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Inductively Coupled Plasma Mass Spectrometer ICPMS-2050

Application News

Analysis of 23 Elements in Wastewater by U.S. EPA Method 6020B Using ICPMS-2050

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User Benefits

- It is possible to measure 23 elements, including trace and high-concentration elements, in wastewater according to EPA Method 6020B.
- The interference of MoO on Cd can be effectively reduced using hydrogen reactions.
- Internal standard fluctuation can be easily observed using the Internal Standard Intensity Fluctuation Graph function of LabSolutions™ ICPMS.

■ Introduction

Because of climate change, population growth and ongoing industrialization, various types of waste are being released into the environment, causing damage to ecosystems. Particularly, the adverse effects of increased heavy metal concentrations in wastewater and the potential effects on human, animal and plant health are of significant concern. Therefore, monitoring these elements in wastewater is one of the most frequently performed environmental analyses.

The U.S. Environmental Protection Agency published EPA Method 6020B to control 23 metals in environmental water using ICP-MS. In this Application News, 23 elements in wastewater were analyzed using the ICPMS-2050. Analytical samples' spike recovery tests and long-term stability tests were performed in accordance with the quality control (QC) requirements of EPA Method 6020b.

■ Analysis Elements

Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Tl, V, Zn (23 elements)

■ Standard Samples

• Calibration Standards

Calibration standards were prepared by mixing commercially available single-element standard solutions and diluting them with a mixture of acid (1 v/v% HNO_3 and 0.5 v/v% HCl). The concentrations in each calibration standard are shown in Table 1.

• Internal Standard Solution

The internal standard solution was prepared by mixing commercially available single-element standard solutions (Bi, Ga, In, Sc) and diluted with a mixture of acid (1 v/v% HNO_3 and 0.5 v/v% HCl). The concentrations of Ga, and Sc in the internal standard solution were 2 mg/L, and the concentrations of Bi and In were 0.5 mg/L.

• Continuing Calibration Verification (CCV) Sample

The CCV sample was prepared by mixing commercially available single-element standard solutions and diluting them with a mixture of acid (1 v/v% HNO_3 and 0.5 v/v% HCl). The concentrations of CCV are shown in Table 1.

• Continuing Calibration Blank (CCB) Sample

The CCB sample was prepared by mixing 1 v/v% HNO_3 and 0.5 v/v% HCl.

■ Samples and Pretreatment

• Spectral Interference Check solution (SIC solution):

ICP-MS Interferents A1 in 5 % HNO_3/tr. HF, 125 mL from SPEX, was used and diluted 10 times.

• Reference material (RM):

The simulated wastewater reference material for metal component analysis (JEMCA 0001-6, JEMCA 0001-7) from the Japan Environmental Measurement and Analysis Association was used.

• Analysis Sample:

Two types of factory wastewater were used. The samples were filtered, and nitric acid was added to make the solution 1 v/v% HNO_3.

■ Equipment Configuration

The configuration of the ICP-MS system is shown in Table 2.

To reduce running costs, the analysis was performed using a mini torch. In addition, to reduce the labor required for sample preparation, the internal standards were added online using an online internal standard kit.

Table 2 ICP-MS System Configuration

System:	ICPMS-2050
Nebulizer:	Nebulizer, DC04
Chamber:	Cyclone Chamber
Torch:	Mini-Torch
Skimmer Cone:	Nickel
Autosampler:	AS-20
Internal Standard Elements:	Online Internal Standard Kit (sample: internal standard = about 9 : 1)

■ Reduction of MoO Interference on Cd and Analytical Conditions

Spectral interference in ICP-MS is caused by polyatomic ions, doubly charged ions, and isobaric ions. Examples of interference caused by overlapping polyatomic ions with the same mass number as the target element include the interference from $^{40}Ar^{16}O^+$ on ^{56}Fe and $^{40}Ar^{38}Ar^+$ on ^{78}Se. Additionally, examples of spectral interference due the analytical sample's to matrix components and liquid properties, such as the chlorine-derived interference of $^{35}Cl^{16}O^+$ on ^{51}V and the interference of $^{95}Mo^{16}O^+$ ions on ^{111}Cd when Mo is present in large quantities.

Methods such as interference correction (inter-element correction, half-mass correction, and interference correction formula) and collision/reaction cells are sometimes used to reduce these spectral interferences.

Table 1 Calibration Standards

(µg/L)	STD0	STD1	STD2	STD3	STD4	STD5	STD6	STD7	STD8	CCV
Ag, Hg, Tl	0	0.1	0.5	1	5	10				1
As, Be, Cd, Co, Cr, Ni, Pb, Sb, Se, V	0	1	5	10	50	100				10
Al, Ba, Cu, Mn, Zn	0	10	50	100	500	1,000				100
Fe	0	10	50	100	500	1,000	2,000			100
K, Mg					1,000	2,000		10,000	20,000	2,000
Ca, Na					5,000	10,000		50,000	100,000	10,000

In this study, we attempted to remove the interference of $^{95}Mo^{16}O^{+}$ on ^{111}Cd by optimizing the collision/reaction conditions. A two-point calibration curve for Cd at concentrations of 0–10 µg/L was created, and the Cd concentration derived from MoO interference in a 2 mg/L Mo standard solution was analyzed using He-collision and H_2-reaction cell gas type, with varying cell voltages. The results are shown in Table 3.

The optimized conditions (indicated by the red box), derived from the Cd concentration due to MoO interference and the intensity of Cd at 10 µg/L, were applied to the wastewater analysis.

In addition to the above Cd analysis conditions, we also attempted changing analytical conditions for removing ClO interference on V. Table 4 shows the analytical conditions for all measured elements.

Table 3 Analytical Results of Cd in Presence of 2 mg/L Mo in Different Collision / Reaction Conditions

Cell Gas Type	**H_2-Reaction**			
Cell gas (mL/min)	6.5	6.5	6.5	6.5
Cell Voltage (V)	-30	-20	-17	-15
Intensity of 10 µg/L Cd (kcps)	25.4	16.9	6.9	2.4
Conc. of Cd in presence of 2 mg/L Mo (Interference from MoO) (µg/L)	0.240	0.008	0.003	N.D.*1
Cell Gas Type	**He-Collision**			
Cell gas (mL/min)	5.5	5.5	5.5	5.5
Cell Voltage (V)	-30	-20	-17	-15
Intensity of 10 µg/L Cd (kcps)	10.2	7.7	5.5	3.4
Conc. of Cd in presence of 2 mg/L Mo (Interference from MoO) (µg/L)	0.514	0.206	0.11	0.067

*1 N.D.: < IDL.

Table 4 Analytical Conditions

RF Power:	1.20 kW
Sampling Depth:	10 mm
Plasma Gas Flowrate:	9.0 L/min
Auxiliary Gas Flowrate:	1.10 L/min
Carrier Gas Flowrate:	0.45 L/min
Dilution Gas Flowrate:	0.40 L/min
Peristaltic Pump Speed:	10 r.p.m

Cell Gas Type:	He	H_2	He (for V)	H_2 (for Cd)
Cell Gas:	5.5 mL/min	6.5 mL/min	5.5 mL/min	6.5 mL/min
Cell Voltage:	-30 V	-30 V	-17 V	-20 V
Energy Filter:	7 V	7 V	7 V	7 V

■ Limit of Quantification and Instrument Detection Limit

A calibration curve was prepared using the calibration standards in Table 1. Table 5 shows the instrument detection limit (IDL) of each analytical element. EPA Method 6020B requires that the laboratory establish the lower limit of quantification (LLOQ) as the lowest point of quantitation, which, in most cases, is the lowest concentration in the calibration curve.

Here, the calibration point for the lowest concentration was determined as LLOQ. The QC requirements for LLOQ in EPA Method 6020B are that the LLOQ is initially verified by analyzing at least seven repeated measurements , the mean recovery should be within ± 35 % of the true value, and RSD should be ≤ 20 %. The LLOQs for all elements analyzed met EPA QC requirements.

Table 5 IDL of Each Analytical Element

Element	Gas Mode	Internal Standard	IDL (µg/L)	Element	Gas Mode	Internal Standard	IDL (µg/L)	Element	Gas Mode	Internal Standard	IDL (µg/L)
^{107}Ag	He	^{115}In	0.005	^{52}Cr	He	^{45}Sc	0.08	^{60}Ni	He	^{71}Ga	0.06
^{27}Al	H_2	^{45}Sc	0.2	^{63}Cu	He	^{71}Ga	0.03	$^{206+207+208}Pb$*1	He	^{209}Bi	0.003
^{75}As	He	^{71}Ga	0.08	^{56}Fe	H_2	^{45}Sc	0.4	^{121}Sb	He	^{115}In	0.02
^{137}Ba	He	^{115}In	0.02	^{200}Hg	He	^{209}Bi	0.02	^{78}Se	H_2	^{71}Ga	0.06
^{9}Be	No Gas	^{45}Sc	0.01	^{39}K	He	^{45}Sc	15	^{205}Tl	He	^{209}Bi	0.003
^{44}Ca	He	^{45}Sc	24	^{24}Mg	He	^{45}Sc	5	^{51}V	He	^{45}Sc	0.1
^{111}Cd	H_2	^{115}In	0.01	^{55}Mn*2	He	^{71}Ga	0.05	^{66}Zn	He	^{71}Ga	0.04
^{59}Co	He	^{45}Sc	0.02	^{23}Na	He	^{45}Sc	20				

*1 The summation of signals at 206, 207, and 208 *m/z* for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

*2 Analysis of Mn used high-resolution mode. The high-resolution mode measures the mass number at every *m/z* = 0.5, half the normal resolution at *m/z* = 1. This has the advantage of separating from the mass number next to it but being less intense. The high-resolution mode is used here to analyze ^{55}Mn when ^{56}Fe is present in large quantities.

■ Analysis and Spike Recovery Test of SIC Solution

To confirm that the interference components don't affect the analysis of wastewater, a sample with the same concentration as the SIC solution described in EPA Method 6020B was prepared and analyzed. The spiked SIC solution includes both analyte elements and matrix/interference elements. The concentration of each element in the SIC solution and spiked SIC solution are shown in Table 6.

From the analysis results of the SIC solution, it was confirmed that the concentrations of all the elements (without matrix/interference elements) were less than two times the LLOQ, which satisfied the requirements of EPA Method 6020B.

The results of the spike recovery test of the SIC solution are shown in Table 7. The mean recoveries are 89 to 105 %, which met EPA QC requirements (100 ± 25 %).

Table 6 Analytes and Interferents with their Respective Concentrations in SIC Solution and Spiked SIC Solution

Analyte / Interferent	SIC Solution (µg/L)	Spiked SIC Solution (µg/L)
Ag, Hg, Tl	0	1
As, Be, Cd, Co, Cr, Ni, Pb, Sb, Se, V	0	10
Ba, Cu, Fe, Mn, Zn	0	100
Mo, Ti	2,000	2,000
Al, K, Mg, P, S	100,000	100,000
C	200,000	200,000
Fe, Na	250,000	250,000
Ca	300,000	300,000

Table 7 Mean Recovery of Spiked SIC Solution (N = 2)

Element	Mean Recovery of Spiked SIC Solution*1	Element	Mean Recovery of Spiked SIC Solution*1
^{107}Ag	95 %	^{55}Mn	98 %
^{75}As	105 %	^{60}Ni	96 %
^{138}Ba	99 %	$^{206+207+208}$Pb*2	99 %
^{9}Be	90 %	^{121}Sb	97 %
^{111}Cd	91 %	^{78}Se	96 %
^{59}Co	95 %	^{205}Tl	89 %
^{52}Cr	97 %	^{51}V	94 %
^{63}Cu	94 %	^{66}Zn	93 %
^{200}Hg	102 %		

*1 Mean recovery: (Concentration of spiked SIC solution – Concentration of SIC solution) / Spike-concentration × 100

*2 The summation of signals at 206, 207, and 208 *m/z* for lead. (To compensate for any differences in the abundances of these isotopes between samples and standards)

■ Analysis Results of Reference Material

To evaluate the accuracy of wastewater analysis, we analyzed the simulated wastewater reference material for metal component analysis (JEMCA 0001-6, JEMCA 0001-7) from the Japan Environmental Measurement and Analysis Association. Table 8 shows the analytical values of RM and the recovery rate for the true value. The recoveries of all elements were within ± 5 %.

Table 8 Analysis Results of JEMCA 0001-6 and JEMCA 0001-7 (N = 2)

JEMCA 0001-6			
Element	Certification Value (mg/L)	Mean Analysis Value (mg/L)	Recovery*1
Mn	0.107	0.108	101 %
Fe	1.97	1.94	98 %
Cu	0.44	0.43	98 %
Cd	0.0029	0.0028	95 %
JEMCA 0001-7			
Element	Certification Value (mg/L)	Mean Analysis Value (mg/L)	Recovery*1
Mn	0.097	0.099	102 %
Fe	1.77	1.74	98 %
Cu	0.49	0.49	100 %
Cd	0.0032	0.0030	95 %

*1 Recovery = Mean analysis value / Certification value × 100

■ Analysis Results of Wastewater and Spike Recovery Test

Analysis of two types of factory wastewater samples and their spiked samples was performed. The relative percent difference (%RPD) and spike recoveries were calculated. The results are shown in Table 9.

The maximum %RPD was 6.5 %, and the spike recoveries were 87 to 104 % for all measured elements. This result satisfied the QC requirements of EPA Method 6020B, which are within 20 % of the %RPD and within 75 to 125 % of the recovery rate. These data confirmed that ICPMS-2050 can provide accurate analysis values.

■ Long-Term Stability

To evaluate the long-term stability of the ICPMS-2050, the two types of factory wastewater were analyzed for approximately 9 hours. CCV and CCB were measured every ten samples (90 samples in total) to confirm the validity of the calibration curves.

All the CCB samples' concentrations were lower than LLOQ. Recoveries of CCV during the analysis are shown in Fig. 1. The CCV recoveries of all the measured elements during the analysis were within 90 to 110 % (red dotted line), which confirmed the validity of the calibration curve during the long-term analysis.

In addition, the internal standard recoveries during analysis are shown in Fig. 2. The intensity of each internal standard element in STD0 was defined as 100 %. All measured internal standard recoveries were within 70 to 130 % (red dotted line). The CCV and internal standard recoveries showed good long-term stability of ICPMS-2050 analysis, which met the QC requirements of EPA Method 6020B.

Table 9 The Analysis Results of Wastewater and Spike Recovery Test (N = 2)

Element	Spike Conc. (µg/L)	Wastewater A				Wastewater B			
		Conc. of Unspiked Sample (µg/L)	Conc. of Spiked Sample (µg/L)	%RPD of Spiked Sample*2	Spike Recovery*3	Conc. of Unspiked Sample (µg/L)	Conc. of Spiked Sample (µg/L)	%RPD of Spiked Sample*2	Spike Recovery*3
^{107}Ag	1	0.008	0.984	2.9	98	0.038	1.02	6.5	98
^{27}Al	100	57.2	151	0.0	94	153	246	2.4	93
^{75}As	10	1.25	11.2	1.8	100	0.98	11.0	1.8	100
^{138}Ba	100	15.6	114	0.9	98	12.5	112	0.0	100
^{9}Be	10	N.D.*1	9.90	0.8	99	0.02	10.2	1.0	102
^{44}Ca	10,000	17,100	26,100	1.5	90	12,700	21,700	0.5	90
^{111}Cd	10	0.06	9.72	0.1	97	5.08	14.6	0.0	95
^{59}Co	10	0.06	9.70	0.4	96	0.35	10.0	1.5	97
^{52}Cr	10	0.14	9.98	0.3	98	1.11	10.9	0.9	98
^{63}Cu	100	6.83	104	1.0	97	8.79	107	0.9	98
^{56}Fe	100	237	324	0.3	87	276	364	2.7	88
^{200}Hg	1	0.04	0.95	4.2	91	0.05	0.98	1.5	93
^{39}K	2,000	2,200	4,130	0.5	97	2,490	4,380	0.2	95
^{24}Mg	2,000	2,640	4,560	0.4	96	1,900	3,890	0.8	100
^{55}Mn	100	102	192	2.1	90	27.0	125	0.8	98
^{23}Na	10,000	12,300	21,600	0.9	93	13,400	22,600	1.8	92
^{60}Ni	10	1.02	10.7	0.9	97	6.59	15.6	0.6	90
$^{206+207+208}$Pb*4	10	0.418	10.3	0.0	99	5.32	15.1	0.0	98
^{121}Sb	10	0.33	10.2	0.0	99	0.49	10.6	0.9	101
^{78}Se	10	0.05	9.75	2.9	97	0.09	9.97	2.7	99
^{205}Tl	1	0.012	1.01	0.0	100	0.007	1.05	1.9	104
^{51}V	10	0.5	9.9	1.9	94	0.4	10.4	1.9	100
^{66}Zn	100	23.8	120	1.7	96	50.9	147	0.0	96

*1 N.D.: < IDL
*2 %RPD: [|First sample analysis value − Duplicate sample analysis value| / (0.5 × |First sample analysis value + Duplicate sample analysis value|)] × 100
*3 Mean recovery: (Concentration of spiked sample − Concentration of sample) / Spike-concentration × 100
*4 The summation of signals at 206, 207, and 208 *m/z* for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

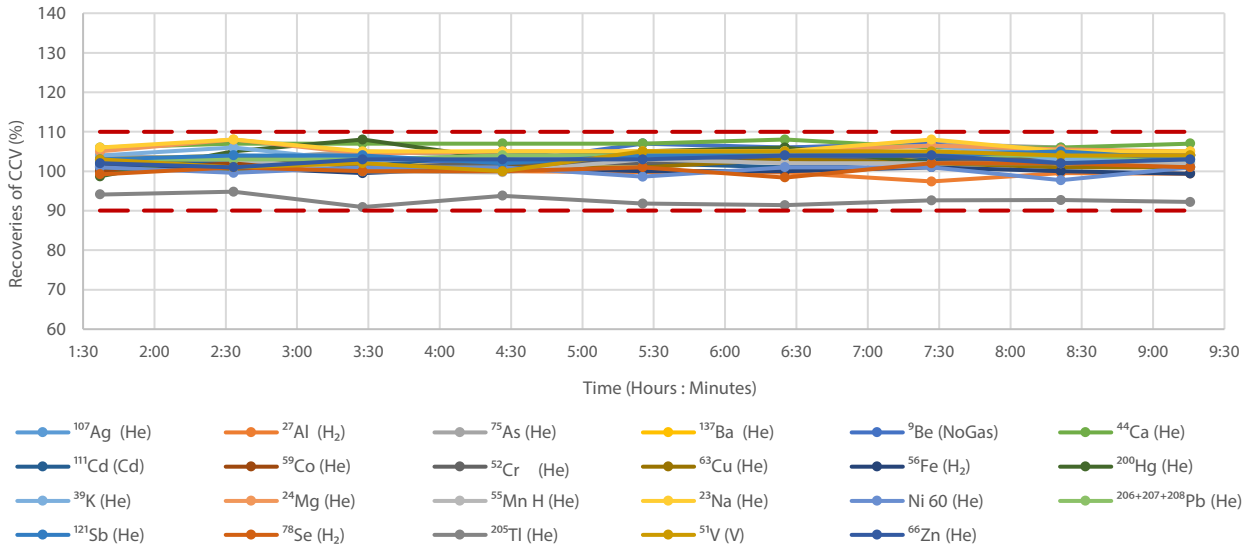

Fig. 1 CCV Recoveries over 9 Hours Analysis

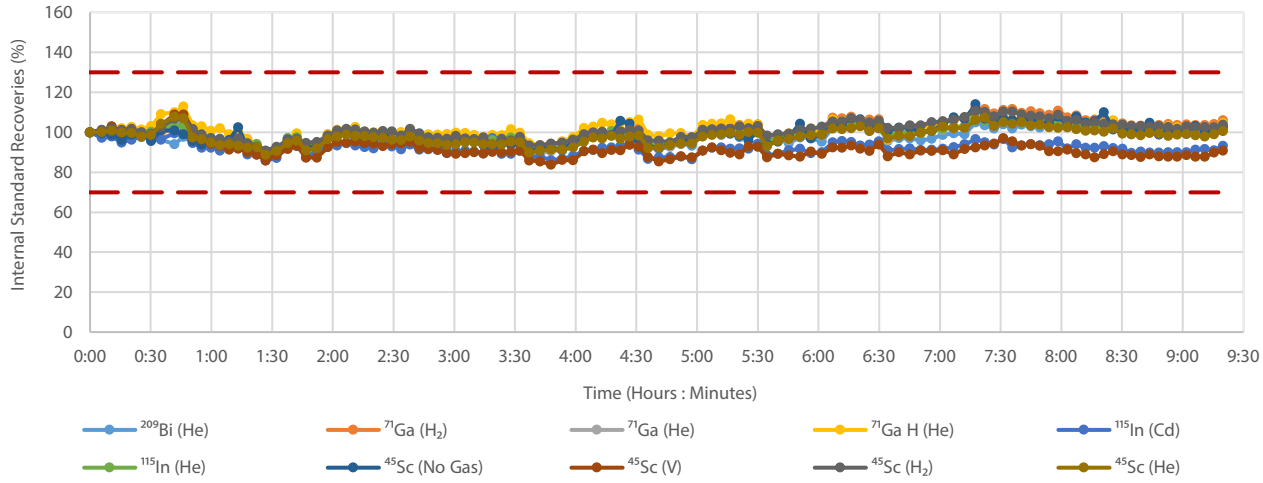

Fig. 2 Internal Standard Recoveries over 8 Hours Analysis

■ The Intensity Fluctuation Graph of Internal Standard by LabSolutions™ ICPMS

When analyzing high-matrix samples such as wastewater over a long period of time, the stability of internal standard elements is often used as a QC requirement to evaluate the robustness of the analysis method.

In general, to ensure no matrix effect exists, the intensities of each internal standard should not decrease below a certain percentage with respect to its intensity during the initial calibration. In EPA Method 6020B, if the intensities decrease more than 30 %, matrix effects must be removed by diluting the affected sample.

LabSolutions™ ICPMS can graphically show the intensity fluctuation of internal standards. Fig. 3 shows an example of the intensity fluctuation graph of internal standards for the wastewater analysis.

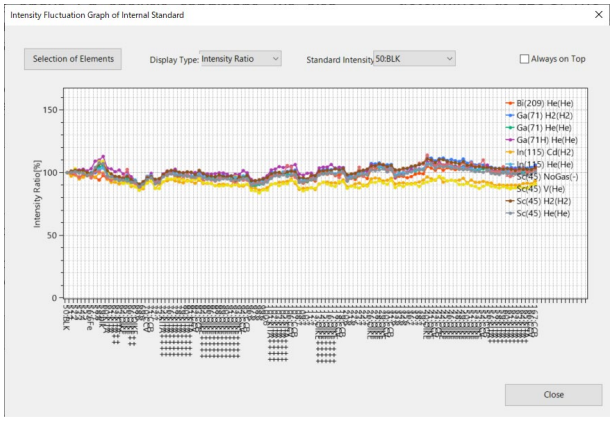

Fig. 3 Fluctuation of Internal Standards Plotted for Each Sample

■ Summary

An ICPMS-2050 was used to analyze 23 elements in wastewater following U.S. EPA Method 6020B. All the analyses met the QC requirements of EPA Method 6020B, confirming the analytical method's usefulness.

IDLs obtained in this analysis were sufficiently low compared with the standard values of each regulation for wastewater analysis, and high-sensitivity analysis was realized. In the spike recovery test with SIC solution and samples, good recoveries were obtained, confirming the accuracy of ICPMS-2050.

In the long-term stability test, the CCV recoveries of all the analytes were within 90 to 110 %. Furthermore, the fluctuation of all internal standards with respect to the intensity during the initial calibration was within the QC requirements of EPA Method 6020B, indicating the high stability of the ICPMS-2050 system.

The ICPMS-2050 mini-torch system provides accurate analysis, high stability, low argon gas consumption and low running costs.

<References>

1) EPA Method 6020B (SW-846), "Inductively Coupled Plasma – Mass Spectrometry," U.S. Environmental Protection Agency, July. 2014

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