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EPA Method 200.8 Using Shimadzu ICPMS-2040

Disclaimer

Shimadzu Scientific Instruments, Shimadzu Corporation, and any associated Shimadzu personnel cannot be held responsible for users' laboratory following or complying with the protocols of EPA Method 200.8. It is the responsibility of the analyst / laboratory to ensure that the laboratory understands the Method and follows all necessary steps to be in compliance with the Method. Furthermore, this document is not a substitute for the laboratory's standard operating procedure (SOP).

Introduction

EPA Method 200.8, adopted in 1994, is a widely used analytical method for the determination of a variety of trace elements in waters and wastes using inductively coupled plasma mass spectrometry (ICP-MS). It covers a range of analytes and is commonly used for environmental analysis due to the high sensitivity of ICP-MS instruments coupled with the relatively high sample throughput on samples requiring analysis of multiple elements.

Along with EPA Method 200.7 (for ICP-OES) and 200.9 (for Atomic Absorption or AA), these methods are among the most commonly used and cited methods for metals in water testing. A comparison of the analytes prescribed in each method is given in **Table 1**. Although many of the analytes are cross-listed for two or more methods, each method stands alone in regards to the total suite of elements analyzed, instrumentation, and sample QA/QC parameters.

The purpose of this document is to provide guidance on how to set up EPA Method 200.8 for metals in water on the ICPMS-2040. This document is to be used in conjunction with, and is *not* a substitute for, the method documentation published by the EPA nor an individual laboratory's SOP.

Table 1. Comparison of common EPA trace element methods

	200.7 (ICP-OES)	200.8 (ICP-MS)	200.9 (AA)
Aluminum	•	•	•
Antimony	•	•	•
Arsenic	•	•	•
Barium	•	•	
Beryllium	•	•	•
Boron	•		
Cadmium	•	•	•
Calcium	•		
Cerium	•		
Chromium	•	•	•
Cobalt	•	•	•
Copper	•	•	•
Iron	•		•
Lead	•	•	•
Lithium	•		
Magnesium	•		
Manganese	•	•	•
Mercury	•	•	
Molybdenum	•	•	
Nickel	•	•	•
Phosphorus	•		
Potassium	•		
Selenium	•	•	•
Silica	•		
Silver	•	•	•
Sodium	•		
Strontium	•		
Thallium	•	•	•
Thorium		•	
Tin	•		•
Titanium	•		
Uranium		•	
Vanadium	•	•	
Zinc	•	•	

Software

The ICPMS-2040 comes equipped with LabSolutions ICPMS Software as a control and analytical software for the instrument. It is critical to the successful validation of EPA Method 200.8 that the software be version 2.03 or newer. Many laboratories choose to export data from LabSolutions ICPMS Software to their LIMS. The software will allow data export in .txt and .csv file formats.

Lab Preparation, Reagents, and Labware

Because the ICPMS-2040 offers extremely high sensitivity for heavy metals analysis, the cleanliness of users' laboratory and reagents is paramount to ensuring high-quality analytical results. To that end, heed the following notes about laboratory site, general cleanliness, and reagents used for sample and standard preparation.

The ideal laboratory in which the ICPMS-2040 is used should be as clean as possible, including minimizing dust and metals anywhere where samples, standards, and reagents are stored, used, prepared, and analyzed. A true 'clean-lab' is not strictly necessary, but all attempts should be made to keep the laboratory as clean as possible, including free of dust and particulate matter.

The primary reagents that are used for sample and standard preparation are nitric acid (HNO_3) and water. The nitric acid must be trace metal grade (or better). That is, the acid should be certified to be sub-ppb levels for heavy metals. Generic 'reagent grade' nitric acid is not sufficient. Similarly, all water used in sample preparation should be ≥18.1 MΩ·cm. Typical 'distilled' or 'de-ionized' water is not sufficient.

Care should be taken to ensure the cleanliness of all labware used in sample collection, storage, preparation, and analysis. We recommend using single-use polypropylene (PP), or polyethylene (PE) labware, including jars, vials, beakers, et cetera. Alternatively, polytetrafluoroethylene (PTFE or Teflon™) is commonly used in very low background metals applications and takes well to multiple cleanings and uses. However, PTFE labware is more costly than PE or PP labware.

Standards

Included in the EPA 200.8 Method Package are a series of standards from Inorganic Ventures listed in **Table 2.**

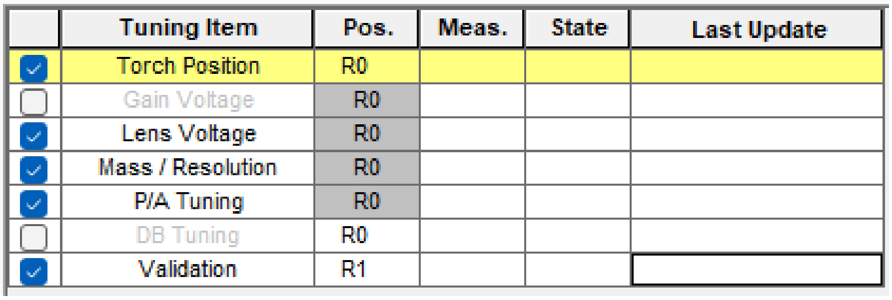
Table 2. EPA 200.8 standards provided from Inorganic Ventures

Standard	Description
WW-MSCAL-1	Mercury calibration standard
WW-MSCAL-2	Multi-element calibration standard
2008CAL-1	Mo and Sb calibration standard
QCP-QCS-3	Mixed element quality control standard
QCP-QCS-4	Mercury quality control standard
GCAUN1	1000 ppm gold for ICP
2008ISS	200.8 Internal Standard
2008TS	Tuning validation solution

This suite of standards, internal standards, and tuning solutions covers the entire range of elements specified in EPA Method 200.8. Many laboratories are interested in running only a handful of metals, most notably lead and copper. If the laboratory is interested in running only a few metals, it is advisable to purchase single-element standards and make their own standards. Using a single element standard, or a mix of them to cover the metals necessary, will provide better detection limits and, more importantly, be cheaper and easier to use.

Instrument Preparation and Tuning

Start the plasma on the instrument and allow it to run for at least 30 minutes prior to tuning the instrument. Optimize the instrument parameters using Shimadzu's ICPMS tuning solution (P/N 220-95357-63). The most important aspects of the tuning procedure are Torch Position, Lens Voltage, Mass Resolution and P/A tuning (**Fig. 1**). To extend the lifespan of the detector, it is only recommended to run Gain Voltage tuning in the Instrument Calibration once or twice a year during the preventive maintenance or when the detector is replaced. These tuning parameters are calibrated using the same tuning solution, which is different from the 200.8 tuning solution. The instrument tuning should be carried out daily.



	Tuning Item	Pos.	Meas.	State	Last Update
☑	Torch Position	R0			
☐	Gain Voltage	R0			
☑	Lens Voltage	R0			
☑	Mass / Resolution	R0			
☑	P/A Tuning	R0			
☐	DB Tuning	R0			
☑	Validation	R1			

Figure 1. ICPMS daily tuning checks.

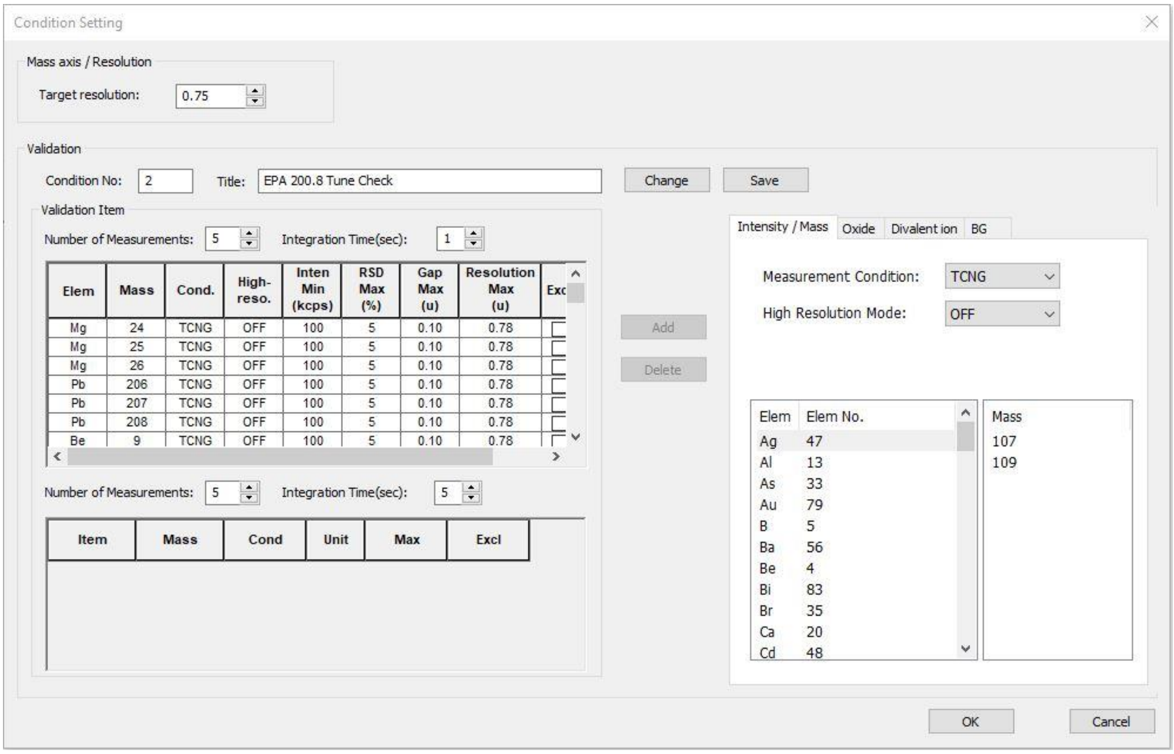
Prepare a 100-fold dilution of the sample 2008TS. Once the instrument's operating parameters have been tuned, validate that the tune is appropriate for the instrument by running the "Validation" portion using the diluted 2008TS sample.

The validation portion must be constructed within the software in the following location: Instrument > Instrument Calibration > Condition Setting. Apply the following parameters (**Fig. 2**; **Table 3**):

The only parameters here that are important, per EPA Method 200.8, are resolution, which should be "around 0.75" and RSD, which should be no more than 5% for five replicate analyses. This custom validation can be saved for later use.

Table 3. Parameters for EPA Method 200.8 Validation

Elem	Mass	Cell Gas	Inten Min (kcps)	RSD Max (%)	Max Gap (u)	Resolution gap (u)	Exclusion
Mg	24	No use	100	5	0.1	0.78	☐
Mg	25	No use	100	5	0.1	0.78	☐
Mg	26	No use	100	5	0.1	0.78	☐
Pb	206	No use	100	5	0.1	0.78	☐
Pb	207	No use	100	5	0.1	0.78	☐
Pb	208	No use	100	5	0.1	0.78	☐
Be	9	No use	100	5	0.1	0.78	☐
Co	59	No use	100	5	0.1	0.78	☐
In	115	No use	100	5	0.1	0.78	☐



Target resolution: 0.75

Condition No: 2
Title: EPA 200.8 Tune Check

Validation Item

Number of Measurements: 5
Integration Time(sec): 1

Elem	Mass	Cond.	High-reso.	Inten Min (kcps)	RSD Max (%)	Gap Max (u)	Resolution Max (u)	Exc
Mg	24	TCNG	OFF	100	5	0.10	0.78	☐
Mg	25	TCNG	OFF	100	5	0.10	0.78	☐
Mg	26	TCNG	OFF	100	5	0.10	0.78	☐
Pb	206	TCNG	OFF	100	5	0.10	0.78	☐
Pb	207	TCNG	OFF	100	5	0.10	0.78	☐
Pb	208	TCNG	OFF	100	5	0.10	0.78	☐
Be	9	TCNG	OFF	100	5	0.10	0.78	☐

Number of Measurements: 5
Integration Time(sec): 5

Item	Mass	Cond	Unit	Max	Excl

Measurement Condition: TCNG
High Resolution Mode: OFF

Elem	Elem No.
Ag	47
Al	13
As	33
Au	79
B	5
Ba	56
Be	4
Bi	83
Br	35
Ca	20
Cd	48

Mass
107
109

Figure 2. Image depicting the EPA Method 200.8 Validation set-up in the LabSolutions ICPMS Software.

Internal Standards

The use of internal standards is mandated by EPA Method 200.8 to control for any fluctuation in signal intensities during the period of analysis. The internal standard provided by Inorganic Ventures (2008ISS) consists of Sc, Y, In, Tb, and Bi. The most effective and efficient way of adding internal standards to all calibration and unknown samples is using an ‘internal standard automatic addition kit’. The final concentration of the internal standard, upon nebulization, is to be 20 – 200 µg/L*.

If mercury is to be analyzed by direct analysis, gold can be added to the internal standard solution such that the concentration of gold is 100 µg/L in all blanks, calibration standards, and samples. This is to aid in mobilizing mercury in samples. Hydrochloric acid can also stabilize the mercury in samples. Hydrochloric acid is also required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, corrections for the chloride polyatomic ion interferences must be applied to all data by setting upt compensation formulas in the LabSolutions ICPMS software.

The internal standard can be prepared ‘in bulk’ when using the internal standard automatic addition kit (P/N: 220-95356-90). Due to the dilution factor of the internal standard automatic addition kit, the concentrations of analytes in the internal standard should be as described in **Table 4***.

It should also be noted that each element requires the use of a single internal standard. The five internal standards used here cover all the elements covered in EPA Method 200.8. However, if the laboratory is only running analysis on one element, only one internal standard will be required. See **Table 5** for a list of analyte elements and their appropriate internal standards.

If tin is in the samples, ^{115}Sn will interfere with ^{115}In. In this case, rhodium (^{103}Rh) can be used as internal standard instead of In.

Table 4. Internal standard concentrations in bulk solution used with Internal Standard Automatic Addition Kit

Internal Standard	**Concentration (µg/L)**
Be	200-2000
Sc	200-2000
Y	200-2000
In	200-2000
Bi	200-2000
Au†	1000

* The internal standard automatic addition kit, when employed per its instruction manual, imparts a ~1:10 dilution of internal standards during mixing. That is to say, a 100 µg/L internal standard from a stock solution will be ~10 µg/L once it reaches the plasma.

†Only to be used when analyzing mercury by "direct analysis".

Table 5. EPA Method 200.8 analytes and their associated internal standards

Analyte	**Recommend Analysis Mass(es)**	**Recommended Internal Standard**
Aluminum	27	^{45}Sc
Antimony	123	^{115}In
Arsenic	75	^{89}Y
Barium	137	^{159}Tb
Beryllium	9	^{45}Sc
Cadmium	111	^{115}In
Chromium	52	^{45}Sc
Cobalt	59	^{45}Sc
Copper	63	^{45}Sc
Lead	206, 207, 208	^{209}Bi
Manganese	55	^{45}Sc
Mercury	202	^{209}Bi
Molybdenum	98	^{89}Y
Nickel	60	^{45}Sc
Selenium	82	^{89}Y
Silver	107	^{115}In
Thallium	205	^{209}Bi
Thorium	232	^{209}Bi
Uranium	238	^{209}Bi
Vanadium	51	^{45}Sc
Zinc	66	^{89}Y

Instrument Detection Limit

Instrument Detection Limits (or IDL) are calculated for EPA Method 200.8 by calibrating the instrument using external standards followed by running ten (10) replicates of a blank solution.

Prepare four external (calibration) standards using the WW-MSCAL-1, WW-MSCAL-2, and 2008CAL-1 solutions such that the analyte concentrations are as follows:

Table 6. Calibration conditions for EPA 200.8

Element	Units	Cal 1	Cal 2	Cal 3	Cal 4
Ag	ug/L	0	10	20	100
Al	ug/L	0	10	20	100
As	ug/L	0	10	20	100
Ba	ug/L	0	10	20	100
Be	ug/L	0	10	20	100
Cd	ug/L	0	10	20	100
Co	ug/L	0	10	20	100
Cr	ug/L	0	10	20	100
Cu	ug/L	0	10	20	100
Hg	ug/L	0	0.5	1	5
Mn	ug/L	0	10	20	100
Mo	ug/L	0	10	20	100
Ni	ug/L	0	10	20	100
Pb	ug/L	0	10	20	100
U	ug/L	0	10	20	100
Sb	ug/L	0	10	20	100
Se	ug/L	0	50	100	500
Th	ug/L	0	10	20	100
Tl	ug/L	0	10	20	100
V	ug/L	0	10	20	100
Zn	ug/L	0	10	20	100

All standards should be prepared in 1-2% HNO_3. It is critical to matrix match all samples and standards. That is, all samples and standards should be acidified and prepared identically.

The blank solution should be comprised of HNO_3 and water used for dilution and preparation of standards and samples. It can be the same solution as “Cal 1” described above.

Open the ICPMS data file entitled ‘EPA 200.8.imd’. Populate the sample table with calibration standards and ten repeated blanks. Ensure that the prepared standards and samples correspond with the correct autosampler positions indicated in the sample table.

Run the calibration and analysis of ten repeated blank samples. The IDL for each analyte is equal to three times the standard deviation of the ten analyses.

Method Detection Limit

Method Detection Limits (or MDL) are calculated for EPA Method 200.8 by calibrating the instrument and running seven (7) replicate analyses of each analyte spiked into reagent water at a concentration of two- to five-times the IDL. This can prove to be a challenge with the pre-packaged standards as there will not be one dilution that will be suitable to analyze all analytes in one seven-sample run. Rather, the analyst will need to analyze multiple dilutions of WW-MSCAL-1, WW-MSCAL-2, and 2008CAL-1 in order to cover all analytes.

Because the IDLs will differ slightly between laboratories, it is the responsibility of the analyst to determine their IDLs and calculate the MDLs for each analyte. The slight variations are a function of individual variations between instruments, sample preparation methods, and reagent and diluent quality. As such, no fixed IDL nor MDL concentrations can be prescribed for each individual instrument.

Open the ICPMS data file entitled ‘EPA 200.8.imd’. Populate the sample table with calibration standards. Ensure that the prepared standards correspond with the correct autosampler positions indicated in the sample table.

Prepare the MDL samples as described above and in the EPA 200.8 Method document. Because seven replicate analysis are required, it is advisable to prepare ~50 mL of these solutions and make repeated measurements from those containers.

Populate the sample table with the appropriate sample names and autosampler vial positions. We recommend using the “R” positions in the center of the AS-20 as these positions will hold 50 mL centrifuge tubes.

Then, run the calibration and seven repeat analyses for each MDL sample. The MDL for each analyte 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.

Linear Dynamic Range

The Linear Dynamic Range (LDR) test ensures that analytes fall within ±10% of their true concentration when analyzed outside of the range of the external calibration solutions. To complete this analysis, the analyst will calibrate the instrument as indicated in **Table 4**. Then, the analyst will run a series of samples prepared from the same stocks as the standards, however, these will be analyzed in increasing concentration. An example of dilutions for each standard for the LDR test are shown in **Table 7**.

Table 7. Suggested dilutions for Linear Dynamic Range test

Standard	LDR 1	LDR 2	LDR 3	LDR 4	LDR 5	LDR 6
WW-MSCAL-1	Blank	1:10000	1:1000	1:100	1:10	1:1
WW-MSCAL-2	Blank	1:10000	1:1000	1:100	1:10	1:1
2008CAL-1	Blank	1:10000	1:1000	1:100	1:10	1:1

Post-analysis Validation (Spike and Recovery)

To finalize method validation, EPA 200.8 requires a spike and recovery analysis. It is critical to this analysis that the instrument be calibrated with solutions made from the WW-MSCAL-1, WW-MSCAL-2, and 2008CAL-1.

Samples for spike-and-recovery should be representative of the type of sample the laboratory is going to run. If the laboratory is engaged in drinking water analysis, a sample of tap water should be prepared as indicated in the Method and analyzed ‘as is’ and after spiking. It is recommended to spike the samples with analytes at concentrations in the middle of the calibration range (**Table 8**).

Table 8. Suggested* spike concentrations

Element	Units	Concentration
Ag	ug/L	50
Al	ug/L	50
As	ug/L	50
Ba	ug/L	50
Be	ug/L	50
Cd	ug/L	50
Co	ug/L	50
Cr	ug/L	50
Cu	ug/L	50
Hg	ug/L	2.5
Mn	ug/L	50
Mo	ug/L	50
Ni	ug/L	50
Pb	ug/L	50
U	ug/L	50
Sb	ug/L	50
Se	ug/L	250
Th	ug/L	50
Tl	ug/L	50
V	ug/L	50
Zn	ug/L	50

*These are suggestions based on the calibration scheme presented here and may be modified

Conclusions

This short document should provide some guidance to the analyst on how to prepare for analysis of waters by EPA Method 200.8 on the Shimadzu ICPMS-2040. This document does not cover the QA/QC procedures moving forward to daily analyses of samples.

As stated at the beginning of the document, this document is not a substitute for an SOP nor is it as comprehensive as EPA Method 200.8 written in its entirety. It is the responsibility of the analyst to conform to all procedures outlined in the Method for full compliance.