SHIMADZU
Excellence in Science

Application News

Inductively Coupled Plasma Mass Spectrometer ICPMS-2050

Analysis of Drinking Water by U.S. EPA Method 200.8 Using ICPMS-2050 with Collision/Reaction Cell

Kosuke Naka

User Benefits

- ICPMS-2050 can achieve accurate analysis and high stability, as well as lower Ar gas consumption and running costs with a mini-torch.
- Se can be measured with higher sensitivity using reaction mode.
- Avoids a complex investigation of conditions by using the analytical conditions from preset methods.

■ Introduction

Method 200.8[1], developed by the U.S. Environmental Protection Agency (EPA), is an ICP-MS method for the analysis of trace elements in groundwater, surface water, and drinking water. EPA 200.8 is a method based on analysis with no gas mode. On the other hand, ICP-MS is commonly equipped with collision/reaction cell technology to eliminate interferences such as polyatomic ions.

In this Application News, drinking water and a certified reference material were analyzed by ICPMS-2050. Most elements were measured in collision mode to eliminate interference, but reaction mode was used to measure Se for higher sensitivity. Spike recovery and long-term stability were evaluated with reference to EPA 200.8 quality control (QC) requirements.

The analytical conditions used in this application can be easily registered from preset methods, enabling measurements to be performed without the need to develop them.

Fig. 1 ICPMS-2050 and AS-20 Equipment

■ Sample Preparation

- Certified Reference Material (CRM) JSAC 0302-4a (The Japan Society for Analytical Chemistry)

JSAC 0302-4a (CRM for river water) was used to evaluate the accuracy of the ICPMS-2050 measurements.

- Drinking Water

Drinking water was prepared to contain 1 v/v% HNO_3 and 100 µg/L Au.

■ Standard Samples

- Calibration Standards

Calibration standards were prepared by mixing standard solutions (Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Hg, Tl, Pb, Th, U) and adding HNO_3 and Au standard solution. Au standard solution is added to retain Hg in solution according to EPA 200.8. The concentrations in each calibration curve sample are shown in Table 1.

- Internal Standard Solution

The internal standard solution was prepared by mixing standard solutions (Li, Sc, Ga, Y, Rh, In, Tb, Ho, Lu, Bi) and adding HNO_3 and Au standard solution. The concentrations in the internal standard solution are shown in Table 2.

- Continuing Calibration Verification (CCV) Samples

CCV was prepared at the same concentration as STD4.

Table 1 Calibration Standards

Elements	Concentration (µg/L)				
	STD1	STD2	STD3	STD4	STD5
Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba, Tl, Pb, Th, U	0	1	10	50	100
Ag	0	1	10	50	
Hg	0	0.05	0.5	2.5	5
Na, Mg, K, Ca	0	250	2500	12500	25000
Au	100				
HNO_3	1v/v%				

Table 2 Internal Standard Solution

Elements	Concentration (µg/L)
Li, Sc, Ga	1000
Y, Rh, In, Tb, Ho, Lu, Bi	100
Au	100
HNO_3	1 v/v%

■ Equipment Configuration and Analytical Conditions

The configuration of the ICP-MS system is shown in Table 3. To reduce running costs, analysis was performed with a mini-torch that consumes less argon gas than a typical plasma torch. To reduce the labor involved in sample preparation, the internal standard sample was added online using an online internal standard kit.

The analytical conditions used are shown in Table 4. The analytical conditions used in this study can be easily registered from LabSolutions™ ICPMS preset methods.

Table 3 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)

Table 4 Analytical Conditions

RF Power:	1.20 kW
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
Collision/Reaction Gas:	He / H_2

■ Collision/Reaction Cell

EPA 200.8 is a method based on analysis in the no gas mode, which corrects for interference using theoretical equations. However, there are also interferences that cannot be corrected by theoretical formulas in ICP-MS analysis. For example, $^{44}Ca^{16}O^+$ interferes with ^{60}Ni due to Ca in drinking water. This interference of polyatomic ions cannot be corrected by theoretical equations, which can lead to measurements that are larger than the true value.

He collision and H_2 reaction are effective means of eliminating the interferences of polyatomic ions. In He collision, interferences are removed by collision of He gas with polyatomic ions. Interference removal of polyatomic ions by collision has the advantage of being versatile, but it also gives rise to collision with the measured elements, which causes the signal degradation of the measured elements. In the H_2 reaction, on the other hand, interferences are eliminated by reaction between H_2 gas and polyatomic ions. Therefore, the signal degradation of the measured elements can be minimized. However, interference ions that do not react with H_2 gas cannot be sufficiently removed.

In this Application News, most elements were measured in He collision and Se was measured in H_2 reaction for accurate analysis. Se is generally analyzed at *m/z* 78. However, ^{78}Se is interfered with by $^{40}Ar^{38}Ar^+$, which comes from argon gas that forms the plasma. Both He collision and H_2 reaction can eliminate this interference. Table 5 shows a comparison of the Instrument Detection Limit (IDL) of Se in He collision and H_2 reaction. In H_2 reaction, the signal degradation of Se is smaller, lower IDL of Se can be achieved than in He collision.

Table 5 Comparisons of IDL in He Collision and H_2 Reaction

Elements	Gas Mode	IDL (µg/L)
^{78}Se	He collision	0.2
^{78}Se	H_2 reaction	0.02

■ Detection Limits

Calibration curves were prepared using the calibration standards shown in Table 1. IDLs and Method Detection Limits (MDLs) determined from calibration curves are shown in Table 6. Following EPA 200.8, IDLs were calculated from 3 times the standard deviation (σ) of 10 measurements of the calibration blank (STD1). MDLs were determined from σ of 7 measurements of blank spiked with concentrations two to five times the estimated detection limit.

IDL = 3 × σ (STD1) × slope of the calibration curve

MDL = t × σ (spiked blank) × slope of the calibration curve

where :

t = Student's t value for a 99 % confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]

σ = standard deviation of the replicate analyses

Table 6 IDLs and MDLs for Each Element

Elements	Gas Mode	Internal Standard Element	IDL (µg/L)	MDL (µg/L)
^{9}Be	No Gas	^{45}Sc	0.008	0.03
^{23}Na	He	^{45}Sc	20	10
^{24}Mg	He	^{45}Sc	0.8	2
^{27}Al	No Gas	^{45}Sc	0.01	0.02
^{39}K	He	^{45}Sc	7	10
^{44}Ca	He	^{45}Sc	9	30
^{51}V	He	^{71}Ga	0.02	0.02
^{52}Cr	He	^{71}Ga	0.009	0.02
^{55}Mn	He	^{71}Ga	0.009	0.03
^{59}Co	He	^{71}Ga	0.004	0.007
^{60}Ni	He	^{71}Ga	0.03	0.03
^{63}Cu	He	^{71}Ga	0.005	0.006
^{66}Zn	He	^{71}Ga	0.02	0.06
^{75}As	He	^{71}Ga	0.03	0.04
^{78}Se	H_2	^{71}Ga	0.02	0.05
^{98}Mo	He	^{103}Rh	0.004	0.004
^{107}Ag	He	^{103}Rh	0.001	0.007
^{111}Cd	He	^{115}In	0.01	0.01
^{121}Sb	He	^{115}In	0.006	0.009
^{137}Ba	He	^{115}In	0.02	0.04
^{202}Hg	He	^{209}Bi	0.006	0.005
^{205}Tl	He	^{209}Bi	0.001	0.003
^{208}Pb	He	^{209}Bi	0.002	0.003
^{232}Th	He	^{209}Bi	0.0007	0.001
^{238}U	He	^{209}Bi	0.0003	0.0009

■ Analysis of CRM JSAC 0302-4a

CRM JSAC 0302-4a was quantitatively analyzed using the calibration curves. The results of CRM analysis are shown in Table 7. Recoveries of 98 to 107 % of the certified value were achieved. These results certify the EPA 200.8 QC requirement of 90 to 110 % CRM recoveries. The accuracy of ICPMS-2050 measurement is confirmed.

Table 7 Result of CRM JSAC 0302-4a Analysis (N = 3)

Elements	Certified Value (µg/L)	Mean Measured Value (µg/L)	Recovery (%)
^{9}Be	0.99	0.98	99
^{23}Na	3900	4030	103
^{24}Mg	3100	3100	100
^{27}Al	79	80.1	101
^{39}K	470	466	99
^{44}Ca	12700	12500	98
^{52}Cr	9.96	9.90	99
^{55}Mn	5.7	5.65	99
^{60}Ni	16.8	18.0	107
^{63}Cu	10.2	10.9	107
^{66}Zn	10.3	10.8	105
^{75}As	5.2	5.32	102
^{78}Se	5.0	5.21	104
^{98}Mo	0.38	0.382	101
^{111}Cd	0.98	1.00	102
^{137}Ba	0.89	0.90	101
^{208}Pb	9.7	10.2	105

Recovery (%) = Mean Measured Value / Certified Value × 100

■ Analysis of Drinking Water and Spike Recovery

Unspiked and spiked drinking water were quantitatively measured using calibration curves, and spike recoveries were calculated. The results are shown in Table 8. Spike recoveries of 94 to 107 % were obtained for all the measured elements. The results meet EPA 200.8 QC requirement of 70 to 130 % recoveries. The matrix of the drinking water had no effect on the ICPMS-2050 analysis.

■ Long-Term Stability

Drinking water was analyzed for about seven hours to evaluate the long-term stability of the ICPMS-2050. CCV was measured every 10 samples to confirm the validity of the calibration curves.

Recoveries of CCV during the analysis are shown in Fig. 2. The CCV recoveries of all the measured elements during the analysis were within the EPA 200.8 QC requirement of 90 to 110 % (red dotted line). If the CCV recoveries fall outside 90 to 110 %, recalibration is required.

The internal standard recoveries during analysis are shown in Fig. 3. All measured internal standard recoveries were within the EPA 200.8 QC requirement of 60 to 125 % (red dotted line). If the internal standard recoveries also fall outside this range, recalibration is needed.

The results of CCV and internal standard recoveries showed good long-term stability of ICPMS-2050 analysis.

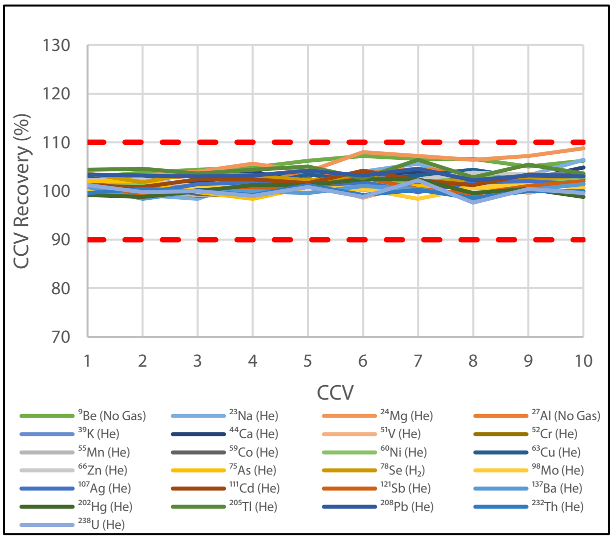

Fig. 2 CCV Recoveries over 7 Hours Analysis

Table 8 Spike Recoveries of Drinking Water

Elements	Unspiked Drinking Water	STD3 Spiked Drinking Water			STD4 Spiked Drinking Water		
	Measured Value (μg/L)	Spike Conc. (μg/L)	Measured Value (μg/L)	Recovery (%)	Spike Conc. (μg/L)	Measured Value (μg/L)	Recovery (%)
^{9}Be	N.D.	10	10.3	103	50	50.0	100
^{23}Na	6530	2500	8990	98	12500	19200	101
^{24}Mg	9200	2500	11600	(96)	12500	22100	103
^{27}Al	8.95	10	18.8	99	50	57.5	97
^{39}K	887	2500	3300	97	12500	12800	95
^{44}Ca	21200	2500	23700	(100)	12500	32900	94
^{51}V	15.8	10	25.9	101	50	64.8	98
^{52}Cr	0.591	10	10.8	102	50	50.6	100
^{55}Mn	0.866	10	10.8	99	50	50.1	98
^{59}Co	N.D.	10	10.6	106	50	51.8	104
^{60}Ni	0.20	10	10.6	104	50	51.5	103
^{63}Cu	0.256	10	10.9	106	50	53.1	106
^{66}Zn	0.33	10	10.9	106	50	52.4	104
^{75}As	0.18	10	10.4	102	50	51.2	102
^{78}Se	0.13	10	10.5	104	50	50.3	100
^{98}Mo	0.135	10	9.7	96	50	50.1	100
^{107}Ag	0.017	10	10.3	103	50	50.5	101
^{111}Cd	N.D.	10	10.5	105	50	51.8	104
^{121}Sb	0.012	10	10.6	106	50	52.0	104
^{137}Ba	0.88	10	11.3	104	50	52.4	103
^{202}Hg	N.D.	0.5	0.536	107	2.5	2.65	106
^{205}Tl	N.D.	10	10.5	105	50	50.6	101
^{208}Pb	0.009	10	10.6	106	50	52.1	104
^{232}Th	0.0064	10	10.1	101	50	51.0	102
^{238}U	0.0458	10	10.4	104	50	52.0	104

N.D. = Not Detected (< MDL)
Recovery (%) = (Spiked Sample – Unspiked Sample) / Spike conc. × 100
( ): According to EPA 200.8, spike recovery calculations are not required if spike concentration is less than 30 % of unspiked sample concentration.

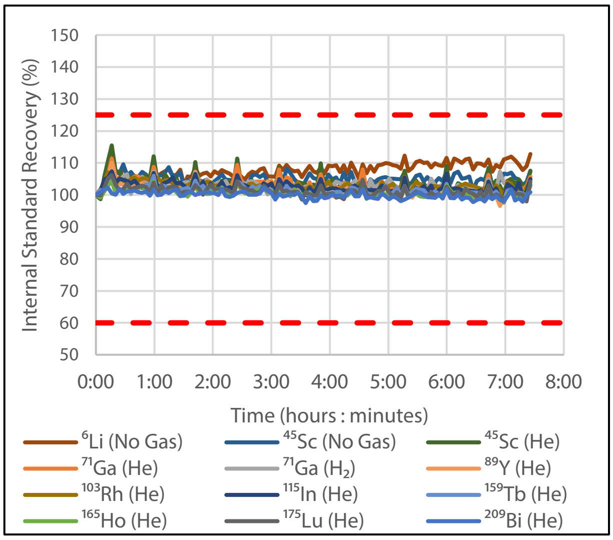

Fig. 3 Internal Standard Recoveries over 7 Hours Analysis

■ Conclusion

In this Application News, drinking water was analyzed using ICPMS-2050. Good recoveries of CRM and spiked samples were obtained, confirming the accuracy of ICPMS-2050 analysis. The CCV recoveries of all the measured elements were within 90 to 110 %. Also, all measured internal standard recoveries were within the EPA 200.8 QC requirement of 60 to 125 %, demonstrating the high stability of the ICPMS-2050.

ICPMS-2050 can achieve accurate analysis and high stability, as well as lower argon gas consumption and lower running costs, thanks to the use of a mini-torch. In addition, the analytical conditions can be easily registered from preset methods, and analysis can be started without the need to develop the analytical method.

<References>

1) EPA Method 200.8 Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry Revision 5.4

<Related Applications>

1. Analysis of Drinking Water by U.S. EPA Method 200.8 Using ICPMS-2040 with Collision Cell, Application News 01-00572_EN

01-00573-EN First Edition: Jul. 2023