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DETERMINATION OF 15 RARE EARTH ELEMENTS BY LIQUID CHROMATOGRAPHY WITH INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRIC DETECTION

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An inductively coupled plasma atomic emission spectrometer (ICP-AES) interfaced with high performance liquid chromatography (HPLC) has been applied to the determination of 15 rare earth elements (14 lanthanide elements and Y). The separation of rare earth elements was performed by HPLC with a cation exchange column using ammonium lactate buffer. The ICP-AES was used as a high-sensitive and an element-selective detector for rare earth elements.

Since industrial utilization of rare earth elements has been extensively expanded,1) the demand for the precise and accurate determination of rare earth elements has increased. The measurements of rare earth elements have been performed by instrumental techniques, such as X-ray fluorescence,2) atomic absorption spectrometry,3) colorimetry,4) neutron activation analysis,5) and isotope dilution mass spectrometry.6) Recently ICP-AES has received much attention for the determination of rare earth elements because ICP-AES has the following advantages: low detection limits, good precision and/or accuracy, and capability of rapid determination of all rare earth elements.7-10) In the determination with ICP-AES, however, many spectral interferences with rare earth elements are prone to be serious problems.8-10) Crock et al. eliminated the interferences by selecting the wavelengths with mathematical corrections and determined rare earth elements in geological materials, which contained almost similar concentration levels of rare earth elements.10)

In this paper ICP-AES interfaced with HPLC is applied to the determination of rare earth elements. In this system, the separation of rare earth elements by HPLC helps to avoid erroneous analytical results from spectral interferences.

The HPLC system consisted of two solvent delivery pumps (Model LC-3A from Shimadzu Co.), an injection valve (Model 7125 from Rheodyne Co.), and a 4 mm i.d. × 25 cm long stainless steel column packed with a cation exchange resin of strong acid type (IEX-210 SC 10 µm from Toyo Soda Co.). The gradient elution was performed by controlling the solvent flow rate from two pumps with a gradient programmer (Model GRE-3A from Shimadzu Co.). The column temperature was maintained at 50 °C with a column oven (Model CTO-2A from Shimadzu Co.). The sample volume injected into the column was 100 µl. The effluent outlet from the column was fed to a cross-flow nebulizer of the ICP spectrometer, which was interfaced with a small diameter Teflon tubing (0.5 mm i. d. × 30 cm long). The ICP-AES system consisted of an ICP torch system with a RF generator (Model ICAP-50A from Nippon Jarrell-Ash Co.), a monochromator (HR 1000 from Jobin Yvon Co.), a photomultiplier (R 787 from Hamamatsu Photonics Co.), and a recorder (Model R-10 from Rikadenki Co.). The torch of the ICP-AES was modified in the hole diameter and shape of the central tube for analyses of high salt content solutions. The monochromator was of the Czerny-Turner type (focal length 1 m) with a holographic grating (2400 grooves/mm) and was controlled by a computer scanning system.

The ICP was operated at 1.2 kW RF power, with 0.8, 1.0, and 16 l/min of flow rates for the carrier, auxiliary, and coolant argon gases, respectively. The flow rate of mobile phase of HPLC was set at 1.4 ml/min, which was a compromise flow rate for both separation by HPLC and detection by ICP-AES. Other experimental conditions were similar to those described in the previous papers.11,12)

Standard solutions of rare earth elements were prepared by dissolving high-purity oxides (>99.9 %) purchased from Wako Chemical Co.

When determining rare earth elements directly with ICP-AES, many spectral interferences with other co-existing rare earth elements cause analytical errors. Table 1 shows spectral interferences with other co-existing elements at the most sensitive spectral lines of analyzed rare earth elements. The values of interferences in Table 1 were indicated as the concentrations of analyzed elements. As can be seen from Table 1, the determination of rare earth elements by ICP-AES is extremely difficult because of interelement interferences. When ICP-AES is combined with HPLC, however, these spectral interferences may be avoided, since rare earth elements can be separated with HPLC before their introduction into the plasma.

Analytical figures of merit for rare earth elements obtained with a HPLC/ICP-AES system are listed in Table 2, in which the determination of rare earth elements was performed using a concentration gradient elution. The wavelengths of analyzed elements used were the same as those shown in Table 1. As can be seen from Table 2, the advantage of this system is capability of the determination without spectral

Table 1. Spectral Interferences of Co-existing Rare Earth Elements at the Most Sensitive Spectral Lines of Analyzed Elements

Analyzed element	Wavelength nm	Interfering elements and interference factor (ng ml^{-1}/10 μg ml^{-1})
Y	371.03	Pr 2.9, Nd 1.8, Sm 1.4, Eu 1.5
La	379.48	Ce 49, Pr 36, Nd 49, Sm 33, Eu 27, Tb 27, Ho 48, Er 41
Ce	413.77	Pr 59, Nd 85, Sm 52, Eu 63
Pr	390.84	Ce 2200, Nd 180, Sm 140, Eu 95, Gd 66, Tb 73, Dy 81, Er 330, Tm 65, Yb 81
Nd	401.23	Ce 1050, Pr 160, Tb 59, Dy 56
Sm	359.26	Y 23, Pr 35, Nd 370, Gd 1200, Tb 50, Dy 47, Ho 47
Eu	381.97	Nd 260, Er 7.0
Gd	342.25	Ce 59, Sm 19, Tb 67, Dy 65, Ho 76, ER 29
Tb	350.92	La 35, Ce 31, Pr 41, Sm 188, Gd 21, Dy 46, Ho 138
Dy	353.17	Nd 35, Eu 21, Tb 45
Ho	345.60	Pr 25, Nd 12, Sm 16, Tb 36, Dy 11
Er	337.27	Tb 160, Dy 42, Ho 23
Tm	313.13	Pr 16, Sm 10, Tb 36, Er 53
Yb	328.94	Pr 1.6, Nd 1.8, Tb 1.3, Dy 3.9, Ho 4.4, Tm 2.2

interferences, since rare earth elements can be detected separately. There were some elements which showed peak overlappings at the wings. Such elements were only elements showing close retention times in elution. When tops of the peaks were measured in determination, the interferences of other rare earth elements were negligibly small. Actually, with the present system spectral interferences were not observed at the concentration below 100 μg ml^{-1} of all rare earth elements, i. e., all the rare earth elements could be determined without the interferences. The detection limits (S/N=2) and reproducibilities are also summarized in Table 2. The calibration curves obtained by peak heights showed linear relationships in the concentration range of 0-500 μg ml^{-1} for all rare earth elements. Analytical results of a U. S. Geological Survey granodiorite rock sample are summarized in Table 3. The rock sample was dissolved by acid digestion procedure using hydrofluoric, nitric, and perchloric acids. The results of a GSP-1 sample show good agreement with the reference values reported in the literature.13)

Consequently, we can see from the results that the HPLC/ICP-AES system is useful for the determination of rare earth elements, even when their concentration levels are widely different from each other.

Table 2. Analytical Figures of Merit for Rare Earth Elements Determined by HPLC/ICP-AES System

Element	RT/min	HW/min	DL(μg ml^{-1})	RSD/%
Lu	3.80	0.49	0.004	3.0
Yb	4.68	0.55	0.001	3.0
Tm	5.78	0.75	0.02	2.6
Er	8.06	0.95	0.04	3.7
Ho	11.44	1.10	0.05	4.8
Y	13.06	0.85	0.005	3.4
Dy	14.60	0.86	0.06	5.0
Tb	18.16	0.80	0.08	6.9
Gd	21.20	0.80	0.07	4.4
Eu	22.36	0.76	0.02	1.2
Sm	23.50	0.78	0.1	4.2
Nd	27.02	0.80	0.1	3.6
Pr	29.06	0.81	0.2	3.4
Ce	32.00	0.95	0.3	7.4
La	37.60	1.17	0.05	4.9

RT, retention time; HW, half width; DL, detection limit; RSD, relative standard deviation (10 μg ml^{-1}); Mobile phase (linear concentration gradient method) 0.4 M ammonium lactate, pH 4.2 (0-8 min) → 0.6 M ammonium lactate, pH 4.2 (18 min) → 1.0 M ammonium lactate, pH 4.2 (31-40 min).

Table 3. Analytical Results of a USGS GSP-1 Standard Rock Sample

Element	GSP-1[a)]	
	Found	USGS[13)]
Y	26	30.4
La	177	191
Ce	386	394
Pr	57	50
Nd	181	188
Sm	31	27.1
Eu	2.8	2.4
Gd	13	15
Tb		1.3
Dy	5.1	5.4
Ho	3.9	<5
Er	4.7	3.0
Tm	2.9	
Yb	2.0	1.8
Lu	0.18	0.23

a) Values are in unit of μg g^{-1}.

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