

Analysis of Trace Elements in Water by EPA Method 200.8 using the Shimadzu ICPMS-2030

No. ICP-005

■ Introduction

This application note describes the methodology and use of the Shimadzu ICPMS-2030 ICP mass spectrometer for the analysis of trace elements in drinking and fresh waters following the EPA 200.8 method. This method is also used for analysis of wastewater. Here, we demonstrate the stability and sensitivity of the ICPMS-2030 for EPA 200.8 analyses.

■ Equipment, Reagents, and Labware

A Shimadzu ICPMS-2030 was used for all analysis in conjunction with a Shimadzu AS-10 Autosampler. In-line addition of internal standards to calibration and unknown samples was accomplished using the Shimadzu Internal Standard Addition Kit. Based on the internal diameter of peristaltic tubing used for sample and internal standard injection, the approximate dilution factor of the internal standard solution was 90%.

High-purity reagents were used during sample preparation and dilution to ensure minimal contamination. Ultra-pure water ($\geq 18.1 \text{ M}\Omega \cdot \text{cm}$; Millipore) along with trace-metal grade nitric acid (Fisher *Optima*) was used for all dilutions and acidifications. For the sake of brevity, we refer to these simply as “water” and “nitric acid”, herein. All labware was cleaned in a solution of 20% nitric acid, triple rinsed with water, and allowed to dry. All standards and unknown samples were prepared in cleaned, single-use containers to minimize any cross-contamination between analytical runs.



Shimadzu ICPMS-2030

■ Tuning, Calibration, Internal Standard, and Instrument Operation Parameters

The instrument was allowed to warm up for ≥ 30 minutes and was tuned prior to analysis using Shimadzu’s ICP-MS tuning solution to ensure proper signal responses, lens voltages, and mass resolution. Following tuning, the condition of the instrument was validated using Inorganic Ventures 200.8 Method Tuning Solution, which contains Be, Mg, Co, In, and Pb. The validation procedure consisted of ensuring a resolution of $\sim 0.75 \text{ amu}$ on ^{24}Mg , ^{25}Mg , ^{26}Mg , ^{206}Pb , ^{207}Pb , and ^{208}Pb . Acceptable instrument stability was determined by running five replicate measurements of the tuning solution and ensuring that relative standard deviations of raw signals for Be, Mg, Co, In, and Pb were $< 5\%$.

A general summary of the operational parameters of the ICPMS-2030 is provided in Table 1.

Table 1: Operating parameters for the Shimadzu ICPMS-2030 while running EPA Method 200.8.

Torch	Shimadzu Mini Torch
Nebulizer	Coaxial
Spray Chamber	Cooled Cyclonic
Spray Chamber Temp.	5° C
RF Power	1.20 kW
Sampling Depth	5 mm
Plasma Gas Flow	8.0 L/min
Auxiliary Gas Flow	1.1 L/min
Carrier Gas Flow	0.70 L/min
Total Ar Flow	9.8 L/min
Number of Scans	10
Scan Time	0.2 sec
Total Integration Time	2 sec

All calibration solutions were prepared from verified multi-element standards provided from Inorganic Ventures, using their EPA 200.8 Method Package. These standards contain the elements specified in method 200.8 (i.e., Al, Ag, As, Ba, Be, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, Th, U, V, and Zn). The concentration of analytes in the calibration solutions are provided in Table 2.

Table 2: Concentration (in ppb) of analytes in calibration solutions for EPA Method 200.8.

	Cal 1	Cal 2	Cal 3	Cal 4
As	0	10	20	100
Ba	0	10	20	100
Be	0	10	20	100
Cd	0	10	20	100
Co	0	10	20	100
Cr	0	10	20	100
Cu	0	10	20	100
Hg	0	0.5	1	5
Mn	0	10	20	100
Mo	0	10	20	100
Ni	0	10	20	100
Pb	0	10	20	100
Pd	0	10	20	100
Ru	0	10	20	100
Sb	0	10	20	100
Se	0	50	100	500
Th	0	10	20	100
Tl	0	10	20	100
U	0	10	20	100
V	0	10	20	100
Zn	0	10	20	100

A multi-element internal standard solution was prepared from a multi-element standard provided by Inorganic Ventures and contained Sc, Y, In, Tb, and Bi. Because Hg was determined using the direct analysis method, Au was added to the internal standard solution and to the blank rinse solution. All of the internal standards were added in-line from a stock of 200 ppb for each analyte. After a ~1:10 dilution during internal standard uptake, the final concentration of the internal standards upon reaching the plasma was ~20 ppb.

■ **Pre-analysis Validation**

To validate the instrument's capability prior to analyzing unknown samples, instrument detection limits (IDL), method detection limits (MDL), and linear dynamic ranges (LDR) were established for each analyte.

The IDL is calculated as three times the standard deviation of 10 replicate measurements of a calibration blank.

The MDL is determined as specified in EPA Method 200.8. Each analyte is spiked into reagent water at a concentration two- to five-times the IDL. Then, seven replicate analyses of that solution are conducted. The MDL is calculated as:

$$MDL = t \times S$$

Where t is Student's t-distribution for 99% confidence level (equals 3.14 for a sample size of seven) and S is the standard deviation of the seven replicate measurements.

The LDR was determined by calibrating the instrument as described in Table 2 and running a series of samples of increasing concentration, outside of the range of the calibration curve, and determining at which concentrations those analytes fell outside of ± 10% of their expected concentration as extrapolated from the calibration curves.

The results of these tests are shown in Table 3.

Table 3: Analytes, analyte mass(es), instrument detection limits (IDL), method detection limits (MDL) and linear dynamic range (LDR).

Analyte	Mass(es)	IDL (ppb)	MDL (ppb)	LDR (ppm)
Al	27	0.0430	0.063	20
Sb	123	0.0099	0.022	20
As	75	0.0166	0.023	20
Ba	137	0.0057	0.006	20
Be	9	0.0004	0.018	40
Cd	111	0.0057	0.017	40
Cr	52	0.0102	0.016	20
Co	59	0.0002	0.024	20
Cu	63	0.0311	0.015	40
Pb	206, 207, 208	0.0142	0.03	20
Mn	55	0.0022	0.064	20
Hg	202	0.0069	0.008	0.5
Mo	98	0.0031	0.007	40
Ni	60	0.0090	0.011	40
Se	82	0.0929	0.111	100
Ag	107	0.0027	0.03	40
Tl	205	0.0002	0.011	40
Th	232	0.0001	0.012	40
U	238	< 0.0001	0.014	40
V	51	0.0023	0.032	20
Zn	66	0.0986	0.065	40

■ Post-analysis Validation

To validate the instrument's analytical capabilities, a series of samples spiked with known concentrations of the analyte elements, as well as a NIST Standard Reference Material (SRM 1643f – Trace Elements in Water) were analyzed. According to EPA Method 200.8, the spike recoveries should be $\pm 30\%$. The results of the spike recovery tests are shown in Tables 4 and 5. The spike recoveries for all analytes fall well within the specified $\pm 30\%$ and, in fact, are within $\pm 10\%$.

Table 4: Concentrations (in ppb) for spike and recovery for a tap water sample. All analytes fall within $\pm 10\%$ recovery. Spike levels were 5 ppb for Hg, 100 ppb for Se, and 20 ppb for all others.

	Sample Conc.	Sample + Spike conc.	% Recovery
Ag	-0.585	18.8	96.9
Al	19.1	39.5	102.0
As	-0.492	20.1	103.0
Ba	22.9	42.4	97.5
Be	-0.45	19.9	101.8
Cd	1.08	20.7	98.1
Co	1.35	20.6	96.3
Cr	1.03	19.9	94.4
Cu	150	170.3	101.5
Hg	0.755	5.3	90.9
Mn	2.7	22.3	98.0
Mo	0.94	21.8	104.3
Ni	2.96	23	100.2
Pb	1.11	21.2	100.5
Sb	1.81	21.9	100.5
Se	-6.66	92.7	99.4
Th	1.9	22.5	103.0
Tl	-0.316	18.9	96.1
U	2.36	22.5	100.7
V	1.61	21.2	98.0
Zn	77.2	98.1	104.5

The long-term stability of the instrument over a typical analytical session, in this case, 10 hours, was assessed by analyzing a series of known samples repeatedly to ensure minimal deviation of signal intensities over time. As shown in Fig. 1 (next page), the ICPMS-2030 demonstrates stable signals over a 10-hour analytical period, indicating that the instrument will provide robust results in high-throughput laboratories.

Table 5: Concentrations (in ppb) of analytes reported in NIST SRM 1643f, Trace Elements in Water, as well as concentrations measured for NIST SRM 1643f using the ICPMS-2030. Note that the NIST sample does not contain Hg, U, or Th.

	NIST SRM 1643f	Measured Conc.	% Recovery
Ag	0.9606	0.991	103.2
Al	132.5	132	99.6
As	56.85	57.9	101.8
Ba	513.1	479	93.4
Be	13.53	12.9	95.3
Cd	5.83	6.12	105.0
Co	25.05	24.7	98.6
Cr	18.32	17.6	96.1
Cu	21.44	21	97.9
Mn	36.77	36.7	99.8
Mo	114.2	108	94.6
Ni	59.2	58.2	98.3
Pb	18.303	17.1	93.4
Sb	54.9	52.3	95.3
Se	11.583	11.63	100.4
Tl	6.823	6.38	93.5
V	35.71	34.9	97.7
Zn	73.7	76.4	103.7

■ Sample Analysis

Drinking water samples from a variety of sources and locations were analyzed to ensure that the above described methodology functions appropriately with real-world samples. The samples were stabilized in 2% HNO₃ prior to analysis. The samples, sample source, and analytical results are presented in Table 6.

Table 6: Concentrations (in ppb) of analytes from residential water samples. Note that Municipal Waters 1 and 2 are from private residences with water sourced from two different regional water utilities. Wells 1 and 2 are from private residences in two different states. An indication of "n.d." specifies that the analyte fell below the level of detection.

	Municipal Water 1	Municipal Water 2	Residential Well 1	Residential Well 2
Ag	n.d.	n.d.	n.d.	n.d.
Al	31.6	25.4	2.43	4.2
As	n.d.	n.d.	n.d.	0.878
Ba	23.8	37	2.79	29.5
Cd	1.07	1.08	1.07	1.08
Co	2.49	1.39	1.24	1.28
Cr	1.12	1.31	1.03	2.15
Cu	29.3	24.8	13.4	1.55
Hg	0.31	0.33	0.37	0.30
Mn	2.3	4.6	1.51	38.5
Mo	0.70	1.5	1.65	0.989
Ni	4.13	4.34	3.12	3.47
Pb	0.98	0.65	0.49	0.49
Sb	1.79	1.81	1.76	1.73
Se	n.d.	n.d.	n.d.	n.d.
Th	1.89	1.4	1.9	1.89
Tl	n.d.	n.d.	n.d.	n.d.
U	2.39	2.39	2.81	2.37
V	1.58	1.67	1.65	1.32
Zn	4.7	25.5	0.83	127

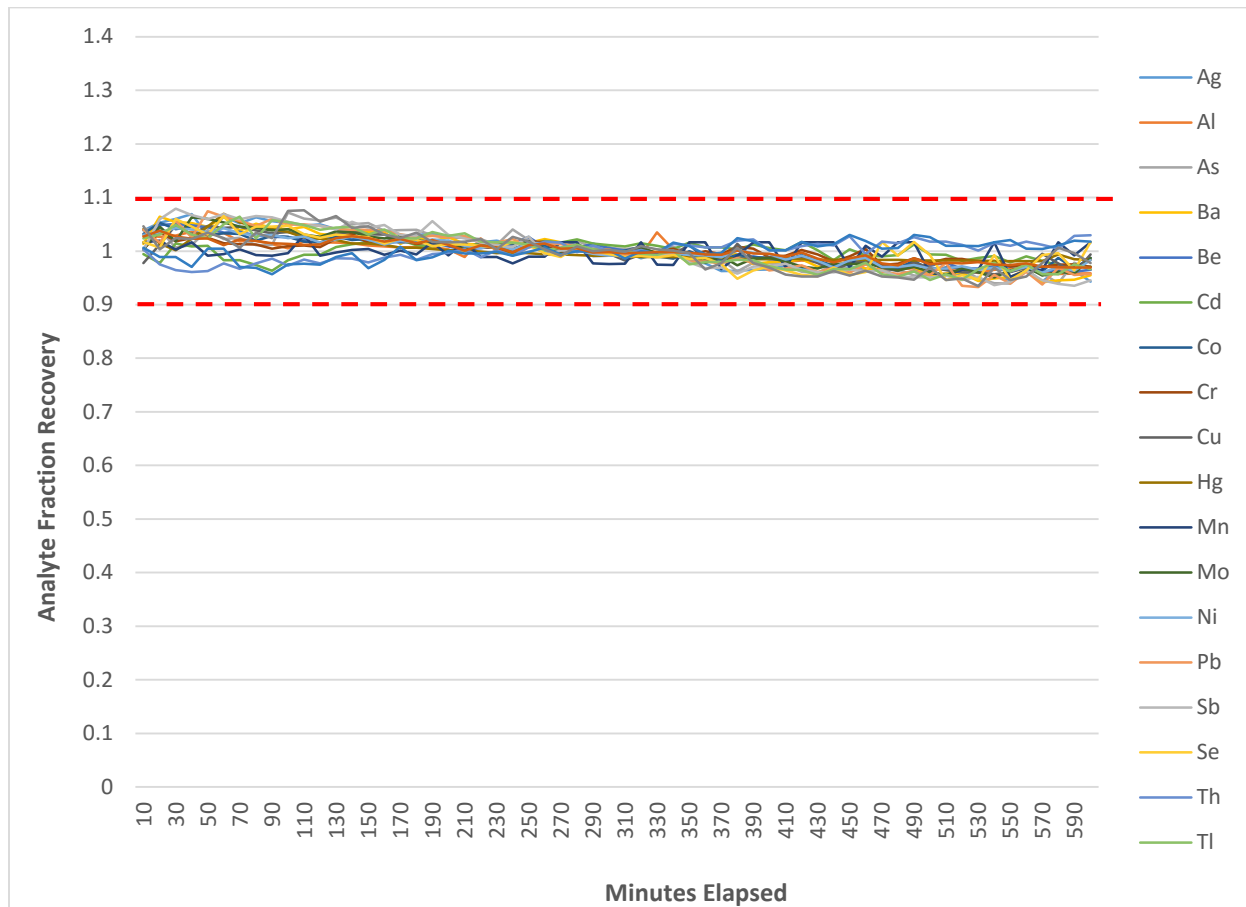


Figure 1: Fraction recovery of analytes over a 10-hour period. The dashed lines represent $100 \pm 10\%$ recovery and shows that all analytes fall within $\pm 10\%$ recovery threshold.

■ Conclusions

The Shimadzu ICPMS-2030 meets or exceeds all of the analytical requirements established in EPA Method 200.8. When equipped with an AS-10 autosampler and the Internal Standard Addition kit, the instrument is capable of handling large sample sets with ease and simplicity.



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