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Application News

No.J109

Inductively Coupled Plasma Atomic Emission Spectrometry

Content Analysis of Toxic Elements in Soil by ICPE-9800 Series

Introduction

Contaminated soil not only leads to contamination of untreated drinking water through permeation into river water and rainwater, it adversely affects health when the soil itself is directly ingested as a child puts the ground into a stoma into a play etc. Therefore, assessment of soil toxicity using a defined method is required. In Japan, the Soil Contamination Countermeasures Law specifies content standards and related inspection methods (measurement method according to soil content investigation). Table 1 shows the established standard values for soil content. The testing method consists of elution tests based on the assumption that when soil is ingested, harmful elements contained in the soil will be absorbed in the body. The apparatus used for the analysis is required to accurately measure those elements at trace concentrations equivalent to or lower than the reference values.
Here, using the Shimadzu ICPE-9800 series multi-type ICP atomic emission spectrometer, we conducted content analysis of soil. The ICPE-9800 series, with its mini-torch plasma and spectrometer capable of simultaneous analysis of all elements at all wavelengths, can be used to conduct high-throughput, low-cost analysis with high sensitivity and high precision.

Table 1 Soil Concentration Standard Values (Unit: mg/kg)

Element	As	B	Cd	Cr^{6+}	Hg	Pb	Se
Soil Concentration Standard Value	150	4000	150	250	15	150	150

Sample

For analysis, we used a sample consisting of a standard substance with certified content (1 mol/L hydrochloric acid content survey method), as specified in the Ministry of the Environment Notification No. 19.
- Soil certified reference material (brown forest soil) JSAC0402, 0403 (The Japan Society for Analytical Chemistry)

Sample Preparation

Sample preparation was conducted according to the Test Solution Preparation Method of Soil Content Survey (Ministry of the Environment Notification No. 19), in conjunction with the total digestion method using a microwave sample preparation system.

- Test Solution Preparation Method for Soil Content Survey (Ministry of the Environment Notification No. 19, March 6, 2003)

Elution was performed using 200 mL of 1 mol/L hydrochloric acid per 6 g of soil sample, and Yb (Ytterbium) and In (Indium) were added as internal standard elements to the obtained eluate, which was then filtered through a 0.45 µm membrane filter. The obtained filtrate was used as the analytical sample.

- Total content digestion method (Digestion using microwave sample preparation system)

Nitric acid and hydrofluoric acid were added to 0.2 g of sample, and digestion was conducted using a microwave sample preparation system. After transferring the digest solution to a fluorine resin beaker, the mixture was heated to near dryness (about 200 °C) on a hot plate. Dilute nitric acid and dilute hydrochloric acid were added to dissolve the contents. Yb and In were added as internal standard elements, and the volume was adjusted to 20 mL using distilled water. This solution served as the analytical sample.

Instrument and Analytical Conditions

Measurement was conducted using the Shimadzu ICPE-9800 series ICP atomic emission spectrometer. The analytical conditions are shown in Table 2.
The ICPE-9800 series, with a newly designed CCD which permits simultaneous measurement of all elements at all wavelengths, is built for high-throughput measurement, even when there are large numbers of samples and target elements. Further, the mini torch which suppresses the plasma gas flowrate, the Eco mode which suppresses gas and power consumption during wait periods, and use of a vacuum spectrometer which does not require purge gas, all serve to greatly reduce running costs as compared with conventional ICP instruments.

Table 2 Analytical Conditions

Instrument	: ICPE-9800 series
Radio frequency power	: 1.2 kW
Plasma gas Flowrate	: 10 L/min
Auxiliary gas Flowrate	: 0.6 L/min
Carrier gas Flowrate	: 0.7 L/min
Sample introduction	: Nebulizer 10
Misting chamber	: Cyclone chamber
Plasma torch	: Mini Torch
Observation	: Axial (AX)
Measurement time	: 2.5 min/sample (Including rinse time)

Analysis

Here, using the internal standard method – calibration curve method, we conducted quantitative analysis of a standard containing seven elements. As internal standard elements, we used Yb and In, which are few concentration in soil.

Analytical Results

Soil samples contain high concentrations of co-existing elements, such as Fe, Al, and Si, etc., and therefore may be the source of spectral interference with respect to trace elements in the matrix. For example, as can be seen in Fig. 1, the spectrum of Fe interferes with that of Cd at 214.438 nm. Correction between elements in which this type of interference (overlapping) occurs refers to the software feature which permits subtraction of the coexisting element spectrum. Table 3 shows the effectiveness of interference element correction (IEC), whereby the accuracy is significantly improved.
The results of the soil content analysis are shown in Table 4. The lower limit of determination is now less than 1/10 that of the reference values for all elements. Good results matching the certified value were also obtained for elements in the low-concentration region below the reference value.

Table 3 Effectiveness of interference element correction (IEC) for Cd at 214.438 nm

JSAC0402 (Total content digestion method)	Cd (mg/kg)	Co-Existing Element (Fe) (%)
Certified value	18.5 ± 1.1	4.2 (Reference value)
Quantitation value (with IEC)	18.4	
Quantitation value (without IEC)	19.9	

Conclusion

The ICPE-9800 series permits quick and accurate measurement of trace elements in the soil, at lower cost.

[References]
1) Soil Contamination Countermeasures Law Enforcement Regulations (Ministry of the Environment Ordinance No. 29, December 26, 2002)
2) Determination of Measurement Methods According to Soil Content Investigation (Ministry of the Environment Notification No. 19, March 6, 2003)
3) JIS K0102-2013 (Testing Method for Industrial Wastewater)
4) US EPA SW-846 Method 3052 (Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices)

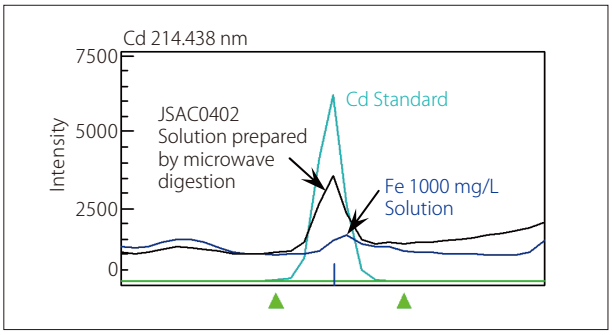

Fig. 1 Spectral Interference of Cd 214.438 nm

Table 4 Results of Soil Content Analysis (Unit: mg/kg)

	Pretreatment	Public Method (Ministry of the Environment Ordinance No. 19)					Total Content Digestion Method			
	Sample Name	Detection Limit	JSAC0402		JSAC0403		JSAC0402		JSAC0403	
Element	Concentration Standard		Quantitation Value	Certified Value	Quantitation Value	Certified Value	Quantitation Value	Certified Value	Quantitation Value	Certified Value
As	150	0.2	11	10.3 ± 0.9	115	111 ± 7	42	41.6 ± 3.2	195	199 ± 15
B	4000	0.02	15.8	15.6 ± 0.9	157.7	157 ± 3		115 ± 15		269 ± 46
Cd	150	0.007	17.1	17.3 ± 0.4	178.2	178 ± 5	18.4	18.5 ± 1.1	182.2	183 ± 7
Cr^{6+}	250	0.02	7.4		64.8		91	90.5 ± 6.9	250.4	257 ± 9
Hg	15	0.1	0.6	0.6 ± 0.1	6.7	7 ± 1		1.3 ± 0.1		11.1 ± 1
Pb	150	0.1	32	32.3 ± 0.8	193	197 ± 4	44	45.2 ± 7.1	216	224 ± 13
Se	150	0.2	3	2.7 ± 0.6	64	63.5 ± 6.4	18	17 ± 1.7	163	169 ± 13

Content reference value : Soil content reference value according to the Soil Contamination Countermeasures Law
Detection limit : 3 times the concentration of the standard deviation obtained from 10 measurements of a calibration curve blank × Dilution factor (200/6)
Cr^{6+} : The content standard is Cr^{6+}, but the analytical value is the total Cr value.

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