

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

### User Benefits

- ICPMS-2030 meets or exceeds all of the analytical requirements established in EPA Method 200.8.
- Exceptional stability of ICPMS-2030 minimizes the downtime of the instrument.
- ICPMS-2030 is equipped with a mini-torch and consumes two thirds of argon gas as conventional plasma torch. The combination of Eco mode (standby mode) and mini-torch dramatically reduces running cost by reducing argon gas consumption.



### ■ Introduction

This application note describes the methodology and use of the Shimadzu ICPMS-2030 inductively coupled plasma 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. The newly developed collision cell in ICPMS-2030 is generally used to remove polyatomic interferences with helium gas. Because a collision cell is not currently adapted in the EPA 200.8 method, correction equations alternatively were used to minimize the effect. Here, we demonstrate the stability and sensitivity of the ICPMS-2030 for EPA 200.8 analyses.

### ■ Equipment, Reagents, and Labware

A Shimadzu ICPMS-2030 in conjunction with a Shimadzu AS-10 Autosampler was used for all analyses. 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 dilution factor of the internal standard solution was 1:10.

High-purity reagents were used during sample preparation and dilution to ensure minimal contamination. Ultra-pure water ( $\geq 18.1 \text{ M}\Omega\text{-cm}$ ) along with trace-metal grade nitric acid was used for all dilutions and acidifications. For the sake of brevity, we refer to these simply as “water” and “nitric acid”, herein. All calibration standards and samples were stabilized in 2%  $\text{HNO}_3$ . All labware was cleaned in a solution of 5% 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.

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

The instrument was allowed to warm up for  $\geq 30$  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 a 200.8 method tuning solution, which contains Be, Mg, Co, In, and Pb. The validation procedure consisted of ensuring a resolution of  $\sim 0.75$  amu on  $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$ ,  $^{26}\text{Mg}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ . 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 certified multi-element standards. 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
Al	0	10	20	100
Ag	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 stock multi-element standard 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 of 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	0.0105	0.0267	20
Sb	123	0.0005	0.0017	20
As	75	0.0053	0.0259	20
Ba	137	0.0006	0.0009	20
Be	9	0.001	0.0012	40
Cd	111	0.0072	0.0132	40
Cr	52	0.0071	0.0256	20
Co	59	0.0002	0.0003	20
Cu	63	0.0024	0.003	40
Pb	206, 207, 208	0.0003	0.0004	20
Mn	55	0.0028	0.0052	20
Hg	202	0.0008	0.0155	0.5
Mo	98	0.0008	0.0011	40
Ni	60	0.0022	0.0031	40
Se	82	0.0087	0.0492	100
Ag	107	0.0004	0.0007	40
Tl	205	0.0001	0.0003	40
Th	232	0.0003	0.0004	40
U	238	< 0.0001	0.0003	40
V	51	0.003	0.0084	20
Zn	66	0.0132	0.0543	40

### ■ Sample Analysis and Post-analysis Validation

To demonstrate the instrument's performance, a series of five drinking water samples as well as a NIST Standard Reference Material (SRM 1643f – Trace Elements in Water) were analyzed. One of the drinking water samples (DW #1) was spiked with known concentrations of the analyte elements. According to EPA Method 200.8, the spike recoveries should be  $\pm 30\%$  of the theoretical values. The results of the recovery tests of drinking water (DW) #1 and NIST SRM are shown in Tables 4 and 5, respectively. The 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.

	Drinking Water (DW) #1	Spiked Drinking Water #1	% Recovery
Ag	<i>n.d.</i>	18.8	94.0
Al	19.1	39.5	102.0
As	<i>n.d.</i>	20.1	100.5
Ba	22.9	42.4	97.5
Be	<i>n.d.</i>	19.9	99.5
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	<i>n.d.</i>	92.7	92.7
Th	1.9	22.5	103.0
Tl	<i>n.d.</i>	18.9	94.5
U	2.36	22.5	100.7
V	1.61	21.2	98.0
Zn	77.2	98.1	104.5

*n.d.* = Not Detected

The recoveries for the tap water and NIST standard are also displayed in Fig. 1 and the acceptable range of  $\pm 10\%$  is highlighted with green horizontal bar.

The long-term stability of the instrument was assessed by analyzing a series of known samples repeatedly for 10 hours. As shown in Fig. 2, the ICPMS-2030 demonstrates stable responses for all target elements over the 10-hour analytical period, indicating that the instrument can provide robust and stable performance in high-throughput laboratories.

**Table 5:** Concentrations (in ppb) of analytes reported and measured in NIST SRM 1643f, and %Recovery. Note that the NIST sample does not contain Hg, U, or Th. All analytes fall within  $\pm 10\%$  recovery.

	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

Four other drinking water samples from a variety of sources and locations were analyzed. The analytical results are presented in Table 6. Note that DW #2 and #3 are sourced from two different regional water utilities, and DW #4 and #5 are from two different household wells.

**Table 6:** Concentrations (in ppb) of analytes from residential water samples.

	DW #2	DW #3	DW #4	DW #5
Ag	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
Al	31.6	25.4	2.43	4.2
As	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.878
Ba	23.8	37	2.79	29.5
Be	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
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	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
Th	1.89	1.4	1.9	1.89
Tl	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
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

*n.d.* = Not Detected

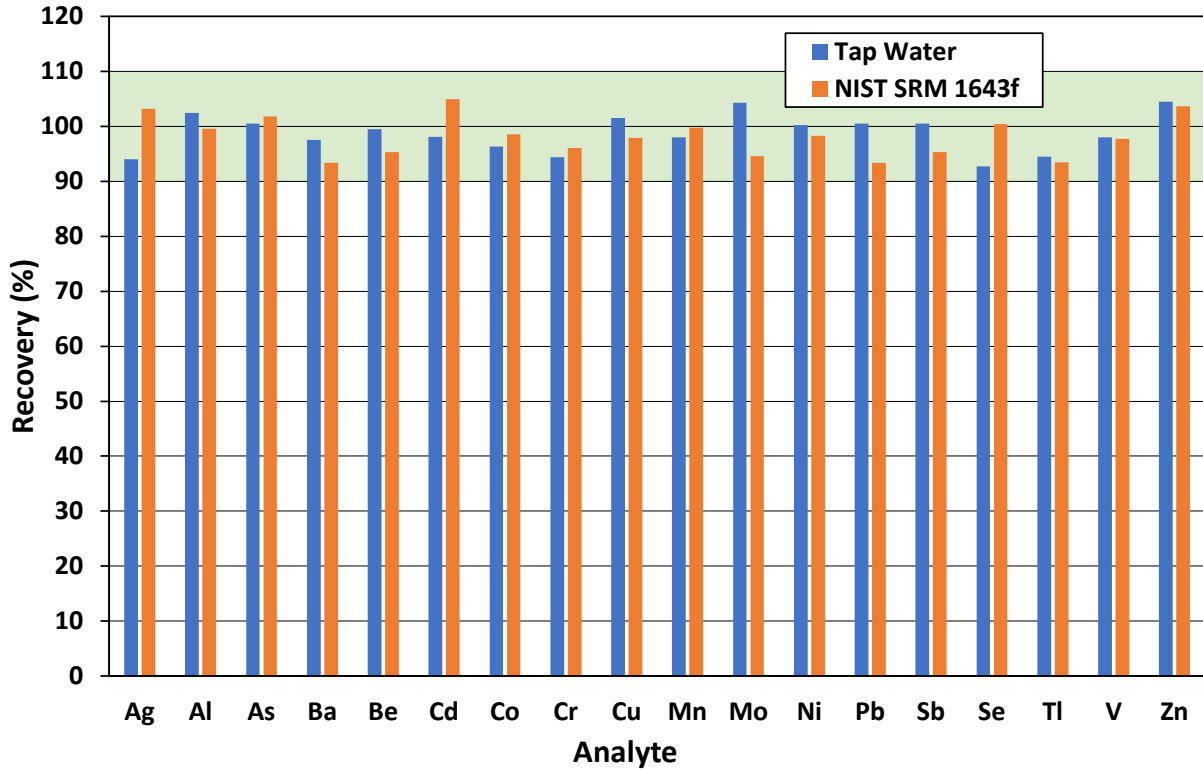


Figure 1: % Recovery for the tap water and NIST standard samples.

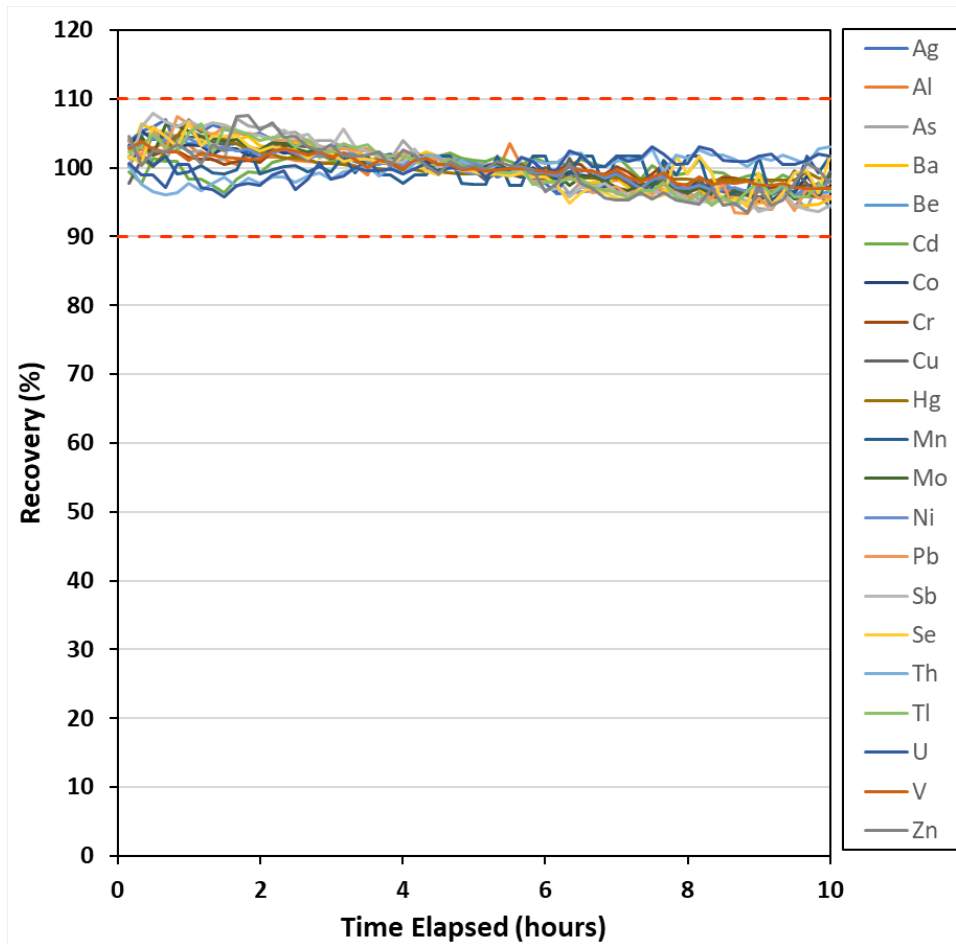


Figure 2: Recovery of analytes over a 10-hour period. The dashed lines represent  $100 \pm 10\%$  recovery and shows that all analytes fall within  $\pm 10\%$  recovery threshold.

■ **Conclusions**

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

conditions in environmental Laboratories minimize the downtime for instrument maintenance. Additionally, the Shimadzu's designed Mini-torch and Eco-Mode operation for stand-by status reduce the gas consumption and running cost.

■ **Parts and Consumables**

Part Number	Item Name	Item Description
220-95356-90	Internal Standard Automatic Addition Kit, ICP/ICPMS	Trident CT Glass Ratchet Connector Internal standard automatic addition kit. Pump tubing sold separately
220-95356-84	Sampler Cone, Nickel	Nickel sampler cone. A graphite gasket is included.
220-95356-85	Skimmer Cone, Nickel	Nickel skimmer cone
018-31558-44	Peristaltic pump tubing, ICPMS	Contour PVC Pump Tube 3tag 0.76mm ID Black/Black, 95mm for sample (PKT 6)
018-31558-43	TUBE,0.25-OB3B-95-F	Peristaltic Pump Tube for Internal Standard Addition, 0.25mm ID Orange/Blue (PKT 6)
220-95357-63	ICPMS Tuning Solution	ICPMS Tuning Solution 250 mL certified reference material.
220-95371-01	Ultrapure Nitric Acid, 67-70%, 500mL	Nitric acid 67-70%, ultrapure for trace metal analysis at the parts-per-trillion (ppt) level. 500 mL in FEP Bottle.
220-95377-11	ICPMS Standards Set for EPA 200.8 Rev. 5.4	Standards Set for EPA 200.8 is a kit of 5 Calibration standards in 125mL vials, 2 Internal Standards Solutions in 125mL, 2 Quality Control solutions in 125mL, 1 Tuning Solutions in 125mL.



**SHIMADZU Corporation**  
www.shimadzu.com/an/

**SHIMADZU SCIENTIFIC INSTRUMENTS**  
7102 Riverwood Drive, Columbia, MD 21046, USA  
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222  
URL: www.ssi.shimadzu.com

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