

# ICP-MS Analysis of Trace and Major Elements in Drinking Water According to US EPA Method 200.8

Using the Agilent 7850 ICP-MS with ISIS 3 and automated Intelligent Sequence QA/QC software



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## Introduction

People around the world rely on access to a supply of clean, safe drinking water (1). But many fresh water sources are contaminated with pollutants from domestic and industrial wastewaters or agricultural, mining, forestry, and construction activities. Regulated analytical testing of potentially harmful elements in ground waters, surface waters, and drinking water is therefore essential to ensure water quality and safety. Labs that perform routine elemental analysis of waters often use ICP-MS because of its low detection limits, wide elemental coverage, and fast, multi-element capability (2). Many regulatory methods for water analysis, such as US EPA 200.8 and ISO 17294-2:2016, specify ICP-MS for the analysis of trace element concentrations (3, 4). EPA method 200.8 defines a procedure for the analysis of 21 elements in waters and wastes using ICP-MS. ISO 17294-2 lists 63 elements that may be measured by ICP-MS (5).

ICP-MS technology developments over the past 30 years have dramatically improved the technique's matrix tolerance, ease of use, and ability to control spectral interferences. These developments have increased productivity, improved accuracy, and reduced detection limits for many trace elements in natural samples. For example, Agilent ICP-MS systems use the Octopole Reaction System (ORS<sup>4</sup>) collision/reaction cell (CRC) with helium (He) collision mode to control polyatomic ion overlaps. He mode uses kinetic energy discrimination (KED) to selectively filter out polyatomic ions, reducing the contribution from these interferences and improving accuracy in waters and other environmental samples. He mode offers both performance and workflow/productivity benefits as it allows the same cell settings to be used for most elements in many common sample types, simplifying routine analysis.

However, EPA 200.8 was first published in 1990, which is long before ICP-MS developments such as CRCs. The most recent version of EPA 200.8 to be distributed is revision 5.4 in 1994, so labs often cannot use modern workflows for certain sample types. In the US, the National Pollutant Discharge Elimination System (NPDES) permit program was created by the 1972 Clean Water Act (6). When EPA 200.8 is used for compliance monitoring of wastewaters under NPDES, the applicable section of the Code of Federal Regulations (CFR) is Title 40, Part 136 (40 CFR Part 136). This regulation permits the use of ICP-MS CRC methods such as He KED to control spectral interferences. However, when EPA 200.8 is used for compliance monitoring of drinking water under the 1974 Safe Drinking Water Act (SDWA), the applicable regulation is 40 CFR Part 141 (7). Section § 141.23 of 40 CFR Part 141 defines inorganic chemical sampling and analytical requirements under the National Primary Drinking Water Regulations (NPDWR). 40 CFR Part 141 § 141.23 mandates the use of traditional correction equations rather than CRC methods to mitigate polyatomic ion interferences that affect trace element analysis by ICP-MS.

Laboratories that run other regulated methods—or use EPA 200.8 for non-SDWA compliance monitoring—can use He KED CRC methods to control polyatomic ion interferences. Also, laboratories that run SWDA drinking water samples may use He KED mode to collect comparative data and troubleshoot data queries, provided the results are not reported for compliance monitoring.

For SDWA compliance analysis, the lack of CRC methods means that analysts must rely on robust ICP plasma conditions to minimize errors due to polyatomic ion overlaps. Plasma robustness in ICP-MS is monitored using the ratio of CeO<sup>+</sup> to Ce<sup>+</sup> (CeO/Ce), which shows how well the plasma is able to break the strong Ce-O bond. A lower CeO/Ce ratio indicates a hotter, more robust plasma, which has more energy available to dissociate other, potentially interfering, polyatomic species. For example, a three times (3x) reduction in the CeO/Ce ratio from 0.03 to 0.01 (3 to 1%) gives a 3x reduction in the level of other, matrix-based polyatomic ions. Agilent ICP-MS typically operate with a CeO/Ce ratio around 1%, the lowest in the industry. The low CeO/Ce ratio helps ensure high data quality, even while operating without He KED mode in compliance with the current 200.8 method.

Routine water analysis is often performed by competitive commercial laboratories that prioritize sample throughput, productivity, and return on investment, along with ease-of-use, and ease of reporting large data sets. In this study, we show how the Agilent 7850 ICP-MS addresses the priorities of laboratories that analyze SDWA samples, such as drinking waters, in accordance with EPA Method 200.8.

To achieve the high sample throughput required by busy commercial laboratories, the 7850 was fitted with the optional Integrated Sample Introduction System (ISIS 3). ISIS 3 uses a loop injection system to reduce sample run times using discrete sampling (DS). For ease-of-use, the predefined preset method "EPA 200.8" was used as the template for the Agilent ICP-MS analysis. Other instrument settings such as the ion lens voltages were autotuned, and the optional Intelligent Sequence software module for ICP-MS MassHunter was used for real-time quality assurance and quality control (QA/QC) of the data.

The Intelligent Sequence software is supplied with templates that predefine QC sample types, QC checks, and action on failure settings for common ICP-MS methods such as EPA 200.8 and EPA 6020. The settings can be easily tailored to meet a lab's specific QA/QC requirements and produce custom protocols by the addition of extra QC samples and acceptance criteria. The advanced QA/QC functionality helps analysts by monitoring the data as it is acquired and comparing measured results to expected values. If a QC failure occurs, the software can automatically trigger an appropriate action rather than wait for intervention by the analyst. Intelligent Sequence can help improve the efficiency and cost-effectiveness of the analytical workflow by avoiding unnecessary sample reruns and saving analyst-time.

In this study, the 7850 ICP-MS was used to analyze 25 major and trace elements in bottled mineral water and tap water samples following EPA Method 200.8. All 21 elements specified in EPA 200.8 were included in the study plus the mineral elements Na, Mg, K, and Ca that are commonly measured to ensure drinking water quality.

## Experimental

### Instrumentation

An Agilent 7850 ICP-MS fitted with the optional ISIS 3 system was used for the analysis. An Agilent SPS 4 autosampler was used to introduce the samples. The standard 7850 sample introduction system was used, comprising a MicroMist nebulizer, Scott-type spray chamber, and one-piece quartz torch with 2.5 mm id injector. The standard interface was used, consisting of a nickel-tipped copper sampling cone and a nickel skimmer cone.

To create the method quickly and easily, analysts can use a preset method provided in the ICP-MS MassHunter software. The choice of preset method will depend on the application, sample type, or total matrix solids (TMS) concentration of the samples. The preset method automatically sets the plasma conditions and other analytical parameters that are required for the chosen sample type or application, simplifying method development. Examples of the predefined parameters that are included in preset methods include a list of analytes and internal standard elements, preferred isotopes and integration times, ORS<sup>4</sup> cell conditions (if permitted), and correction equations.

In this study, the EPA 200.8 preset method was selected in ICP-MS MassHunter. The parameters in the shaded rows in Table 1 were set automatically and the lens voltages were autotuned. ISIS 3 operating parameters are shown in Table 2. When EPA 200.8 is used for compliance monitoring of drinking waters, the method does not allow CRC gas modes to be used to resolve polyatomic ion interferences on analyte ions. Therefore, all elements were measured in no gas mode (no cell gas added to the ORS<sup>4</sup> cell). To correct for interferences, the mathematical correction equations defined in EPA 200.8 were used (3). These correction equations (Table 3) are predefined in the ICP-MS MassHunter EPA 200.8 preset method, so analysts do not need to input them manually.

**Table 1.** Agilent 7850 ICP-MS operating conditions. The shaded parameters were defined automatically by selecting the EPA 200.8 preset method in ICP-MS MassHunter.

ICP-MS Parameter	No Gas Mode
Plasma Mode	Low matrix*
RF Power (W)	1550
Spray Chamber Temp (°C)	2
Sampling Depth (mm)	8
Nebulizer Gas Flow (L/min)	1.08
Lens Tune	Autotune
Energy Discrimination (V)	5.0
Number of Elements	25 analytes, 8 ISTDs

\*Under these low matrix tune conditions, the 7850 ICP-MS has an extremely robust plasma, indicated by the low CeO/Ce ratio of 0.01 to 0.012 (1.0 - 1.2%).

**Table 2.** Agilent ISIS 3 parameters.

Parameter	Setting		
	Time (s)	Pump Speed (%)	Valve
Loop Volume (mL)	1.0		
Sample Load	10	35	Load
Stabilize	12	5	Inject
Probe Rinse	5	5	Load
Rinse 1	15	5	Load
Rinse 2	15	5	Load
Optional Loop Probe Wash	5	70	Load
Optional Loop Wash	5	5	Inject

**Table 3.** Correction equations defined in US EPA 200.8, predefined in the ICP-MS MassHunter EPA 200.8 preset method.

Parameter	Setting
<sup>6</sup> Li	$Mc(6) = M(6) \times 1.0 - M(7) \times 0.082$
<sup>51</sup> V	$Mc(51) = M(51) \times 1.0 + M(52) \times 0.353 - M(53) \times 3.127$
<sup>75</sup> As	$Mc(75) = M(75) \times 1.0 - M(77) \times 3.1270 + M(82) \times 2.549$
<sup>82</sup> Se	$Mc(82) = M(82) \times 1.0 - M(83) \times 1.0078$
<sup>98</sup> Mo	$Mc(98) = M(98) \times 1.0 - M(99) \times 0.146$
<sup>111</sup> Cd	$Mc(111) = M(111) \times 1.0 - M(108) \times 1.073 + M(106) \times 0.764$
<sup>115</sup> In	$Mc(115) = M(115) \times 1.0 - M(118) \times 0.016$
<sup>208</sup> Pb	$Mc(208) = M(208) \times 1.0 + M(206) \times 1.0 + M(207) \times 1.0$

## Standard and sample preparation

The calibration standards, internal standard (ISTD) solution, and samples were prepared in an acid matrix of 1% HNO<sub>3</sub> and 0.1 mg/L gold (Au(III) chloride). The Au(III) chloride was added to help retain Hg in solution in accordance with EPA 200.8. Calibration standards for most elements were prepared using the Agilent Environmental Calibration Standard (part number 5183-4688) multi-element stock solution. A single element standard was used for Hg (Kanto Chemicals, Japan). Five-point calibrations including the calibration blank were prepared at the concentration ranges given in Table 4.

The ISTD solution (Agilent part number 5183-6525) containing 2 mg/L <sup>6</sup>Li, Sc, Ge, Rh, In, Ir, and Bi was added to the samples automatically online, using the standard ISTD mixing connector (G3280-67062). The ISTD flow rate was approximately 15 times less than the sample flow rate, due to the use of the standard narrow internal diameter ISTD pump tubing.

**Table 4.** Details of concentration of calibration standards (µg/L) and composition of internal standard solution at 2 mg/L.

	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
Trace Elements	0	1	10	100	
Major Elements*	0	100	1000	10,000	25,000
Hg	0	0.1	0.5	2	
Au	100	100	100	100	100
ISTD	<sup>6</sup> Li, <sup>45</sup> Sc, <sup>72</sup> Ge, <sup>103</sup> Rh, <sup>115</sup> In, <sup>159</sup> Tb, <sup>175</sup> Lu, <sup>209</sup> Bi				

\*Na, Mg, Ca, and K

For the in-run QC, the diluent, 1% HNO<sub>3</sub>, was used as the continuing calibration blank (CCB). A mid-concentration calibration standard (trace elements at 50 µg/L, mineral elements at 5000 µg/L, and Hg at 1 µg/L) was used as the Lab Fortified Blank (LFB). The CCB and continuing calibration verification (CCV, prepared at the same concentration as the LFB) solutions were measured periodically throughout the sample sequence and at the end of the run.

Standard reference material (SRM) NIST 1643f Trace Elements in Water (NIST, Gaithersburg, MD) was used to evaluate the accuracy of the ICP-MS method. The SRM was analyzed as received (undiluted).

A bottled mineral water (sample 1) and two tap water samples (samples 2 and 3) from different sources in Tokyo, Japan were analyzed in this study. The bottled water was bought in a store in Tokyo. The water samples were analyzed repeatedly with the QC block (CCB and CCV solutions) inserted automatically after every 10 water samples.

Matrix spike samples (which are referred to as Laboratory Fortified Sample Matrix (LFM) samples in EPA 200.8) were prepared by spiking the bottled water with low and high concentration spikes. For the low spiked sample, trace elements were spiked at 10 µg/L, mineral elements at 1000 µg/L, and Hg at 0.2 µg/L. For the high spiked sample, trace elements were spiked at 50 µg/L, mineral elements at 5000 µg/L, and Hg at 1 µg/L.

## Results and discussion

### Instrument and method detection limits

All analytes were measured using the 7850 ICP-MS acquisition parameters listed in Table 1. Isotopes recommended in EPA 200.8 were used for all analytes. Following EPA 200.8, three sigma instrumental detection limits (IDLs) were calculated from 10 measurements of the blank (Table 5). The IDLs obtained for the critical trace analytes easily met the EPA 200.8 requirements, confirming the high sensitivity of the 7850 ICP-MS for the 200.8 method. Method detection limits (MDLs) were calculated from seven measurements of a blank fortified (spiked) at a concentration of two to five times the estimated IDL.

**Table 5.** Selected ISTD, integration time, IDLs, and MDLs for each analyte.

Element and Mass number	ISTD	Integration Time (s)	EPA 200.8 IDL (µg/L)	7850 IDL (µg/L)	MDL (µg/L)
9 Be	45 Sc	1	0.02	0.0002	0.014
23 Na	45 Sc	0.1	-	0.122	1.48
24 Mg	45 Sc	0.1	-	0.010	0.010
27 Al	45 Sc	0.3	0.02	0.011	0.013
39 K	45 Sc	0.1	-	2.65	12.6
43 Ca	45 Sc	0.1	-	3.79	3.47
51 V	45 Sc	0.3	0.006	0.006	0.020
52 Cr	45 Sc	0.3	0.04	0.011	0.035
55 Mn	45 Sc	0.3	0.007	0.002	0.011
59 Co	45 Sc	0.3	0.002	0.0004	0.017
60 Ni	72 Ge	0.3	0.07	0.005	0.008
63 Cu	74 Ge	0.3	0.004	0.001	0.023
66 Zn	74 Ge	0.3	0.07	0.004	0.068
75 As	74 Ge	0.3	0.02	0.019	0.032
82 Se	74 Ge	0.5	1.3	0.050	0.067
98 Mo	103 Rh	0.5	0.005	0.0008	0.015
107 Ag	103 Rh	0.3	0.004	0.001	0.017
111 Cd	115 In	0.3	0.02	0.005	0.017
123 Sb	115 In	1	0.008	0.0007	0.014
137 Ba	175 Lu	0.3	0.03	0.001	0.015
202 Hg	175 Lu	1	0.2	0.0003	0.001
205 Tl	175 Lu	0.3	0.014	0.0004	0.013
Pb*	175 Lu	1	0.015	0.0005	0.016
232 Th	175 Lu	0.3	0.005	0.0007	0.015
238 U	175 Lu	0.3	0.005	0.0001	0.014

\*Pb was measured as the sum of the three most abundant isotopes, 206, 207, and 208.

### Real-time QA/QC by Intelligent Sequence

It can be time-consuming for analysts to manually check all the sample and QC data against the various QA/QC criteria specified in EPA 200.8, either during or at the end of the analytical sequence. To help analysts assess the data, the Intelligent Sequence software (optional module for ICP-MS MassHunter, part number G7206C) provides comprehensive QA/QC by evaluating data quality in real time.

The Intelligent Sequence module contains preconfigured templates for US EPA 200.8. The software can also be tailored to meet specific QA/QC requirements and produce custom protocols by the addition of QC samples and criteria. In the Intelligent Sequence setup pane, analysts can see all the QC parameters including pass/fail criteria and actions on failure in one window. Predefined report templates are provided for EPA 200.8, and report templates can also be specified for each sample type.

Figure 1 shows examples of the “Action on Failure” settings and actual sequence in the Intelligent Sequence window for EPA 200.8. These settings are predefined in the EPA 200.8 batch template. The software then monitors the data during the analytical sequence. If there are any failures with any of the samples or QC standards against the criteria, an error flag will be shown immediately in the Data Analysis table. Appropriate action will then be applied, with no operator input required.

Intelligent Sequence generates real-time reports, such as tuning reports, calibration reports, QC flag reports, and analytical results. This auto reporting provides valuable information for every sample, eliminating manual reporting procedures. All required information is included on one page. By looking at the reports, analysts can see if each sample has passed or failed the QC criteria, such as DL limits, ISTD recoveries, and QC recoveries.

Error Action			Criteria1
Title	Action	#Allowed Failure 1	
1st Error by ISTD check	SameSmpl	0	
2nd Error by ISTD check	NextSmpl		
1st Error by QC check	SameSmpl	0	
2nd Error by QC check	Cal-SameSmpl		
▶ 3rd Error	Abort		

Sample Name	Conc. [ ppb ]	Conc. [ ppb ]	Conc. [ ppb ]	Conc. [ ppb ]	Conc. [ ppb ]
50 ppb	10.254	10.263	10.482	10.280	9.897

  

Task Name	Status
17 preset 7850 EPA 200.8_	Aborted by QC Failure

**Figure 1.** Example of QC action on failure settings and error sequence in the Intelligent Sequence window. Up to three actions can be set for both ISTD and QC check solutions. If the concentration in a sample is out of the specified range, Intelligent Sequence automatically highlights the error. In this example, the QC sample was expected to contain analytes at 50 µg/L rather than 10 µg/L. The QC flags (red highlights) clearly signal the error. Error actions were performed in sequence, and finally the batch sequence was aborted according to the third error action.



## Laboratory fortified sample matrix spike recoveries

To determine whether the sample matrix contributes bias to the analytical results, LFM spike samples were measured, and spike recoveries were calculated. Table 7 shows the matrix spike recoveries of high and low-level spiked samples of the bottled water. Recoveries were between 93 and 108% for all elements apart from the low-level spike for Ca. The recovery for Ca in the low spike was not calculated, as the spiked concentration of 1000 mg/L was less than 30% of the native concentration in the sample. The excellent recovery of 94% for Ca in the high spike sample indicates the accuracy of the 7850 ICP-MS method for the determination of Ca.

**Table 7.** LFM spike recoveries of bottled water.

Element	Bottled Water	Bottled Water + Low Spike			Bottled Water + High Spike		
	Measured Conc, µg/L	Low Spike Conc, µg/L	Measured Conc, µg/L	Recovery %	High Spike Conc, µg/L	Measured Conc, µg/L	Recovery %
9 Be	0.007	10	9.31	93	50	54.0	108
23 Na	7970	1000	8970	100	5000	13200	105
24 Mg	2100	1000	3110	101	5000	7310	104
27 Al	0.232	10	10.2	99	50	48.3	96
39 K	1880	1000	2790	91	5000	6700	96
43 Ca	9270	1000	**	**	5000	14000	94
51 V	0.065	10	10.0	100	50	49.2	98
52 Cr	0.013	10	9.45	94	50	47.9	96
55 Mn	0.056	10	9.95	99	50	48.5	97
59 Co	0.026	10	9.40	94	50	47.2	94
60 Ni	0.064	10	9.73	97	50	50.3	100
63 Cu	0.045	10	10.1	100	50	50.4	101
66 Zn	0.407	10	10.3	99	50	49.6	98
75 As	0.418	10	10.1	97	50	48.9	97
82 Se	0.060	10	10.1	100	50	48.7	97
98 Mo	0.022	10	9.79	98	50	50.7	101
107 Ag	0.034	10	9.98	99	50	50.5	101
111 Cd	0.007	10	9.61	96	50	48.1	96
123 Sb	0.335	10	10.2	98	50	51.4	102
137 Ba	2.488	10	12.0	95	50	50.2	95
202 Hg	0.001	0.5	0.486	97	1	0.984	98
205 Tl	0.003	10	9.51	95	50	49.4	99
Pb*	0.013	10	9.48	95	50	50.4	101
232 Th	0.029	10	10.1	101	50	49.9	100
238 U	0.008	10	10.0	100	50	49.3	99

\*Pb was measured as the sum of the three most abundant isotopes, 206, 207, and 208.

\*\*No recovery calculation required as the concentration of the Ca low-level spike is less than 30% of the sample background concentration.

## Conclusion

The Agilent 7850 ICP-MS with ISIS 3 was used to measure 25 elements in drinking waters according to US EPA Method 200.8. To simplify method development and save analyst-time, an EPA 200.8 preset method that includes all the analytical, QC, and reporting requirements was used, and the 7850 was autotuned.

The 7850 ICP-MS method easily passed the detection limit and data-quality requirements outlined in EPA 200.8.

- For all the critical trace analytes, the IDLs were below EPA 200.8 specifications, confirming the high sensitivity of the 7850 ICP-MS for the method.
- All recoveries of ISTDs in three drinking water samples were within  $\pm 10\%$ , easily within the EPA 200.8 specified limits of 60 to 125%. Also, all the CCV recoveries were within  $\pm 10\%$ , demonstrating the stability of the method over nine hours.
- The predefined instrument operating conditions remained stable over the nine-hour analytical sequence with no retuning or recalibration required.
- Accurate measurements of all certified analytes in the NIST 1643f Trace Elements in Water SRM were obtained, with recoveries between 98 and 106% of the certified values.
- There was no bias to the analytical results from the sample matrix, as shown by recoveries between 93 and 108% for high and low-level spikes in bottled water.

The ICP-MS data was automatically checked against the EPA 200.8 QA/QC acceptance criteria in real time using the Intelligent Sequence program for ICP-MS MassHunter.

- Intelligent Sequence can show all the QC setting information in one window.
- The analyst can set up to three error actions per each QA/QC acceptance criterion.
- Intelligent Sequence provides QC functions such as predefined action on failure, error flagging of any out-of-range data, and auto reporting for each sample.
- Intelligent Sequence can generate reports for different sample types, e.g., general samples, ISTD checks, CCV recoveries, CRM recoveries, and matrix spike recoveries.

Using Intelligent Sequence software to monitor data quality prevents errors from being overlooked. The software also saves analysts a lot of time from having to manually check the data, freeing them to work on more productive tasks. No failures were reported throughout the run in this study.

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## Consumables list

Consumable Description	Agilent Part Number
Sampler cone: nickel-tip with copper base. Standard cone used with x-lens for most routine applications	<a href="#">G3280-67040</a>
ICP-MS skimmer cone: nickel. Standard cone used with x-lens for most common applications	<a href="#">G3280-67041</a>
Easy-fit peristaltic pump tubing, standard for sample uptake, recommended for aqueous, acid, or alkaline matrix, 1 pack of 12 pieces	<a href="#">5005-0020</a>
Easy-fit peristaltic pump tubing, standard for ISTD uptake, recommended for aqueous, acid, or alkaline matrix, 1 pack of 12 pieces	<a href="#">5005-0021</a>
Easy-fit peristaltic pump tubing, long-life, standard for spray chamber drain, 1 pack of 12 pieces	<a href="#">5005-0022</a>
Environmental calibration standard, 100 mL	<a href="#">5183-4688</a>
Internal standard mix, 100 mL	<a href="#">5183-4681</a>

[www.agilent.com/chem/7850icp-ms](http://www.agilent.com/chem/7850icp-ms)

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