Lab Director Approval: Shene A. Jones / 08/19/2021
QA Manager Approval: Jeffrey Moore / 08/19/2021

EPA Method 200.7 - Inductively Coupled Plasma-Atomic Emission Spectroscopy

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at https://epd.georgia.gov/about-us/epd-laboratory-operations. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1 Scope and Application

Method 200.7 is used to determine metals in ground water, surface water, drinking water wastewater, sludges and soils by ICP-AES. Samples analyzed by this method must be acceptable for analysis by direct aspiration or prepared by EPA Method 200.2 This method is used to analyze the following metals:

Compound	CAS No.
Aluminum	7429-90-5
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Cadmium	7440-43-9
Calcium	7440-70-2
Chromium	7440-47-3
Cobalt	7440-48-4
Copper	7440-58-8
Iron	7439-89-6
Lead	7439-92-1
Magnesium	7439-95-4
Manganese	7439-96-5
Molybdenum	7439-98-7
Nickel	7440-02-0
Potassium	7440-09-7
Selenium	7782-49-2
Silver	7440-22-4
Sodium	7440-23-5
Strontium	7440-24-6
Thallium	7440-28-0
Tin	7440-31-5
Vanadium	7440-62-2
Zinc	7440-66-6

1.2 Restricted Procedure
This procedure is restricted to use by an analyst experienced in the operation of an optical ICP. Additionally, the analyst must complete the requirements of the GaEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GaEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2 Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions. (See SOP reference 13.7)

2.2 Lower Level Check Standard (LLCS): A standard analyzed at lower end of the curve usually at report limit.

2.3 Interference Check Solution (INCK): A standard solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine of correcting known inter-element spectral interferences. Commonly referred to as Spectral Interference Check (SIC)

2.4 Instrument Detection Limit (IDL): The concentration equivalent to analyte signal which is equal to 3 times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the same wavelength.

2.5 MDL standard (ML) = Method Detection Limit Spike Standard (MDL_{spike}): An MDL_{spike} is analyzed with every batch of samples and is carried through the same procedure as the samples being analyzed. One or more MDL_{spike} samples may be used per batch if needed.

2.6 Manganese (Mn) Profile: Manfacturer recommended procedure using Manganese to establish optimum alignment of the Spectrum's Optics for ICP01 and ICP03

2.7 Spectrometer Optimization: An automatic procedure that ensures the wavelengths are correctly located on the detector for ICP02.

2.8 MDL_{blank} is analyzed with evert batch of samples and is carried through the same procedure as the samples analyzed. One or more MDL_{blank} samples may be used per batch if needed.

3 Interferences

3.1 Method interferences may be caused by background emission, stray light from the line emission from high concentration elements, spectral overlap from another analyte, or unresolved overlap of molecular band spectra.

3.1.1 Subtracting the background adjacent to the analytical wavelength peak compensates for stray light and background emission. This is automatically performed by the instrument software for every analytical scan. Background correction locations are chosen to be free of off-line spectral interference or reflect the same change in the background intensity as does the analytical peak.

3.1.2 Spectral overlaps are compensated for by the use of interelement correction factors (IECs). IECs are determined by analyzing potential interfering elements individually at different concentrations and monitoring the apparent concentrations (both positive and negative) of all other elements. For ICP01, Arsenic is corrected with Aluminum, Selenium is corrected with Iron, Titanium is corrected with Calcium and Thallium is corrected with Magnesium. The correction equations and coefficients are determined by the instrument software and are automatically applied for every analytical scan.

3.1.3 Physical interferences are effects associated with the sample nebulization and transport such as changes in viscosity and surface tension. Physical interferences are corrected by using a peristaltic pump for sample delivery and maintenance to keep the sample introduction system clean.

3.1.4 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally these interferences are not a major concern with ICP spectroscopy, but are minimized by matrix matching the standard matrix to the sample matrix and by acid digesting all samples. The presence of chemical interferences is monitored for by the use of matrix spikes and matrix spike duplicates.

3.1.5 Memory interferences occur when elements from a previous sample contribute to the signal measured in a new sample. Memory effects usually arise from a dirty sample introduction system and are minimized by proper instrument maintenance. Memory interferences are detected by analyzing a rinse blank after a sample with an analyte concentration exceeding the linear dynamic range and by periodic analysis of the continuing calibration blank (CCB).

4 Safety

Refer to Laboratory Chemical Hygiene Plan, online revision. (See SOP reference 13.8)

5 Apparatus and Equipment

5.1 Computer controlled ICP spectrometer with background correction.
5.2 Peristaltic pump for sample delivery.
5.3 Computer controlled autosampler.
5.4 High purity Argon gas supply at 50 PSI to 90 PSI
5.5 Auto sampler tubes
5.6 Electronic balance
5.7 Air displacement pipettors capable of delivering volumes between 0.001 ml and 1 ml with an assortment of tips. Air displacement pipettes and auto-pipettors may also be described as mechanical pipettes.
5.7.1 Each day of use, the volume dispensed by each mechanical pipette must be verified for the specific volume for which the pipette is being used.
5.7.1.1 Mechanical pipette volumes are verified by measuring the weight of a volume of water dispensed by the unit. At room temperature, 1 ml of water is equal to 1 g. Pipettes must be capable of ± 2.5% accuracy and within 2.5% precision RSD.
5.7.1.2 Auto-pipettors may be verified by measuring the volume dispensed with a graduated cylinder. The volume dispensed must be within ±2.5% of the nominal weight.
5.7.1.3 Air displacement pipettes must be professionally calibrated every 6 months.
5.8 Assorted HDPE labware

5.9 Assorted HDPE Digestion tubes
5.10 Assorted HDPE Centrifuge tubes
5.11 Hot Block Digesters capable of maintaining a temperature of 95°C for samples digested by EPA method 200.2
5.12 Disposable polypropylene ribbed watch glasses for digestion
5.13 Assorted certified volumetric labware

6 Reagents and Standards

All reagents and standards must be logged into the standard log notebook, the container must be labeled with the standard number, expiration date, name, and initials of the person who prepared the solution.

6.1 1000 mg/kg Yttrium solution for the "bullet" test purchased from an outside vendor.
6.2 Reagent grade 6% (v/v) nitric acid and 5% (v/v) hydrochloric acid mixture as running buffer for all non-drinking water samples and the calibration blank. In a vented fume hood, add 1000ml of 18MΩ water to a 2L HDPE container. Slowly add 120ml of nitric acid and 100ml of Hydrochloric acid. Bring to volume with 18MΩ water.
6.3 1:1 Nitric Acid Solution: Inside a vented fume hood, add 400mL of 18MΩ water to a clean 1L HDPE container. Slowly add 500mL of concentrated Ultra Trace Metal Grade Nitric Acid and bring to volume with 18MΩ water.
6.3.1 Acidified Blank solution: In a vented fume hood, add 500mL of 18MΩ water to a 1L HDPE container. Slowly add 5mL of 1:1 Nitric Acid Solution (6.3) and bring to final volume with 18MΩ.
6.4 18MΩ water: Purified water which does not contain any measurable quantities of target elements or interfering elements for each element of interest. Milli-Q water is used by the EPD Metals Lab. Milli-Q water has a resistivity of 18.2 [MΩ.cm] @ 25°C and a TOC of 50µg/L or less.
6.5 Calibration standards (described in section 8).
6.6 Initial Calibration Verification standard (ICV) (described in section 8).
6.7 Continuing Calibration Check standard (CCC) (described in section 8).
6.8 1% Nitric Acid Buffer solution: Add 500ml of 18MΩ water to a clean 2L HDPE container. In a vented fume hood, slowly add 20mL of concentrated Ultra Trace Metal Grade Nitric Acid. Bring to final volume with 18MΩ water.
6.9 1000ug\mL Scandium Stock Solution purchased from an outside vendor.
6.9.1 30 mg\L Scandium Internal Standard Solution: Add 250ml of blank solution (6.2) to a clean 1L HDPE container. Add 15mL of Scandium stock solution (6.9). Bring to final volume of 500mL with blank solution (6.2). Please note, final volumes may vary with varying concentrations of Scandium stock used to make internal standard solution. Also, final concentration of Scandium Internal Standard Solution may vary depending on instrument dynamics.

7 Sample Collection

Water samples and liquid waste samples for metal analysis are collected in wide and narrow mouth plastic (HDPE) bottle. Samples are preserved with sufficient HNO_3 to lower the pH below 2. One to two bottles are required for each sample. Analysis must be performed within 6 months after preservation.

Soil and sediment samples for metal analysis are collected in a 500 ml wide mouth plastic (HDPE) bottle. Samples must be cooled to 0-6^{0}C (not frozen) after sample collection. Analysis must be performed within 180 days.

8 Calibration

8.1 Calibration Standards: The ICP-OES is calibrated daily prior to analysis. The calibration curve consists of at least a blank two calibration standards.

Table 8.1.1A - Calibration Standard Names for **ICP 01**

Standard Name	Concentration µg/L
Calibration Standard 1 (Blank)	Calibration Blank(Final con: 5%HCL and 6%HNO3)
Calibration Standard (Std 2) Same as Standard 4 for ICP02\ICP03	Std 2 (Final con: Ag2000ppb, Se50000ppb &Metals 10000ppb)

Table 8.1.1B - Calibration Standard Names for **ICP 02**

Standard Name	Concentration µg/L
Calibration Standard 1 (Blank)	Calibration Blank(5%HCL and 6%HNO3)
Calibration Standard (Std 2) same as MDL concentration	K 500, Tl 200, Se 190, As 80, Al 50. Ca, Mg, and Na 100, Cr, Cu, Fe, Ni, and Zn 20. Ag, Ba, Be, Cd, Co, Mn, Ti, and V 10
Calibration Standard (Std3) same as CCC concentration	Ag 1000, Se 25000 and Metals 5000
Calibration Standard (Std4) same as Std 2 for ICP 01	Ag 2000, Se 50000 and Metals 10000

Table 8.1.1C - Calibration Standard Names for **ICP 03**

Standard Name	Concentration µg/L
Calibration Standard 1 (Blank)	Calibration Blank(5%HCL and 6%HNO3)
Calibration Standard (Std 2) same as MDL concentration	K 500, Tl 200, Se 190, As 80, Al 50. Ca, Mg, and Na 100, Cr, Cu, Fe, Ni, and Zn 20. Ag, Ba, Be, Cd, Co, Mn, Ti, and V 10
Calibration Standard (Std3) same as CCC concentration	Ag 1000, Se 25000 and Metals 5000
Calibration Standard (Std4) same as Std 2 for ICP 01	Ag 2000, Se 50000 and Metals 10000

8.2 Calibration Verification: The calibration is verified by analyzing the initial calibration verification (ICV) standard daily after calibration. The ICV is usually from a second source vendor or if from the same vendor as the curve it must have a different lot number than CCC. The % drift must be ≤5% from the expected values.

Table 8.2.1 - ICV Concentration

Elements:	Concentration ug/L
Metals	5000
Ag	1000
Se	25000

8.3 Continuing calibration check (CCC) and Continuing calibration blank (CCB): Analyze immediately after calibration, after every ten samples, and at the end of an analytical sequence. (See SOP Table 14.2 for acceptance criteria)

Table 8.3.1A - CCC Concentration

Elements:	Concentration ug/L
Metals	5000
Ag	1000
Se	25000

8.4 An interference check standard (INCK) is analyzed prior to analyzing any samples. The INCK standard for drinking water parameters
must be +/-10% of true value. All-other non-drinking water samples must be +/-20%. The Interference Check Standard (INCK) concentrations are as follows:

Table 8.4.1 - Interference Check Standard Concentrations

Element	**Solids Concentration (mg/kg)**	**Liquids Concentration (mg/L)**
Aluminum	500	500
Antimony	0	0
Arsenic	0	0
Barium	1	1
Beryllium	1	1
Cadmium	2	2
Calcium	500	500
Chromium	1	1
Cobalt	1	1
Copper	1	1
Iron	200	200
Lead	2	2
Magnesium	500	500
Manganese	1	1
Molybdenum*	0	0
Nickel	2	2

Potassium	0	0
Selenium	0	0
Silver	2	2
Sodium	0	0
Strontium*	0	0
Thallium	0	0
Tin*	0	0
Vanadium	2	2
Zinc	2	2
*Molybdenum, Strontium, and Tin are not a requirement for this method and will be available upon request		

8.5 $\text{MDL}_{\text{spike}}$/Lower Level Check Standard (LLCS) – analyzed with each analytical sample batch. For ICP01 run immediately after calibration as standard 3.

Table 8.5.1 – MDL/LLCS Concentration

Elements:	Concentration ug/L
K, Tl	500, 200
Se, As, Al	190, 80, 50
Ca, Mg, and Na	100
Cr, Cu, Fe, Ni, and Zn	20
Ag, Ba, Be, Cd, Co, Mn, Ti, and V	10

8.6 Manganese Profile for ICP01

8.6.1 Automatic or manual check to be performed daily before calibration for ICP01.

Table 8.6.1.1A - Mn Profile for **ICP01**

Standard Name:	Concentration ug/L	Acceptance Criteria
Mn	1000ppb	± 1.0 peak unit shift from central position of zero

8.7 Spectrometer Optimization for ICP02

8.7.1 This procedure is automatically run when the plasma is turned on. It is manufacturer recommended that this procedure is performed daily before calibration for the ICP02. Please note: No standard is required to perform this procedure because the routine uses plasma wavelength positions.

8.8 Spectrometer Optimization for ICP03

8.8.1 This procedure is run using both Axial and Radial Views. No preference is given to which view is run first. It is recommended that this procedure is performed prior to calibration.

Table 8.8.1.1A - Mn Profile for **ICP03**

Standard Name:	Concentration ug/L	Acceptance Criteria
Mn Axial View	1ppm	Instrument will alert if failed with following comment: align view may not be correct. The following plausibility checks have not been met: The peak signal\peak intensity value is less than 10,000 counts per second.
Mn Radial View	10ppm	Instrument will alert if failed with following comment: align view may not be correct. The following plausibility checks have not been met: The peak signa\peak intensity value is less than 10,000 counts per second.

9 Quality Control

9.1 For digested samples: Record all reagents used, volumes, standard or lot numbers, time, and sample IDs on the digestion log. Fill out a run log with every use of the instrument. The run log must include all samples and standards in the order they were analyzed.

9.2 Verify the pipette calibration by following procedure outlined in section 5.7. Record the pipette number, the volumes and the weights on the digestion sheet.

9.3 Refer to Tables 14.1.1-14.1.7 for reporting limits (PQLs) and Table 14.2 for Quality Control Procedures associated with this method. For Quality Control Acceptance Criteria for this method, refer to Appendix A, Table A.1 for SOP 2-013.

9.4 Control Limits

9.4.1 The default control limits from EPA Method 200.7 are 85 – 115% recovery for LCS recoveries. The EPD Laboratory applies LCS recovery limits to LCSDs. Note, unless specified by method, the EPD Laboratory does not validate batch quality based on LCSD recoveries.

9.4.2 By default, the EPD Laboratory sets LCS/LCSD precision control limits to be 0 – 15% RPD.

9.4.3 10% of all routine samples must be spiked. See Section 9.5 modification below. EPA Method 200.7 requires recovery control limits of 70 – 130% for matrix spikes. The EPD Laboratory applies MS recovery limits to MSDs.

9.4.4 By default, the EPD Laboratory sets default MS/MSD precision control limits to be 0 – 15% RPD. MS/MSD precision limits are not dependent on control charting results.

9.4.5 LCS and LCSD recovery and precision control limits are updated through the use of control charts by Drinking Water. MS/MSD control limits are static at the default limit.

9.4.6 See Administrative SOP for Control Charting and Control Limits for further details.

9.5 Batch samples in groups of no more than 20. For each batch, analyze a Matrix Spike

(MS) and a Matrix Spike Duplicate (MSD) for a minimum of 10% of routine samples**.**

9.5.1 For batches of 1 to 10 routine samples, one MS/MSD pair must be spiked. For batches of 11 to 20 routine samples, two MS/MSD pairs must be spiked using different samples for each pair.

9.6 Method Detection Limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

9.6.1 The actual MDL varies depending on the instrument and matrix.

9.6.2 The MDL study must be determined annually for each instrument prior to results being reported for that instrument. The MDL determined for each analyte must be less than the reporting limit for that analyte.

9.6.3 The MDL study for all analytes must be performed initially on a new instrument, after major instrument repairs, changes to procedures and with Drinking Water Initial Demonstrations (see 9.6.3.1). There are two ways to perform the MDL study. The first is with seven $\text{MDL}_{\text{spikes}}$ (ML) and seven $\text{MDL}_{\text{blanks}}$ over 3 separate days. The second way is by analyzing the $\text{MDL}_{\text{spike}}$ sample ($\text{ML}_{\text{sample}}$) with every batch.

9.6.3.1 To perform the seven $\text{MDL}_{\text{spike}}$ and seven $\text{MDL}_{\text{blank}}$ MDL study over three separate days, prepare seven blanks and seven spiked blanks. The seven spiked blanks are spiked at the lowest calibration point on the curve. The seven sets of $\text{MDL}_{\text{spikes}}$ and $\text{MDL}_{\text{blanks}}$ pairs are analyzed over three separate days. Please note, there may or may not be a non-analysis day between each of the three days.

9.6.3.2 A continuous MDL study format: One blank is spiked per batch and identified as the MLsample. The MLsample is at the lowest point on the calibration curve. The method blank for each batch is the MDLblank.

9.7 The results of the MDLblank will be entered into Labworks using the Method Blank test code. The MDLspike result will be entered using the prefix $ML followed by the test code. The instrument used for the MDLsample and MDLblank, will be selected using prefix INSTR followed by the instrument number.

Please note, A continuous MDL study must be generated yearly and cover a 2-year period.

Note: The default control limits are presented to assist in defining control limits established with control charts for Drinking water sample analysis and are not used as batch acceptance criteria. All samples from programs other than Drinking water will use method default limits for batch acceptance criteria.

Table 9.4.1. – Default Quality Assurance Criteria for Method EPA 200.7

QC Type	Analyte	Accuracy(%R) LCL UCL	Precision (%RPD)
LCS/LCSD	All metals	85 – 115	0 – 15
MS/MSD	All metals	70 – 130	0 – 15

10 Procedure

10.1 All drinking water and non-drinking water samples must have the pH checked a minimum of 16 hours after preservation. For drinking water samples ($ICPIOC), the turbidity must also be checked a minimum of 16 hours after preservation. If the pH is < 2 and the turbidity is < 1 NTU for drinking water samples ($ICPIOC), the sample is poured for analysis by direct aspiration. All other samples must be digested by EPA Method 200.2 (Refer to SOP 2-002 – EPA 200.2 Sample. Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements) See SOP reference 13.9
Please note, any drinking water samples ($ICPIOC) with a turbidity result >1, must be digested using EPA Method 200.2.
10.2 Start the instrument and allow at least 45 minutes to warm up.
10.3 Profile/Optimize the instrument according to manufacturer specifications.
10.4 Calibrate the instrument by using at least one blank and two standards. Please note: ICP01 uses the LLCS as the lowest level standard for calibration and is run immediately after calibration as standard 3 (LLCS).
10.5 Analyze the ICV standard.
10.6 Analyze the CCC and CCB immediately after calibration. A CCC and CCB must be analyzed at the start of each batch, after every ten samples in a batch, and as the last samples analyzed in a batch. The CCC and CCB do not count towards the sample total in a batch.
10.7 Analyze the INCK standard.
10.8 Analyze the LLCS. Please note, the LLCS is only run in this order for ICP02 and ICP03.
10.9 Determine the instrument detection limits (IDLs).
10.9.1 Change the number of repetitions from 3 to 10.
10.9.2 Aspirate the running calibration blank (see 6.2) and analyze for 10 repetitions. and analyze for 10 repetitions.
10.9.3 Calculate the IDL for each element by multiplying the standard deviation (SDev) by 3. This result must be below the reporting limit for each analyte.
10.9.4 Change the number of repetitions back to 3.
10.10 Analyze the MDL standard.
10.11 Analyze the matrix blank.
10.12 Analyze the LCS and LCSD.
10.13 Begin analyzing samples.
10.14 Matrix spike and Matrix spike duplicate
10.14.1 A matrix spike must be analyzed for every ten samples in a batch.
10.14.2 A matrix spike duplicate must be analyzed for every ten samples in a batch.
10.15 Dilute any sample above Linear Detection Range calibration blank solution. The upper LDR limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed.

11 Calculations

11.1 Evaluation of the Linearity of the Initial Calibration
Correlation coefficient of 0.995 is required.

11.1.1 The external standard calibration is calculated by the instrument software and is documented in the instrument software.

11.2 Mean ($\overline{X}$):

$$\overline{X} = \frac{X_1 + X_2 + \cdots X_n}{n}$$

11.2.1 Where:

$X_1 + X_2 + \cdots X_n$ = The sum of a set of values X_i, i = 1 to n
n = The number of values in the set

11.3 Standard Deviation (n – 1) (σ_{n-1}):

$$\sigma_{n-1} = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \overline{X})^2}{n-1}}$$

11.3.1 Where:

$\overline{X}$ = Mean of the values
X_i = Individual values 1 through i
n = Number of values

11.4 Percent Relative Standard Deviation (%RSD):

$$\%RSD = \frac{\sigma_{n-1}}{\overline{X}} * 100$$

11.4.1 Where:

σ_{n-1} = Sample Standard Deviation
$\overline{X}$ = Mean of the values

11.5 Relative Percent Difference (%RPD or RPD):

$$\%RPD = \frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} * 100$$

11.5.1 Where:

$|X_1 - X_2|$ = Absolute difference between two values

$\frac{(X_1 + X_2)}{2}$ = Average of two values

11.6 Percent Drift, %Drift:

$$\%Drift = \frac{(Concentration_{Calculated} - Concentration_{Expected})}{Concentration_{Expected}} * 100$$

11.6.1 Where:

$Concentration_{Calculated}$ = Concentration calculated from result
$Concentration_{Expected}$ = Theoretical concentration of the standard

11.7 Percent Recovery:

11.7.1 LCS/LCSD:

$$\%Recovery = \frac{Conc_{spiked}}{Conc_{expected}} * 100$$

11.7.1.1 Where:

$Conc_{spiked}$ = Concentration found in the spiked sample
$Conc_{expected}$ = Expected concentration

11.7.2 MS/MSD:

$$\%Recovery = \frac{Conc_{spiked} - Conc_{unspiked}}{Conc_{expected}} * 100$$

11.7.2.1 Where:

$Conc_{spiked}$ = Concentration found in the spiked sample
$Conc_{unspiked}$ = Concentration found in unspiked sample
$Conc_{expected}$ = Expected concentration

11.8 Sample Concentration

Liquid Sample Concentration: Concentration = CD_f Where C = concentration from instrument D_f = dilution factor $D_f = \frac{D}{S}$ Where D = dilution volume in liters. S = Sample aliquot volume in liters.	Concentration = $\frac{CVD_f}{DW}$ Where C = concentration from instrument in mg/L. V = final digestion volume in L. D_f = dilution factor. DW = sample weight in kg after drying to constant weight at 60°C ± 5°C.
Use the following formula if there is insufficient sample to dry for digestion: Concentration = $\frac{CVD_F P_s}{WW}$ Where C = concentration from instrument in mg/L V = final digestion volume in L. D_f = dilution factor. WW = wet weight of sample (not dried). P_s = percent solids Percent Solids = $\frac{DW}{WW}$ Where DW = sample weight in kg after drying to constant weight at 60°C ± 5°C WW = wet weight of sample (not dried).	Waste Concentration Calculation: Concentration= $\frac{CVD_F}{WW}$ Where C= concentration from instrument in mg/L V = final digestion volume in L. D_f= dilution factor WW = wet weight of sample.

Aqueous sample results are expressed in ug/L or mg/L
Waste sample results are expressed in mg/kg wet weight
Solid sample results are expressed in mg/kg dry weight

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures. (See SOP reference 13.4)

13 References

13.1 EPA Method 200.7, Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, EMMC Version, Revision 4.4, 1994.
13.2 GA EPD Laboratory SOPs – Initial Demonstration of Capability SOP 6-001, online revsion and/or Continuing Demonstration of Capability SOP 6-002, online revision.
13.3 GA EPD Laboratory SOP – EPD Laboratory Procedures for Control Charting and Control Limits SOP, SOP 6-025, online revision.

13.4 GA EPD Laboratory SOP – EPD Laboratory Waste Management SOP, SOP 6-015, online revision.
13.5 Manual for the Certification of Laboratories Analyzing Drinking Water, EPA/815-R-05-004, January 2005.
13.6 GA EPD Laboratory SOP – Determination of Method Detection Limits SOP, SOP 6-007, online revision.
13.7 GA EPD Laboratory Quality Assurance Plan, online revision.
13.8 GA EPD Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.
13.9 EPA Method 200.2, Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, U.S. EPA Office of Research and Development: Cincinnati, OH, Revision 2.8, May 1994
13.10 Poly Scan 61E Spectrometer Operator’s Manual, Thermo Jarrell Ash Corporation, 1992.
13.11 Thermo Scientific, ICAP 7000 Plus Series, ICP-OES, Software Manual, Otegra ISDS Software 2.8 SR3, BRE0009693 Revision C, January 2018.

14 Practical Quantitation Limits (PQLs), Precision and Accuracy Criteria, and Quality Control Approach

See Appendix A, Table A.1 for Precision and Accuracy Criteria

Table 14.1.1 Reporting Limits for EPA 200.7 $ICPIOC

Method	Analyte	Matrix (Drinking Water)	
		RL	Unit
200.7	Sodium	1000	ug/L

Table 14.1.2 Reporting Limits for EPA 200.7 $ICP_SOURCE

Method	Analyte	Matrix (Drinking Water)	
		RL	Unit
200.7	Calcium	1000	ug/L
	Magnesium	1000	ug/L
	Potassium	5000	ug/L
	Titanium	10	ug/L
	Vanadium	10	ug/L
	Sodium	1000	ug/L

Table 14.1.3 Reporting Limits for EPA 200.7 $CAMG

Method	Analyte	Matrix Water	
		RL	Unit
200.7	Calcium	0.15	mg\L
	Magnesium	0.15	mg\L

Table 14.1.4 Reporting Limits for EPA 200.7 $FEMN

Method	Analyte	Matrix Water	
		RL	Unit
200.7	Iron	20	ug/L
	Manganese	10	ug/L

Table 14.1.5 Reporting Limits for EPA 200.7 $ICP_W

Method	Analyte	Matrix (Water, Water Quality Metals)	
		RL	Unit
200.7	Silver	10	ug/L
	Aluminum	100	ug/L
	Arsenic	80	ug/L
	Barium	10	ug/L
	Beryllium	10	ug/L
	Calcium	1000	ug/L
	Cadmium	10	ug/L
	Cobalt	10	ug/L
	Chromium	20	ug/L
	Copper	20	ug/L
	Iron	20	ug/L
	Potassium	5000	ug/L
	Magnesium	1000	ug/L
	Manganese	10	ug/L
	Sodium	1000	ug/L
	Nickel	20	ug/L
	Lead	90	ug/L
	Antimony	120	ug/L
	Selenium	190	ug/L
	Titanium	10	ug/L
	Thallium	200	ug/L
	Vanadium	10	ug/L
	Zinc	20	ug/L

Table 14.1.6 Reporting Limits for EPA 200.7 $ICP_M and $TMDL

Method	Analyte	Matrix (Water, Munici Perm Prog)	
		RL	Unit
200.7	Aluminum	100	ug/L
	Beryllium	10	ug/L
	Calcium	1000	ug/L
	Cobalt	10	ug/L
	Iron	20	ug/L
	Potassium	5000	ug/L
	Magnesium	1000	ug/L
	Manganese	10	ug/L
	Sodium	1000	ug/L
	Titanium	10	ug/L
	Vanadium	10	ug/L

Table 14.1.7 Reporting Limits for EPA 200.7 $ICP_S

Method	Analyte	Matrix (Soil/Sediment)	
		RL	Unit
200.7	Silver	0.01	mg/kg
	Aluminum	0.01	mg/kg
	Arsenic	0.08	mg/kg
	Barium	0.01	mg/kg
	Beryllium	0.01	mg/kg
	Calcium	1	mg/kg
	Cadmium	0.01	mg/kg
	Cobalt	0.01	mg/kg
	Chromium	0.02	mg/kg
	Copper	0.02	mg/kg
	Iron	0.02	mg/kg
	Potassium	5	mg/kg
	Magnesium	1	mg/kg
	Manganese	0.01	mg/kg
	Sodium	1	mg/kg
	Nickel	0.02	mg/kg
	Lead	0.09	mg/kg
	Antimony	0.12	mg/kg
	Selenium	0.19	mg/kg
	Titanium	0.01	mg/kg
	Thallium	0.20	mg/kg
	Vanadium	0.01	mg/kg
	Zinc	0.02	mg/kg

Table 14.2 Summary of Calibration and QC Procedures for EPA Methods 200.7

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
200.7	Metals by ICP	Analyst Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of a QC sample, a method blank and a unknown sample. In addition, the analyst must prepare at least one standard. For drinking water samples, MDL study must be performed. See 9.6.3.1	Once per analyst.	Average of 4 LCS recoveries between 85-115%. Recovery of unknown sample between 85-115%.	Recalculate results, correct problem, then rerun the initial demonstration for those analytes that did not meet criteria	
		Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	Every 6 Months after IDC.	QA Acceptance Criteria: **For DW** - SOP 2-013, Appendix A. **For All other programs -** Method Default Limits, See SOP 2-013, Section 9.4.	Correct the problem, then rerun the continuing demonstration for those analytes that did not meet criteria	
		MDL Study Initial	New instrument start-up, major instrument repair and analyst initial demonstration for drinking water analysis	Minimum Detection Limits established shall be <the RLs in Table 14.1. All Spiked MDLs must have a value greater than 0	Re-do MDL Study	None

Table 14.2 Summary of Calibration and QC Procedures for EPA Methods 200.7

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
200.7	Metals ICP	MDL Study Continuous	Generated yearly over a two-year period	All analyte concentrations must be <RL	Redo initial MDL Study	Corrective Action Report
		MDL_{spike}	Once per analytical batch or as needed to acquire data points for SOP 6-007, online revision	All batch QC must meet established criteria. All spiked MDL's must have a value greater than 0	Re-run the MDL once and initiate a corrective action. If the MDL fails a second time, do not use MDL data. Update corrective action, and use associated sample data .	None
		MDL_{blank} Can be combined with Matrix Blank	Once per analytical batch.	All batch QC must be valid.	Rerun once, if still out of limits, correct problem and reanalyze affected batch if MDLblank is matrix blank	
		Analysis of PE sample.	Once every 12 months.	All analyte results acceptable per the auditing agency.	Correct the problem.	
		Linear Dynamic Range (LDR).	Once every 12 months or whenever major maintenance is preformed on the instrument that might affect the instruments detector.	Consecutive levels of increasing concentrations must be within 10% of expected value. See 10.15.		

Table 14.2 Summary of Calibration and QC Procedures for EPA Methods 200.7

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
200.7	Metals by ICP	Automatic or Manual Mn profile (ICP01).	Daily before calibration.	± 1.0 unit shift.	If automatic peak shift fails criteria, adjust manually. If still outside of criteria, correct the problem and reanalyze profile.	
		Spectrometer Optimization (ICP02).	Daily before calibration.	Automatic when plasma is ignited. Success or Fail message.	If fails, correct the problem and restart the instrument.	
		Spectrometer Optimization (ICP03)	Daily before calibration	See table 8.8.1.1A	Correct the problem and reanalyze profile.	
		Initial Calibration. Minimum of 1 blank and two standards	Daily prior to sample analysis.	Correlation coefficient ≥0.995.	Correct the problem and recalibrate.	
		Interference Check Sample (INCK).	Daily after calibration.	For drinking water samples, spiked element recoveries between 90% and 110% of the absolute value of the true value. All non-drinking water samples, spiked element recoveries between 80% and 120% of the absolute value of the true value. All other element concentrations must be below the RL.	Rerun once if still outside of acceptance criteria, correct the problem and calculate new interelement correction factors and recalibrate.	
		Lower Level Check Standard (LLCS).	Daily after calibration but before analyzing samples.	All analyte recoveries between 50-150%.	Rerun once, if still outside of acceptance critieria, correct the problem and recalibrate.	
		Instrument detection limit standard (IDL).	Daily after calibration.	3 times standard deviation of 10 replicates <analyte RL.	Reun once, if still outside of acceptance criteria, correct the problem, recalibrate.	
		Initial Calibration Verification (ICV).	Daily after calibration.	All analyte recoveries between 95% and 105% of true value.	Rerun once, if still outside of acceptance criteria, correct the problem and recalibrate.	

Table 14.2 Summary of Calibration and QC Procedures for EPA Methods 200.7

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
200.7	Metals by ICP	Continuing Calibration Blank (CCB).	Daily immediately after calibration and immediately after CCC. After every 10 samples, and at end of analysis sequence.	All analyte concentrations <RL.	Rerun once, if still out of control, correct the problem, recalibrate, and reanalyze all samples since the last acceptable CCB.	If unable to re-analyze, flag with a "B".
		Continuing Calibration Check (CCC).	Daily immediately after calibration, after every 10 samples, and at end of analysis sequence.	Initial analyte recoveries between 95% and 105%. Subsequent analyte recoveries between 90% and 110%.	Rerun once, if still out of control, correct the problem, recalibrate, and reanalyze all samples since the last acceptable CCC.	
		Laboratory Control Sample (LCS).	Once per analytical batch.	For drinking water samples, all analyte recoveries between QC charting limits (See SOP 2-013, Appendix A, Table A.1). For non-drinking water samples, all analyte recoveries between 85% and 115%.	Rerun once, correct the problem and recalibrate, if still outside of acceptance criteira, redigest, and reanalyze all samples in the batch.	If unable to re-analyze, flag with a "J".
		Laboratory Control Sample Duplicate (LCSD).	Once per analytical batch.	For drinking water samples, all analyte precision ≤ QC charting limits (See SOP 2-013, Appendix A, Table A.1). For all other test codes precision≤ 15 RPD.	If precision fails, rerun once, correct the problem and recalibrate, if still outside of acceptance criteira correct the problem, redigest, and reanalyze all samples in the batch. The EPD Lab does not validate results based on LCSD recoveries.	If unable to reanalyze, flag with a "J".
		Matrix Blank.	Once per analytical batch.	All analyte concentrations must <RL.	Rerun once, correct the problem and recalibrate, if still outside of acceptance criteria, correct the problem, redigest, and reanalyze all samples in the batch.	If unable to reanalyze, flag with a "B".

Table 14.2 Summary of Calibration and QC Procedures for EPA Methods 200.7

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
200.7	Metals by ICP	Matrix Spike/Matrix Spike Duplicate.	Every 10 samples.	All analyte recoveries between 70 – 130%.	If recovery is outside QC limits but CCC, CCB, ICV, and LCSD are acceptable matrix effect is suspected.	Inform data user that data is suspect due to matrix effect. Comment report.
		Matrix Spike Duplicate.	Every 10 samples.	≤15 RPD	If recovery is outside QC limits but CCC, CCB, ICV, and LCS are acceptable, matrix effect is suspected.	Inform data user that data is suspect due to matrix effect. Comment report.
		Internal Standard	Every standard and sample except for Mn profile. Internal Standard only used for ICP03		Dilute and reanalyze.	None

Appendix A for Method 200.7 Inductively Coupled Plasma-Atomic Emission Spectroscopy

Table A.1 Water, Water Quality Metals ($ICP_W)

QC Type	Analyte	Accuracy (%R) LCL	UCL	Precision (%RPD)
LCS/LCSD	**Silver**	**85**	**115**	**15**
	Aluminum	**85**	**115**	**15**
	Arsenic	**85**	**115**	**15**
	Barium	**85**	**115**	**15**
	Beryllium	**85**	**115**	**15**
	Calcium	**85**	**115**	**15**
	Cadmium	**85**	**115**	**15**
	Cobalt	**85**	**115**	**15**
	Chromium	**85**	**115**	**15**
	Copper	**85**	**115**	**15**
	Iron	**85**	**115**	**15**
	Potassium	**85**	**115**	**15**
	Magnesium	**85**	**115**	**15**

	Manganese	**85**	**115**	**15**
	Sodium	**85**	**115**	**15**
	Nickel	**85**	**115**	**15**
	Lead	**85**	**115**	**15**
	Antimony	**85**	**115**	**15**
	Selenium	**85**	**115**	**15**
	Titanium	**85**	**115**	**15**
	Thallium	**85**	**115**	**15**
	Vandium	**85**	**115**	**15**
	Zinc	**85**	**115**	**15**
MS/MSD	**Metals(Silver-Zinc)**	**70**	**130**	**15**

Control Limits are static by EPA Method/EPD Lab default. Static Limits are generated for trend monitoring purposes.

Table A.2 Water, Munici Perm Prog ($ICP_M)

QC Type	**Analyte**	**Accuracy (%R)** **LCL**	**UCL**	**Precision** **(%RPD)**
LCS/LCSD	**Aluminum**	**85**	**115**	**15**
	Beryllium	**85**	**115**	**15**
	Calcium	**85**	**115**	**15**
	Cobalt	**85**	**115**	**15**
	Iron	**85**	**115**	**15**
	Potassium	**85**	**115**	**15**
	Magnesium	**85**	**115**	**15**
	Manganese	**85**	**115**	**15**
	Sodium	**85**	**115**	**15**
	Titanium	**85**	**115**	**15**
	Vanadium	**85**	**115**	**15**
MS/MSD	**Metals(Aluminum-Vanadium)**	**70**	**130**	**15**

Control Limits are static by EPA Method/EPD Lab default. Static Limits are generated for trend monitoring purposes.

Table A.3 Approval Water ($ICP_SOURCE)

QC Type	**Analyte**	**Accuracy (%R)** **LCL**	**UCL**	**Precision** **(%RPD)**
LCS/LCSD	**Calcium**	**90**	**110**	**10**
	Magnesium	**90**	**115**	**10**
	Potassium	**90**	**113**	**10**
	Sodium	**87**	**114**	**10**
	Titanium	**90**	**112**	**10**
	Vanadium	**90**	**113**	**10**
MS/MSD	**Metals(Calcium-Vanadium)**	**70**	**130***	**15***

***MS/MSD Control Limits are static by EPA Method/EPD Lab default. Static Limits are generated for trend monitoring purposes.**

Control chart date generated from 1/1/2018-1/1/2020

Table A.4 Water ($CAMG)				
QC Type	**Analyte**	**Accuracy (%R)**		**Precision (%RPD)**
		LCL	**UCL**	
LCS/LCSD	**Calcium**	**85**	**115**	**15**
	Magnesium	**85**	**115**	**15**
MS/MSD	**Metals(Calcium-Magnesium)**	**70**	**130**	**15**
Control Limits are static by EPA Method/EPD Lab default. Static Limits are generated for trend monitoring purposes.				

Table A.5 Water ($TMDL)				
QC Type	**Analyte**	**Accuracy (%R)**		**Precision (%RPD)**
		LCL	**UCL**	
LCS/LCSD	**Aluminum**	**85**	**115**	**15**
	Beryllium	**85**	**115**	**15**
	Calcium	**85**	**115**	**15**
	Cobalt	**85**	**115**	**15**
	Iron	**85**	**115**	**15**
	Potassium	**85**	**115**	**15**
	Magnesium	**85**	**115**	**15**
	Manganese	**85**	**115**	**15**
	Sodium	**85**	**115**	**15**
	Titanium	**85**	**115**	**15**
	Vanadium	**85**	**115**	**15**
MS/MSD	**Metals(Aluminum-Vanadium)**	**70**	**130**	**15**
Control Limits are static by EPA Method/EPD Lab default. Static Limits are generated for trend monitoring purposes.				

Table A.6 Water ($FEMN)				
QC Type	**Analyte**	**Accuracy (%R)**		**Precision (%RPD)**
		LCL	**UCL**	
LCS/LCSD	**Iron**	**85**	**115**	**15**
	Manganese	**85**	**115**	**15**
MS/MSD	**Metals(Iron-Magnesium)**	**70**	**130**	**15**
Control Limits are static by EPA Method/EPD Lab default. Static Limits are generated for trend monitoring purposes.				

Table A.7 Water ($ICPIOC)

QC Type	Analyte	Accuracy (%R) LCL	 UCL	Precision (%RPD)
LCS/LCSD	**Sodium**	**87**	**114**	**10**
MS/MSD	**Metals- Sodium**	**70**	**130***	**15***
***MS/MSD Control Limits are static by EPA Method/EPD Lab default. Static Limits are generated for trend monitoring purposes. Control chart date generated from 1/1/2018-1/1/2020**				

Sections 2, 3, 6, 8, 9, 10, and 14 updated. Appendix A added.