

Application News

Inductively Coupled Plasma Atomic Emission Spectrometry

Analysis of Soil

1. Soil Contamination Countermeasures Law

Recently, along with redevelopment at old factory sites, etc., ground contamination with heavy metals and volatile organic compounds has become increasingly obvious. Due to this situation, the "Soil Contamination Countermeasures Law" was enacted on May 29, 2002 to protect the public health, and enforcement of the law began on February 15, 2003. Since it is probable that exposure to specific toxic substances over a long period of time results in high concentrations in the ground surface layer, and that these toxins enter the soil directly, maximum concentration standards were set for nine items. Twenty-five substances were specified as risks with respect to infiltration into underground water. Accordingly, it is necessary to conduct risk assessment with respect to these items at sites that are being investigated.

Table 1 shows the specific toxic substances (heavy metals), as well as the specified standard criteria and measurement methods.

Table 1: Target Analytes and Standard Criteria (Heavy Metals, etc)

Test Method Standard	Underground Water Infiltration Risk		Direct Uptake Risk	Measurement Method
	Dissolution Test		Total Content Test	
	Soil Dissolution Criteria (mg/L)	*2nd Dissolution Criteria (mg/L)	Soil Content Criteria (mg/kg)	
Cadmium	0.01	0.3	150	Flame AAS, Graphite Furnace AAS, ICP-AES, ICP-MS
Lead	0.01	0.3	150	Flame AAS, Graphite Furnace AAS, ICP-AES, ICP-MS
Hexavalent Chromium	0.05	1.5	250	Spectrophotometry, Flame AAS, Graphite Furnace AAS, ICP-AES, ICP-MS
Arsenic	0.01	0.3	150	Spectrophotometry, Hydride Generation AAS, Hydride Generation ICP
Total Mercury	0.0005	0.005	15	Reduction Vaporization AAS
Selenium	0.01	0.3	150	Spectrophotometry, Hydride Generation AAS, Hydride Generation ICP
Boron	1	30	4000	Spectrophotometry, ICP, ICP-MS

*Guidelines for Soil Remediation Water Shields / Sealing Enclosures

2. Analysis by ICP-AES

ICP emission spectrometry (ICP-AES) is highly sensitive, allows simultaneous analysis of multiple elements, and features a wide dynamic range. It can therefore be used for efficient analysis not only of the principle high-concentration constituents, but of toxic trace elements as well. We introduce here the use of the multi-type ICPE-9000 ICP emission spectrometer for quantitative analysis of soil contaminants.

■ Sample

- Soil contaminant standard SRM2710, 2711 (NIST)
- Volcanic ash soil standard JSAC0411 (Japan Society for Analytical Chemistry)

■ Sample Pretreatment

Official Method (Soil Content Investigation Test Solution Preparation (Ministry of Environment Notification No. 19, March 6, 2003))

- (1) According to the test solution preparation method for the soil content investigation, dissolve a 6 g soil sample in 200 mL of 1 mol/L hydrochloric acid (for hexavalent chromium, 5 mM Na₂CO₃ + 10 mM NaHCO₃ basic buffer solution), and pass the obtained solution through a 0.45 μm membrane filter.
- (2) Transfer the obtained filtrate to a PTFE beaker, and add 20 mL of high-purity nitric acid.
- (3) Cover it with a PTFE watch glass, and heat it on a hot plate (about 200°C), until the liquid volume decreases to about 20 mL.
- (4) Transfer the digested solution to a polypropylene vessel, and bring volume to 200 mL using pure water.
- (5) Measure out two 50 mL aliquots of the solution obtained in step (4) into 2 vessels, add the internal standard Y to each vessel, and add the standard solution of analytes to one of the vessels. Bring the solutions to 100 mL using ultra pure water, and use these as the analytical sample and standard addition sample, respectively.

Total Decomposition Method (Microwave High-Pressure Digestion)

- (1) Weigh out 0.2 g of sample into a PTFE vessel, add 10 mL nitric acid, 3 mL

hydrogen peroxide and 5 mL hydrofluoric acid, and let stand for about four hours (preliminary reaction).

- (2) Digest using a microwave digester.
- (3) After digestion, transfer the sample to a PTFE beaker, and heat on a hot plate (about 200°C) to dry to hardness.
- (4) Add 20 mL dilute nitric acid (1:10), and heat for about one hour to decompose the contents.
- (5) Transfer the solution to a plastic vessel, add the internal standard Y, bring to a volume of 20 mL using pure water, and use this as the analytical sample.

■ Table 2: Analytical Conditions

Instrument	: ICPE-9000
Radio Frequency Power	: 1.2 (kW)
Cooling Gas	: 10 (L/min)
Plasma Gas	: 0.6 (L/min)
Carrier Gas	: 0.7 (L/min)
Sample Introduction	: Coaxial Nebulizer
Sample Aspiration	: 1.0 (mL/min)
Misting Chamber	: Cyclone Chamber
Attached Instruments	: Mini Torch
View Direction	: Axial

■ Calibration Curve Sample

Prepare a standard solution (1000 ppm) for use in atomic absorption analysis, and appropriately dilute with ultra pure water.

■ Analysis

Using the ICPE-9000, we conducted quantitation for the specific harmful pollutants cadmium, lead, total chromium, arsenic, total mercury, selenium and boron. Moreover, the same analysis was conducted using ICP-MS (Shimadzu ICPM-8500) to confirm the quantitation values.

■ Results

* Qualitative Analysis

Fig. 1 shows the semi-quantitation results obtained in qualitative analysis. A single analysis with the ICPE-9000 can provide both qualitative and quantitative analysis information. These semi-quantitation values are estimated concentrations calculated from information in the database.

* Spectral Interference and Correction

Soil samples contain high concentrations of various coexisting elements, like iron and aluminum, and these can cause spectral interference in the spectra of analyte trace elements. For instance, the spectrum of the arsenic is adjacent to the wavelength of cadmium at 228.802 nm. Fig. 2 shows an example of spectral interference with the multi-type ICPE-9000 and the high-resolution sequential-type ICPS-8100. With the ICPE-9000, the arsenic spectrum overlaps the center of the cadmium spectrum. However, in the case of the high-resolution sequential-type ICPS-8100, the two spectra are separate, with the cadmium spectrum nearly unaffected. When trace analysis is conducted on a sample containing high concentrations of coexisting elements, it can be said that a high-resolution ICP instrument is advantageous.

When this type of spectral interference occurs, the accuracy of the analysis values can be improved by conducting inter-element correction. Table 3 shows the influence of arsenic on the cadmium quantitation value when using the ICPE-9000. When the sample contains a high concentration of arsenic, a positive error is caused in the cadmium quantitation result. Inter-element correction is a method of subtracting the amount of interference imparted to the analyte from the coexisting element (interfering element) by estimating the degree of interference. By conducting this inter-element correction, it is clear that an accurate quantitation value is obtained regardless of the interference.

* Quantitative Analysis

Table 4 shows the quantitation results using the official method (hydrochloric acid dissolution) and the total decomposition method (microwave digestion).

In the microwave digestion method, the results agree well with the certified values for all elements except chromium using both ICP-AES and ICP-MS. Chromium in soil often exists in a difficult-to-dissolve state (as oxide, etc.), preventing its

complete extraction even using microwave digestion. In this situation, the entire quantity can be extracted using the alkali fusion method adopted in the sediment test method, etc.

A comparison of the official method and the total decomposition method reveals that the official method results have lower values. The method of preparing the test solution for the soil content test is for risk assessment of soil uptake, so the method taking into consideration the correlation with absorption in the digestive tract (bioavailability) is adopted. Thus, compared with the total decomposition methods (alkali fusion and high-pressure digestion using hydrofluoric acid), the quantitation values show a lower tendency.

Table 5 shows quantitation results by the official method, Fig. 3 the spectral profiles, and Fig. 4 the calibration curves.

The quantitation results for most of the elements agree with those by ICP-MS down to the low concentrations. Moreover, good recovery percentages are shown in the spike and recovery test. It is clear that toxic elements in soil can be accurately analyzed with high sensitivity using the ICPE-9000.

Reference Materials

- Environmental Quality Standards for Soil (Ministry of Environment Notification No.46, August 23, 1991)
- Soil Contamination Countermeasures Law Enforcement Regulation (Ministry of Environment Ordinance No. 29, December 26, 2002)
- Matters Providing for Measurement Method of Soil Dissolution Test (Ministry of Environment Notification No. 18, March 6, 2003)
- Matters Providing for Measurement Method of Soil Content Test (Ministry of Environment Notification No. 19, March 6, 2003)
- Notification of Enforcement Order of Partial Revision of Water Quality Pollution Prevention Law, March 8, 1993
- JIS K0102_ (Testing methods for industrial wastewater)
- Microwave Assisted Acid Digestion Of Siliceous And Organically Based Matrices Method 3052 (EPA Method 3052) December 1996
- 3rd Japan Society for Environment Chemistry Conference, Soil / Sediment Pollution Research Group Lecture Meeting Presentation Preview (2003)

Sample Name: SRM2711_HCl_6 g/200 mL/2						
1000 mg/L or greater						
1 mg/L or greater	Ag 3.5	Al 177	Ba 3.3	Ca 110	Cu 3.2	
	Fe 72	K 12	Mg 36	Mn 6.7	Na 2.2	Pb 17
	S 3.1	Si 40	Y 13	Zn 1.1		
1 µg/L or greater	As 720	B 120	Be 6.8	Cd 830	Ce 290	Cr 52
	Gd 78	La 110	Li 9.8	Ni 140	P 900	Sr 230
	Ti 270	U 730	V 54	Yb 3.8		
Up to 1 µg/L						
Below Detection Limit µg/L	Au < 59	Bi < 370	Co < 57	Dy < 34	Er < 33	Eu < 4.8
	Ga < 78	Ge < 570	Hf < 100	Hg < 14	Ho < 13	I < 330
	In < 280	Ir < 1300	Lu < 110	Mo < 100	Nb < 21	Nd < 120
	Os < 1200 +	Pd < 54	Pr < 67	Pt < 1000	Rb < 44000 +	Re < 97
	Rh < 360	Ru < 120	Sb < 340	Sc < 3.4	Se < 560	Sm < 87
	Sn < 240	Ta < 130	Tb < 27	Te < 620	Th < 2400	Tl < 390
	Tm < 12	W < 210	Zr < 5.9			

Figure 1: Semi-Quantitation Results for Soil

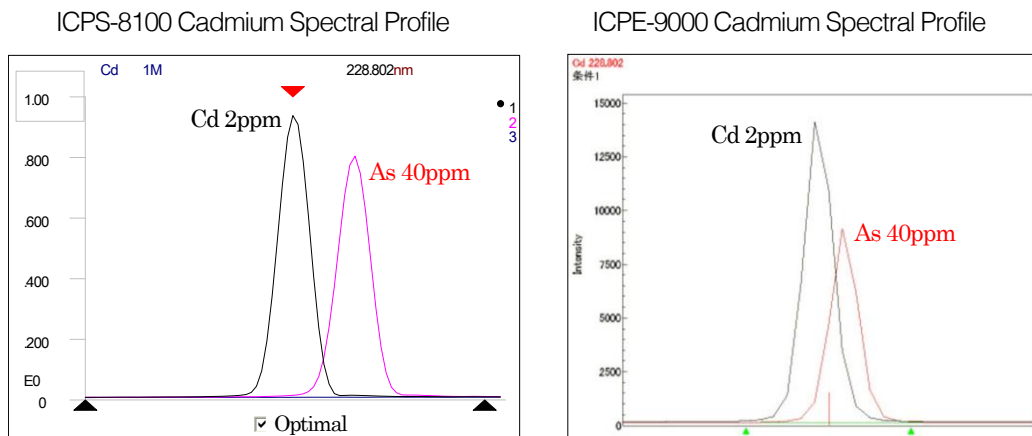


Figure 2: Spectral Interference of Arsenic on Cadmium

Table 3: Effect of Arsenic on Cadmium Quantitation Value in ICPE-9000, Inter-Element Correction Effect (Unit: mg/kg)

Sample Name	Inter-Element Correction Quantitation Result		Certified Value	As Concentration
	Pre-Correction	Post-Correction		
SRM2710	25.9	21.8	218 ± 02	626
SRM2711	42.1	41.5	41.7 ± 025	105

Table 4: Content Test Results
(Official Method – Total Decomposition Method Comparison) (Unit: mg/kg)

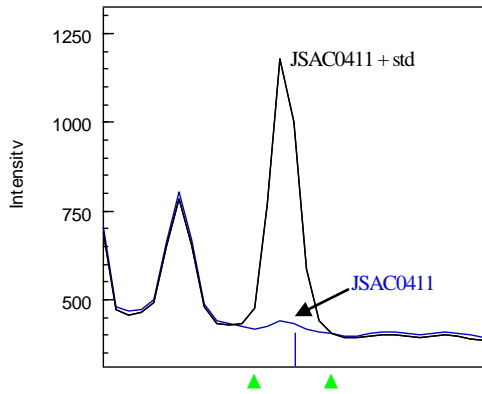
Element	Content Standard	Sample	NIST (SRM2711)		
		Detection Limit	Certified Value	HCl Dissolution Quantitation Results	Microwave Digestion Quantitation Results
Cd	150	0.02	41.7 ± 0.25	37.8	41.5
Pb	150	0.1	1162 ± 31	1040	1135
Cr	250	0.02	47	2.0	41.0
As	150	0.8	105 ± 8	70	105
Hg	15	0.3	6.25 ± 0.19	1	6.3
Se	150	0.4	1.52 ± 0.14	N.D	N.D
B	4000	0.03		4.9	45.0
Cu		0.1	114 ± 2	73	114
Mn		0.02	638 ± 28	326	635
Ni		0.04	20.5 ± 1.1	5.0	20.4
Zn		0.04	350.4 ± 4.8	119	345

Table 5: Content Test Results (Official Method) (Unit: mg/kg)

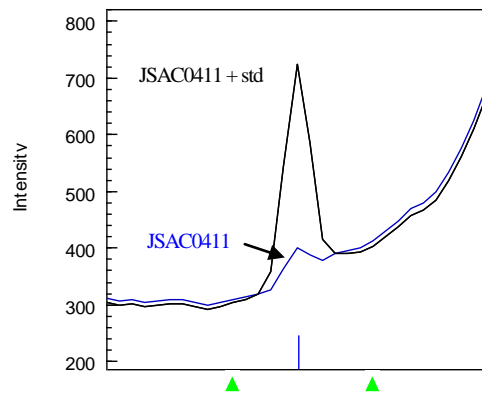
Element	JSAC0411				
	Certified Value	ICPE-9000			ICP-MS
		Quantitation Results	Spike/Recovery (%)	Measurement Solution Addition Conc. (mg/L)	Quantitation Results
Cd	0.274 ± 0.023	0.2	103	0.1	0.18
Pb	18.9 ± 2.6	12	99	1	12.2
Cr	23.5 ± 1.8	1.3	101	0.1	1.30
As	11.3 ± 0.5	1	93	0.1	0.92
Hg	±	0.3	100	0.1	0.13
Se	1.32 ± 0.27	N.D	108	0.1	0.26
B		0.5	105	0.05	0.55
Cu	26.7 ± 1.1	9.0	-	-	-
Mn	943 ± 28	309	-	-	-
Ni	11 ± 1	3.7	-	-	-
Zn	64.6 ± 2	2.9	-	-	-

Measurement Solution Addition Concentration = Concentration in Solid / 66

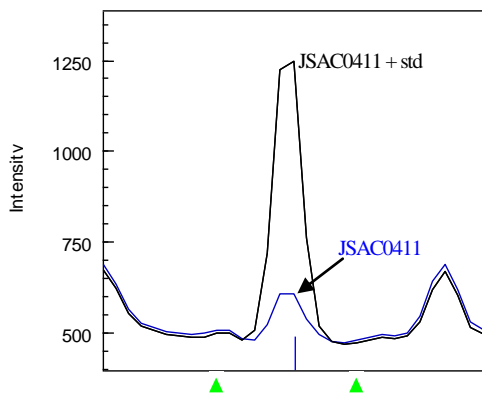
Cd 228.802 Best
Cond 1



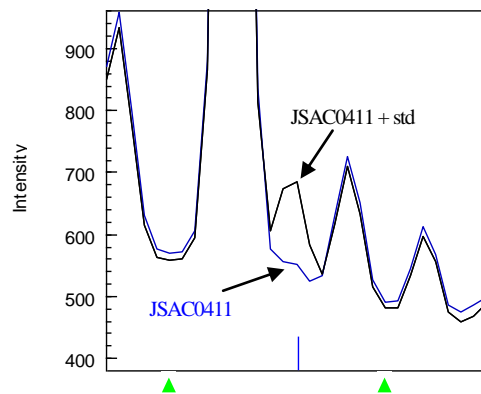
Pb 220.353 Best
Cond 1



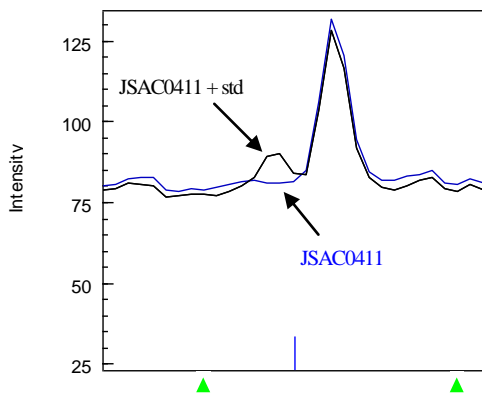
Cr 267.716 Best
Cond 1



B 249.678 Best
Cond 1



Hg 184.950
Cond 1



As 189.042
Cond 1

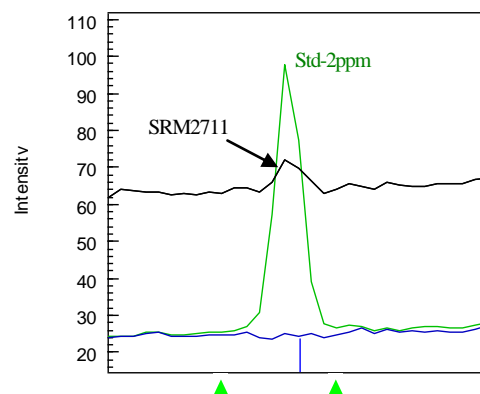


Figure 3: Spectral Profiles of Soil

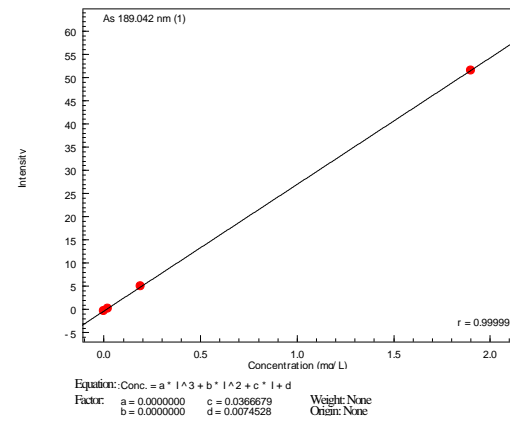
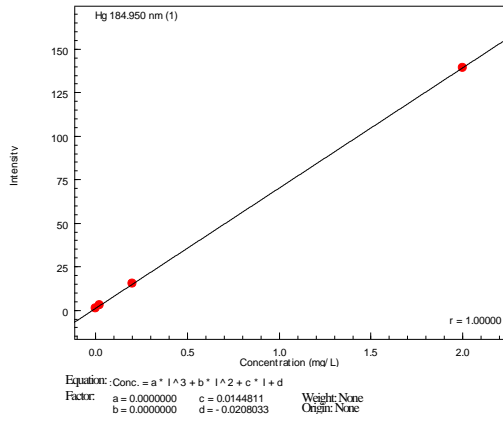
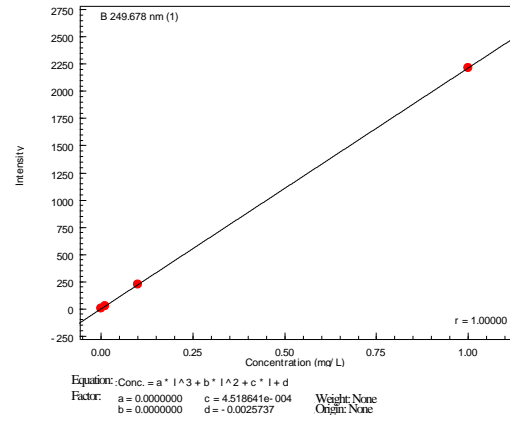
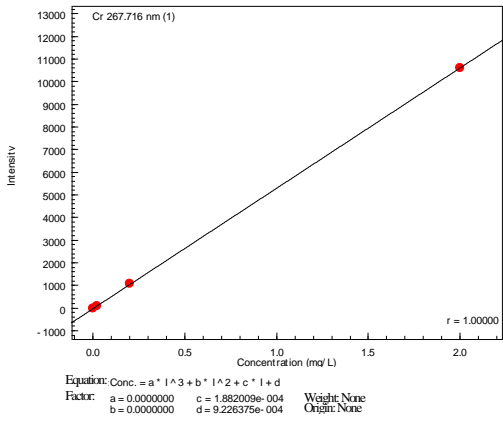
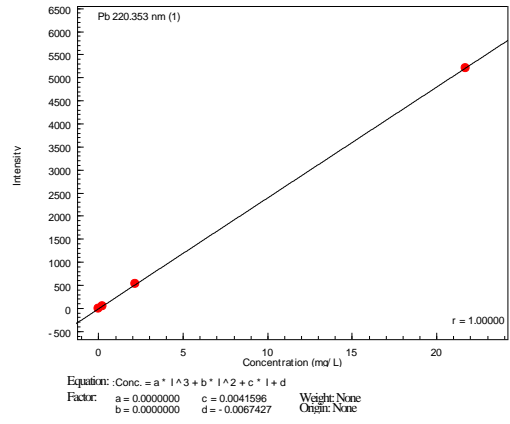
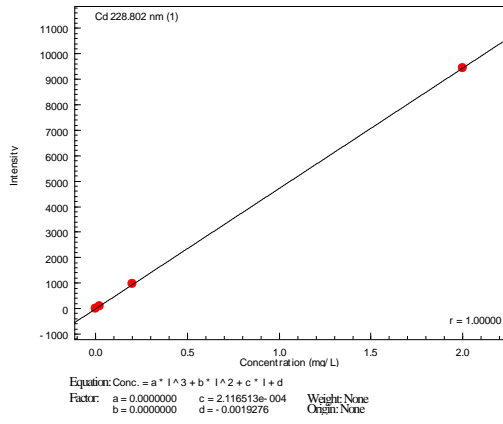


Figure 4: Calibration Curves