Multielement Determination of Rare Earth Elements by Liquid Chromatography/Inductively Coupled Plasma Atomic Emission Spectrometry

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The rapid determination of rare earth elements (REEs) has been investigated by an on-line system of high performance liquid chromatography/multichannel inductively coupled plasma atomic emission spectrometry. In the present system, all REEs could be detected simultaneously in a single chromatographic measurement without spectral interferences. Utilizing a cation exchange column and 2-hydroxy-2-methylpropanoic acid aqueous solution as the mobile phase, the detection limits of 0.4—30 ng ml^{-1} for all REEs were obtained. The system was applied to the determination of REEs in geological standard rock samples and rare earth impurities in high purity rare earth oxides. The REEs in standard rocks could be determined by the present HPLC/ICP-AES system without pretreatment after acid digestion, although the detection limits were not sufficient for the analysis of rare earth oxides.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a useful method for trace analysis with analytical feasibilities of simultaneous multielement detection, high sensitivity and wide dynamic range in the working calibration curve. The determination of rare earth elements (REEs) by ICP-AES, however, is still troublesome because spectral interferences due to major constituents and co-existing REEs are often serious. Till now, thus, the mutual spectral interferences of REEs have been often reported.[1—6] Although knowledge on the spectral interference has been accumulated and the resolution of commercial spectrometers has been improved, such spectral interferences cannot be eliminated completely when the samples containing various REEs at the different concentration levels are analyzed by ICP-AES. An interference correction coefficient method is usually employed for the determination of REEs by ICP-AES,[7—11] but such correction is not always accurate enough, especially when large interferences exist. In order to obtain the accurate analytical results, therefore, mutual separation of REEs is desirable to reduce the interferences.

Mutual separation of REEs has been performed by ion exchange chromatography. In particular, high performance liquid chromatography (HPLC) allows rapid separation within several ten minutes. Yoshida and Haraguchi[12,13] combined HPLC directly with ICP-AES and succeeded in the determination of REEs without spectral interference. However, since their ICP-AES instrument was equipped with a monochromator which could detect only one element at once, they had to repeat the chromatographic measurements after re-adjusting the monochromator wavelength in order to detect another REE. Nakamura et al.[14] also determined REEs by an HPLC/ICP AES system. Although they reduced the time for analysis utilizing silica-ODS (octadecyl silane) column for HPLC, they also had to repeat the measurements in a similar manner to Yoshida and Haraguchi.[12,13] Tielrooy et al.[15] used HPLC/ICP-AES equipped with a sequential slew-scanning monochromator, which enabled sequential wavelength adjustment for the detection of all REEs during a chromatographic measurement. In their study, reproducibility of wavelength adjustment was important, although multichannel spectrometer (polychromator) does not involve such a problem. Aulis et al.[16] employed HPLC/multichannel ICP-AES system for the determination of REEs in geological samples, but they used HPLC for the separation of major components from REEs, not for the separation of mutual REEs.

Recently, ICP mass spectrometry (ICP-MS) has been developed and widely used in trace analysis, and the HPLC/ICP-MS systems for REE determination were

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proposed.[17,18] It is apparent that the detection limits for REEs obtained by ICP-MS are superior generally by 2 or 3 orders of magnitude to those obtained by ICP-AES. ICP-AES, however, is a quite stable and reliable method, when the concentration of the analyte is sufficiently higher than the detection limit and spectral interference is negligible. Hence, establishment of the determination of REEs by ICP-AES is still required for practical analysis.

In the present study, a multichannel ICP-AES spectrometer was utilized together with HPLC to perform interference-free and simultaneous multielement REE determination. The on-line system of HPLC/multichannel ICP-AES is more simple and reliable than HPLC/sequential ICP-AES because all REEs were detected during one chromatographic measurement without wavelength adjustment of the spectrometer. The present system, thus, allows the most convenient and time-saving determination of REEs because of complete mutual separation of REEs by HPLC and simultaneous multielement detection by ICP-AES. The system was applied to the determination of REEs in geological standard rock samples and high purity rare earth oxides without pretreatment.

Experimental

Chemicals. The mobile phase for HPLC was prepared by dissolving 2-hydroxy-2-methylpropanoic acid (α-HIBA) or ammonium lactate in water and the pH was adjusted by adding aqueous ammonia solution. α-HIBA and ammonium lactate were of analytical reagent grade purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo) and Katayama Chemical Co. (Nagoya), respectively. They were used without further purification. Aqueous ammonia solution, nitric acid, hydrochloric acid, and perchloric acid used were of extra pure grade, and hydrofluoric acid was of semiconductor manufacturing grade. The standard solutions of REEs and diverse elements were prepared by diluting the commercial standard solutions (1000 $\mu g\,ml^{-1}$) for atomic absorption analysis. Deionized water was used to prepare all reagents and samples.

Apparatus. The HPLC system consisted of two pumps (model LC-9A from Shimadzu, Kyoto) for gradient elution, an injection valve (model 7125 from Rheodyne, Cotati, CA, USA) with a 20—400 μl sample loop, and a cation exchange column (TSKgel SP-2SW or IC-Cation-SW from Tosoh, Tokyo). Both of the two columns were of silica-based cation exchange resin (5 μm), and they were different only in column length; SP-2SW was 4.6 mm i.d.×250 mm long and IC-cation-SW 4.6 mm i.d.×100 mm long. The ICP-AES system for the detection of REEs was Plasma AtomComp MkII from Jarrell–Ash (Franklin, MA, USA) equipped with a 45-channel polychromator, and the data acquisition system was modified as described later. The outlet of the column was connected to the nebulizer of the ICP-AES by means of a Teflon® tubing (0.25 mm i.d.×300 mm long).

Data Acquisition System of Time-Sequence ICP-AES Measurement. For the measurement of simultaneous multielement-detected chromatogram, the data acquisition system in the ICP-AES instrument was modified by replacing the original DEC PDP-8 computer with an NEC PC-9801RX personal computer. The time-sequence data acquisition system (model CDR-80) including the computer software was developed by Nippon Jarrell–Ash Co. (Kyoto) with cooperation of our laboratory. As the result, the present time-sequence measurement program allowed to detect up to 39 elements simultaneously, in which the emission signal for each element examined could be acquired at each time-interval in the range of 0.2—10 s. In the chromatogram measurement, 1600 data points as the total were available, and then the retention time in the range of 0—5.33 min in the shortest and 0—266 min in the longest could be observed in the present time-sequence program. In the present experiment, the emission signal was observed at each 2.5 s and the chromatogram was drawn by connecting those emission data observed.

Results and Discussion

Optimization of Separation Conditions for Rare Earth Elements by HPLC. For the separation of REEs by ion-exchange chromatography, aqueous solutions of α-HIBA[19] and lactate[20] are known as good eluting solutions. In the present study, thus, these two solutions were employed as the mobile phase in HPLC for the mutual separation of REEs, although the lactate aqueous solution was used in the previous work.[13] The experimental conditions such as the concentration, pH and flow rate of the mobile phase, and gradient elution program were optimized in order to obtain good separation efficiencies of mutual REEs. The ranges of the conditions examined are as follows: concentration, 0.04—0.4 M (1 M=1 mol dm^{-3}); pH, 3.6—4.0; flow rate, 0.8—1.2 ml min^{-1}. The chromatograms obtained under the optimized conditions are shown in Figs. 1 and 2, together with the experimental conditions. As is seen in Figs. 1 and 2, separations between Y and Dy, and between Gd and Eu were better in the case of α-HIBA than ammonium lactate. Thus, α-HIBA was mainly used as the mobile phase in the further investigation.

The influence of the column temperature was also investigated. The chromatogram obtained by keeping the column temperature at 42 °C was scarcely different from that in Fig. 1, which was obtained at room temperature maintained at 23±1 °C. Accordingly, the chromatogram measurement was performed at room temperature.

Since acid digestion is usually performed in analysis of geological materials by ICP-AES, the analytical sample solutions contain certain amount of acids used. Thus, influence of acid concentration on the separation of REEs by HPLC was examined by using the test solutions containing Lu and Yb (10 $\mu g\,ml^{-1}$ each) in various concentrations of nitric acid (0.05—1 M) as samples. With increasing the acid concentration, separation of Yb from Lu was deteriorated, and finally two peaks overlapped into one apparent peak. Consequently, the acid concentration of 0.1 M HNO_3 was optimal for the mutual separation of REEs, and thus the chromatogram

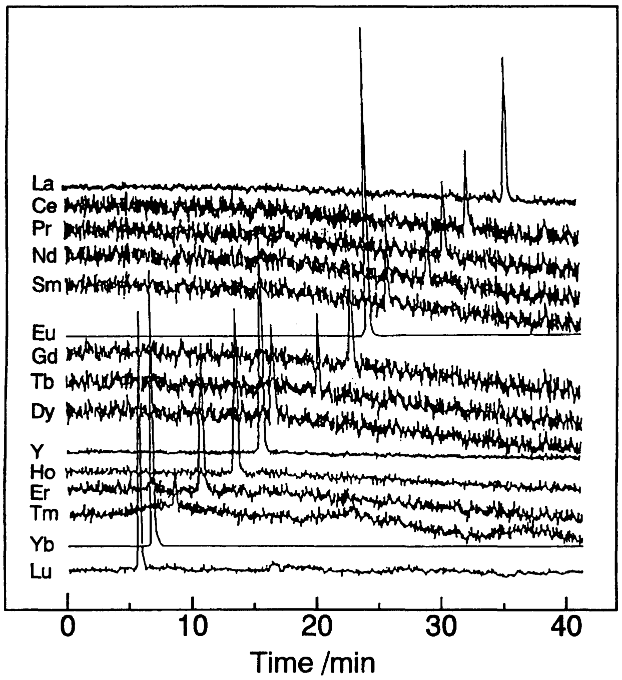

Fig. 1. Chromatogram of REEs obtained by HPLC/ICP-AES system using α-HIBA as the mobile phase. Sample: 500 ng ml^{-1} of each REE in 0.1 M HNO_3, Injection volume: 400 µl, Column: SP-2SW, Mobile phase A: 0.06 M α-HIBA (pH 3.90), Mobile phase B: 0.40 M α-HIBA (pH 3.90), Gradient program: A 100% (0 min) → A 90%, B 10% (15 min) → B 100% (40 min), Flow rate: 1.0 ml min^{-1}. Chromatogram for each element is drawn in arbitrary scale.

shown in Fig. 1 was measured in 0.1 M HNO_3.

Optimization of Analytical Conditions in ICP-AES. The carrier gas flow rate, observation height, incident RF power and mobile phase flow rate were optimized to obtain the largest signal-to-background (S/B) ratios of the emission signals for REEs. In the optimization experiment, 20 µl of 10 µg ml^{-1} Lu solution was injected into the HPLC/ICP-AES system and the signals were monitored under various experimental conditions. At any flow rate of the mobile phase, the largest S/B ratio for Lu was obtained under the conditions of the carrier gas flow rate of 0.47 ml min^{-1}, observation height of 18 mm above load coil and incident RF power of 1.0 kW. These results indicate that the flow rate of the mobile phase did not influence significantly on the S/B ratio in the ICP-AES measurement. Thus the flow rate of the mobile phase which gave the best separation in HPLC was selected to be 1.0 ml min^{-1} for α-HIBA and 1.4 ml min^{-1} for ammonium lactate.

The optimized conditions for the ICP-AES measurement are summarized in Table 1. Under these conditions, no clogging or carbon deposition on the plasma torch was observed, even when the present on-line HPLC/ICP-AES was used for the REE determination.

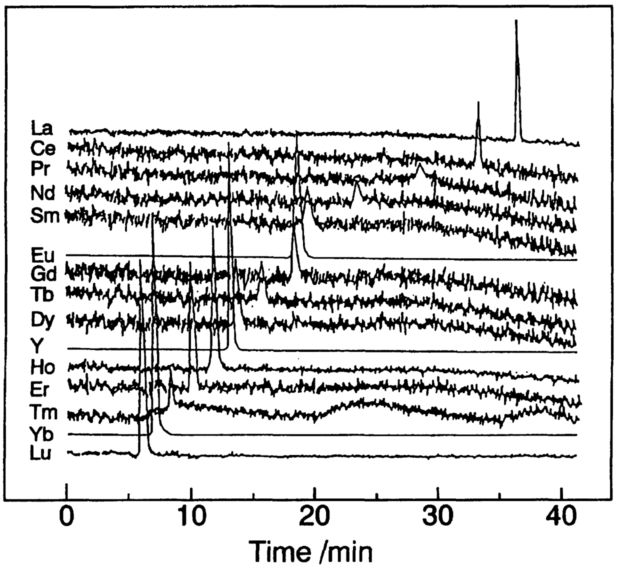

Fig. 2. Chromatogram of REEs obtained by HPLC/ICP-AES using ammonium lactate as the mobile phase. Mobile phase A: 0.1 M ammonium lactate (pH 4.20), Mobile phase B: 0.4 M ammonium lactate (pH 4.20), Gradient program: A 100% (0 min) → A90%, B10% (constant for 10—25 min) → B 100% (40 min), Flow rate: 1.4 ml min^{-1}. Other experimental conditions were the same as Fig. 1.

Table 1. Operating Conditions for Measurements of ICP-AES

Plasma Conditions :	
Incident power	1.0 kW
Reflected power	<30 W
Coolant gas flow rate	17 l min^{-1}
Intermediate gas flow rate	1.0 l min^{-1}
Carrier gas flow rate	0.47 l min^{-1}
Observation height	18 mm above load coil
Nebulizer:	Cross-flow type
Polychromator:	Paschen-Runge (75 cm focal length)
Grating	2400 grooves mm^{-1}
Entrance slit width	25 µm
Exit slit width	50 µm

Separation Characteristics of Diverse Elements from Rare Earth Elements. In the ICP-AES measurement, spectral interference is a serious problem because many elements including rare earth elements provide a large number of emission lines in the UV and shorter visible wavelength region. Correction of spectral interference is often made by using the spectral interference correction coefficient method. However, such correction is sometimes inaccurate because of over-correction for trace elements, when various major elements co-exist at the high concentration level. Therefore, the on-line separation of trace elements from major elements has been investigated to eliminate spectral interference, as mentioned earlier. In the present experiment, mutual separation of rare earth elements with a ion-exchange column was successfully achieved by using α-HIBA, as is shown in Fig. 1. Accordingly, spectral interferences between REEs were almost negligible.

The diverse elements except for REEs co-existing in the sample solution often cause spectral interference with trace elements, and thus the separation characteristics of diverse elements were also examined under the same separation conditions as REEs. The retention times of rare earth elements and diverse elements obtained by the present HPLC/ICP-AES using α-HIBA as the mobile phase are summarized in Table 2. These elution characteristics are also schematically illustrated in Fig. 3 to show the peak width broadening in the chromatograms. The results in Table 2 and Fig. 3 were obtained by injecting the 400 μl solutions of diverse elements into the HPLC/ICP-AES system. The concentrations of the elements in the test solutions are shown in Fig. 3. These concentrations were decided, considering the elemental concentrations in geological rock standard samples.

As can be seen from Table 2, K, Ti, P, Zr, V, and Cr eluted out of the column prior to REEs, while Mg, Ca, Mn, and Sr did after REEs. Consequently these elements caused no spectral interferences with REEs. On the other hand, the chromatographic peaks of Fe, Cu, Al, Na, Zn, and Ni appeared in the retention time range of REEs. Among these elements, the elements except Fe did not cause serious spectral interferences with REEs, when their concentration levels were at the orders in the geological rock samples.

The spectral interference of Fe with Lu, Yb, and Tm should be taken into account because the Fe peaks overlapped with those of Lu, Yb, and Tm. Iron is usually one of major constituents in rock samples, in which the concentrations of Lu, Yb, and Tm are quite low. Thus, the spectral interference of Fe with Lu, Yb, and Tm was corrected by the back-ground correction method, where the peak areas of Lu, Yb, and Tm on the broad peak of Fe were estimated by the curve fitting method.

As will be described later, it was difficult to determine Tm for all the rock samples analyzed because of its poor detection limit in the present system. On the other hand, the detection limits of Yb and Lu were quite good, and thus they could be determined for all the rock samples except JB-1, although the rather lower analytical data were obtained in some cases. Such lower analytical values may be ascribed to inaccurate correction of spectral interference.

Analytical Figures of Merit. The detection limits of REEs obtained by the present HPLC/ICP-AES system are summarized in Table 3, where they are shown for the mobile phases of α-HIBA and ammonium lactate and also for direct nebulization. The detection limits were defined as the concentrations corresponding to twice of the standard deviation of the signal intensity estimated from the 10-times duplicate measurement of a blank solution. The detection limits obtained using α-HIBA and ammonium lactate were almost the same, but slightly better for α-HIBA. This is because clearer separation with sharp peaks was achieved by the use of α-HIBA.

In the HPLC/ICP-AES system, the signals of REEs were detected as the broadened chromatographic peaks, and hence these detection limits were worse than those obtained by direct nebulization without HPLC. The degree of deterioration in the detection limit, however, was less than one order of magnitude, as is seen in Ta-

Table 2. Retention Times of Rare Earth Elements and Diverse Elements by HPLC Using α-HIBA as the Mobile Phase[a)]

Rare earth elements	Retention time min	Diverse elements	Retention time min
Lu	7.47	Cr,Ti	3.38
Yb	8.08	V	3.50
Tm	9.32	K	3.75
Er	10.75	Zr	3.92
Ho	12.83	P	4.05
Y	14.55	Fe	7.17
Dy	15.08	Cu	13.05
Tb	18.55	Al	18.38
Gd	23.13	Na	20.63
Eu	24.67	Ni	27.67
Sm	26.58	Zn	27.88
Nd	30.13	Mg	37.67
Pr	31.42	Mn	39.5
Ce	33.17	Ca	41.72
La	36.22	Pb,Ba,Sr	>45.00

a) The experimental conditions are the same as those employed in Fig. 1.

Table 3. Detection Limit Obtained by HPLC/ICP-AES and Conventional ICP-AES with Direct Nebulization

Elements	Wavelength[a)]	Detection limit/ng ml^{-1}		
	nm	HPLC/ICP-AES		Conventional
		α-HIBA	Ammonium lactate	direct nebulization
Y	377.43 II	2	2	0.9
La	398.85 II	3	2	3
Ce	418.66 II	30	50	10
Pr	422.29 II	20	100	3
Nd	430.36 II	20	70	3
Sm	442.43 II	20	40	2
Eu	381.97 II	1	2	0.3
Gd	303.28 II	20	20	6
Tb	367.64 II	30	20	2
Dy	340.79 II	10	10	2
Ho	345.60 II	5	2	0.3
Er	369.27 II	10	9	4
Tm	313.13 II	30	20	20
Yb	328.94 II	0.4	1	0.1
Lu	261.54 II	1	2	0.6

a) II indicates the ionic emission line.

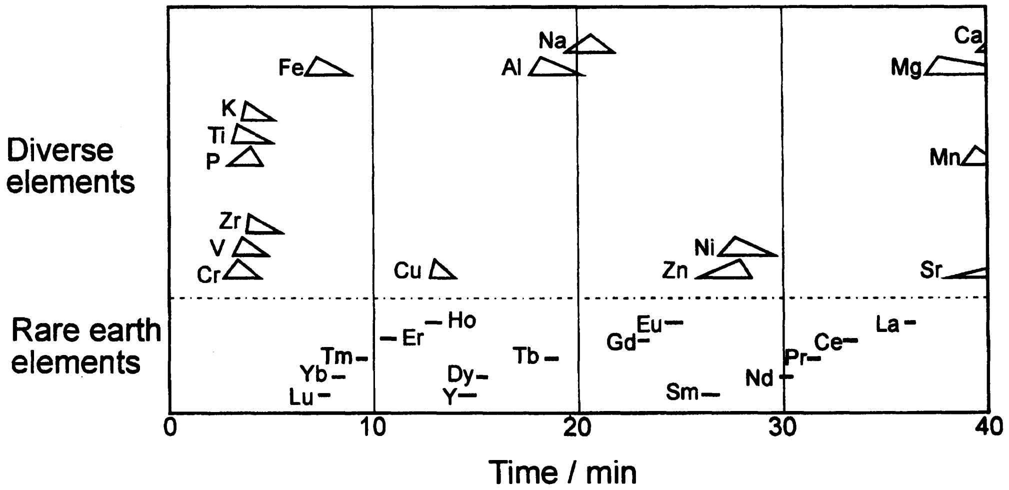

Fig. 3. Schematic representation of chromatograms for diverse elements and REEs. Elemental concentrations in the sample solution: 1000 µg ml^{-1} for each of Fe, Al, Na, Mg, Ca; 100 µg ml^{-1} for each of K, Ti, P, Mn; 10 µg ml^{-1} for each of Cr, V, Zr, Cu, Zn, Ni, Sr; 500 ng ml^{-1} for each REE. Other conditions were the same as Fig. 1.

ble 3. Considering the reduced spectral interferences, the use of the HPLC/ICP-AES system may provide some advantages for the determination of REEs. It is also pointed out here that the detection limits for conventional direct nebulization in Table 2 were obtained from the measurement of the pure standard solutions containing only one REE, and thus the detection limit and accuracy would be deteriorated when the real samples containing various REEs are analyzed.[21,22]

In the present HPLC/ICP-AES measurement, quantitation of REEs was performed by the peak-area integration. To estimate experimental precision, relative standard deviation of the signal intensities was calculated from ten consecutive measurements of the Lu solution. In the case of peak-area measurement, relative standard deviation was about 2%, when Lu concentration was above 100 ng ml^{-1}. When the peak-height measurement was employed, relative standard deviation was more than 4% even at the Lu concentration of 10 µg ml^{-1}. Then, in the present study, quantitative analysis was carried out based on the peak-area measurement. When a sequential slew-scanning monochromator was used for the detector of a HPLC/ICP-AES system, the peak-area measurement was difficult because wavelength adjustment was incomplete to observe the whole chromatographic peak within a short time between the end of the elution of one element and the beginning of the next elution of the other element.[15] In the present system, a polychromator was used, and thus the signal integration of a whole peak for peak-area measurement could be carried out with aid of the computer without the problem of wavelength adjustment.

Determination of REEs in Standard Rock Samples. The present HPLC/ICP-AES system was applied to the determination of REEs in seven standard rock samples issued from the Geological Survey of Japan (GSJ). The rock samples were decomposed by acid digestion as follows.

First, powdered rock sample was dried at 110 °C for 4 h. Then 0.4 g of the sample was weighed in a Teflon® breaker and wetted with a small amount of water. Five ml of concentrated nitric acid was added and heated nearly to dryness. Then 20 ml of 50% (w/w) hydrofluoric acid was added and heated to dryness. Furthermore, 5 ml of 60% (w/w) perchloric acid was added to the residue and heated until white fume of perchloric acid appeared. After standing cool, 2 ml of concentrated nitric acid was added and evaporated to dryness again. Finally, the residue was dissolved to 25 ml with 0.1 M nitric acid. In the determination of REEs, 400 µl of the sample solution was injected into the ion exchange column of HPLC.

When a shorter column (IC-Cation-SW) was used for the analysis of rock samples containing large amount of diverse elements, separation of REEs from diverse elements was incomplete, and thus the determination of REEs was almost impossible. When a longer SP-2SW column was utilized, REEs and diverse elements were much better separated, as is schematically shown in Fig. 3, and then REEs could be determined more accurately and precisely.

Table 4 shows the analytical results for REEs in the GSJ standard rock samples along with the certified values.[21] The experimental conditions were the same as those in Fig. 1. The results in Table 4 were the mean values in 3—5 times repeated measurements. In general, reproducibility was within 2—20% as the relative standard deviation, depending on the concentrations of REEs in rock samples. The analytical results were almost consistent with the certified values. Disagreement between observed and certified values for heavy REEs in JG-1 may be attributed to incomplete decomposition of heavy REE-rich refractory minerals by the present acid digestion method.[9] Terbium and Tm for all samples

Table 4. Analytical Results for Geological Standard Rock Samples Determined by the HPLC/ICP-AES System[a]

Element	Concentration/μg g^{-1}													
	JA-1		JA-2		JA-3		JB-1		JB-2		JB-3		JG-1	
	Obs.	Ref.	Obs.	Ref.	Obs.	Ref.	Obs.	Ref.	Obs.	Ref.	Obs.	Ref.	Obs.	Ref.
Y	26.7	30.6	15	18.1	18	21.3	14	24.4	22	24.9	24	27.0	17	28.5
La	4.7	5.1	15	16.3	9.8	9.00	30	37.9	2.3	2.37	9.0	8.89	22	22.4
Ce	12.9	13.5	32	32.7	22	23.3	57	66.7	6.3	6.77	19.3	21.5	44.8	45.9
Pr	1.8	1.98	4.6	4.38	3.0	2.25	7.8	7.02	1.7	0.96	3.3	3.39	4.3	5.21
Nd	11	11.0	14	13.8	12	12.3	21	26.7	5.4	6.70	16.5	15.4	19.9	19.5
Sm	3.6	3.52	2.8	3.12	3.0	3.14	4.5	5.07	2.5	2.25	3.9	4.27	5.3	4.67
Eu	1.1	1.17	0.87	0.94	0.86	0.85	1.34	1.50	0.88	0.86	1.3	1.31	0.73	0.74
Gd	4.5	4.36	4.1	3.11	1.9	2.94	4.8	4.91	3.7	3.28	4.3	4.47	3.6	4.20
Tb	N.D.	0.77	N.D.	0.42	N.D.	0.52	N.D.	0.84	N.D.	0.62	N.D.	0.75	N.D.	0.83
Dy	4.8	4.53	2.4	3.01	3.3	2.97	3.8	4.07	3.90	3.66	4.5	4.55	3.7	3.93
Ho	1.1	0.94	0.61	0.46	0.74	0.48	0.69	0.80	0.85	0.81	0.90	0.79	0.77	0.83
Er	3.1	3.01	1.8	1.37	1.9	1.46	2.1	2.27	2.4	2.63	2.6	2.61	1.68	1.83
Tm	N.D.	0.48	N.D.	0.3*	N.D.	0.3*	N.D.	0.35	N.D.	0.45	N.D.	0.41	N.D.	0.44
Yb	2.8	2.92	1.4	1.67	1.9	2.18	1.4	2.16	2.2	2.51	2.3	2.62	1.6	2.49
Lu	0.44	0.47	0.25	0.27	0.40	0.32	N.D.	0.31	0.14	0.39	0.37	0.39	0.37	0.39

N.D.: not detected. a) The reference values were cited from Ref. 23. The values with asterisk are preferable values, and others are the recommended values.

and Lu for JB-1 could not be determined because of their very low concentrations and spectral interferences of Fe.

Determination of REE Impurities in Rare Earth Oxides. The present HPLC/ICP-AES system was further applied to the determination of impurity REEs in Y_2O_3 (99.99%), La_2O_3 (99.5%), and Pr_6O_{11}, Er_2O_3, and Yb_2O_3 (99.9%), purchased from Wako Pure Chemical Industries Ltd. (Osaka). These rare earth oxides were dissolved with nitric acid. The sample solutions injected into the system for analysis contained 2000 μg ml^{-1} of major REEs. Only Yb in Pr_6O_{11} and Gd in Yb_2O_3 could be determined by the present HPLC/ICP-AES system, and their concentrations (in solid sample) were 11.5 μg g^{-1} and 3730 μg g^{-1}, respectively. The same samples were analyzed also by inductively coupled plasma mass spectrometry (ICP-MS; model SPQ-6500 from Seiko Instrument Inc., Tokyo) after further dilution. The concentrations of major REEs in the analysis solution for the ICP-MS measurement were 500 μg ml^{-1}. The concentrations of Yb in Pr_6O_{11} and Gd in Yb_2O_3 determined by ICP-MS were 13.6 and 3840 μg g^{-1}, respectively. They were in good agreement with the results by HPLC/ICP-AES. Other impurity REEs were also determined by ICP-MS, and the analytical results for Pr_6O_{11} and Yb_2O_3 are shown in Table 5. As in seen from Table 5, the concentrations of impurity REEs in REE oxides were much lower than the detection limits of the present HPLC/ICP-AES system. In the previous study,[13] many rare earth impurities in rare earth oxide reagents could be determined by the similar HPLC/ICP-AES system. The detection limits of the present HPLC/ICP-AES were almost similar to those in the previous study,[13] and rare earth oxides analyzed in the previous and present studies were of the same grade purchased from the same manufacturer. The present result suggests that purity of commonly available rare earth reagents was markedly improved in last decade.

Table 5. Concentrations of Impurity Rare Earth Elements in Yb_2O_3 and Pr_6O_{11} Determined by ICP-MS

Element	Concentration / μg g^{-1}	
	Pr_6O_{11}	Yb_2O_3
Y	0.743	0.458
La	0.379	0.125
Ce	1.70	0.862
Pr	---	1.93
Nd	1.07	0.811
Sm	0.291	4.31
Eu	0.180	0.174
Gd	1.20	3840
Tb	—[a]	0.374
Dy	0.258	0.098
Ho	0.022	0.067
Er	1.44	1.03
Tm	0.046	—[a]
Yb	13.6	---
Lu	0.093	—[a]

a) Not determined because of spectral interferences due to major REE.

Conclusion

The on-line separation/detection system of HPLC/multichannel ICP-AES was developed for the simultaneous multielement determination of REEs. Using an ion-exchange column and α-HIBA as the mobile phase, REEs were almost completely separated, which was helpful to eliminate mutual spectral interference of REEs. In the present HPLC/ICP-AES system, only Fe, Na, and Al provided the overlapped peaks with some of REEs, and spectral interferences of Fe with Lu, Yb, and Tm had to be taken into consideration. Rare earth elements in geological standard rock samples were successfully determined by the present system, although the analytical sensitivities of the present system were not sufficient for analysis of impurity REEs in high purity REEs. Thus it can be concluded that the online HPLC/ICP-AES system is useful as a conventional method for the multielement determination of REEs at the concentration level higher than ca. 1 $\mu g\,g^{-1}$.

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