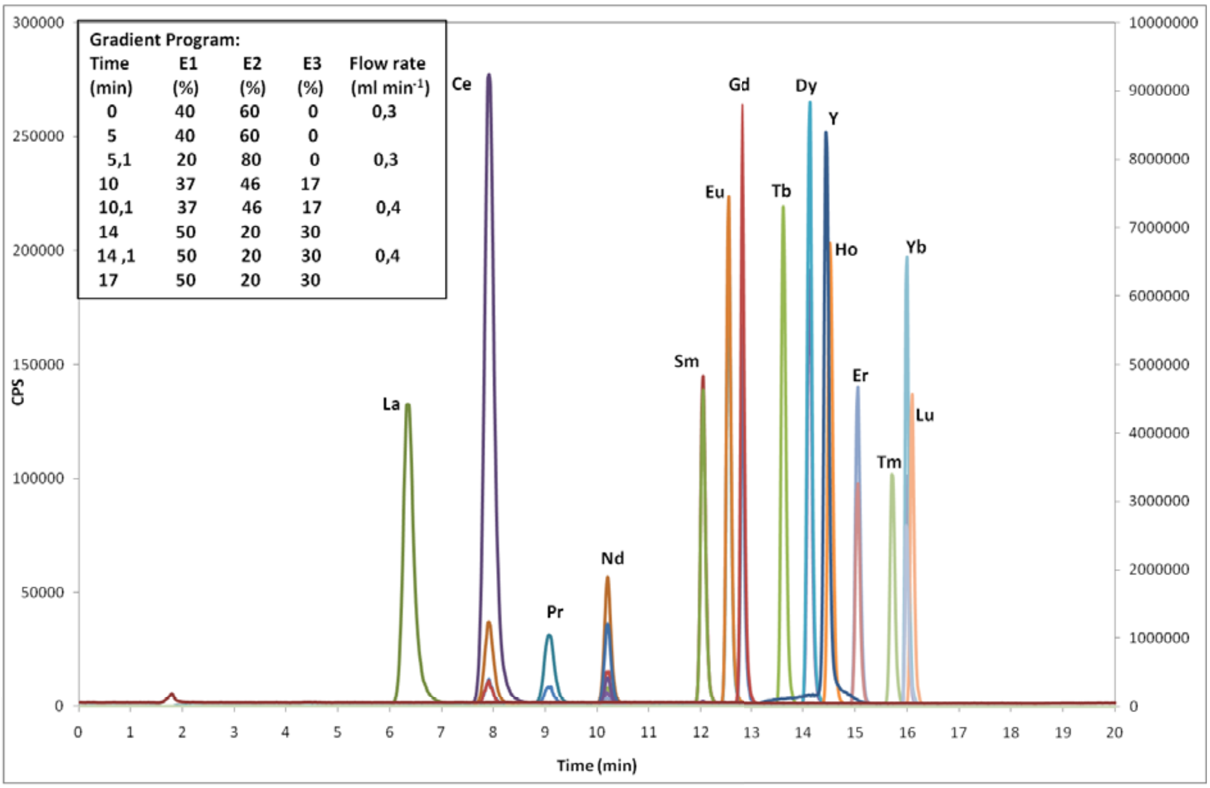
Chromatogram 7. Here the pH of eluents E2 and E3 was adjusted to 4,3.



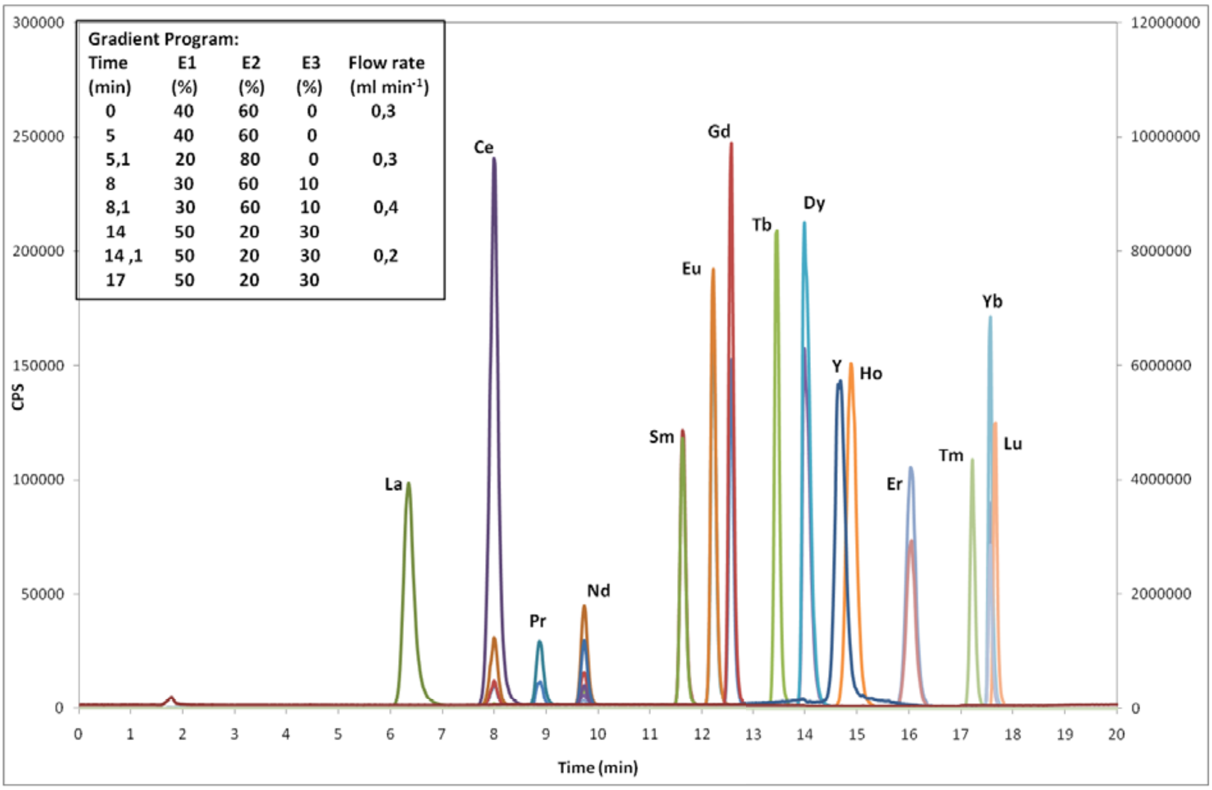
Gradient Program:

Time (min)	E1 (%)	E2 (%)	E3 (%)
0	35	65	0
5	35	65	0
5,1	35	50	15
8	35	50	15
8,1	35	43	22
14	50	20	30

Chromatogram 8



Chromatogram 9



A-3. Measured Data

This appendix contains the measured data on REE concentration (mg kg^{-1}) that was obtained for each analyzed sample using the proposed method (without Tm correction). The reference values are from [51].

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
BCR-2														
	27,0	59,9	7,6	31,2	6,47	1,86	7,14	1,09	6,78	1,39	3,94	0,59	3,68	0,54
	29,6	64,5	6,9	35,1	7,46	2,27	7,96	1,30	8,16	1,60	4,32	0,63	4,02	0,57
Mean value	28,3	62,2	7,3	33,1	6,96	2,06	7,55	1,19	7,47	1,49	4,13	0,61	3,85	0,56
s	1,8	3,3	0,5	2,8	0,70	0,29	0,57	0,15	0,98	0,15	0,27	0,03	0,25	0,02
%RSD	6,4	5,2	6,4	8,3	10,1	14,0	7,6	12,5	13,1	10,3	6,5	5,6	6,4	3,3
Ref. value	24,9	52,9	6,7	28,7	6,58	1,96	6,75	1,07	6,41	1,28	3,66	0,54	3,38	0,5
BHVO-2														
	15,0	38,1	5,2	23,1	4,66	1,51	5,28	0,83	4,94	0,92	2,41	0,32	1,81	0,25
	15,5	41,8	4,9	25,9	5,56	1,83	5,87	1,00	5,80	1,08	2,65	0,37	2,17	0,24
Mean value	15,2	40,0	5,0	24,5	5,11	1,67	5,58	0,92	5,37	1,00	2,53	0,35	1,99	0,25
s	0,3	2,6	0,3	2,0	0,63	0,23	0,42	0,12	0,61	0,11	0,17	0,03	0,26	0,00
%RSD	2,2	6,6	5,0	8,3	12,4	13,5	7,5	13,3	11,3	11,3	6,7	9,8	12,9	0,8
Ref. value	15,2	37,5	5,35	24,5	6,07	2,07	6,24	0,92	5,31	0,98	2,54	0,33	2,0	0,27
BIR-1														
	0,722	2,34	0,44	2,82	1,13	0,54	2,13	0,42	3,24	0,69	2,07	0,32	2,08	0,31
	0,422	1,72	0,35	2,34	0,99	0,48	1,76	0,37	2,91	0,62	1,87	0,26	1,73	0,26
	0,820	2,46	0,38	2,38	0,95	0,44	1,71	0,35	2,63	0,58	1,75	0,27	1,63	0,24
Mean value	0,655	2,17	0,39	2,52	1,02	0,49	1,87	0,38	2,93	0,63	1,89	0,28	1,82	0,27
s	0,207	0,40	0,05	0,26	0,09	0,05	0,23	0,04	0,31	0,05	0,16	0,03	0,24	0,04
%RSD	31,6	18,2	11,6	10,5	9,3	10,3	12,5	9,8	10,6	8,3	8,7	12,4	13,1	14,3
Ref. value	0,615	1,92	0,37	2,38	1,12	0,53	1,87	0,36	2,51	0,56	1,66	0,25	1,65	0,25

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
BRP-1														
	43,8	101,0	12,2	50,0	8,2	2,4	8,5	1,29	7,8	1,49	3,9	0,51	2,86	0,39
	43,0	97,8	12,4	49,5	8,4	2,5	8,7	1,43	8,6	1,64	4,1	0,57	3,27	0,44
	41,2	94,7	12,4	53,5	10,4	3,1	10,1	1,48	8,7	1,62	4,3	0,60	3,57	0,49
Mean value	42,6	97,9	12,3	51,0	9,0	2,7	9,1	1,40	8,4	1,59	4,1	0,56	3,23	0,44
s	1,3	3,2	0,1	2,1	1,2	0,4	0,9	0,10	0,5	0,08	0,2	0,04	0,35	0,05
%RSD	3,1	3,2	1,0	4,2	13,7	14,9	9,8	6,9	6,1	5,0	5,2	7,5	11,0	11,3
Ref. value	42,6	93,3	12,3	51,9	11,2	3,42	10,4	1,52	8,5	1,62	4,2	0,57	3,48	0,50

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
OKUM														
	0,69	1,42	0,26	1,51	0,63	0,29	1,09	0,22	1,57	0,35	1,11	0,16	0,99	0,14
	0,78	1,37	0,27	1,61	0,83	0,33	1,30	0,23	1,68	0,38	1,16	0,17	1,05	0,16
	0,44	0,82	0,16	1,05	0,52	0,23	0,95	0,18	1,34	0,28	0,86	0,14	0,86	0,13
Mean value	0,63	1,20	0,23	1,39	0,66	0,28	1,12	0,21	1,53	0,34	1,04	0,16	0,97	0,14
s	0,17	0,33	0,06	0,30	0,16	0,05	0,18	0,03	0,17	0,05	0,16	0,02	0,10	0,01
%RSD	27,6	27,7	26,1	21,3	24,0	18,0	15,8	12,8	11,3	15,3	15,1	10,2	10,3	9,2
Ref. value	0,41	1,29	0,24	1,51	0,71	0,30	1,15	0,22	1,61	0,35	1,04	0,15	1,01	0,15
OPC-1														
	25,4	49,9	7,16	27,9	6,10	1,35	4,94	0,64	3,67	0,75	1,96	0,30	1,77	0,25
	26,6	49,5	6,61	26,4	5,28	1,07	4,31	0,52	2,97	0,59	1,58	0,24	1,37	0,21
	22,4	39,7	5,78	23,8	5,28	1,18	4,50	0,61	3,43	0,63	1,72	0,28	1,68	0,26
Mean value	24,8	46,4	6,52	26,0	5,55	1,20	4,58	0,59	3,36	0,66	1,76	0,28	1,61	0,24
s	2,2	5,8	0,69	2,1	0,48	0,14	0,32	0,06	0,36	0,09	0,19	0,03	0,21	0,02
%RSD	8,9	12,5	10,7	7,9	8,6	11,7	7,1	10,3	10,6	13,2	11,0	10,5	13,1	9,3
Ref. value	23,1	42,9	6,22	23,6	4,39	0,98	3,63	0,51	2,79	0,54	1,49	0,21	1,32	0,19

	La	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
OU-1														
	17,6	37,7	5,5	19,0	3,0	0,7	3,3	0,60	3,76	0,80	2,21	0,34	2,13	0,303
	18,1	40,8	4,6	17,9	2,8	0,7	2,9	0,52	3,49	0,73	2,19	0,32	2,04	0,301
Mean value	17,9	39,2	5,1	18,4	2,9	0,7	3,1	0,56	3,63	0,76	2,20	0,33	2,09	0,302
s	0,4	2,2	0,6	0,8	0,2	0,0	0,3	0,06	0,19	0,05	0,01	0,02	0,06	0,001
%RSD	2,2	5,7	11,5	4,5	5,3	2,2	9,8	10,4	5,3	6,6	0,6	4,6	3,0	0,4
Ref. value	18,8	38,0	4,7	18,7	3,9	1,0	3,7	0,61	3,65	0,75	2,20	0,34	2,2	0,34
SCO-1														
	29,0	57,7	6,9	25,5	4,7	1,0	4,3	0,6	3,9	0,80	2,3	0,35	2,20	0,34
	28,5	58,2	5,9	26,9	5,0	1,0	4,4	0,7	4,3	0,89	2,4	0,38	2,36	0,35
Mean value	28,7	58,0	6,4	26,2	4,8	1,0	4,3	0,7	4,1	0,84	2,3	0,36	2,28	0,34
s	0,4	0,4	0,7	1,0	0,2	0,0	0,1	0,0	0,3	0,06	0,0	0,03	0,12	0,01
%RSD	1,3	0,6	10,8	3,9	4,3	4,8	1,5	5,1	7,1	7,3	1,5	7,0	5,1	2,0
Ref. value	29,5	62	7,1	26	5,3	1,19	4,6	0,7	4,2	0,97	2,5	0,42	2,27	0,34
WGB-1														
	7,26	15,72	2,14	9,39	2,28	1,02	2,64	0,42	2,69	0,53	1,51	0,21	1,31	0,20
	7,16	18,03	2,94	10,42	2,98	1,34	3,18	0,54	3,33	0,63	1,79	0,26	1,61	0,23
	9,30	19,17	2,41	11,36	2,80	1,27	3,11	0,53	3,43	0,66	1,89	0,26	1,58	0,22
Mean value	7,91	17,64	2,50	10,39	2,68	1,21	2,98	0,50	3,15	0,61	1,73	0,24	1,50	0,21
s	1,21	1,76	0,41	0,99	0,36	0,17	0,29	0,06	0,40	0,07	0,20	0,03	0,16	0,02
%RSD	15,3	10,0	16,3	9,5	13,5	13,9	9,8	13,1	12,7	11,1	11,4	12,8	10,9	7,8
Ref. value	7,80	17,00	2,23	10,00	2,80	1,27	2,94	0,47	2,92	0,58	1,65	0,23	1,42	0,21

A-4. Tm correction

This appendix shows the measured REE concentration (mg kg-1) for MUH-1 and OKUM ontained using the proposed method and the corresponding concentration value obtained before and after correction with Tm for comparison.

OKUM

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu
Before Tm correction													
Sample													
O01	0,451	1,533	0,245	1,458	0,667	0,275	1,117	0,209	1,558	0,338	1,061	0,973	0,143
O02	0,280	0,909	0,162	0,954	0,450	0,205	0,803	0,143	1,086	0,233	0,742	0,657	0,099
O03	0,307	1,031	0,176	1,102	0,486	0,210	0,854	0,166	1,220	0,262	0,805	0,748	0,111
Mean value	0,346	1,158	0,194	1,172	0,535	0,230	0,925	0,173	1,288	0,278	0,870	0,793	0,118
s	0,092	0,331	0,044	0,259	0,116	0,039	0,169	0,033	0,243	0,054	0,169	0,163	0,023
%RSD	26,5	28,6	22,8	22,1	21,8	17,0	18,2	19,1	18,9	19,6	19,4	20,5	19,3
After Tm correction													
O01	0,453	1,540	0,246	1,465	0,670	0,276	1,123	0,210	1,566	0,340	1,066	0,978	0,144
O02	0,416	1,350	0,240	1,417	0,668	0,305	1,192	0,213	1,612	0,346	1,102	0,975	0,147
O03	0,402	1,349	0,231	1,442	0,636	0,274	1,117	0,217	1,596	0,343	1,054	0,979	0,145
Mean value	0,424	1,413	0,239	1,441	0,658	0,285	1,144	0,213	1,591	0,343	1,074	0,977	0,146
s	0,026	0,110	0,008	0,024	0,019	0,017	0,042	0,004	0,024	0,003	0,025	0,002	0,002
%RSD	6,2	7,8	3,3	1,7	2,9	6,0	3,6	1,9	1,5	0,9	2,3	0,2	1,2
Ref. value	0,413	1,294	0,237	1,505	0,711	0,300	1,147	0,224	1,610	0,351	1,042	1,009	0,148

MUH-1

	La	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**	**Lu**
Before Tm correction													
Sample													
M01	0,143	0,209	0,032	0,157	0,051	0,020	0,089	0,018	0,139	0,032	0,100	0,106	0,017
M02	0,157	0,222	0,034	0,168	0,062	0,024	0,101	0,020	0,148	0,034	0,107	0,113	0,018
M03	0,154	0,224	0,035	0,183	0,059	0,023	0,104	0,021	0,148	0,035	0,105	0,113	0,018
M04	0,158	0,233	0,034	0,181	0,061	0,025	0,106	0,021	0,157	0,036	0,110	0,119	0,019
Mean value	0,153	0,222	0,034	0,172	0,058	0,023	0,100	0,020	0,148	0,034	0,105	0,113	0,018
s	0,007	0,010	0,002	0,012	0,005	0,002	0,008	0,001	0,007	0,002	0,005	0,005	0,001
%RSD	4,5	4,6	4,6	7,0	8,6	9,8	7,5	6,0	4,9	4,9	4,3	4,4	5,5
After Tm correction													
M01	0,155	0,226	0,034	0,170	0,055	0,021	0,096	0,020	0,151	0,035	0,108	0,115	0,018
M02	0,174	0,246	0,038	0,186	0,069	0,027	0,112	0,022	0,163	0,037	0,118	0,125	0,019
M03	0,163	0,236	0,037	0,193	0,062	0,024	0,109	0,022	0,157	0,036	0,111	0,120	0,019
M04	0,158	0,233	0,034	0,181	0,061	0,025	0,106	0,021	0,157	0,036	0,110	0,118	0,019
Mean value	0,162	0,235	0,036	0,183	0,062	0,024	0,106	0,021	0,157	0,036	0,112	0,120	0,019
s	0,008	0,008	0,002	0,010	0,006	0,002	0,007	0,001	0,005	0,001	0,004	0,004	0,001
%RSD	5,2	3,5	6,1	5,2	9,1	9,6	6,4	5,4	3,3	2,7	4,0	3,4	3,6

A-5. Photos

1. Sample sintering. The sample and some Na_2O_2 were placed in carbon crucibles for sintering in a muffle furnace.

2. Resin Dowex 50W-X8.

3. Eluent evaporation after cation exchange matrix separation

4. HPIC system.