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Simultaneous Multielement Determination of Major, Minor, and Trace Elements in Soil and Rock Samples by Inductively Coupled Plasma Emission Spectrometry.

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A simple and convenient analytical method for simultaneous multielement determination of soil and rock samples has been investigated by inductively coupled plasma emission spectrometry. Spectral interferences due to major elements were examined in detail, and the correction coefficients for minor and trace elements were estimated for correction of matrix effects. The determinations of minor and trace elements as well as major elements could be performed without matrix matching of the standard solutions. The present method investigated has been applied to the analysis of various soil and rock samples, and the analytical results have been compared with those obtained by atomic absorption spectrometry.

An inductively coupled plasma (ICP) is an efficient excitation source in emission spectrochemical analysis for major, minor and trace elements in various samples.[1] As has been extensively studied,[2–8] ICP optical emission spectrometry (ICP-OES) provides high sensitivities for a variety of elements, wide linear dynamic ranges of calibration curves, and less chemical and ionization interferences, along with simultaneous multielement detection capability. However, spectral interferences with major elements in samples, which originate from spectral line overlapping, stray light or scattering due to strong emission lines, and continuous emission backgrounds, are severe problems in the determination of trace elements.[9,10] Usually in conventional analyses, the concentrations of major elements in sample solutions and those in standard solutions are matched as closely as possible in order to compensate the matrix effects. This experimental procedure requires the different sets of standard solutions for samples with different matrices, and so it is not easily applicable to or convenient for rapid analysis of a number of samples. The soil or rock samples have been analysed by ICP-OES.[11–16] Since the matrix compositions of soil or rock samples are complicated, spectral interferences mentioned above should be carefully corrected for accurate analyses. In addition, the chemical reagents used for digestion are often prone to contamination and physical interference as well as spectral interference. Generally, acid digestion is preferable to alkali fusion in the viewpoints of contamination from chemicals used and nebulization interference. Hence, acid digestion method has been employed in the present experiment.

Furthermore, we have investigated a conventional method for analysis of digested soil and rock samples without matrix-matching of major elements. The changes of background intensities for trace elements at the monitored wavelengths due to major elements are estimated as the correction coefficients for background correction. The background correction method examined is applied to the analysis of soil and rock samples, and the analytical values are compared with those obtained by atomic absorption spectrometry.

Experimental

Instruments. An ICP emission spectrometer (Mode Plasma Atomcomp Mk II) from Jarrell-Ash Co. was used with a crossflow type nebulizer. The instrumental components and operating parameters for the emission measurements are summarized in Table 1. The solution was fed to the nebulizer through a Teflon capillary tube. The analytical lines employed are shown in Table 2. The calibration curves were made by joining the points for the blank and standard with the straight lines.

Chemicals and Standard Solutions. All the chemicals used were of analytical or spectrochemical reagent grade. Commercially available standard solutions (1000 μg/ml) for atomic absorption spectrometry (Wako Pure Chemicals Co.) were used for the stock solutions except for K, Na, Be, P, Pb, Sc and Y, which were prepared from proper compounds or metals according to the recommended methods.[17] Working standard solutions for calibration curves were simply prepared by mixing and/or diluting the stock solutions in four groups. The combinations of elements for working standard solutions

Table 1. Instrumentation and operating parameters

ICP spectrometer	Jarrell-Ash Plasma Atomcomp MkII
Frequency	27.12 MHz
Output power	1.1 kW
Coolant gas	argon 16.0 l/ml
Auxiliary gas	argon 0.8 l/ml
Carrier gas	argon 1.0 l/ml
Nebulizer	cross-flow type
Observation height	17 mm above work coil
Polychromator	Paschen-Runge type (75 cm focal length)
Grating	2400 grooves/mm
Reciprocal linear dispersion	0.54 nm/mm at 270 nm
Entrance slitwidth	25 μm
Exit slitwidth	50 μm (100 μm for Na and K)
Monochromator	Ebert type (50 cm focal length)

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Table 2. Compositions of mixed standard solutions for calibration curves and analytical wavelengths

Standard I			Standard II			Standard III			Standard IV		
	Concn μg ml^{-1}	Wavelength nm		Concn μg ml^{-1}	Wavelength nm		Concn μg ml^{-1}	Wavelength nm		Concn μg ml^{-1}	Wavelength nm
Al	500	I 308.2	As	5	I 193.6	Be	5	II 313.0	Si	50	I 288.2
Ca	100	II 317.9	Ba	5	II 483.4	Bi	5	I 223.0[a]			
Fe	300	II 259.9	Cr	5	II 205.5[a]	Cd	5	I 228.8[a]			
K	40	I 766.5	Ga	1	I 417.2	Co	5	II 228.6			
Mg	40	II 279.1	Mn	5	II 257.6	Cu	5	I 324.7			
Na	30	I 589.0	P	5	I 214.9[a]	La	5	II 398.8			
Ti	30	II 334.9	Pb	5	II 220.3	Mo	5	II 202.0			
			Sr	5	II 421.5	Ni	5	II 231.6[a]			
			V	1	II 292.4	Sb	5	I 217.5			
			Zr	2	II 343.7	Sc	5	II 361.3			
						Sn	5	I 189.9			
						Y	5	II 371.0			
						Zn	5	I 213.8[a]			

a) 2nd order.

are summarized in Table 2.

Standard I is composed of major elements in usual soil samples, and these concentrations are similar to the average values of the digested solutions of soil samples. Standards II and III are composed of minor and trace elements. Standard IV for Si was prepared to check the suitability of the digestion procedure, because incomplete digestion resulted in abnormally high concentration of Si in the digested solutions.

In order to minimize the variation of the nebulization efficiency due to the differences of the viscosities of the solutions, the acid contents in each standard solution were adjusted to be 3% $HClO_4$ and HCl so as to match those in the digested sample solutions.

Digestion Procedure. About 0.5 g of powdered soil or rock sample was dried at 110 °C for 4 h, and taken into a Teflon beaker. Ten ml of concd HNO_3 was added in the beaker, and heated to near dryness on a hot plate at 200 °C. Five ml of HF was added into the dried residue, and heated again to dryness. After cooling, 3 ml of HNO_3 and 5 ml of $HClO_4$ were added, and heated for about 3 h until white fume of $HClO_4$ appeared. The digested sample was diluted with 20 ml of distilled water and 3 ml of HCl, and filtered with a 5 A filter paper. Finally, the filtrate was filled up to 100 ml with water.

According to the digestion procedure described above, the final concentration of $HClO_4$ was about 3%, and the content of total salts (major components) was less than 0.5%. As mentioned earlier, the concentrations of $HClO_4$ in the standard solutions were adjusted to be 3%. It was reported that the spectral interferences by major elements were linear in the concentration range of the total salts less than 0.5%.[16] It should be noted that the decomposition of oxide minerals such as chromite and zircon by the digestion method above may not be complete. In general, however, the contents of such minerals in soil samples are not significant.

Table 3. Detection limits, elemental contents of soil, and analytical recoveries

Element	Detection limit (μg ml^{-1})	Detection limit for soil (μg g^{-1})	Average[a] content in soil μg g^{-1}	Recovery %
As	0.4	80	6	102.4
Ba	0.001	0.2	500	100.4
Be	0.0006	0.12	6	101.6
Bi	0.04	8	—	99.6
Cd	0.004	0.8	0.06	103.3
Co	0.02	4	8	102.9
Cr	0.008	1.6	100	102.3
Cu	0.004	0.8	20	104.3
Ga	0.05	10	30	104.5
La	0.02	4	30	100.5
Mn	0.005	1	850	93.5
Mo	0.02	4	2	98.3
Ni	0.02	4	40	102.2
P	0.2	40	650	99.9
Pb	0.2	40	10	99.5
Sb	0.1	20	—	101.1
Sc	0.002	0.4	7	99.1
Sn	0.04	8	10	98.4
Sr	0.003	0.6	300	100.0
V	0.01	2	100	101.7
Y	0.004	0.8	50	99.8
Zn	0.007	1.4	50	104.3
Zr	0.01	2	300	106.2

a) Cited from Ref. 18.

Results and Discussion

Detection Limits and Recoveries. The detection limits, average contents of minor and trace elements in soils,[18] and the recoveries of elements in the digestion procedure are summarized in Table 3. The detection limits were defined as the analyte concentrations equivalent to twice the standard deviations of the background emission intensities in the presence of major elements at the average concentration levels in the soil samples. The detection limits were obtained under the compromised operating conditions shown in Table 1. The compromised conditions were chosen to make the detection limits as low as possible and to avoid the spectral interferences of major elements as much as possible.

TABLE 4. CORRECTION COEFFICIENTS FOR SPECTRAL INTERFERENCES OF MAJOR ELEMENTS AT EMISSION LINES OF MINOR AND TRACE ELEMENTS[a)]

Element	Major elements						
	Al	Ca	Fe	K	Mg	Na	Ti
Sn	1.60	—	0.318	—	0.063	—	5.10
As	23.9	—	2.92	—	0.206	—	0.400
Mo	1.17	—	0.187	—	0.067	—	0.042
Cr	0.354	—	0.052	—	0.026	—	0.026
Zn	0.038	—	0.048	0.031	0.052	0.031	0.117
P	1.48	0.199	1.84	—	0.819	—	0.367
Sb	1.01	—	1.78	0.030	0.248	0.037	0.344
Pb	1.21	—	0.563	—	0.259	—	1.81
Bi	0.046	—	0.291	—	0.351	—	2.15
Co	0.024	—	0.181	—	0.048	0.001	1.256
Cd	0.006	—	0.032	—	0.018	—	0.013
Ni	—	—	0.232	—	0.230	—	0.036
Mn	0.187	0.009	0.134	—	0.015	—	0.038
V	0.027	0.025	0.297	—	0.264	0.011	0.587
Be	—	—	—	—	—	—	0.007
Cu	0.006	0.007	0.031	0.005	0.009	0.002	1.73
Zr	0.003	0.016	0.093	—	—	0.007	0.081
Sc	—	—	0.004	0.002	0.007	0.004	0.016
Y	—	0.009	0.010	—	—	0.003	0.085
La	0.015	0.633	0.008	—	0.002	0.016	0.123
Ga	0.017	0.213	0.263	—	—	—	5.81
Sr	—	0.005	0.001	—	—	0.001	0.001
Ba	0.001	0.002	0.005	—	—	0.001	0.005

a) Spectral interference is expressed as the analyte concentration (ng/ml) equivalent to the background emission intensity which is provided with 1 μg/ml of major element.

TABLE 5. EFFECTS OF MAJOR ELEMENTS ON NET INTENSITIES OF MINOR AND TRACE ELEMENTS

Element	Net intensity without major elements[a)]	Net intensity with major elements[a)]	Relative intensity[b)]
Sn	8540	8750	1.02
As	10820	10940	1.01
Mo	2090	2110	1.01
Cr	9850	10140	1.03
Zn	22510	23320	1.04
P	1450	1380	0.95
Sb	6500	6470	0.99
Pb	9650	9120	0.94
Bi	5900	6190	1.05
Co	9920	10150	1.02
Cd	3360	3360	1.09
Ni	4760	4760	1.00
Mn	2700	2750	1.02
V	1520	1540	1.02
Be	18770	17680	0.94
Cu	12390	14270	1.15
Zr	3450	3210	0.93
Sc	3770	3670	0.97
Y	14330	12890	0.90
La	4780	4750	0.99
Ga	16900	15020	0.89
Sr	11450	11630	1.02
Ba	11400	11590	1.02

a) The values when each element is aspirated at the concentration given in Table 2. All intensities are shown as the arbitrary unit. b) Relative intensity is expressed as the ratio of net intensities observed without and with major elements.

The detection limits for soil, which were converted as the minimal detectable contents in soil samples from the detection limits for the standard solutions, are also shown in the second column of Table 3. It can be seen from Table 3 that the determinations of elements except for As, Bi, Cd, Mo, Pb, and Sb are possibly made in terms of soil samples.

The recoveries summarized in Table 3 were obtained by digesting about 0.5 g of soil sample with 50 μg of each element added, and measuring the emission intensities simultaneously. The recovery values obtained were good enough to apply the present method to the soil analysis.

Spectral Interferences. The changes of background intensities due to major elements were investigated by observing intensity profiles near analytical lines of minor and trace elements. The profiles were obtained by moving a refractor quartz plate behind the entrance slit. The profile measurements allowed to distinguish the emission signals caused by spectral interferences from those due to impurities. Consequently, the spectral interference due to major elements such as Al, Ca, Fe, K, Mg, Na, and Ti were estimated as correction coefficient expressed as the analyte concentration (ng/ml) equivalent to the background emission intensity which is provided with 1 μg/ml of each major element. The results are summarized in Table 4. For example, the interference with 1000 μg/ml of Al is equivalent to 23.9 μg/ml of As. The largeness of the interference is generally dependent on the operating conditions of the instrument, especially on the RF power. Therefore, the interference data such as those shown in Table 4 should be estimated under each operating condition and also with each instrument.

The effects of major elements on emission intensities of minor and trace elements were observed as the changes of net intensities at various emission lines with and without major elements. The results are shown in Table 5, along with relative intensities. In the experiment, the concentrations of major, minor and trace elements were the same as those shown in Table 2. As can be seen in Table 5, the changes of net intensities caused by major elements are negligibly small at the tested concentrations of minor and trace elements except for Ga, Zr, Cd, Cu, and Y. However, such changes must be carefully examined at the lower concentrations of analytes.

In order to make accurate background correction, the linearity of the spectral interferences with the major element concentration must be investigated at each emission line. The interferences of Ti and K with Cu are, for example, shown in Fig. 1. The interference at Cu I 324.7 nm caused by Ti is proportional to the Ti concentration, while that by K is not. Generally, the interferences were proportional to the concentration of major elements (Al, Ca, Fe, Mg, and Ti) at the level

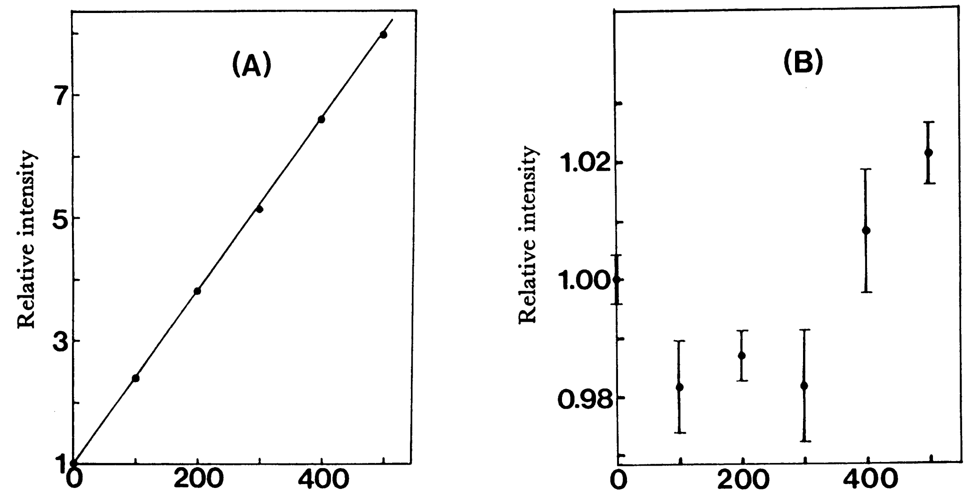

Fig. 1. Spectral interference of copper at the 324.7 nm emission line with titanium and potassium. (A) Interference of titanium, (B) interference of potassium.

Table 6. Additivity of interferences of major elements

Interfering element	Concentration μg ml^{-1}	Apparent intensity$^{a)}$ Cr	Cu	La
Al	100	74.5	1	4
Ca	100	−4.5	1.5	115
Fe	100	13	9	5
K	100	−6.5	−4	−4
Mg	100	6.5	4	3.5
Na	100	−9.5	−2.5	−3
Total interference$^{b)}$		73.5	9	120.5
Total interference without Na and K$^{c)}$		89.5	15.5	127.5
Observed interference of mixed solution$^{d)}$		91	14	115

a) The values are the apparent intensities (arbitrary unit) caused by 100 μg/ml of each interfering element. b) Sum of the apparent intensities caused by 6 interfering elements. c) Sum of the apparent intensities caused by 4 interfering elements (Al, Ca, Fe, Mg). d) Observed apparent intensity of mixed solution.

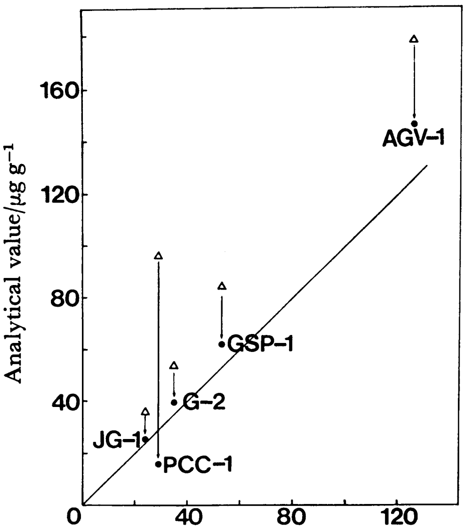

Fig. 2. Correlations of recommended values for vanadium in rock samples with analytical values obtained by ICP-OES. △: Observed value, ●: corrected value.

less than 500 μg/ml. On the other hand, the linearity of spectral interferences was not found in the case of Na and K, but the interferences due to Na and K were rather small compared to those due to other major elements, or sometimes negative for most minor and trace elements. This result suggests that the interferences due to Na and K are physical ones caused by nebulization changes. In most cases, however, the interferences due to Na and K could be neglected in the background correction except for the case at their high concentration levels.

The additivity of the spectral interferences due to major elements, when the mixed solution of major elements are aspirated, should be also examined for the background correction. In Table 6, the sum of the apparent intensities at the emission lines of Cr, Cu, and La caused by 100 μg/ml of each major element is compared with those caused by the mixed solution which contains all the major elements at the level of 100 μg/ml. As can be seen from Table 6, the interferences due to major elements without Na and K is more similar to the observed interference of the mixed solution than that due to all major elements including Na and K.

Standardization of Analytical Method. The present analytical method was standardized by analysing some standard rock samples of which elemental compositions were known. It is, also, desirable to analyse standard soil samples, but such standard soil samples have not been available yet. The rock samples studied are AGV-1, GSP-1, G-2, and PCC-1 from the United States Geological Survey, and JG-1 from the Geological Survey of Japan.

The correlation between the analytical and recommended values for V in the standard rock samples are shown in Fig. 2, where the observed and corrected

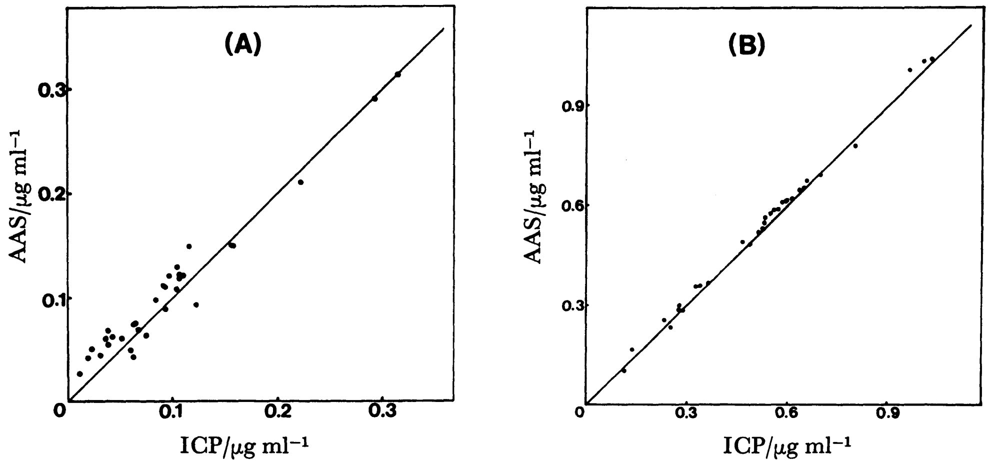

Fig. 3. Correlations of analytical results for cobalt and zinc in soil samples obtained by ICP-OES and AAS. (A) Cobalt, (B) zinc.

Table 7. Analytical results of rock sample (G-2)

Element	Reported values[a)] μg g^{-1}	ICP-OES Observed values μg g^{-1}	ICP-OES Corrected values μg g^{-1}	AAS Observed values μg g^{-1}
Al	81500	80300	80300	77100
Ca	13900	13500	13400	13400
Fe	18500	21100	21100	17300
K	37400	36700	36500	36500
Mg	4600	4500	4500	4120
Na	30200	29600	29400	30200
Ti	3000	3100	3100	3690
Be	2.6	3.1	3.0	
Ba	1870	1850	1850	
Cr	7	40	8.0	
Cu	11.7	13	8.9	8.9
Ga	22.9	73	25.4	
La	96	103	91	
Mn	260	310	267	260
P	610	690	560	
Pb	31.2	140	30.2	26.3
Sr	479	467	467	
V	35.4	53.6	39.6	
Zn	85	111	107	95

a) Cited from Ref. 19.

values are indicated as △ and ●, respectively. As can be seen in Fig. 2, most of the corrected values agree well with the recommended values reported in the literature. In the case of PCC-1, the lower value for V was obtained, compared with the recommended value. Since the content of Mg in PCC-1 is relatively high (1200 μg/ml), the over-correction might be made. When the concentrations of some major elements are high like in the case of PCC-1, the over-correction of the spectral interferences is generally made because of the deviation from the linearity of the interference at the high concentration range of major elements.[20)]

Analytical results for the standard rock sample G-2 by the present method are shown in Table 7, along with the results obtained by atomic absorption spectrometry (AAS) and the reported values. It can be seen from Table 7 that the present data are almost consistent with those in the literature values for most elements. Thus the present method is well standardized for the rock and soil samples with complicated matrices.

Application to Simultaneous Multielement Determinations of Soil Samples. The present ICP-OES method has been applied to the simultaneous multielement determinations of 40 soil samples from South-East Asian countries. No adjustment of the operating parameters were required during the experimental period for total analysis time of 3 h. The analytical results for some elements were cross-checked with those obtained by AAS. In Fig. 3, the correlations of analytical results obtained for Zn and Co by ICP-OES are shown, respectively.

The extensive data shown in Table 7 and Figs. 2 and 3 suggest that a single set of the calibration standard solutions (see Table 2) suffices for the quantitative determination of the elements at the minor and trace concentration levels in a variety of sample matrices. It should, however, be noted here that the matrix matching of acid contents and the background correction for major elements are strongly recommended for accurate determination of minor and trace elements, when ICP-OES is applied.

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