A comparison of INAA and high performance liquid chromatography for the determination of rare earth elements in geological materials

A. M. G. Figueiredo,* N. M. P. de Moraes, H. M. Shihomatsu

Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, Caixa Postal 11 049, CEP 05422-970, São Paulo, SP, Brazil

Procedures for the determination of traces of rare earth elements (REE) in geological samples by instrumental neutron activation analysis (INAA) and high resolution liquid chromatography (HPLC) are presented. The international standard reference materials AGV-1, GSP-1 and G-2 (USGS) were tested for the determination of REE concentrations using both techniques. The results obtained showed good agreement with certified values, giving relative errors less than 10%. By using INAA, the REE La, Ce, Nd, Sm, Eu, Tb, Yb and Lu were determined. All the REE, except Dy and Y, were determined when HPLC was employed. The application of INAA and HPLC to the determination of REE in geological samples is also discussed.

Introduction

Trace element geochemistry is an important tool for understanding the global geodynamical processes. Rare earth elements (REE's) have been widely used in petrogenetic studies of igneous rocks, since they allow the comprehension of the main processes involved in the generation of the magma.[1] In order to study REE geochemistry, a large number of samples is needed, and accurate and rapid analytical techniques must be available. Among the different analytical procedures used to determine REE's, instrumental neutron activation analysis (INAA) and high performance liquid chromatography (HPLC) have special place due to their high sensitivity, accuracy and precision, for most of the REE's.[2] INAA has the advantage of being a non-destructive and multi-elemental technique. The sample does not have to be put into solution, and this fact provides relative freedom from analytical blanks. INAA has been widely used for the determination of REE's in geological samples due to their nuclear characteristics, particularly appropriate to neutron activation.[3] More recently, studies employing HPLC technique have shown that this analytical technique can provide rapid and accurate results for the determination of all the REE's.[4] The selectivity, the necessity of few milligrams of the sample and analysis of several elements simultaneously in short time are some advantages of this technique. On the other hand, HPLC requires the chemical dissolution of the sample, as well as a previous separation of REE's from most of major rock components to prevent overloading and precipitation of interfering elements in the column, besides their interference with the post-column reaction detection.

In the present paper, INAA and HPLC were applied to the determination of REE elements in the geological reference materials AGV-1, G-2 and GSP-1 (USGS). The accuracy, detection limits, advantages and disadvantages of each technique are discussed.

Experimental

Instrumental neutron activation analysis (INAA)

About 100 mg of the sample were accurately weighed in polyethylene vials. Elemental synthetic standards of the REE's were prepared by dissolving their respective calcined oxides (Johnson Mathey Chemical Limited) with nitric acid and diluting with distilled water. In the case of Ce, a standard solution (NIST) was used. Aliquots of these solutions were pipetted onto 1 cm^2 pieces of Whatman No. 40 filter paper, evaporated to dryness under an infrared lamp, and sealed in polyethylene envelopes.

Samples and standards were irradiated for 8 hours at a thermal neutron flux of $10^{12} \text{ n·cm}^{-2}\text{·s}^{-1}$, at the IEA-R1 nuclear reactor of the Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP). The geological reference materials GS-N and BE-N (IWG-GIT) were used as internal standards. The measurements of the induced gamma-ray activity were carried out in a GMX20190 hyperpure Ge detector (Canberra). The multichannel analyser was an 8192 channel Canberra S-100 plug-in-card in a PC computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma-ray of ^{60}Co. Two series of counting were performed; the first was done from the 5th day after irradiation, for the determination of La, Sm, Nd, Yb and Lu, and the second from the 15th day after irradiation for the determination of Ce, Eu, Tb, Yb and Sc. The counting times varied from 1 to 2.5 hours. The gamma-ray spectra were processed by using an in-house gamma-ray software which locates peak positions and calculates the energies and net areas.

* E-mail: grafigue@curiango.ipen.br

High performance liquid chromatography (HPLC)

Sample dissolution/group separation of the REE samples: 200 mg were digested in PTFE bombs with 8 ml of 40% hydrofluoric acid and 0.5 ml of 65% nitric acid at 160 °C for 18 hours. After the dissolution, the solution was passed through the quartz column of 0.8 cm of inside diameter containing 14 cm of Dowex 50W-X8 cation-exchange resin conditioned with 2M hydrochloric acid and the interfering matrix elements were eluted with 80 ml of 2M hydrochloric acid. The column was subsequently neutralized with water and the REEs, as a group, were eluted with 40 ml of 8M nitric acid. This REE fraction was evaporated to dryness, and dissolved in the mobile phase prior to injection into the HPLC system. Details of the sample dissolution and group separation of REE's were described elsewhere.[5]

HPLC procedure: The analyses were performed in a liquid chromatograph Waters Model 625, equipped with a linear gradient programmer, a Rheodyne 9125 load injection valve, a constant-flow peristaltic pump, a Waters 490 programmable multiwavelength spectrophotometric detector and a Waters RDM module (post-column reagent) used to transfer the solution of the colorimetric agent (PAR). The output of the detector is linked to a Shimadzu CLASS-LC10 data system. Aliquots of 30 to 100 µl of the REE fraction from the group separation were injected in a Nova-Pak C-18 reverse phase column. The mobile phase used was the α-hydroxibutiric acid (α-HIBA) with n-octane sodium sulphonate (OS) as a column modifying agent. The concentration of the mobile phase was linearly programmed from 0.01 to 0.4M for 30 minutes, keeping the pH (3.8), the flow-rate of the mobile phase (1 ml·min^{-1}) and the OS concentration (0.01M) constants. The eluted REE were detected after a post-column reaction with 4-(2-pyridylazo)resorcinol (PAR), 0.05 mg·l^{-1} in 2M ammonium hydroxide and 1M acetic acid. This reagent was added to the eluent in a T type mixing tee at 0.5 ml·min^{-1}, and the eluted metals were monitored by a UV/Vis detector at 535 nm. The concentration of the REE's in the samples were calculated with the non-linear regression program in the LC-10 system. The regression equations were obtained by the areas of several standards covering the concentration range expected for the samples.

Results

The results obtained as well as the certified values[6] are presented in Table 1. Figure 1 shows the data normalized to certified values. The values obtained by INAA and HPLC are the mean of three replicate analyses of the samples, and the errors associated with the data represent one standard deviation. The results obtained by INAA agreed with the certified values (relative errors less than 8%), and presented good precision, with relative standard deviations less than 10%. The results for Tb presented higher deviations between the replicates (12% in G-2 and 19% in GSP-1).

Table 1. REE concentration in the geological reference material AGV-1, G-2 and GSP-1 by INAA and HPLC (in mg·g^{-1})

| Element	AGV-1 INAA	AGV-1 HPLC	AGV-1 Certified value	G-2 INAA	G-2 HPLC	G-2 Certified value	GSP-1 INAA	GSP-1 HPLC	GSP-1 Certified value
Y	–	–	–	–	10.9 ± 0.6	11	–	–	–
La	39.3 ± 0.7	36 ± 2	38	92 ± 2	96 ± 2	89	179 ± 3	183 ± 11	184
Ce	68.7 ± 0.6	69 ± 3	67	167 ± 3	161 ± 12	160	424 ± 13	426 ± 15	399
Pr	–	6.7 ± 0.5	7.6	–	19.2 ± 0.6	18	–	51.9 ± 0.3	52
Nd	33.1 ± 0.2	35 ± 4	33	56.0 ± 0.7	50 ± 2	55	198 ± 9	180 ± 3	196
Sm	5.88 ± 0.07	5.4 ± 0.2	5.9	7.35 ± 0.07	7.1 ± 0.6	7.2	25 ± 1	27.1 ± 0.2	26.3
Eu	1.68 ± 0.04	1.57 ± 0.07	1.64	1.42 ± 0.03	1.4 ± 0.03	1.4	2.29 ± 0.02	2.4 ± 0.1	2.33
Gd	–	5.17 ± 0.05	5.0	–	4.14 ± 0.09	4.3	–	12.9 ± 0.3	12.1
Tb	0.72 ± 0.06	0.66 ± 0.04	0.70	0.52 ± 0.06	0.38 ± 0.01	0.48	1.28 ± 0.25	1.38 ± 0.04	1.34
Dy	–	–	–	–	1.8 ± 0.2	2.4	–	–	–
Ho	–	0.71 ± 0.06	0.67	–	0.37 ± 0.04	0.4	–	1.20 ± 0.06	1.01
Er	–	1.7 ± 0.1	1.7	–	0.81 ± 0.07	0.92	–	2.4 ± 0.1	2.7
Yb	1.70 ± 0.05	1.69 ± 0.04	1.72	0.81 ± 0.02	0.7 ± 0.06	0.8	1.75 ± 0.06	1.74 ± 0.03	1.7
Lu	0.25 ± 0.02	0.23 ± 0.03	0.27	0.11 ± 0.01	0.098 ± 0.005	0.11	0.23 ± 0.02	–	0.214
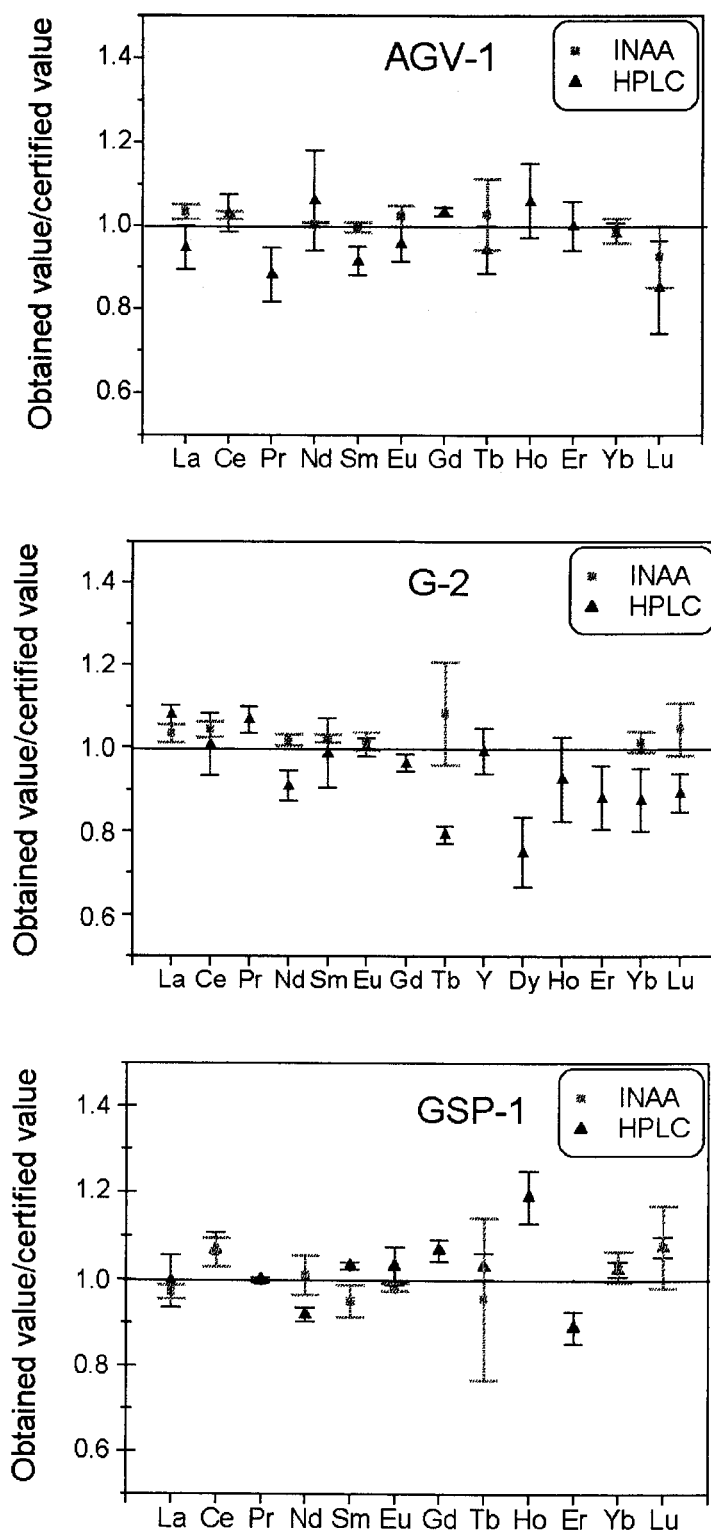
Fig. 1. REE concentration obtained by INAA and HPLC (mean of three replicate analysis) normalized to certified values. The errors associated to the data represent one standard deviation

The relative errors obtained by HPLC varied from 1 to 8%, for most elements. For the reference materials GSP-1 and AGV-1, it was not possible to calculate the concentration of Dy and Y, due of their very close retention times and very different concentrations. In the case of G-2, the concentration of Dy and Y are of the same order of magnitude, and it was possible to determine them.

The experimental quantitative detection limits, for the analytical conditions described, were between 25 to 75 ng·g^{-1} by using HPLC, depending on the molar absorptivity of the elements. The detection limits for INAA according to the CURRIE[7] criterion ranged from 10 to 100 ng·g^{-1}, except for Nd and Ce which gave values of 1000 and 350 ng·g^{-1}, respectively.

Discussion

Both analytical techniques are equally suitable for the precise and accurate REE determination in most common silicate rocks, providing results in good agreement with literature values (relative errors less than 10% for the majority of the elements analyzed). We observed more accurate results by using INAA. On the other hand, Pr, Gd, Dy, Ho and Er were not determined by INAA. To determine all the REE's, a chemical separation after analysis must be employed to avoid spectral interferences. It must be emphasized that, with the eight REE determined by INAA (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu), it is possible to obtain the so-called chondrite normalized diagrams,[8] widely used in geochemical studies to understand the long-term diagenesis of REE.

HPLC is a very effective technique, giving results for almost all REE. One advantage of HPLC, compared to INAA, is the lower detection limits achieved. A pre-separation of REE as a group from major elements like Ca and Fe in silicate rocks improves the sensitivity and selectivity in REE determination. This procedure makes the method more laborious and susceptible to contaminations from reagents. The capability of analyzing solid samples is definitely the most important advantage of INAA. Main drawbacks of INAA are the high cost and safety requirements to handle radioactive materials.

Nuclear facilities are becoming less available in the last years. HPLC is an alternative approach for the determination of REE and its contribution to analytical geochemistry must increase in the next years.

References

1. P. HENDERSON (Ed.), Rare Earth Element Geochemistry, Elsevier, Amsterdam, 1984, p.115.
2. R. M. CASSIDY, Chem. Geol., 67 (1998) 185.
3. E. L. HOFFMAN, J. Geochem. Explor., 44 (1992) 297.
4. R. KURODA, M. ADACHI, K. OGUMA, Y. SATO, Chromatographia, 30 (1990) 263.
5. N. M. P. DE MORAES, S. S. IYER, Anal. Chim. Acta, 236 (1990) 487.
6. K. GOVINDARAJU, Geostand. Newsl., Spec. Issue, 13 (1989).
7. L. A. CURRIE, Anal. Chem., 40 (3) (1968) 586.
8. C. G. CORYELL, J. W. CHASE, J. W. WINCHESTER, J. Geophys. Res., 68 (1963) 559.