Multielement Determination of Rare Earth Elements in Rock Sample by Liquid Chromatography / Inductively Coupled Plasma Mass Spectrometry

Tadashi Hamanaka,† Akihide Itoh, Shinya Itoh, Hideyuki Sawatari, and Hiroki Haraguchi*
Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01
†*Analysis & Physical Properties Center, Central Research Laboratory, SHOWA DENKO K.K., Ohnodai 1-1-1, Midori-ku, Chiba 267*

(Received January 23, 1995)

Rare earth elements in geological standard rock sample JG-1 (granodiolite) issued from the Geological Survey of Japan have been determined by a combined system of liquid chromatography and inductively coupled plasma mass spectrometry.

In recent years, inductively coupled plasma mass spectrometry (ICP-MS) have been extensively used for ultratrace analysis of various samples.[1,2] As is well known, ICP-MS has excellent analytical feasibilities of good sensitivity, multielement detection capability, wide dynamic range, and less interelement interferences.[3] In particular, the detection limits of most elements obtained by ICP-MS are much better, for example, by 2-3 orders of magnitude compared to those by inductively coupled plasma atomic emission spectrometry (ICP-AES).

In last decade, the present authors have reported the ultratrace determination of rare earth elements (REEs) by ICP-AES and ICP-MS.[4-6] Yoshida and Haraguchi performed the determination of REEs by using a combined system of liquid chromatography (LC) / ICP-AES, [4,5] where a monochromator was used for spectral measurement. Thus, they had to measure a single element chromatogram at one time for each sample injection, although the system was helpful to avoid spectral interferences with co-existing REEs. More recently, a simultaneous multielement detection system using ICP-AES was explored for chromatographic measurement and applied to the determination of REEs.[6] In the present paper, a combined system of LC and ICP-MS was developed for multielement separation and detection of REEs, where the chromatograms of 15 REEs including yttrium could be measured simultaneously.

An ICP-MS instrument used was of model SPQ 8000A from Seiko Instrument Co. A liquid chromatograph of model LC-9A from Shimadzu Instrument Co. was employed for ion exchange separation of REEs and other ions, where the ion exchange column of TSKgel SP-2SW from TOSOH was used. The exit of the LC column was connected to the capillary of the nebulizer for ICP-MS with a Teflon tubing (0.25 mm i.d.). The operating and experimental conditions of the ICP-MS and LC instruments are summarized in Table 1. The standard rock sample JG-1 (granodiolite) issued from the Geological Survey of Japan was decomposed by acid digestion (HNO_3/HF) and alkali fusion (Suprapur® 99.5% Na_2CO_3 from MERCK). Since analytical values in acid digestion provided somewhat lower concentrations for REEs compared to those in alkali fusion and the certified values, alkali fusion was employed for sample digestion in the following experiment. In alkali fusion, 0.2120 g of powdered granodiolite sample was decomposed and diluted with 0.1 M (M = mole / dm^3) HNO_3 to 100 ml. This final solution was provided to the determination of REEs as the analysis solution.

Table 1. Instrumentation and operating conditions for liquid chromatography/ICP-MS

ICP-MS		SPQ 8000A from Seiko
	RF power	1.3 kW
	RF frequency	27.12 MHz
	carrier gas flow rate	Ar 1.0 l / min
	auxiliary gas flow rate	Ar 1.0 l / min
	coolant gas flow rate	Ar 16 l / min
	sampling depth	10 mm above load coil
Data acquisition(multielement mode by peak hopping)		
	measurement positions	15 m/z per 1 measurement
	dwell time	100 ms at each m/z
	data plot	1 point per 5 s measurement
Liquid chromatograph		LC-9A from Shimadzu
	Ion exchange column	TSKgel SP-2SW from TOSOH 4.6 mm i.d. x 250 mm long
	mobile phase	α -HIBA
	flow rate	1.0 ml / min
	sample injection volume	100 μl

The concentrations of major constituents in the analysis solution of rock sample after alkali fusion were determined by ICP-AES, and they were as follows (unit in μg / ml) ; Na 2800, Al 159, K 70.0, Ca 33.1, Fe 32.6, Mg 9.46, Ti 3.31. The original concentration of Na was supposed to be 53.3 μg / ml in the analysis solution, and then large excess of Na was added from the fusion reagent.

The ion exchange separation of REEs was first investigated under isocratic elution using a single concentration of 0.15 M 2-hydroxy-2-methylpropanoic acid (α -HIBA) as a mobile phase, where pH of the mobile phase was adjusted to 3.9. The chromatogram obtained with detection of ICP-MS is shown in Figure 1, where the signal intensity of each REE was expanded to be seen as almost the same peak height. As can be seen in Figure 1, light REEs (La, Ce, Pr, Nd, Sm, Eu, and Gd) are quite well separated from each other, while heavy REEs (Tb, Dy, Er, Tm, Tb, and Lu) are not well separated. It is thus noted here that isocratic separation using a single concentration of α -HIBA as the mobile phase is not effective for the determination of REEs by ICP-MS. Therefore, the concentration gradient elution of REEs was examined by using the same ion exchange column. In gradient elution, two (A and B) solutions with different concentration of α -HIBA were used as the mobile phase; A and B solutions were 0.06 M and 0.25 M, respectively. The gradient program was as follows; 100% A solution for first 15 min, (90% A solution + 10% B solution) from 15 min to 30 min, and then 100% B solution from 30 min to 50 min. The chromatogram obtained by LC / ICP-MS under the gradient elution is shown in Figure 2. It is seen that all REEs except for Yb and Lu are quite well separated. Thus, REEs were determined by the peak area measurement in the chromatogram as shown in Figure 2. Under the elution conditions as in Figure 2, the chromatographic separation for major constituents was also investigated by using the same ion exchange column with simultaneous multielement detection of ICP-AES.[6,7] In the chromatogram obtained, Na, K, Fe, and Al were eluted in the retention time range of REEs. However, these elements did not interfere with the determination of REEs, because their mass numbers were completely different from those of REEs.

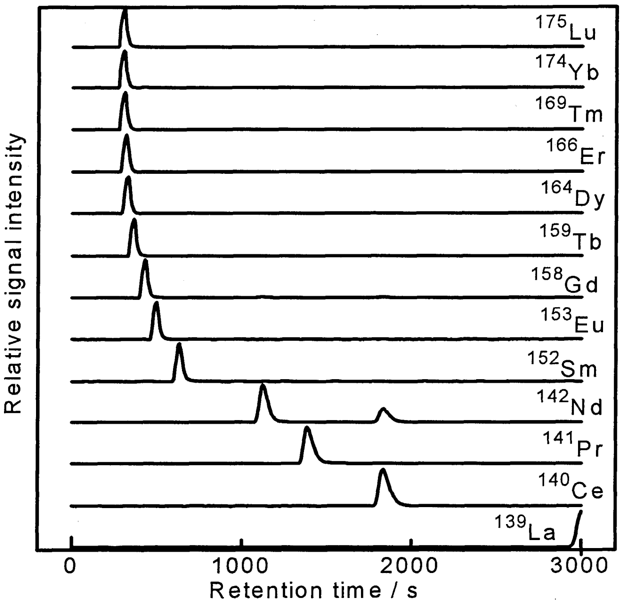

Figure 1. Chromatogram of rare earth elements in rock sample (JG-1) detected by ICP-MS
Mobile phase:α-HIBA (0.15 M) under isocratic elution. Other conditions as in Table 1.

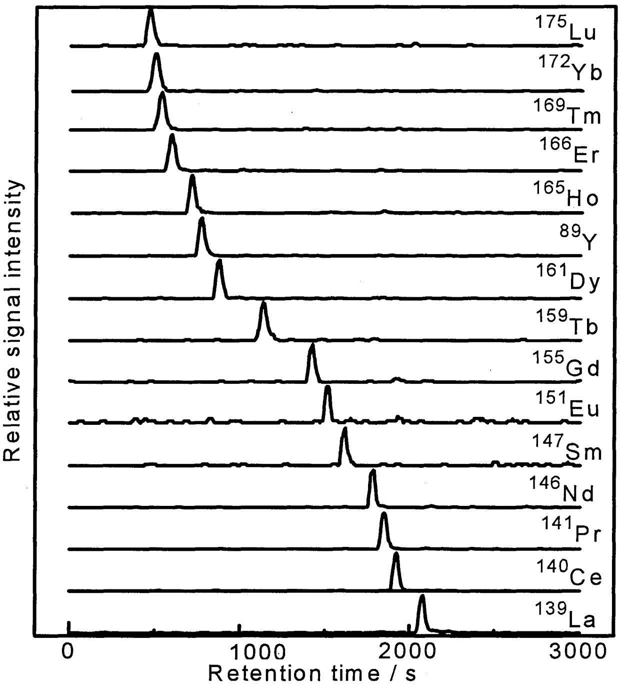

Figure 2. Chromatogram of rare earth elements in rock sample (JG-1) detected by ICP-MS.
Mobile phase: α-HIBA under gradient elution program. Other conditions as in Table 1.

Table 2. Analytica results for rare earth elements in rock sample determined by LC / ICP-MS
Sample: JG-1 issued from the Geological Survey of Japan

Element	Observed value μg / g	Certified value[a)] μg / g	CV[b)]
Y	22.4	28.5	0.090
La	24	22.4	0.020
Ce	47.8	45.9	0.050
Pr	4.3	5.2	0.034
Nd	20.6	19.5	0.040
Sm	5.4	4.7	0.050
Eu	0.78	0.74	0.029
Gd	3.6	4.2	0.089
Tb	0.81	0.83	0.061
Dy	4.8	3.9	0.049
Ho	0.98	0.83	0.067
Er	1.7	1.8	0.12
Tm	0.42	0.44	0.094
Yb	2.6	2.5	0.029
Lu	0.40	0.39	0.020

a) Cited from Ref. 8, b) Coefficient of variation(n=3)

In the determination of REEs by LC/ICP-MS, the standard solution containing all REEs (20 ng / ml each) was injected into the column, and each REE was standardized by the peak area measurement similar to the case of the sample. The analytical results are summarized in Table 2, together with the certified values.[8] It was found that the observed values were in good agreement with the certified values. These results indicate that the present LC / ICP-MS system is useful for the determination of REEs in the samples with complex matrices.

References

1 C. Vandecasteele and C. B. Block, “Modern Methods for Trace Element Determination,“ John Wiley & Sons, Chichester (1993).

2 A. Montaser and D. W. Golightly, “Inductively Coupled Plasmas in Analytical Atomic Spectrometry,” VCH Publisher, New York (1992).

3 K. E. Jarvis. A. L. Gray, and R. S. Houk, “Handbook of Inductively Coupled Plasma Mass Spectrometry, “ Blackie Academic & Professional, London (1992).

4 K. Yoshida, K. Fuwa, and H. Haraguchi, *Chem. Lett.*, **1993**, 879.

5 K. Yoshida and Haraguchi, *Anal. Chem.*, **56**, 2580 (1984).

6 H. Sawatari, T. Asano, X. Hu, A. Itoh, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, in press.

7 A. Itoh, M. Aikawa, H. Sawatari, A. Hirose, and H. Haraguchi, *Chem. Lett.*, **1993**, 1017.

8 S. Itoh, S. Terashima, N. Imai, H. Kamioka, N. Mita, and A. Ando, *Bull. Geol. Surv. Japan.*, **43**, 659(1992)