

## Measurement of Chromium in Soil by Atomic Absorption Spectrophotometry

The Soil Contamination Countermeasures Law was implemented in Japan in 2003. It prescribes soil elution standards and soil content standards for hexavalent chromium, as well as metals such as cadmium and lead. Although trivalent and hexavalent are typical atomic valencies for chromium, the

standard value is prescribed for hexavalent chromium. This Application News introduces an example of chromium analysis on a commercial soil standard sample (JSAC 0401 Brown Forest Soil, manufactured by The Japan Society for Analytical Chemistry).

### ■ Sample Preparation

Figs. 1 and 2 show outlines of the sample preparation methods for the elution standard (Ministry of the Environment Bulletin 18, 6 March 2003) and the content standard (Ministry of the Environment Bulletin 19, 6 March 2003) of hexavalent chromium.

A slightly acidic sample is prepared for the elution standard, while an alkaline sample is prepared for the content standard. 1mol/L hydrochloric acid is used as the eluate to prepare samples for content testing of heavy metals besides chromium.

Take 50g or more prepared sample  
 ↓ Add extract (pH 5.8 to 6.3) (liquid/solid ratio: 10/1)  
 Shaking (6 hours)  
 ↓  
 Centrifuge (3000rpm, 20 minutes)  
 ↓  
 Filter (0.45μm membrane filter)  
 ↓  
 Use filtrate as sample.

Fig.1 The Outline of Preparation for the Elution Standard

Take 6 g or more prepared sample  
 ↓ Add extract (5 mM NaCO<sub>3</sub>+10 mM NaHCO<sub>3</sub>)  
 (liquid/solid ratio : 100/3)  
 Shaking (2 hours)  
 ↓  
 Filter (0.45μm membrane filter)  
 ↓  
 Use filtrate as sample.

Fig.2 The Outline of Preparation for the Content Standard

As the sample was considered to be sufficiently homogenous this time, elution was conducted with 1/10 the sample volume for the official method. The liquid/solid ratio was unchanged.

Table 1 Certified Values of the Reference Soil JSAC 0401

Element	Certified value mg/kg (ppm)
Cd	4.25±0.41
Pb	26±4
Cr	<b>50.4±5.1</b>
As	10.62±0.65
Se	0.27±0.05
Be	5.28±0.35
Cu	15.3±1.3
Zn	66.8±2.7
Ni	18.9±1.3
Mn	266±9
V	65.0±2.6
Al	65000*
Fe	30000*
K	17000*
Si	350000*

The number with "\*" indicates reference data

### ■ Analytical Methods and Conditions

As prescribed in the official method above, the sample solution was analyzed according to the analysis method for hexavalent chromium in section 65.2 of JIS K0102-1988 "Testing Methods for Industrial Wastewater."

JIS K0102 lists the following five analysis methods for hexavalent chromium:

1. Diphenylcarbazide absorptiometry
2. Flame atomic absorption spectrophotometry
3. Furnace atomic absorption spectrophotometry
4. ICP plasma spectrometry
5. ICP mass spectrometry

Furnace atomic absorption spectrophotometry was used for this test.

Analysis methods other than diphenylcarbazide absorptiometry offer no selectivity for hexavalent chromium. Therefore, with these methods, if the sample contains trivalent chromium, it must be eliminated by co-precipitation with iron.

Separation by co-precipitation with iron was not conducted for this test. Instead, nitric acid was added to a fixed amount of sample solution and thermal decomposition conducted. A measured volume of this solution was appropriately diluted to create the measured sample. An AA-6300 was used for the measurements. Table 2 and 3 show the major measurement parameters.

Table 2 Optics parameters

Measurement wavelength	357.9nm
Slit width	0.7nm
Current value	10mA
Lighting mode	BGC-D2

Table 3 Atomizing Parameters

Temperature program	Drying 150°C (20 s), 250°C (10 s) Incineration 1000°C (25 s) Atomization 2400°C (3 s) Cleaning 2600°C (2 s)
Tube type	Pyro-coated graphite tube
Sample injected volume	5µL
Interference suppressant	5µL, 500ppm magnesium nitrate
Signal processing	Area

## Results

Fig. 3 shows the calibration curve. Figs. 4 and 5 show some measured peak profiles.

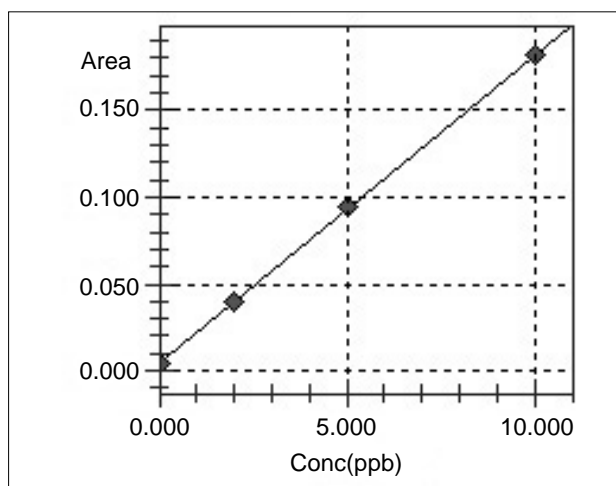


Fig.3 Calibration Curve for Cr

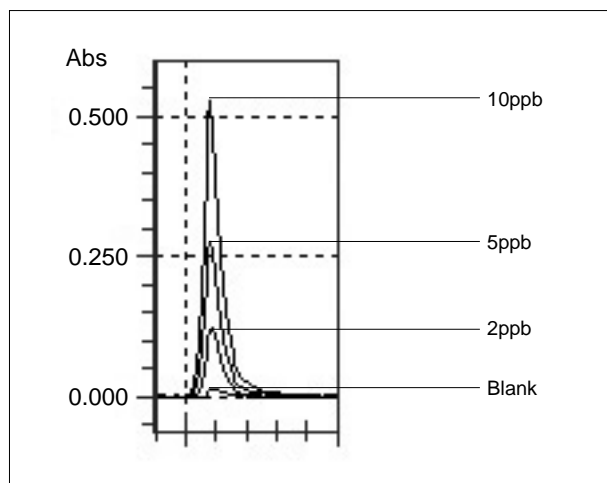


Fig.4 Peak Profiles of Cr standard

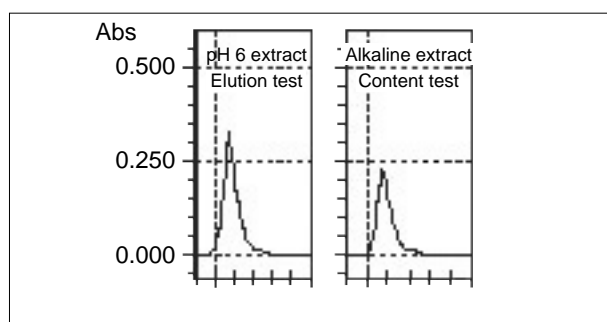


Fig.5 Peak Profiles of Sample

Table 4 lists the measured results. As the elution concentration is dependent on the chemical species and elution conditions, treatment conforming to the test method must be conducted.

Table 4 Measurement results of Cr in Reference Soil JSAC 0401

Sample preparation method	pH6 extract (elution test)	Alkaline extract (content test)
Concentration in sample solution (mg/L)	0.160	0.0519
Liquid/solid ratio	10/1	100/3
Concentration in soil (mg/kg)	1.60	1.73