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

Akihide ITOH*, Tadashi HAMANAKA**, Wei RONG**, Katsuya IKEDA**, Hideyuki SAWATARI***, Koichi CHIBA** and Hiroki HARAGUCHI**

**Research Center for Advanced Waste and Emission Management, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

***Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

****Faculty of Education, Miyagi Institute of Education, Aramaki, Sendai 980-0845, Japan*

A system of liquid chromatography combined with inductively coupled plasma mass spectrometry (ICP-MS) has been applied to the determination of rare earth elements (REEs) in geochemical standard reference samples. In liquid chromatography, a strong ion-exchange resin was employed as a stationary phase and ammonium lactate was used as a mobile phase. Multielement detection by ICP-MS was performed in the peak hopping mode to measure the chromatograms for all REEs at the corresponding mass numbers. REEs in the standard rock sample (GSJ JB-1) and the standard sediment sample (Pond Sediment; NIES No.2) were determined by the present measurement system without any correction of the matrix effect and polyatomic ion interferences.

Keywords Inductively coupled plasma mass spectrometry, rare earth element, geochemical sample, ion exchange chromatography

Recently, inductively coupled plasma mass spectrometry (ICP-MS) has been increasingly used for trace elements in various samples because ICP-MS generally provides much better detection limits by 2–4 orders of magnitude for most elements.¹ However, it is noted here that since matrix effects are often serious in ICP-MS, ICP-AES is still useful for the determination of major, minor and some trace elements, when the concentrations of these analyte elements are higher than 1 µg/ml in the analysis solution. In addition, ICP-AES provides better analytical precision than does ICP-MS. Thus, it is desirable to use ICP-MS and ICP-AES, depending on the concentration levels of the analyte elements as well as analytical purposes.

The concentrations and distribution patterns of rare earth elements (REEs), for example in rock samples, generally provide important information about the geochemical evolution and origins of magmatic rocks. Thus, REEs in geological or geochemical samples, such as rocks, sediments and soils, have been determined by neutron activation analysis, inductively coupled plasma atomic emission spectrometry (ICP-AES), and thermal-ionization mass spectrometry.¹ The present authors previously reported on the determinations of REEs in rock samples^{2,3} and rare earth ores⁴ by con-

ventional ICP-AES with pneumatic nebulization. In addition, we explored the combined LC (liquid chromatography)/ICP-AES system as the analytical method for the determination of REEs in rock samples and REE oxides, where a monochromator system for single-element detection^{5,6} and a polychromator system for simultaneous multielement detection⁷ were employed. In these LC/ICP-AES systems, the main purpose of using LC was to separate the coexisting diverse elements and REEs in rock and other samples so as to eliminate interelement spectral interferences.

Recently, ion chromatography combined with ICP-MS was applied to the determination of REEs.⁸ The present authors also reported a LC/ICP-MS system for the chromatographic determination of REEs.⁹ Since ICP-MS generally provides much better detection sensitivities for REEs than does ICP-AES^{10,11}, the analytical results for REEs obtained by the LC/ICP-MS system appeared to be more reliable than those by the LC/ICP-AES system.^{9,12} Thus, in the present experiment the determination of REEs in geological samples has been investigated in more detail by the LC/ICP-MS system. Furthermore, ICP-AES and the LC/ICP-AES system were also used for determining the matrix elements and for investigating the separation efficiencies of the matrix elements from REEs in the sample solutions.

T. H. present address: Nippon Denso Co. Ltd., 1-1, Showa-machi, Kariya, 448-8661, Japan.

Experimental

Instrumentation

A liquid chromatograph (Model LC-9A, Shimadzu Instrument Co., Kyoto) was used for ion-exchange separation of REEs and concomitant ions with a strong ion-exchange column (TSKgel SP-2SW, TOSOH, Tokyo), where two pumps were used for concentration gradient elution. The sample injection volume into LC was 100 μ l. In ion-exchange separation, ammonium lactate was used as the mobile phase under the concentration gradient program. The experimental conditions for LC operation are given in Table 1.

An ICP-MS instrument (Model SPQ8000, Seiko Instrument Co., Chiba) was used with a concentric nebulizer for pneumatic nebulization. The conventional operating conditions of the ICP instrument are summarized in Table 1. The capillary of the nebulizer in ICP-MS was connected through a Teflon tubing to the exit of the LC column to construct a LC/ICP-MS system. Thus, REEs were on-line detected by ICP-MS after ion-exchange separation with LC. In a chromatogram measurement, ICP-MS was operated in the peak hopping mode for multielement detection, where the ICP-MS signals at 15 m/z positions were measured during a single mass-range scanning. The dwell time at each m/z was 100 ms, and the chromatograms were drawn by plotting the data every 5 s. The total acquisition time for chromatogram measurements was 2400 s, which resulted in observations of each chromatogram with 480 points at each m/z . The thus-measured chromatograms are shown in Figs. 1, 3 and 4. In these chromatograms, the maximum intensity of each peak was normalized to 1 according to the computer program employed in the present experiment, although the

peak intensities were obtained as the real ion counts. In addition, the curves of the chromatograms were smoothed by taking the average of each 5 points.

Chemicals and samples

The chemicals used were of analytical-reagent grade. The working standard solution of REEs was prepared by mixing the commercially available standard stock solutions of REEs (1000 μ g/ml each) for atomic absorption spectrometry, which were purchased from Wako Chemicals Co. (Osaka). Lactic acid and an aqueous ammonia solution were also purchased from Wako Chemicals Co. The ammonium lactate solutions (pH 4.2) used for the mobile phase were prepared by mixing lactic acid and ammonia solutions. The rock and sediment standard reference samples, issued by the Geological Survey of Japan (Tsukuba) and the National Institute for Environmental Studies (Tsukuba), respectively, were used for analysis. The samples were digested by alkali fusion using LiBO_2 (>99%) from E. MERCK (Darmstadt, Germany), and finally dissolved with 0.1 M HNO_3 . The digested samples were subjected to analysis without any further pretreatment.

Results and Discussion

Chromatographic separation of REEs

The chromatograms for REEs (20 ng/ml each in 0.1 M HNO_3) in the mixed standard solution were measured by the present LC/ICP-MS system, and are shown in Fig. 1. In this chromatographic measurement, a strong ion-exchange column of TSKgel SP-2SW was used for separating REEs, and the elution was performed using an ammonium lactate solution as the mobile phase under the following concentration gradient program. In the concentration gradient program, two solutions (**A** and **B**) with different concentrations of ammonium lactate were used as the mobile phase; the **A** and **B** solutions were 0.1 M and 0.4 M of ammonium lactate aqueous solution (pH 4.2), respectively. The gradient program was operated as follows: a 100% **A** solution was gradually decreased down to 90% and **B** was alternately increased up to 10% for the first 15 min, the mixture of 90% **A** solution and 10% **B** from 15 min to 25 min, and then **B** solution gradually up to 100% from 25 min, and finally to 40 min.

The retention times of REEs obtained from the chromatograms shown in Fig. 1 are summarized in Table 2, together with those obtained using α -HIBA (2-hydroxy-2-methylpropanoic acid) as the mobile phase, which was examined in a previous study.⁹ It can be seen in Fig. 1 that the peak-profile overlappings are observed in the cases of Lu-Yb-Tm-Er and Eu-Sm. In such cases, the differences in the retention times were smaller than 100 s, as is seen in Table 2. However, the present chromatograms for REEs measured in the peak hopping mode were independently observed at each m/z under the mass-separated conditions. Thus, the

Table 1 Instrumentation and experimental conditions for the LC / ICP-MS system

ICP-MS	SPQ8000 from Seiko
RF power	1.3 kW
carrier gas flow rate	Ar 1.0 l/min
auxiliary gas flow rate	Ar 1.0 l/min
outer gas flow rate	Ar 16 l/min
sampling depth	10 mm above load coil
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 (strong cation exchange resin) 4.6 mm i.d. $\times$ 250 mm long
mobile phase	ammonium lactate
elution program	concentration gradient
flow rate	1.0 ml/min
sample injection volume	100 μ l

Fig. 1 Chromatograms of rare earth elements in a mixed standard solution with multielement detection of ICP-MS. LC elution, concentration gradient (see text); mobile phase, ammonium lactate; separation column, cation exchange resin; flow rate, 1 ml/min; injection volume, 100 μ l.

Table 2 Retention times of rare earth elements obtained by the present LC/ICP-MS system

Element	Retention time/s	
	Ammonium lactate	α -HIBA ^a
Lu	510	465
Yb	540	490
Tm	595	530
Er	685	600
Ho	840	705
Y	890	770
Dy	965	870
Tb	1155	1130
Gd	1340	1420
Eu	1400	1515
Sm	1485	1615
Nd	1685	1785
Pr	1905	1850
Ce	2010	1915
La	2180	2070

a. Cited from ref. 9.

overlappings of the peak profiles were not seriously prone to mutual interferences in the determination of REEs by LC/ICP-MS.

In comparison with the results obtained by using ammonium lactate and α -HIBA as the mobile phase, the better peak resolution of the chromatographic peaks for REEs were obtained rather in the case of α -HIBA. However, better analytical results, especially in terms

Table 3 Detection limits obtained by the LC/ICP-MS system

Element	m/z	Detection limit ^a /ng ml ⁻¹	
		LC/ICP-MS ^b	Conventional ICP-MS
Y	89	0.49	0.0027
La	139	0.23	0.006
Ce	140	0.13	0.0056
Pr	141	0.044	0.0041
Nd	146	0.051	0.0050
Sm	147	0.054	0.0029
Eu	151	0.055	0.0024
Gd	155	0.032	0.0043
Tb	159	0.063	0.0036
Dy	161	0.027	0.0028
Ho	165	0.010	0.0027
Er	166	0.018	0.0065
Tm	169	0.010	0.0022
Yb	172	0.022	0.0030
Lu	175	0.027	0.0030

a. Detection limits for the standard solution of REEs with direct nebulization.

b. The concentration gradient elution was employed, as described in the text.

of precision, were obtained in the case of ammonium lactate. This may be because the slow elution (longer retention time) of REEs was achieved in the case of ammonium lactate, which allowed a more precise chromatogram measurement in the peak-hopping mode.

Detection limits of REEs obtained by LC/ICP-MS

The detection limits obtained by the present LC/ICP-MS system are summarized in Table 3 together with those obtained by conventional ICP-MS with pneumatic nebulization. The detection limit in LC/ICP-MS was estimated as the concentration corresponding to 3-times the standard deviation (σ), which was calculated from the blank intensity measured at each m/z of REEs with flowing only the mobile phase (0.1 M ammonium lactate solution). The present detection limits were poorer by 10 – 180 times for Y, La, Ce, Pr, Nd, Sm, Eu, and Tb compared to those obtained by conventional ICP-MS, while they were less than 10 times for other REEs. It is noted that the detection limits in LC/ICP-MS were poorer for light REEs than those for heavy REEs. Even so, LC/ICP-MS was applicable to the determination of REEs because the natural abundances of light REEs are significantly higher than those of heavy REEs. The present LC/ICP-MS system, thus, provided the following advantages over the conventional ICP-MS, even though the detection limits were fairly deteriorated. First, spectral interferences due to polyatomic ions could be eliminated because of mutual separation of REEs as well as major elements. Second, such mutual separation also helped to reduce matrix effects due to major elements. Thus, it was not necessary to make any internal-standard correction in the present experi-

Table 4 Concentration of major elements in standard rock sample (GSJ JB-1) and sediment sample (NIES No. 2) determined by ICP-AES

Element	Rock sample		Sediment sample	
	Observed, %	Certified, %	Observed, %	Certified, %
Na	2.04	2.05	0.57	0.57
Mg	4.52	4.66	0.85	0.81
Al	7.07	7.69	10.5	10.6
Si	24.2	24.48	22.0	22.0
K	1.09	1.19	0.52	0.68
Ca	6.64	6.61	0.80	0.81
Ti	0.79	0.80	0.60	0.64
Fe	6.17	6.29	6.8	6.53
Total	53.03	53.77	42.64	42.64

mental system.

Chromatographic retention behaviors of major elements

The concentrations of major elements in the rock and sediment samples examined here were determined by ICP-AES (inductively coupled plasma atomic emission spectrometry), where the ICP-AES instrument (Model Plasma AtomComp MK II from Jarrell-Ash, Franklin, MA, USA) was operated under the usual experimental conditions.⁷ Before the analysis, the rock and sediment samples were digested, as mentioned later. The analytical results are summarized in Table 4, together with the certified values. As can be seen in Table 4, the concentrations of the alkali and alkaline earth elements (Na, K, Mg, and Ca) in the rock sample were much higher than those in the sediment sample. In general, a large amount of major constituents in the samples often causes matrix effects in the ICP-MS measurement. Thus, the ion-exchange separation of the major elements in the rock sample was further examined using the LC/ICP-AES system.

In a chromatogram measurement by LC/ICP-AES, the same ion-exchange column and experimental conditions as those shown in Fig. 1 were employed. The LC/ICP-AES measurement system, which was developed in the present laboratory, was used in the experiment in similar manner to the previous experiment.⁷ The test solution for the chromatogram measurements was prepared so as to match the concentrations of the major elements with those in the digested rock sample solution, in which Li was also added, because LiBO₂ was used for fusion of the samples.

The ion-exchange chromatograms of the major elements are shown in Fig. 2. Compared to the chromatograms in Fig. 1, it can be seen from Fig. 2 that the retention times of Ca, Si, Ti, and Fe were shorter than those of REEs, and those of K and Mg were much longer. Thus, these elements may not interfere with REEs in the chromatographic measurement by LC/ICP-MS. However, Li, Na, and Al eluted in the retention

Fig. 2 Chromatograms of the major constituents in the standard rock sample (JB-1) with multielement detection by ICP-AES. Chromatographic experimental conditions, same as in Fig. 1. Concentrations of major concentrations in the test solution of rock sample (JB-1): Li 4.17 µg/ml, Na 39.6 µg/ml, Mg 87.7 µg/ml, Si 137 µg/ml, K 21.1 µg/ml, Ca 128 µg/ml, Fe 120 µg/ml.

time range of REEs. The peak-profile overlappings are observed for the cases of Li-Er, Na-Y, and Al-Tb. Thus, the matrix effects of these elements should be taken into consideration in the LC/ICP-MS measurement.

Determination of REEs in standard rock and sediment samples

The standard rock sample (JB-1: basalt) issued from the Geological Survey of Japan was analyzed by the present LC/ICP-MS system. The rock sample (ca. 0.2 g) was digested by alkali fusion using LiBO₂ (ca. 0.3 g) in a platinum crucible, which was heated on a burner for 15 min. After cooling, the residue was dissolved in 100 ml of 0.1 M HNO₃. The rock sample solution was subjected to analysis by the LC/ICP-MS system without any further pretreatment. Element-selective chromatograms of REEs in the rock sample are shown in Fig. 3. In the determination procedure, the standard solution of REEs was first injected into LC for standardization, and then the rock-sample solution was injected for analysis. REEs were determined by the peak-area measurement method. The analytical results are summarized in Table 5, along with the certified values and relative standard deviation. As can be seen in Table 5, the observed values in the present method are almost in good agreement with the certified values¹³, although the values for light REEs (Y – Sm) were rather smaller than the certified values.

REEs in the pond-sediment reference material (NIES

Fig. 3 Chromatograms of rare earth elements in the standard rock sample (JB-1) with multielement detection of ICP-MS. Experimental conditions, same as in Fig. 1.

Fig. 4 Chromatograms of rare earth elements in the standard sediment sample (NIES No. 2) with multielement detection of ICP-MS. Experimental conditions, same as in Fig. 1.

Table 5 Analytical results for the determination of rare earth elements in the standard rock sample (GSJ JB-1) and sediment sample (NIES No. 2) obtained by the LC/ICP-MS system

Element	Rock sample			Sediment sample		
	Observed/ $\mu\text{g g}^{-1}$	RSD ^a	Certified ^b / $\mu\text{g g}^{-1}$	Observed/ $\mu\text{g g}^{-1}$	RSD ^a	Certified ^c / $\mu\text{g g}^{-1}$
Y	18.9	0.076	24.4	23.5	0.068	23.2
La	33.6	0.031	37.9	15.7	0.088	16.7
Ce	56.2	0.013	66.7	31.8	0.042	36.1
Pr	6.5	0.036	7.0	4.1	0.037	4.2
Nd	22.8	0.029	26.7	16.4	0.033	18.4
Sm	4.6	0.029	5.1	3.8	0.026	4.1
Eu	1.4	0.061	1.5	1.1	0.038	1.2
Gd	4.4	0.039	4.9	4.2	0.019	4.6
Tb	0.80	0.16	0.84	0.6	0.039	0.7
Dy	3.7	0.022	4.1	4.1	0.041	4.6
Ho	0.7	0.047	0.8	0.8	0.11	0.9
Er	2.3	0.057	2.3	2.5	0.056	2.7
Tm	0.30	0.072	0.35	0.4	0.034	0.4
Yb	2.1	0.033	2.2	2.5	0.097	2.6
Lu	0.32	0.096	0.31	0.4	0.038	0.4

a. Relative standard deviation, which was estimated from the 3-times measurements. b. Cited from ref. 13. c. Cited from ref. 14.

No. 2) issued from the National Institute for Environmental Studies of Japan, which was collected from a pond in the campus of the University of Tokyo, located in the central part of Tokyo City, were also determined by the LC/ICP-MS system. The sediment sample was digested in a similar manner to the rock sample using LiBO_2 . Chromatograms of REEs for the sediment sample are shown in Fig. 4. The determination of REEs was also performed by the peak-area measurement method. The analytical results are also sum-

marized in Table 5, along with the certified values. As can be seen in Table 5, the observed values for all REEs in the sediment sample are in good agreement with the certified values.¹⁴

It is noted here that the concentrations of REEs in the rock and sediment samples are almost at the same level for each other, though rather smaller values were obtained for light REEs in the rock sample examined in the present experiment, as mentioned above. The deviation in the analytical values for light REEs in the rock

sample may be partly due to the poorer detection limits for light REEs than those for heavy REEs, obtained in the present LC/ICP-MS system. Another reason is possibly ascribed to some matrix effects caused by the major constituents.⁶ It is noted here that the concentrations of alkali and alkaline earth elements (Na, K, Mg and Ca) in the rock sample were much higher than those in the sediment sample. It can be seen in Table 5 that the observed value of Y in the rock sample was significantly smaller than its certified value. As can be seen in Fig. 2, the retention time of Na was almost consistent with that of Y. Thus, it is considered that the coexistence of a large amount of Na in the rock sample possibly resulted in a smaller value of Y determined by LC/ICP-MS. It was reported in a previous paper¹⁵ that a large amount of coexisting Na suppressed the ion counts of alkaline-earth elements in the ICP-MS measurement. This result was interpreted by suppression of ionization due to easily ionizable elements (EIEs). The Na concentration of the rock sample was larger by about 4 times than that of the sediment sample. Therefore, the smaller observed value of Y in the rock sample might be caused by ionization suppression due to Na, which co-eluted at almost the same retention time as Y in the LC separation. Although no correction was made in terms of matrix effects due to Na in the present experiment, matrix matching of the working standard solution with the sample solution may be recommended to obtain more accurate analytical values, even in the LC/ICP-MS measurement, when the concentrations of the major constituents, especially in the case of easily ionizable elements, are too high. Since the ionization energies of Li and Al are larger than that of Na, the matrix effects due to Li and Al were perhaps negligibly small in the present case.

The system of liquid chromatography combined with ICP-MS has been applied to the determination of rare earth elements (REEs) in geochemical reference materials: rock sample (GSJ JB-1) and sediment sample (Pond Sediment; NIES No.2). As a result, REEs in these samples could be determined by the present measurement system without any correction of the matrix effect and polyatomic ion interferences, although possi-

ble ionization interference of Na with Y and light REEs in the rock sample was observed. Thus, the present method is applicable to the determination of REEs in geological samples decomposed by alkali fusion, because sample pretreatment is minimized with the aid of precolumn separation of the analytes from concomitant elements.

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