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Versatile Simultaneous Multielement Measurement System with Combination of ICP-MS and ICP-AES through Optical Fiber

Hideyuki Sawatari, Eiji Fujimori, Akihide Itoh, Masahide Aikawa, and Hiroki Haraguchi*

Department of Applied Chemistry, School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-01

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A hyphenated system of inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) combined with aid of optical fiber was developed for versatile simultaneous multielement measurement of the elements from the major to ultratrace levels. In the present system, the emission signals from the argon ICP equipped for ICP-MS were led through optical fiber to a sequential-type monochromator for ICP-AES measurement. In consequence, the dynamic range of 9 orders of magnitude from a few pg ml^{-1} up to ca. 1000 μg ml^{-1} was obtained, which allowed the simultaneous determination of a variety of elements in the wide concentration range by ICP-MS and/or ICP-AES. The present system was applied to simultaneous multielement analysis of rock and seawater samples.

Nowadays inductively coupled plasma mass spectrometry (ICP-MS) is extensively used for ultratrace analysis of various samples.[1,2] The ICP-MS instruments provide the detection limits at a few-ppt (pg ml^{-1}) level for many elements. The linear dynamic range of 4 or 5 orders of magnitude and capability of multielement detection are also excellent analytical features of ICP-MS. The direct determination of major constituents by ICP-MS, however, is often difficult because the analytes at the concentration over 1 ppm (μg ml^{-1}) usually cause saturation of a detector for ICP-MS. Thus, when the determinations of both major and trace constituents are required, the major constituents must be separately determined by ICP-AES directly or by ICP-MS after further dilution of the sample solution, and then trace ones by ICP-MS. It is time-consuming to carry out such separate measurements for major and trace constituents. The separate determination for major and trace constituents also encounters difficulty when analysis is performed with limited sample amount.

Since a factor to restrict the upper limit of determination in ICP-MS is saturation of a conventional detector (secondary electron multiplier operated in ion counting mode), some commercial ICP-MS instruments have a low or no gain detector in order to extend the dynamic range to the higher concentration. Detuning of instrumental operating conditions to reduce the sensitivity is also made for the determination of analytes at the high concentration level. Considering the operation system for the mass spectrometer, however, it takes time to change the gain of the detector or other operating conditions. Therefore, the determination of analytes at both high and low concentration levels in a single measurement is not possible by employing such alternative methods.

Inversely, inductively coupled plasma atomic emission spectrometry (ICP-AES) is widely used as a reliable method for multielement analysis at the ppb and ppm levels.[3] As is well known, almost the same argon plasma is used as an ion source in ICP-MS and as a light source in ICP-AES.[4] Thus, exploitation to construct a combined system of ICP-MS and ICP-AES with a single plasma enables rapid simultaneous multielement determination at the quite wide concentration range from the lower ppt to the higher ppm levels. Such a system also helps save consumption of argon gas used for ICP-MS and ICP-AES measurements.

From the viewpoint of practical analysis, ICP-MS is prone to isobaric and polyatomic interferences as well as matrix effects, while ICP-AES often suffers from severe spectral interferences. Consequently, such interferences provide inaccurate analytical results in both ICP-MS and ICP-AES, although the causes of interferences are different from each other. A combined system of ICP-AES and ICP-MS is also helpful to intercalibrate the analytical data obtained by independent two methods for the analytes at the ppb level.

Several works[5—7] were reported about the combined system of ICP-MS and ICP-AES. Garbarino et al.[5] constructed a combined system of ICP-AES and ICP-MS by attaching two polychromators to an ICP-MS instrument with two sets of fiber optic cables. They measured major and trace elements simultaneously in geological and environmental standard samples, and correction for polyatomic interference in ICP-MS due to major constituents were made by using the analytical data for the major constituents determined by ICP-AES. Lepla et al.[6] developed a similar combined system which was equipped with a photodiode array detector. They operated the system under various experimental conditions and reported that there was no optimum conditions common to both ICP-MS and ICP-AES measurements. Although Garbarino et al.[5] and Lepla et al.[6] used commercial ICP-MS instruments to construct a combined system, Hobbs and Olesik[7] used a laboratory-made ICP-MS. They performed simultaneous time-resolved measurement of mass spectrometric signal and emission signal with their combined system, and analyzed signal fluctuations in ICP-MS and ICP-AES.

Among the previous works,[5—7] the systems of Lepla et al.[6] and Hobbs and Olesik[7] were not used for practical analysis. Garbarino et al.[5] analyzed standard reference samples using their combined system, but the analytical feasibilities including the detection limits for their system were not well evaluated. Nowadays, a commercial combined system of ICP-MS and ICP-AES (model POEMS from Thermo Jarrell Ash, Franklin, MA, USA) has become available. The commercial system is combined with an optical alignment using a mirror and consists of a quadrupole mass spectrometer and an echell polychromator with a solid state multichannel detector.

In the present study, a combined system of ICP-MS and ICP-AES (hereafter abbreviated as "ICP-MS/AES") was constructed by attaching a monochromator through fiber optics to a commercial ICP-MS instrument, and analytical performance of the system including the detection limits and practical analysis was evaluate in detail.

Experimental

Instrumentation. A schematic diagram of the combined system is shown in Fig. 1. An ICP-MS instrument used was of model SPQ8000 from Seiko Instrument Inc. As a spectrometer for emission measurement, the monochromator of a sequential ICP-AES instrument of model SPS1500V from Seiko was used after detaching its plasma torch. The emission signals from the plasma of ICP-MS were introduced to the monochromator by means of a fiber optic cable of 3 m in length. The cable consisted of 21 optical fibers (model ST-U200D-SY from Mitsubishi Cable Industries Ltd.), and the core diameter of each optical fiber was 200 μm. The emission light was collected just in front of the sampling cone tip using a quartz lens and focused on an end of the fiber optic cable. Focal length of the lens was 15 mm and the image of the plasma with a reduction of 1/3 was formed. The other end of the cable was mounted at the position where a plasma torch for ICP-AES was originally placed. The emission light through the cable was introduced into the monochromator and detected by a photomultiplier. Sequential multielement analysis was possible by the ICP-AES spectrometer used in the present experiment. The operating conditions and specifications of the system are listed in Table 1.

Table 1. Operating Conditions of ICP-MS and Specifications of Monochromator

ICP-MS	
Rf frequency	27.12 MHz
Rf power	1.2 kW
Outer Gas	Ar 16 l min^{-1}
Intermediate Gas	Ar 1.0 l min^{-1}
Carrier Gas	Ar 0.41 l min^{-1}
Sampling depth[a)]	8 mm
Sampling cone	Copper, 1.1 mm orifice diameter
Skimmer cone	Copper, 0.35 mm orifice diameter
Scanning mode	Peak hopping
Data points	3 points/peak
Dwell time	10 ms/point
Integration	100 times
Monochromator	
Mounting	Czerny–Turner
Focal length	1000 mm
Grating	3600 grooves mm^{-1}
Entrance slit width	20 μm
Exit slit width	30 μm

a) Distance between work coil and top of sampling cone.

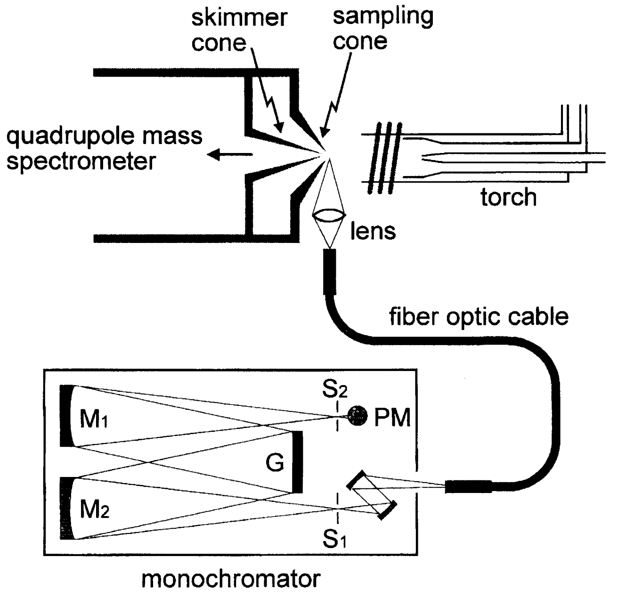

Fig. 1. Schematic diagram of the ICP-MS/AES combined system. S_1: entrance slit, S_2: exit slit, M_1, M_2: mirror, G: grating, PM: photomultiplier.

Chemicals. The standard solutions were prepared by diluting the commercial standard solutions of 1000 μg ml^{-1} for atomic absorption analysis. The blank solution contained the same concentration of the acid as the standard solutions, which was 0.1 M (M=mol dm^{-3}) of nitric acid in most cases.

Results and Discussion

Operating Conditions for Simultaneous ICP-MS and ICP-AES Measurements. The instrumental operating conditions of the combined ICP-MS/AES system were first optimized for the ICP-MS measurement. The conditions examined were Rf power, carrier argon gas flow rate, and sampling depth. In this experiment, sampling depth which was the distance between the work coil and the sampling orifice in the ICP-MS instrument, corresponding to the observation height in ICP-AES, provided most significant influence to the signal-to-background ratio (S/B) in the emission measurement. Thus, the effect of sampling depth on yttrium signal was examined in detail, and the result is shown in Fig. 2. As is seen in Fig. 2, the S/B of the emission signal at Y II 377.4 nm was remarkably larger, when the sampling depth was longer. In this case, the sensitivity of the mass spectrometric signal ($^{89}Y^+$) became inversely poorer. These results are similar to those reported in the previous works.[5,6] That is, the experimental conditions for the combined ICP-MS/AES system could not be optimized at the best conditions common to both ICP-MS and ICP-AES measurements. In the present experiment, the sampling depth was set at 8 mm, considering the sensitivity in the mass spectrometry.

Detection Limits Obtained by ICP-AES in the Combined System. The detection limits obtained by ICP-AES in the present combined system were investigated, and the results are summarized in Table 2. For comparison, the detection limits were also estimated with a conventional ICP-AES instrument, and the results are shown in Table 2, too. The conventional ICP-AES instrument used here was of model SPS1500V from Seiko Instruments Inc., which was the same instrument that was used in the combined system. In estimation of the detection limits, the emission signal for the blank solution was integrated for 10 s, and the detection limits were calculated as the concentration corresponding to 3 times of the standard deviation of the blank signals, which were measured 20 times.

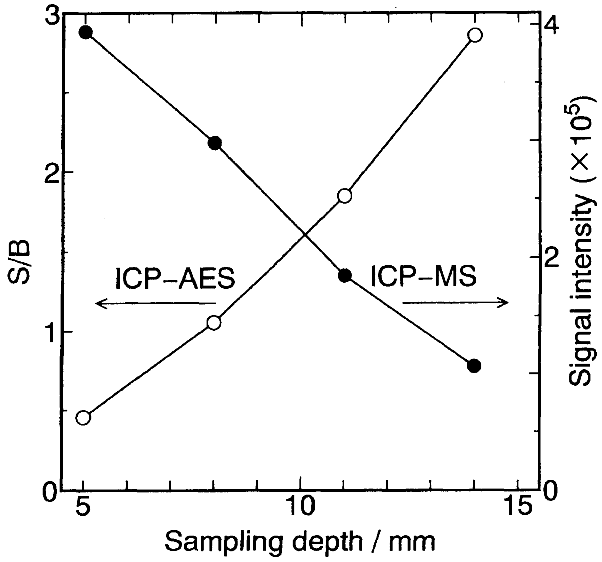

Fig. 2. Effects of sampling depth on S/B for emission signal at Y II 377.4 nm (○) and intensity for mass signal of $^{89}Y^+$ (●). The value on the horizontal axis is the sampling depth in ICP-MS, which corresponds to the observation height in ICP-AES. Other operating conditions were the same as Table 1. Analysis solution: 100 ppb Y in 0.1 M HNO_3.

The detection limits obtained by ICP-AES in the combined system were worse than those obtained by conventional ICP-AES. Compared with conventional ICP-AES, the emission measurement in the combined system had disadvantages such as transmittance loss in the optical fiber and the operating conditions, as mentioned above. In general, the deterioration factor in the detection limits was about 10, while it was about 50 because of low transmittance of the optical fiber in the shorter wavelength region. The wavelength dependence of transmittance for the optical fiber used in the present experiment is shown in Fig. 3. As is seen in Fig. 3, the transmittance in the UV (ultraviolet) region below 400 nm was significantly smaller, although the "UV-grade" optical fiber was used. Even so, the detection limits in the ICP-AES measurement by the present system were good enough, because the emission measurement in the combined system was mainly applied to the determination of major components and the analytes at the trace concentration level could be determined by mass spectrometry.

The detection limits obtained by ICP-MS in the present system are also shown in Table 2. They are almost the same as those obtained by conventional ICP-MS instrument. Of course, the detection limits obtained by ICP-MS are superior to those by ICP-AES in the present combined system. In consequence, mul-

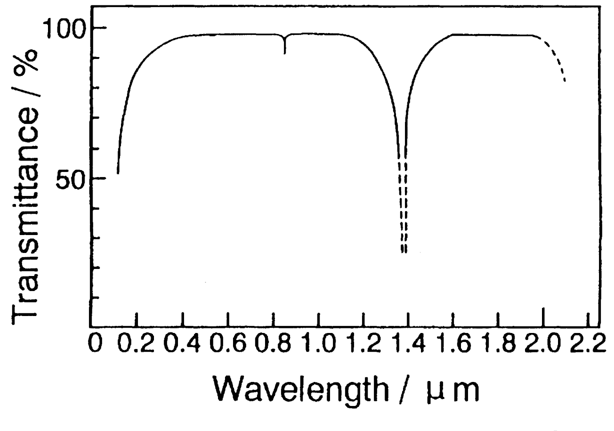

Fig. 3. Wavelength dependence of transmittance characteristics of the optical fiber (1 m in length). Cited from the catalog of Mitsubishi Cable Industries Ltd. with some modification.

Table 2. Detection Limit Obtained by the Present Combined System and Conventional ICP-AES (ng ml^{-1})

Element	ICP-AES				ICP-MS	
	Wavelength$^{a)}$ nm	Present system	Conventional system	Ratio$^{b)}$	Mass number	Present system
Ba	455.4 II	1.8	0.32	5.6	138	0.013
Sr	407.7 II	0.53	0.04	13	88	0.012
Ca	393.4 II	0.36	0.02	18	44	0.32
Eu	382.0 II	2.1	0.42	5	151	0.0004
La	379.4 II	5.9	0.31	19	139	0.0006
Y	377.4 II	5.5	0.27	20	89	0.0004
Zr	343.8 II	14	1.8	7.8	90	0.034
Ti	334.9 II	4.2	0.30	14	48	0.062
Cu	324.7 II	7.6	2.3	3.3	63	0.025
Al	308.2 I	51	12	4.3	27	0.092
Ga	294.4 I	75	7.8	9.6	69	0.0062
Si	288.2 I	37	4.6	8.0	29	2.7
Mg	279.5 II	0.85	0.11	7.7	24	0.12
V	268.7 II	47	2.6	18	51	0.0081
Fe	259.8 II	18	0.81	22	57	0.54
Mn	257.6 II	3.0	0.18	17	55	0.0035
B	249.7 I	12	3.1	3.9	10	8.0
Be	234.9 II	0.41	0.079	5.2	9	1.9
Ni	231.6 II	81	1.5	54	60	0.0071
Co	228.6 II	34	1.1	31	59	0.0049
Cd	226.5 II	20	1.5	13	114	0.0015
Zn	213.8 I	8.7	0.44	20	64	0.030
P	213.6 I	270	13	21	31	2.8
W	207.9 II	320	11	29	184	0.0060
Cr	205.5 II	130	2.0	65	52	0.0058
Mo	202.0 II	130	5.1	25	98	0.0063
As	193.6 I	440	1.7	259	75	0.011
Sn	189.9 II	600	10	60	120	0.028

a) I and II indicate atomic and ionic lines, respectively. b) Ratio was calculated as [(detection limit by present system)/(detection limit by conventional system)], which thus means the deterioration factor in the emission measurement by the present combined ICP-MS/AES system.

tielement determination of major, trace and ultratrace constituents was possible by the present combined system.

Linearities of Calibration Curves of ICP-MS/AES System. In order to examine the linearity of the calibration curve in the combined ICP-MS/AES system, the calibration curves of ICP-MS and ICP-AES were measured by nebulizing the various concentrations of the yttrium solutions into the argon plasma. The calibration curve obtained by the present system is shown in Fig. 4. In ICP-MS measurement, the detection limit of Y was 0.4 ppt and the calibration curve was linear up to ca. 1 ppm. On the other hand, in ICP-AES measurement, the detection limit of Y was 5.5 ppb and the calibration curve was linear up to ca. 1000 ppm. As the result, the total linear dynamic range obtained by the combined system was almost 9 orders of magnitude. In general, the analytes in the range of ppt and ppb can be determined by ICP-MS, while those in the range of ppm and sub-ppm can be determined by ICP-AES. Since the linear calibration curves of ICP-MS and ICP-AES overlap with each other in the ppb range, as can be seen in Fig. 4, the analytes at the ppb concentration level could be determined by both of the two methods. This indicates that the intercalibration of analytical results is possible using one system by ICP-MS and ICP-AES.

Analytical Precision in the ICP-MS/AES System. In order to investigate the effect of the fiber optics on the emission measurement by the present system, the solution containing 100 ppb of Sr was measured 10 times at 5 min intervals, and the precision of the emission signal (407.7 nm) as well as mass spectrometric signal ($^{88}Sr^{+}$) were estimated as relative standard deviation (RSD). The RSD calculated from 10 times measurements was 1.9% for ICP-AES and 3.2% for ICP-MS. These values were almost comparable with those obtained by conventional ICP-AES and ICP-MS independently. In the ICP-AES measurement by the present system, the precision was almost constant at the same concentration because of the stable measurement system. On the other hand, the precision for ICP-MS was significantly poor due to instrumental drift, although

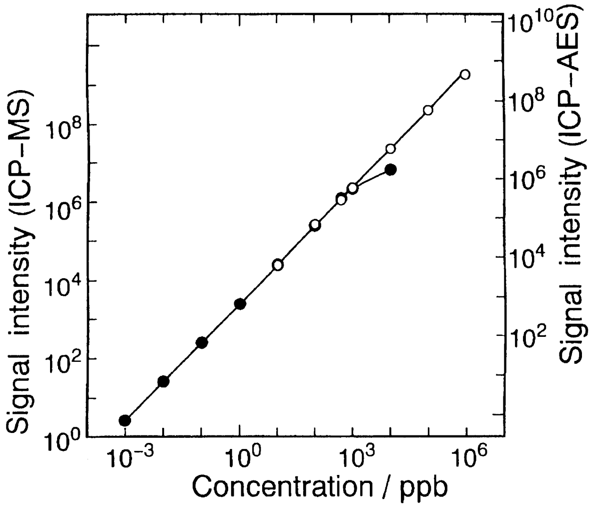

Fig. 4. Calibration curve for yttrium obtained by ICP-MS/AES combined system. ● MS ($^{89}Y^+$); ○ AES (Y II 377.4 nm).

the use of the internal standard method could improve to some extent the precision in ICP-MS. These results indicate that the use of fiber optics does not influence the analytical precision in the ICP-AES measurement. Hence, although major constituents can be determined by an ICP-MS instrument with a low gain detector, as mentioned earlier, ICP-AES has an advantage in the determination of major constituents from a viewpoint of precision.

Determination of Major and Minor Elements in Standard Rock Sample. The present system was applied to the simultaneous determination of major elements, alkaline earth and rare earth elements in geological standard rock sample (JB-1a; basalt) issued from the Geological Survey of Japan (Table 3). About 0.1—0.2 g of the powdered sample was decomposed by hydrofluoric acid and perchloric acid. After heating to near dryness, the residue was dissolved to 100 ml with 1 M nitric acid. The solution was further diluted 10 times with 1 M nitric acid and provided to analysis. In the analysis solution, 10 ppb each of Ge, In, and Re were added as the internal standard elements in the determination by ICP-MS. The internal standard correction was made in almost similar manner to that reported earlier.[8] For the analytes in the mass range of $m/z<74$, $74<m/z<115$, $115<m/z<187$, the signal intensities of Ge, Ge and In, In and Re were used for the correction, respectively. In the determination by ICP-AES, internal standardization was not carried out.

The results for JB-1a (basalt) are shown in Table 3. Magnesium, Fe, Al, and Ti were determined by ICP-AES, and Mn, Sr, and Ba were determined by both ICP-AES and ICP-MS. Sodium, P, K, and rare earth elements were determined by ICP-MS. Difference between the observed and reference values were within 5% except Y, Pr, Dy, and Ho. For Mn, Sr, and Ba, the results obtained by ICP-MS and ICP-AES were in good agreement with the reference values.

Table 3. Concentration of Major Composition, Alkaline Earth, and Rare Earth Elements in JB-1a Determined by ICP-MS/AES Combined System

Composition	Observed[a]		Reference[b]
	ICP-AES	ICP-MS	
Major composition/%			
TiO_2	1.29 ±0.01		1.3
Al_2O_3	14.4 ±0.1		14.51
Fe_2O_3 (total)	9.00 ±0.26		9.10
MnO	0.143±0.003	0.142±0.002	0.15
MgO	7.66 ±0.14		7.75
CaO	9.10 ±0.11		9.23
Na_2O		2.76 ±0.11	2.74
K_2O		1.42 ±0.06	1.42
P_2O_5		0.254±0.006	0.260
Alkaline earth and rare earth elements/$\mu g\,g^{-1}$			
Sr	464 ±7	437 ±3	443
Ba	503 ±5	481 ±5	497
Y		19.9 ±0.2	24.0 ±2.7
La		36.2 ±0.4	38.1 ±1.9
Ce		63.4 ±0.6	66.1 ±5.3
Pr		6.71 ±0.13	7.3 ±0.8
Nd		24.7 ±0.8	25.5 ±2.1
Sm		4.9 ±0.3	5.07±0.4
Eu		1.49 ±0.10	1.47±0.1
Gd		4.7 ±0.3	4.54±0.4
Tb		0.676±0.025	0.69±0.08
Dy		3.92 ±0.16	4.19±0.4
Ho		0.73 ±0.04	0.64±0.09
Er		2.10 ±0.10	2.18±0.6
Tm		0.30 ±0.02	0.31±0.06
Yb		2.01 ±0.13	2.1 ±0.2
Lu		0.29 ±0.02	0.32±0.05

a) Mean and standard deviation obtained from 10 times measurement of the same analysis solution. b) Reference values for rare earth elements were cited from Ref. 7 and others were from Ref. 8. The errors are the standard deviation of more than four reported values.

Since the monochromator utilized in the present study could not detect emission lines with wavelength longer than 500 nm, Na and K could not be determined by emission spectrometry. They could be determined by ICP-MS in the present experiment. In addition, although P could not be determined by ICP-AES because of insufficient detection limit, ICP-MS allowed the simultaneous determination of P and other elements.

Determination of Trace Elements in Seawater. Trace metals in coastal seawater collected at Nagoya port (Aichi prefecture, Japan) were concentrated by a factor of 500 with use of chelating resin (Chelex 100),[11] and determined by the present combined system. In the present experiment, the volumes of the sample seawater and the analysis solution after the pretreatment were 1 l and 2 ml, respectively. Although the large preconcentration factor as 500 was desirable to determine trace metals as many as possible, the concentrations of some of the trace metals in the sample seawater resulted in so

Table 4. Trace Metal Concentration in Coastal Seawater Determined by ICP-MS/AES Combined System

Element	Concn/ng ml^{-1}	Element	Concn/ng ml^{-1}
Al$^{a)}$	17	Zr	0.01
Sc	0.0013	Mo$^{a)}$	9.1
Ti	0.066	Cd	0.050
V	2.6	Sn	0.041
Mn$^{a)}$	42	La	0.013
Fe$^{a)}$	4.2	Ce	0.015
Ni	3.9	Tb	0.0005
Cu	0.92	Lu	0.0011
Zn	8.2	W	0.16
Ga	0.012	Pb	0.071
Y	0.045	U	3.8

a) Determined by ICP-AES of the combined system. Other elements were determined by ICP-MS.

high that the determination by ICP-MS after 500-times preconcentration was difficult. Thus, the concentration levels of such elements in the analysis solution became preferable to the determination by ICP-AES. In addition, the volume of the analysis solution was only 2 ml which was too small for the separate analysis by ICP-MS and ICP-AES. Hence, the present ICP-MS/AES combined system was employed to determine Al, Mn, Fe, and Mo by the emission measurement and other elements by the mass spectrometric measurement. Similar to the rock analysis described above, the internal standardization was carried out for ICP-MS measurement. The results are shown in Table 4. As is seen in Table 4, 22 trace and ultratrace metals in total could be determined by the present ICP-MS/AES system. Then it is concluded that the present system is very valuable and versatile when the analytes at various concentration levels in small sample amount or volume should be determined.

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