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Application News

ICP Mass Spectrometer

Content Analysis of Heavy Metals in Soil by ICP-MS

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User Benefits

- High-sensitivity analysis at less than 1/100 of Japan’s soil content standard is possible.
- Correction methods and H_2 reaction conditions reduce interference from rare earth elements when measuring As and Se.
- Variation in measurement sensitivity due to the soil matrix is small, enabling stable measurement even when measuring multiple samples over a long time.

■ Introduction

Soil pollution occurs when chemical or hazardous substances in the soil harm the environment and human health. Soil pollution may be caused by natural phenomena, but most is caused by human activities such as leakage of hazardous substances from industrial activities and improper disposal of waste.

In Japan, soil surveys are conducted in accordance with the Soil Contamination Countermeasures Act to prevent harm to human health. These surveys are mandatory when facilities using specified hazardous substances are decommissioned or when the characteristics of land over a certain size have changed. Two types of tests are conducted: soil leaching tests and soil content tests. Soil leaching tests are conducted to evaluate the risk of ingesting groundwater containing hazardous substances leached from the soil, and soil content tests are conducted to evaluate the risk of directly ingesting hazardous substances from the soil through the mouth or skin. The number of such soil surveys is increasing year by year, and since many samples need to be analyzed simultaneously, even in laboratories that accept them, stable and robust analysis equipment is required.

In this Application News, soil content tests were conducted on five types of soil samples using an ICPMS-2050. The results of the validity of the analysis, the influence of interference from rare earth elements (REE), and long-term stability are also presented.

■ Samples

Soil A, Soil B, Soil C, Soil D, Soil E

■ Sample Pretreatment

The sample pretreatment method is shown below. Preparation of the test solution for the soil content test is described in the Ministry of the Environment Notification No. 19, “Determination Method for Soil Content Survey”1). The prepared test solution is then measured using the analytical methods specified in the appended table.

Since the pretreatment method for Cr (VI) in the soil content test differs from that for other elements, a separate pretreatment was performed.

However, Cr (III) is not removed by the iron coprecipitation method in this analysis, so the values are expressed as total Cr.

< Pretreatment of Elements Other than Cr >

1. Mix the soil with 1 mol/L hydrochloric acid at a ratio of 3 % by weight
2. Set the shaker to about 200 times per minute and shake horizontally for 2 hours continuously.
3. Allow the sample solution to stand, then filter the supernatant through a membrane filter with a pore size of 0.45 µm.
4. Take 25 mL of the filtrate, add 1.25 mL of nitric acid, boil for 10 minutes, and adjust the volume to 50 mL with pure water.
5. Take 2 mL of the sample, add 0.45 mL of nitric acid, and adjust the volume to 50 mL with pure water.

< Pretreatment for Cr >

1. Mix the soil with the extract (Sodium carbonate 0.005 mol/L, sodium bicarbonate 0.01 mol/L) at a ratio of 3 % by weight
2. Set the shaker to about 200 times per minute and shake horizontally for 2 hours continuously.
3. Allow the sample solution to stand, then filter the supernatant through a membrane filter with a pore size of 0.45 µm.
4. Take 25 mL of the filtrate, add 1.25 mL of nitric acid, boil for 10 minutes, and dilute to 50 mL with pure water.
5. Take 2 mL of the sample, add 0.45 mL of nitric acid, and dilute to 50 mL with pure water.

*For the spiked samples in the recovery test, a concentration equivalent to 1/10 of the soil content standard was added.

■ Calibration Samples

Single-element standard solutions were mixed to prepare calibration samples. The concentration range of the calibration curve was set to 1/100 of the soil content standard converted into the measurement solution. The calibration sample concentrations are shown in Table 1.

Table 1 Calibration Sample Concentrations (µg/L)

Elem.	std0	std1	std2	std3	std4	std5	std6
As	0	0.9	1.8	3.6	9	18	90
B	0	24	48	96	240	480	2400
Cd	0	0.27	0.54	1.08	2.7	5.4	27
Cr	0	1.5	3	6	15	30	150
Pb	0	0.9	1.8	3.6	9	18	90
Se	0	0.9	1.8	3.6	9	18	90
HNO_3	1 %(v/v)						
HCl	0.18 %(v/v)						

Internal Standard Solution

Single-element standard solutions were mixed, and internal standard solutions (Be 500 µg/L, Ga 5000 µg/L, In, Tl 200 µg/L) were prepared with 1 % (v/v) nitric acid and 0.18 % (v/v) hydrochloric acid. Internal standard elements were added using the Internal Standard Automatic Addition Kit. The measurement was conducted while mixing the internal standard solution with the sample at a ratio of 1:9.

Instrument Configurations and Analysis Conditions

The instrument configuration and analysis conditions are shown in Tables 2 and 3, respectively. Shimadzu’s original mini torch was used. The mini torch consumes only 2/3 of the argon gas of a typical torch, which can significantly reduce running costs.

Table 2 Instrument Configurations (µg/L)

Instrument	:	ICPMS-2050
Nebulizer	:	Nebulizer DC04
Torch	:	Mini Torch
Chamber	:	Cyclone Chamber
Sampling Cone	:	Nickel
Skimmer Cone	:	Nickel
Internal Standard Elements	:	Internal Standard Automatic Addition Kit

Table 3 Analysis Conditions

RF Power	:	1.2 kW		
Sampling Depth	:	7 mm		
Plasma Gas Flowrate	:	9.0 L/min		
Auxiliary Gas Flowrate	:	1.1 L/min		
Carrier Gas Flowrate	:	0.60 L/min		
Dilution Gas Flowrate	:	0.25 L/min		
Peristaltic Pump Speed	:	15 r.p.m		
Cell Gas	:	NoGas	He	H_2
Cell Gas Flowrate	:	-	5 mL/min	7 mL/min
Cell Voltage	:	-	-30 V	-21 V
Energy Filter	:	-	7 V	7 V

■ Dealing with Interference from REEs

In ICP-MS measurements, measurements are made for each *m/z*, which represents the ratio of mass number to charge number. Therefore, when an element with a mass number twice the measured *m/z* becomes a divalent ion, it becomes the same m/z and causes interference . This interference may be a problem when the sample contains a lot of REEs, which have low second ionization energies and tend to become divalent ions in the plasma.

Depending on the sampling location, soil may contain REEs, and as shown in Table 4, ^{150}Nd, ^{150}Sm, ^{156}Gd, and ^{156}Dy may interfere with the measurement of ^{75}As and ^{78}Se.

This study examines the amount of interference caused by REEs under He collision conditions, and evaluates the effect of two interference correction functions (Interelement correction[*1], half-mass correction[*2]) available on the ICPMS-2040/2050. The interference cancellation effect of Se under H_2 reaction conditions was also verified.

*1 Interelement Correction(IEC):

First, a single element standard solution of interfering elements is measured and the divalent ion production ratio (IEC factor) is calculated. When measuring a sample, the intensity of interfering elements is multiplied by the IEC factor to calculate the amount of interference with the measured element and then subtracted.

Example: IEC Formula for Gd relative to ^{78}Se
$I(^{78}Se)$ after correction $= I(^{78}Se) - I(^{157}Gd) \times$ IEC factor

*2 Half-Mass Correction:

A high-resolution mode that can measure *m/z* in increments of 0.5 is used to measure the intensity of divalent ions at the odd mass number of interfering elements for each sample. Divalent ions with odd-numbered mass numbers are detected at *m/z* 0.5. Since there are no other elements at the same *m/z*, only the divalent ion intensity can be accurately measured. Using the fact that divalent ions are generated in the same manner as the abundance ratio (AR) of the interfering elements, the interference amount at the *m/z* of the measured element is calculated and subtracted.

Example 1: Half-Mass Correction Formula for Nd and Sm relative to As

$$^{75}\mathrm{As} = I(m/z\ 75) - I(m/z\ 74.5) \times (^{150}\mathrm{Sm\ AR})/(^{149}\mathrm{Sm\ AR}) - I(m/z\ 72.5) \times (^{150}\mathrm{Nd\ AR})/(^{145}\mathrm{Nd\ AR})$$

Example 2: Half-Mass Correction Formula for Gd relative to Se

$$^{78}\mathrm{Se} = I(m/z\ 78) - I(m/z\ 77.5) \times (^{156}\mathrm{Gd\ AR})/(^{155}\mathrm{Gd\ AR})$$

Table 4 Elements Interfering with As and Se as Divalent Ions

Measured Element					Interfering Elements as Divalent Ions				
Mass	Elem.	AR (%)	Elem.	AR (%)	Mass	Elem.	AR (%)	Elem.	AR (%)
72	Ge	27.5			144	Nd	23.8	Sm	3.1
72.5					145	Nd	8.3		
73	Ge	7.8			146	Nd	17.2		
73.5					147	Sm	15.0		
74	Ge	36.5	Se	0.9	148	Nd	5.8	Sm	11.2
74.5					149	Sm	13.8		
75	As	100			150	Nd	5.6	Sm	7.4
75.5					151	Eu	47.8		
76	Ge	7.7	Se	9.4	152	Sm	26.8	Gd	0.2
76.5					153	Eu	52.2		
77	Se	7.6			154	Sm	22.8	Gd	2.2
77.5					155	Gd	14.8		
78	Se	23.8	Kr	0.36	156	Dy	0.06	Gd	20.5
78.5					157	Gd	15.7		

■ Interference of Nd and Sm on As

Fig. 1 shows the recovery rates of quantitative values in a sample containing 5 µg/L of As and 100 µg/L of Nd and Sm. The recovery rate was evaluated in two types of samples, one in a blank solution and the other in a soil solution, to confirm the influence of the matrix on the quantitative values.

Under He collision conditions, the quantitative value of As was 110 to 134 % due to interference by Nd and Sm, but the interference was corrected normally by using IEC and half-mass correction, and good results were obtained. No difference in the correction effect between the blank solution and the soil solution was observed.

In the measurement of As under H_2 reaction conditions, the interference removal effect of divalent ions is not as effective as that for Se, as described in the next section. Furthermore, there is a possibility that the removal of interference from ^{40}Ar^{35}Cl is not sufficient. Therefore, the He collision condition is recommended for the measurement of samples containing hydrochloric acid, such as soil content tests.

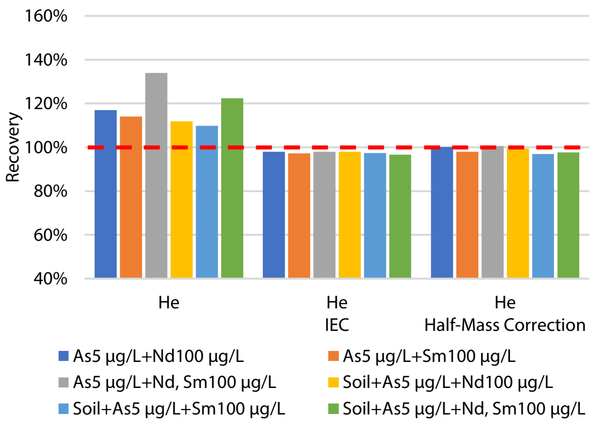

Fig. 1 Effect of Nd and Sm Interference on As

■ Interference of Gd on Se

Fig. 2 shows the recovery rate of quantitative values in a sample containing 5 µg/L Se and 100 µg/L Gd. There is also a risk of interference from ^{156}Dy divalent ions on ^{78}Se, but ^{156}Dy is only 0.02 %, so only Gd was examined this time.

Under He collision conditions, the interference from divalent ions was larger than that from As, and the quantitative value of Se was 191 to 262 %. The half-mass correction for this interference was effective in both the blank solution and the soil solution, but the interelement correction resulted in over-correction, with the quantitative values in the soil solution being about 10 % lower.

On the other hand, under the H2 reaction conditions, Gd interference was eliminated regardless of the presence of the matrix. In Se measurements, the interference from Ar and Gd was greatly reduced by using H2 reaction conditions, enabling high-sensitivity measurements.

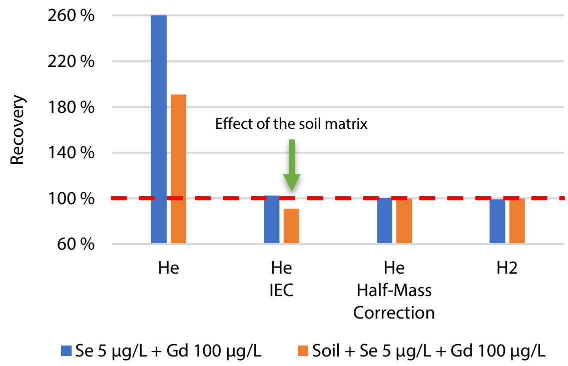

Fig. 2 Effect of Gd Interference on Se

■ Discussion on Each Correction Method

This section considers the measurement of Se under He collision conditions, where IEC was overcorrected in the soil solutions.

In IEC, the divalent ion production ratio (IEC factor) is calculated by measuring a single-element standard solution of the interfering elements at the beginning of a series of measurements. When measuring samples with high matrix concentrations, such as soil samples, the ionization state in the plasma may be different from the state during the calculation of the IEC factor, leading to errors in the correction. In this case, only Se was over-corrected. However, even in the case of As, if the amount of interference correction increases due to the higher content of REEs, the correction error may affect the quantitative value.

On the other hand, in the half-mass correction method, the amount of interference for the measured element is estimated for each sample based on the measurement results of different mass numbers of the interfering element itself, so it is not affected by differences in the divalent ion production ratio. Thus, the half-mass correction method can be said to be less affected by the matrix than IEC.

However, it is important to note that the sensitivity of the half-mass correction method may decrease when measurements are made in the high-resolution mode. As shown in Fig. 3, the intensity in high resolution mode is about 1/3 to 1/2 of that in standard resolution mode. Inter-element correction is the preferred method for microanalysis where measurement sensitivity is a priority. In this way, the ICPMS-2040 Series and ICPMS-2050 Series can use two different correction methods according to the measurement conditions and requirements.

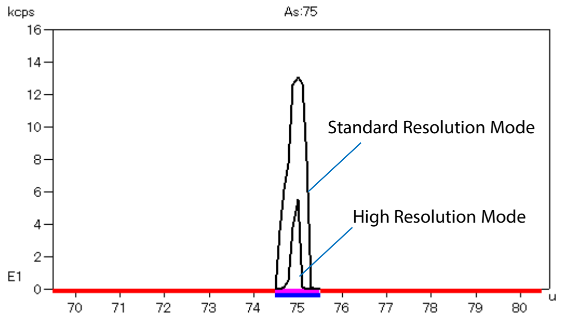

Fig. 3 Differences in Intensity Due to Resolution

■ Soil Content Test Results and Validation of Measurement

Table 5 shows the results of measurement under the optimum correction method and collision reaction cell conditions. The lower limit of quantification (LOQ), calculated from the standard deviation σ of 10 repeated measurements of Std 0 achieved 1/100 or less of the soil content standard[2)], indicating that the measurement sensitivity is sufficient.

In addition, in the validation of the measurement by the spike recovery test, the recovery rate was 98 to 103 %, and it was confirmed that the effect of non-spectral interference from the soil matrix was small.

Table 5 Measurement Results

Element		**^{75}As**	**^{11}B**	**^{111}Cd**	**^{52}Cr***	**^{208}Pb**	**^{78}Se**
Gas Mode		He	No Gas	He	He	He	H_2
Internal Standard Element		^{71}Ga	^{9}Be	^{115}In	^{71}Ga	^{205}Tl	^{71}Ga
Interference Correction		Harf-Mass correction	-	-	-	-	-
LOD in Solution 3σ µg/L		0.005	0.07	0.001	0.008	0.001	0.01
LOQ in Solution 10σ µg/L		0.02	0.2	0.003	0.03	0.003	0.04
Concentration of Samples in Solution µg/L	Soil A	0.438	4.00	0.138	<	5.91	0.06
	Soil B	0.357	1.63	0.053	<	2.02	<
	Soil C	0.257	1.50	0.023	<	2.16	<
	Soil D	0.127	1.11	0.433	<	2.86	<
	Soil E	0.403	2.97	0.085	<	12.5	0.02
Recovery	Spike Conc. µg/L	9	240	2.7	15	9	9
	Soil A	101 %	98 %	100 %	103 %	100 %	101 %
	Soil B	103 %	99 %	101 %	102 %	100 %	102 %
	Soil C	102 %	99 %	102 %	102 %	100 %	103 %
	Soil D	101 %	101 %	98 %	102 %	99 %	99 %
	Soil E	102 %	99 %	102 %	102 %	99 %	102 %
LOD in Soil 3σ mg/kg		0.009	0.1	0.002	0.01	0.002	0.02
LOQ in Soil 10σ mg/kg		0.03	0.4	0.005	0.04	0.005	0.06
Concentration of Samples in Soil mg/kg	Content Test Standard	150	4000	45	250	150	150
	Soil A	0.727	6.64	0.229	<	9.81	0.10
	Soil B	0.595	2.72	0.088	<	3.37	<
	Soil C	0.426	2.49	0.038	<	3.58	<
	Soil D	0.211	1.84	0.719	<	4.75	<
	Soil E	0.664	4.89	0.141	<	20.6	0.03

< : Less than detection limit

* In the soil content standard, the standard value is set as Cr (VI), but the analytical value is the concentration of total Cr.

■ Confirmation of Long-Term Stability

A solution containing 1/10 of the soil content standard was added to the soil measurement solution, and 50 consecutive measurements were taken to confirm sensitivity variation over a long measurement period . Fig. 4 shows the intensity variation of the internal standard elements. The intensity variation based on the initial measurement result was 88 to 104 %, and no significant variation was observed even over a long measurement period.

Fig. 5 shows the variation in the quantitative values of each measured element after internal standard correction. The variation in quantitative values over 50 consecutive measurements was 98 to 103 %, indicating high reproducibility and stability. This confirmed that any sensitivity variation that occurred during the measurements was sufficiently corrected by internal standard correction.

To avoid introducing unnecessary samples into the measurement, the measurement was conducted under the rinse conditions shown in Table 6. After the measurement, the rinse operation is performed in the following order: auxiliary rinse, solvent rinse, and sample rinse. As shown in the upper part of Fig. 6, in the normal rinsing operation, the auto-sampler nozzle moves from the measurement sample to the rinse liquid after the measurement is completed, so that the measurement solution fills the piping at that time. On the other hand, as shown in the lower part of Fig. 6, the auxiliary rinse operation is started ahead of the measurement end timing by using the advance rinse function. Since, at the end of a measurement, the auxiliary rinse liquid has already reached a position immediately before the nebulizer, no unnecessary samples are introduced. By using the advance rinse function in this way, sample consumption can be reduced, sensitivity variation can be suppressed, and measurement time can be shortened.

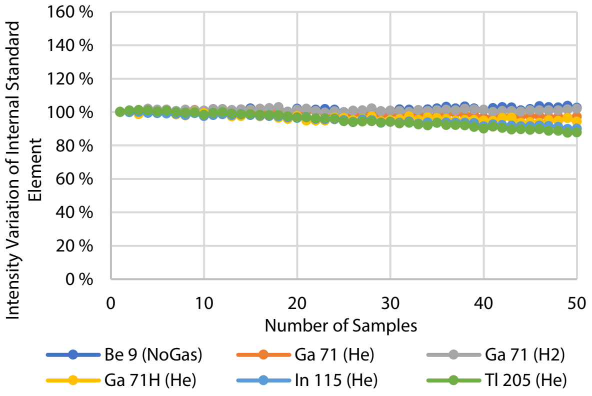

Fig. 4 Intensity Variation of Internal Standard Elements during Continuous Measurement of 50 Samples

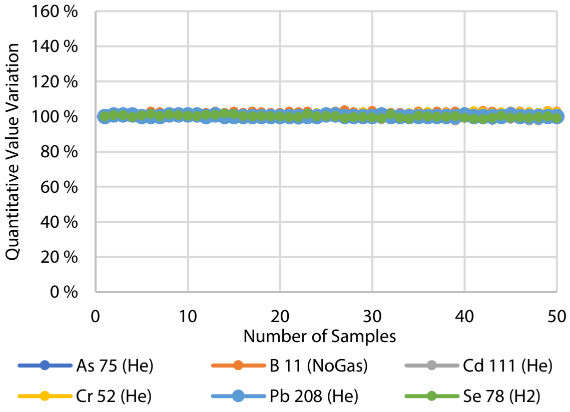

Fig. 5 Quantitative Variation of Each Element during Continuous Measurement of 50 Samples

Table 6 Rinse Conditions (Seconds)

Peristaltic Pump Action	Low (15 r.p.m)	High (45 r.p.m)
Auxiliary Rinse Time (Advance Rinse Time)	130 (90*)	-
Solvent Rinse Time	-	20
Sample Rinse Time	40	40

*Advance rinse is performed during sample measurement.

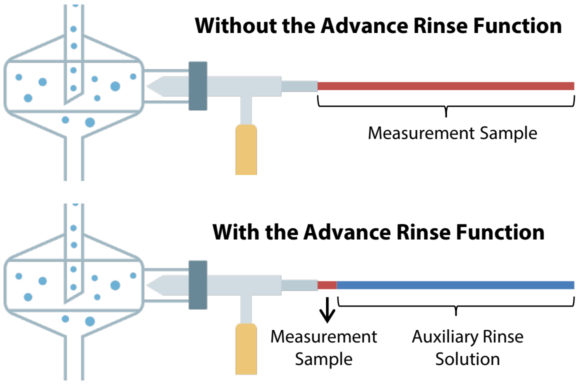

Fig. 6 Condition Inside Piping at End of Measurement

■ Conclusion

Soil content tests were conducted using the ICPMS-2050. The measurement sensitivity was 1/100 or less of the soil content standard, and the validity of the measurements was shown by recovery tests, which confirmed that the influence of the matrix was minimal.

Interelement correction and half-mass correction are effective for interference from REE, and the correction method can be selected depending on the measurement requirements. Furthermore, it was shown that for Se measurement, the interference from Ar and Gd can be largely eliminated by using H2 reaction conditions.

Regarding long-term stability, the variation of the measurement sensitivity was small, and the quantitative values remained stable even when high-matrix samples derived from soil were repeatedly measured. Furthermore, by using the advance rinse function, the sample introduction volume can be reduced, shortening measurement times and improving stability.

<References>

1) The Ministry of the Environment Notification No. 19, “Determination Method for Soil Content Survey”

2) The Ministry of the Environment Notification No. 29 (2002), “The Ordinance for Enforcement of the Soil Contamination Countermeasures Act”

<Related Application>

1. Quantitative Analysis of Leaching of Heavy Metals in Soil Using ICP-MS Application News No. 01-00892-EN

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