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

Method 6020B Determination of Trace Metals in Waters and Wastes by Inductively Coupled Plasma Mass Spectrometers (ICP-MS)

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

1.1 Method 6020B is used to determine trace metals in ground waters, surface waters, drinking waters, wastewaters, sludges, and soils by ICP-MS. An aliquot of the sample is accurately measured and refluxed with Hydrochloric and Nitric acids to solubilize analytes. Samples analyzed by this method must first be prepared by one of the following EPA methods: SW846-3010A, SW846-3015, SW846-3050B, and SW846-3051. The sample is centrifuged or allowed to settle overnight prior to analysis.

1.2 Method SW846-6020B 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	7440-50-8
Iron	7439-89-6
Lead	7439-92-1
Magnesium	7439-95-4
Manganese	7439-96-5
Mercury	7439-97-6
Molybdenum	7439-98-7
Nickel	7440-02-0
Potassium	7440-09-7
Selenium	7782-49-2
Silver	7440-22-4

Sodium	7440-23-5
Thallium	7440-28-0
Vanadium	7440-62-2
Zinc	7440-66-6

1.3 Restricted Procedure

This procedure is restricted to use by an analyst experienced in the operation of ICP-MS. 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

Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions. (See SOP reference 13.6.)

2.1 Control Definitions.

2.1.1 Interference Check Standard Solution (INCK): A standard used to correct inter-elemental effects caused by spectral overlaps. Interference Check Solution is also commonly referred to as ICS, IEC and SIC.

2.1.2 Instrument Detection Limit Standard (IDL): The concentration equivalent to an analyte signal which is equal to 3 times the standard deviation of a series of 10 replicate measurements of the calibration blank (see 6.5) signal at the same wavelength.

2.1.3 MDL standard (ML): Method Detection Limit Spike Standard (MDL_{spike}): An aliquot of Acidified Blank Solution (see 6.2.1) spiked at the lowest level of the calibration curve for each analyte. MDL_{spike} is analyzed with every batch of samples and is carried through the same procedure as the samples being analyzed.

2.1.4 Calibration Blank: An aliquot of 6% HNO_3 and 5% HCL used to establish the calibration curve. The calibration blank will be used for initial and continuing calibration blank determinations.

2.1.5 Method Blank (MB): An aliquot of 6% HNO_3 and 5% HCL used to monitor possible contamination resulting from the sample preparation and digestion procedure.

2.1.6 Initial Calibration Verification (ICV): A second source standard that is used to verify the correctness of the primary source calibration curve. The ICV can be analyzed at or near the mid-level of the calibration curve with an acceptance range of 90-110% of the true value. The ICV must be analyzed immediately after calibration.

2.1.7 Low-Level read back or verification (LLV): A standard at the lowest concentration in the calibration curve. The LLV should quantitate to within 80-120% of the true value. **Please note: The LLV is a read back of calibration standard number 2 (see table 8.1.2).**

2.1.8 Continuing Calibration Check (CCC): A standard prepared using the same acid matrix and stock standards employed when preparing the calibration standards. The CCC should be prepared so as to contain metal concentrations equal or nearly equivalent to the midpoint concentration of the calibration curve. The acceptance range is 90-110%. **Please note: The CCC is also known as the mid-level check.**

2.1.9 Laboratory Control Sample (LCS): Aliquot of Acidified Reagent Water (see 6.2.1) that is spiked with a known amount of analytes and carried through the entire procedure from digestion to analysis.

2.1.10 Laboratory Control Sample Duplicate (LCSD): For the purposes of calculating laboratory precision, an LCSD is carried through the entire procedure as described in section 2.1.9.

2.1.11 Linear Dynamic Range (LDR): The concentration range over which the analytical working curve remains linear. Any sample with an analyte concentration above LDR, must be diluted. The response of the dilution must be between the reporting limit and the LDR. If it is not, adjust the dilution ratio accordingly and reanalyze.

2.1.12 Serial Dilution (DD): One Matrix Spike diluted 1:5 with an acceptance range criteria of 0-20%. One DD is needed per batch.

3 Interferences

3.1 Isobaric elemental interferences: isotopes of different elements which form singly or doubly charges ions of the same mass-to-charge ratio cause isobaric interferences. Tuning the instrument to generate low abundances of doubly charged ions and oxides minimizes isobaric elemental interferences.

3.2 Abundance sensitivity: abundance sensitivity is the contribution by the wings of a mass peak to adjacent peaks. The potential for these interferences is recognized and the spectrometer resolution is adjusted to minimize them by daily tuning procedure according to instrument manufacturer recommendations.

3.3 Isobaric polyatomic ions interferences: isobaric polyatomic interferences are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest and cannot be resolved by the mass quadrupole. Most of the common interferences have been identified. Interference equations are used to correct these interferences. ^{82}Kr is also monitored with each run due to its interference with both arsenic and selenium.

3.4 Physical interferences: physical interferences are associated with the actual transport of the sample to the plasma, through the plasma, and the transmission of the ions through the mass quadrupole. Internal standards are used to compensate for these interferences.

3.5 Memory interferences: memory interferences are caused when isotopes from a previous sample contribute to the signal from another isotope. Rinse and analysis delay times are used to eliminate these interferences. Continuing calibration blanks are used to document to absence of memory effects throughout the run.

4 Safety

4.1 Refer to Laboratory Chemical Hygiene Plan, Revision 2 or later. (See SOP reference 13.7)

5 Apparatus and Equipment

5.1 ICPMS-Perkin Elmer ELAN 9000 or equivalent capable of providing resolution greater than or equal to 1 atomic mass units (AMU) at 10% peak height. The system must have a mass range of at least 6 to 240 AMU.

5.2 High purity argon gas supply.

5.3 Top loading electronic balance.

5.4 Air displacement pipettes capable of delivering volumes between 0.001 mL and 1mL with an assortment of tips. Air displacement pipettes and auto-pipettes may also be described as mechanical pipettes.

5.4.1 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.

5.4.1.1 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 1g. Pipettes must be capable of ± 2.5% accuracy and within 2.5% precision RSD.

5.4.1.2 Auto-pipettes may be verified by measuring the volume dispensed with a graduated cylinder. The volume dispensed must be within ± 2.5% of the nominal weight.

5.4.1.3 Air displacement pipettes must be professionally calibrated every 6 months.

5.5 Assorted HDPE Labware items.

5.6 Assorted HDPE Digestion Tubes.

5.7 Assorted HDPE Centrifuge Tubes.

5.8 Hot block digester capable of maintaining a temperature of at least 95ºC.

5.9 Disposable polypropylene ribbed watch glasses.

5.10 Auto sampler tubes.

5.11 Assorted glass Class A volumetric labware.

5.12 Plastic Digestion Rack.

6 Reagents and Standards

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

6.2 Reagent water: 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] @ 25ºC and a TOC of 50 µg/L or less.

6.2.1 Acidified Reagent Water: An Aliquot of 6% HNO3 and 5% HCL Calibration Blank Solution stored in same containers as samples and used for digesting the Method Blank, LCS, LCSD, MDL and unknown.

6.3 Concentrated Ultra trace metal grade Nitric acid.

6.3.1 1% Nitric Acid Solution: With caution, inside a vented fume hood, add 1000 mL of 18MΩ water (see 6.2) to a clean 2000mL HDPE container. Slowly add 20mL of concentrated Nitric Acid (see 6.3) and bring to 2000mL with 18MΩ water. Cap tightly and slowly invert several times to mix solution.

6.4 Concentrated Ultra trace metal grade hydrochloric acid.

6.5 Calibration Blank Solution (6% HNO_3 and 5% HCL): With caution, inside a vented fume hood, add 1000 ml of 18MΩ reagent water to a 2000mL HDPE container. Slowly add 120 ml of concentrated Nitric Acid (see 6.3) and 100ml of concentrated Hydrochloric Acid (see 6.4). **Caution: solution will get hot**. Allow solution to cool to room temperature, then dilute to 2000ml with 18.2 MΩ water (see 6.2). Cap tightly and slowly invert several times to mix solution.

6.6 Tuning Solutions:

6.6.1 Tuning Stock Intermediate Solution: Add 0.5ml of 1000µg/ml single element vendor stock standards of Magnesium (Mg), Barium (Ba), Beryllium (Be), Cerium (Ce), Cobalt (Co), Indium (In), Lead (Pb), and Rhodium (Rh). Bring to volume of 50ml with 1% Nitric Acid Blank Solution (see 6.3.1). The final concentration is 10µg/ml. This solution is prepared every two months.

6.6.2 Tuning Stock Solution: Add 0.050ml of the tuning stock intermediate solution (see 6.6.1) and bring to final volume of 50ml with 1% Nitric Acid Blank Solution (see 6.3.1). The final concentration is 0.010µg/ml. Prepare solution every two weeks.

6.7 Internal Standard Solutions (ISTD):

6.7.1 ISTD- Intermediate Solution #1- Lithium-6 Solution: Dissolve 0.25 g of Lithium-6, Li_2 carbonate, 95% atom ($^6Li_2CO_3$) into 20ml of 1% Nitric Acid Blank Solution (see 6.3.1). This solution may take several minutes to dissolve. The final concentration is 2000µg/ml. This solution is prepared every two months.

6.7.2 ISTD- Intermediate Solution #2: Add 0.5ml of 1000 µg/ml single element vendor stock standards for Germanium (Ge), Indium (In), Lutetium (Lu), Scandium (Sc) and Lithium-6 Solution (See 6.7.1). Bring to final volume of 50ml with 1% Nitric Acid Blank Solution (see 6.3.1). The final concentration of Ge, In, Lu and Sc is 10µg/ml. The final concentration of Lithium-6 solution is 20µg/ml. This solution is prepared every two months.

6.7.3 ISTD- Internal Standard Solution: Inside a vented fume hood, add 1000ml of 18MΩ reagent water to a 2L HDPE container. Slowly add 20mL of concentrated Nitric Acid (see 6.3). Add 2.0ml of ISTD-Intermediate Solution #2 (see 6.7.2) and bring to final volume with 18MΩ reagent water (see 6.3.1). Invert slowly to mix. This solution is prepared every two weeks.

6.8 Interference Check Standards (INCK)

6.8.1 INCK Stock #1: This standard is purchased from an outside vendor.

Table 6.8.1.1- INCK stock #1	
Analyte	**Concentration (µg/ml)**
Aluminum (Al)	1000
Calcium (Ca)	1000
Iron (Fe)	1000

Potassium (K)	1000
Magnesium (Mg)	1000
Sodium (Na)	1000
Phosphorus (P)	1000
Sulfur (S)	1000
Molybdenum (Mo)	20
Titanium (Ti)	20
Carbon (C)	2000
Chlorine (Cl)	10000

6.8.2 INCK Stock #2: This standard is purchased from an outside vendor.

Table 6.8.2.1- INCK stock #2

Analyte	**Concentration (µg/ml)**
Silver (Ag)	10
Arsenic (As)	10
Cadmium (Cd)	10
Cobalt (Co)	10
Chromium (Cr)	10
Copper (Cu)	10
Manganese (Mn)	10
Nickel (Ni)	10
Zinc (Zn)	10

6.8.3 Interference Check Solution #1 (ICS 1): This solution is prepared every two weeks from INCK stock #1 (See 6.8.1.1) in Calibration Blank Solution (See 6.5). **Note: Molybdenum is the only spiked analyte required for this solution with limits of 80-120% of the true concentration.** The absolute value of the un-spiked required analytes must be less than the reporting limit.

Table 6.8.3.1 (ICS 1)

Analyte	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/L)
Aluminum	1000	2.5	50000
Calcium	1000		50000
Iron	1000		50000
Potassium	1000		50000
Magnesium	1000		50000

Sodium	1000		50000
Phosphorus	1000		50000
Sulfur	1000		50000
Molybdenum	20		1000
Titanium	20		1000
Carbon	2000		100000
Chlorine	10000		500000
Total Volume of Standard Aliquots			2.5 ml
Final Volume of ICS#1 Standard in calibration blank solution (see 6.5)			50 ml

6.8.4 Interference Check Solution#2 (ICS1,2): This solution is a combination of INCK stock #1 (see 6.8.1.1) and INCK stock #2 (see 6.8.2.1). This solution is prepared every two weeks in Calibration Blank Solution (See 6.5).

Table 6.8.4.1 (ICS 1,2)

Analyte	**Initial Concentration (µg/ml)**	**Aliquot (ml)**	**Final Concentration (µg/L)**
Aluminum	1000	2.5	50000
Calcium	1000		50000
Iron	1000		50000
Potassium	1000		50000
Magnesium	1000		50000
Sodium	1000		50000
Phosphorus	1000		50000
Sulfur	1000		50000
Molybdenum	20		1000
Titanium	20		1000
Carbon	2000		100000
Chlorine	10000		500000
Silver	10	0.1	20
Arsenic	10		20
Cadmium	10		20
Cobalt	10		20
Chromium	10		20
Copper	10		20
Manganese	10		20
Nickel	10		20
Zinc	10		20
Total Volume of Aliquots INCK #1(see 6.8.1.1)			2.5 ml
Total Volume of Aliquots INCK #2 (see 6.8.2.1)			0.1
Final Volume of ICS#1 Standard in calibration blank solution (see 6.5)			50ml

7 Sample Collection

7.1 Water samples, liquid waste samples and soil samples are collected in narrow and wide mouth plastic (HDPE) bottles. Water and liquid waste 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. **Please note, samples are keep in a cold storage area between 0℃-6℃ (but never frozen) until ready for analysis.**

8 Calibration

8.1 Calibration Curve

The ICP-MS is calibrated daily using a multipoint calibration curve. All calibration standards are prepared in Calibration Blank Solution (see 6.5). Refer to the calibration standard concentration table below for standard concentrations. Minimum acceptable correlation coefficient is 0.995 using linear regression. All calibration stock standards are prepared from a multi-element mix solution purchased from an outside vendor. Calibration standards are prepared every two weeks.

Table 8.1.1 Calibration Standard Names

Name	Use
6020 Calibration Standard 1 (blank)	Calibration Blank
6020 Calibration Standard 2,3,4,5,6,7	Calibration Standard
6020 ICV	Second Source Calibration
6020 CCC	Initial and Continuing Calibration Check
6020 CCB	Initial and Continuing Calibration Blank

Table 8.1.2 Calibration Standard Concentrations Concentration (ug/L)

Element	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6	Standard 7
Metals	0.00	1	10	25	50	100	200
Ag	0.00	0.20	2.00	5	10.0	20.0	40.0
Se	0.00	5.00	50	125	250	500	1000
Al, Ca, Fe, Mg, Na, K	0.00	20	200	500	1000	2000	4000
Initial concentration of calibration stock standard solution for Metals: 1000µg\ml, Ag: 200µg\ml, Se: 50µg\ml, Al, Ca, Fe, Mg, Na, K: 20000µg\ml. All standards final volume of 50ml using calibration blank solution (see 6.5)							

8.2 Calibration Verification: An ICV, CCB and CCC are analyzed immediately after calibration. A CCC and CCB are also analyzed before each batch, after every ten samples and at the end of an analytical sequence. The LLV is analyzed after the calibration but before analysis of the batch begins (see 2.1.8).

Table 8.2.1 - ICV Concentrations

Element	Concentration in ug/L
Metals	100
Ag	20
Se	500

Al, Fe, Ca, Mg, Na, K	2000
Initial concentration of Second Source Standard for Metals: 1000µg\ml, Ag: 200µg\ml, Se: 50µg\ml, Al, Ca, Fe, Mg, Na, K: 20000µg\ml All standards final volume of 50ml using calibration blank solution (see 6.5)	

Table 8.2.2 - CCC Concentrations

Element	Concentration in ug/L
Metals	100
Ag	20.0
Se	500
Al, Fe, Ca, Mg, Na, K	2000

Note: **The CCC is usually verified using Calibration Standard 6**

9. **Quality Control** - Refer to Table 14.1 for Reporting Limits (PQLs), Table 14.2 for Quality Control Acceptance Criteria, and Table 14.3 for Quality Control Procedures associated with this method.

Table 9.1 - LCS and LCSD Concentrations

Element	Concentration in ug/L
Metals	100
Ag	20
Se	500
Al, Fe, Ca, Mg, Na, K	2000

9.1.1 Analyze the LCS and LCSD with each batch using recovery default control limits of 80-120%. The EPD applies LCS recovery limits to LCSDs. **Note, unless specified, the EPD Laboratory does not validate batch quality based on LCSD recoveries**. By default, the EPD Laboratory precision control limits are 0-20%. See table 9.3.1 for default Quality Assurance Criteria. The LCS and LCSD are usually spiked around the mid-point of the calibration curve with a known amount of each target analyte.

Table 9.2 - MS and MSD Concentration

Element	Concentration in ug/L
Metals	100
Ag	20
Se	500
Al, Fe, Ca, Mg, Na, K	2000

9.2.1 At minimum, 10% of all routine samples must be spiked. Method 6020B requires recovery limits of 75-125% for matrix spike. The EPD Laboratory applies MS recovery limits to MSDs. By default, the EPD Laboratory sets MS/MSD precision control limits to be 0-20%. See table 9.3.1 for default Quality Control Acceptance Criteria. The MS and MSD are usually spiked around the mid-point of the calibration curve with a known amount of each target analyte.

9.3 Default Quality Assurance Criteria for Method 6020B

Table 9.3.1 – Default Quality Assurance Criteria for Method 6020B

QC Type	Analyte	Accuracy (%R) LCL	 UCL	Precision (%RPD)
LCS/LCSD	All metals	80	120	0 - 20
MS/MSD	All metals	75	125	0 - 20

10 Procedure

10.1 Remove sample bottles and Acidified Blank Solution (see 6.2.1) from cold storage area and allow equilibration to room temperature prior to sample preparation and/or analysis.

10.2 Verify each auto pipette by dispensing the volume to be used into a tared pan on the balance (see sections 5.4.1-5.4.1.2).

10.3 All samples are digested by the appropriate digestion method (see section 1.1).

10.4 Start the ICPMS and allow 30 minutes for the instrument to warm up.

10.5 Tune the instrument (see 6.6). Print the tuning reports and include in the data pack. ***Please note, internal standard is not used for tuning***. Record the tuning standard number on run log.

10.6 Calibrate the instrument using multiple level standards (see section 8.1). Make sure probe is in the internal standard solution to perform calibration and for analysis of all samples and standards. The calibration standards are prepared bi-weekly in calibration blank solution (see 6.5).

10.7 Analyze the ICV. All analyte recoveries must be between 90% and 110% of the true value.

10.8 Analyze the CCC and CCB. A CCC and CCB are also analyzed before each batch, after every ten samples, and at the end of an analytical sequence. The CCC and CCB do not count towards the sample total in a batch.

10.9 Analyze the ICS 1 and ICS 1, 2 (see 6.8.3.1 and 6.8.4.1). All monitored analyte recoveries between 80-120%. The absolute value of the un-spiked required analytes must be less than the reporting limit.

10.10 Analyze the LLV (see 2.18). All analyte recoveries between 80-120% of the true value.

10.11 Determine the instrument detection limits (IDLs).

10.11.1 Change the number of repetitions from 3 to 10.

10.11.2 Aspirate the running matrix (see 6.5) and analyze for 10 repetitions.

10.11.3 Calculate the IDL for each element by multiplying the standard deviation (SD) by 3. All anlayte recoveries must be below reporting limit after calculation.

10.11.4 Change the number of repetitions back to 3.

10.12 Analyze the MDL standard (see 2.1.3).

10.13 Analyze the matrix blank (see 6.5). Some batches (such as TCLP) may have more than one matrix blank per batch. All matrix blanks must be analyzed and used for QC purposes.

10.14 Analyze the LCS and LCSD. See table 9.3.1 for acceptance criteria.

10.15 Begin analyzing samples.

10.15.1 A matrix spike must be analyzed for every ten samples in a batch.

10.15.2 A matrix spike duplicate must be analyzed for every ten samples in a batch.

10.15.3 Analyze a serial diluted duplicate (DD) by preparing a 5x dilution of the MS (see 2.1.14). All analytes should agree to within ±20% of the original determination. If not, then a chemical or physical interference must be suspected.

10.15.4 TCLP batches will have a sample duplicate in addition to the spike duplicate. The purpose of the sample duplicate is to provide QC for the tumbling process.

11 Calculations.

11.1 Evaluation of the Linearity of the Initial Calibration Correlation Coefficient of at least 0.995 is required.

11.2 The internal standard calibration is calculated by the instrument software and is documented in the instrument software.

11.3 Mean ($\overline{X}$)

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

11.3.1 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

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

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

11.4.1 Where:

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

11.5 Percent Relative Standard Deviation (%RSD):

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

11.5.1 Where:

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

11.6 Relative Percent Difference (%RPD or RPD):

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

11.6.1 Where:

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

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

11.7 Percent Recovery:

11.7.1 LCS/LCSD:

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

11.7.1. 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 un-spiked sample

$Conc_{expected}$ = Expected concentration

11.8 Sample Concentration

$$Concentration = \frac{CVD_F}{DW}$$

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:

$$\text{Concentration} = \frac{CVD_f}{WW} X \frac{100}{P_S}$$

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

$$\text{Percent Solids} = \frac{DW}{WW} X100$$

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:

$$\text{Concentration} = \frac{CVD_F}{WW}$$

Where C= concentration from instrument in mg/L
V = final digestion volume in L.
D_f= dilution factor
WW = wet weight of sample.

Please note: Aqueous sample results are reported in ug/L, solids are reported in mg/kg dry weight, wastes are reported in mg/kg wet weight.

12 Waste Management

See GA EPD Laboratory SOP – EPD Laboratory Waste Management Standard Operating Procedure. (See SOP reference 13.4)

13 References

13.1 Method 6020B, Inductively Coupled Plasma- Mass Spectrometry, SW-846 Update V, Revision 2- July 2014.
13.2 GA EPD Laboratory SOPs- Initial Demonstration of Capability SOP 6-001, online revision 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 GA EPD Laboratory SOP- Determination of Method Detection Limits SOP, 6-007, online revision.
13.6 GA EPD Laboratory Quality Assurance Plan, online revision.
13.7 GA EPD Laboratory SafetyPlan/Chemical Hygiene Plan & Fire Safety Plan, online revision.
13.8 Methods for the Determination of Metals in Environmental Samples, Supplement I, Environmental Monitoring Systems Laboratory, Office of Research and Development USEPA, Cincinnati, Ohio, 45268, June 1999-EPA/625/R-96/10a.

14 Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 14.1Reporting Limits for Method 6020B TAL ($IMSTL)

		Matrix Aqueous	
Parameter/Method	**Analyte**	**RL**	**Units**
SW846-6020B	Antimony	60	ug/L
	Arsenic	10	ug/L
	Barium	200	ug/L
	Beryllium	5	ug/L
	Cadmium	5	ug/L
	Chromium	10	ug/L
	Cobalt	50	ug/L
	Copper	25	ug/L
	Lead	3	ug/L
	Nickel	40	ug/L
	Selenium	5	ug/L
	Silver	10	ug/L
	Thallium	10	ug/L
	Vanadium	50	ug/L
	Zinc	20	ug/L

Table 14.2 Acceptance Criteria for Method 6020B TAL ($IMSTL)

Method	Analyte	LCS Accuracy Aqueous (%R)	LCSD Precision Aqueous (%RPD)	Matrix Spike Accuracy Aqueous (%R)	Matrix Spike Duplicate Precision Aqueous (%RPD)
SW846-6020B	Antimony	80-120	≤20	75-125	≤20
	Arsenic	80-120	≤20	75-125	≤20
	Barium	80-120	≤20	75-125	≤20

Method	Analyte	LCS Accuracy Aqueous (%R)	LCSD Precision Aqueous (%RPD)	Matrix Spike Accuracy Aqueous (%R)	Matrix Spike Duplicate Precision Aqueous (%RPD)
	Beryllium	80-120	≤20	75-125	≤20
	Cadmium	80-120	≤20	75-125	≤20
	Chromium	80-120	≤20	75-125	≤20
	Cobalt	80-120	≤20	75-125	≤20
	Copper	80-120	≤20	75-125	≤20
	Lead	80-120	≤20	75-125	≤20
	Molybdenum	80-120	≤20	75-125	≤20
	Nickel	80-120	≤20	75-125	≤20
	Selenium	80-120	≤20	75-125	≤20
	Silver	80-120	≤20	75-125	≤20
	Thallium	80-120	≤20	75-125	≤20
	Vanadium	80-120	≤20	75-125	≤20
	Zinc	80-120	≤20	75-125	≤20

Table 14.3Summary of Calibration and QC Procedures for Method EPA 6020B ($IMSTL)

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SW846-6020B	Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Mercury, Molybdenum, Nickel, Potassium, Selenium, Silver, Sodium, Thallium, Vanadium, Zinc	Analyst Initial Demonstration (IDC)	Once per analyst.	2 matrix blanks <RL. Average of 4 LCS recoveries between 80-120%. Recovery of unknown sample between 80%-120%.	Recalculate results, correct problem, and rerun the initial demonstration for those analytes that did not meet criteria.	
		Continuing Demonstration (CDC)	Every 6 Months after IDC.	2 matrix blanks < RL plus 4 LCS recoveries between 80%-120% or Unknown sample between 80%-120% or PE.	Correct the problem and run the CDC for those anlaytes that did not meet criteria.	
		MDL$_{spike}$	Once per batch.	All batch QC must be valid.	Rerun once, if still fails, correct problem and reanalyze affected batch.	
		MDL Study	Annually or whenever major maintenance is performed on the instrument.			

Table 14.3Summary of Calibration and QC Procedures for Method EPA 6020B ($IMSTL)

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SW846-6020B	Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Mercury, Molybdenum, Nickel, Potassium, Selenium, Silver, Sodium, Thallium, Vanadium, Zinc	MDL_{blank} Can be combined with Matrix Blank	Once per analytical batch.	All batch QC must be valid.	Rerun once, if still fails, correct problem and reanalyze affected batch.	
		Analysis of PE sample	Once every 12 months.	All analyte results acceptable per the auditing agency.	Investigation to root cause failure.	
		Instrument Tune	Daily before calibration.	See table 14.4 for manufacturer suggested criteria	If fails, inspect sample introduction system and connections for possible problems and retune instrument.	
		Linear Dynamic Range (LDR)	Annually or whenever major maintenance is performed on the instrument.	Consecutive levels of increasing concentrations must be within 10% of expected value.	Any sample above LDR must be diluted to within LDR parameters.	
		Initial Calibration. Using 7 standards including a blank	Daily initial calibration prior to sample analysis.	Correlation coefficient $\geq$0.995.	Correct the problem and recalibrate	
		Interference Standards (ICS 1) (ICS1,2)	Daily after calibration and once every twelve hours of continuing sample analysis.	Spiked elements required between 80-120% recovery. The absolute value of the other required elements concentrations must be below the reporting level.	Rerun once, if still out of control limits, correct the problem, and recalibrate.	
		IDL Calculation	Daily after calibration.	3x standard deviation of 10 reps < analyte RL.	Rerun once, if still out of control, correct the problem, recalibrate.	
		Initial Calibration Verification (ICV)	Daily after calibration.	All analyte recoveries between 90% and 110%of the true value.	Rerun once, if still out of control correct the problem and recalibrate. .	

Table 14.3Summary of Calibration and QC Procedures for Method EPA 6020B ($IMSTL)

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SW846-6020B	Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Mercury, Molybdenum, Nickel, Potassium, Selenium, Silver, Sodium, Thallium, Vanadium, Zinc	Continuing Calibration Check (CCC).	Daily after calibration, before each batch, after every 10 samples, at the end of each batch and at end of analysis sequence.	All analyte recoveries between 90-110%.	Rerun once, if still out of control, correct the problem, recalibrate, and reanalyzes all samples since the last acceptable CCC.	
		Continuing Calibration Blank (CCB).	Daily after calibration, before each batch, after every 10 samples, at the end of each batch and at end of analysis sequence.	All analyte concentrations must be below the analyte reporting limit.	Rerun once, if still out of control, correct the problem, recalibrate, and reanalyze all samples since the last acceptable CCB.	
		Laboratory Control Sample (LCS).	Once per batch.	All analyte recoveries between 80-120%.	Rerun once, if still out correct the problem, recalibrate. If fails, redigest batch if sample amounts permit, and reanalyze all samples in the batch.	If insufficient sample for redigestion, flag with "J".
		Laboratory Control Sample Duplicate (LCSD) Precision	Once per batch.	≤ 20RPD precision	Rerun once, if still out correct the problem and recalibrate. If fails, redigest batch if sample amounts permit, and reanalyze all samples in the batch.	If insufficient sample for redigestion, flag with "J".
		Laboratory Control Sample Duplicate Recovery	Once per batch.	All analyte concentrations between 80-120%.	Comment sample.	

Table 14.3Summary of Calibration and QC Procedures for Method EPA 6020B ($IMSTL)

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
SW846-6020B	Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Mercury, Molybdenum, Nickel, Potassium, Selenium, Silver, Sodium, Thallium, Vanadium, Zinc	Matrix Blank (MB)	Once per batch.	All analyte concentrations must be RL.	Rerun once, if still out correct the problem and recalibrate. If fails, redigest batch if sample amounts permit, and reanalyze all samples in the batch. Comment report if reanalysis has contamination.	Flag data with "B"
		Matrix Spike (MS)	Every 10 samples.	All analyte recoveries between 75-125%.	Rerun once. If recovery exceeds QC limits but CCC, CCB, ICV, LCS and LCSD are acceptable, matrix effect is suspected.	Comment report.
		Matrix Spike Duplicate. (MSD)	Every 10 samples.	All analyte recoveries between 75-125%. MSD precision ≤ 20.	Rerun once. If recovery exceeds QC limits, matrix effect is suspected.	Comment report.
		Dilution Test: dilute one matrix spike per batch fivefold with matrix blank.	Once per batch	Original and diluted results must be within 20 RPD of each other.	Rerun once. If RPD >20 matrix interference must be suspected.	Comment data about suspected matrix interference.
		Internal Standards	Every sample and standard except tuning.	All internal standard recoveries must be between 60%-125%.	Dilute and reanalyze.	

Table 14.4Tuning Criteria Method 6020B ($IMSTL)

Mass 220 counts	<100
Cerium Oxide ratio	<3%
Ba^{++} ratio	<5%
Mass calibration of $^{24, 25, 26}$Mg and $^{206, 207, 208}$Pb	± 0.1 AMU of unit mass.
RSD of 5 replicates of a 10 ug/L solution of ^{9}Be, ^{24}Mg, ^{59}Co, ^{115}In, and ^{208}Pb	< 5
^{24}Mg counts of a 10 ug/L solution	>5,000 CPS

Table 14.4Tuning Criteria Method 6020B ($IMSTL)

^{115}In counts of a 10 ug/L solution	>10,000 CPS
^{208}Pb counts of a 10 ug/L solution	>7,500 CPS
Peak width of $^{24, 25, 26}$Mg and $^{206, 207, 208}$Pb	Between 0.6 and 0.8 AMU at 10% peak height.

Appendix A for Method 6020 Determination of Trace Metals in Waters and Wastes by ICPMS

Table A.1 TAL ($IMSTL)

QC Type	Analyte	Accuracy (%R) LCL UCL	Precision (%RPD)
LCS/LCSD	**Antimony**	**85 - 115**	**15**
	Arsenic	**85 - 115**	**15**
	Barium	**85 - 115**	**15**
	Beryllium	**85 - 115**	**15**
	Cadmium	**85 - 115**	**15**
	Chromium	**85 - 115**	**15**
	Cobalt	**85 - 115**	**15**
	Copper	**85 - 115**	**15**
	Lead	**85 - 115**	**15**
	Molybdenum	**85 - 115**	**15**
	Nickel	**85 - 115**	**15**
	Selenium	**85 - 115**	**15**
	Silver	**85 - 115**	**15**
	Thallium	**85 - 115**	**15**
	Tin	**85 - 115**	**15**
	Vanadium	**85 - 115**	**15**
	Zinc	**85 - 115**	**15**
MS/MSD	**Metals(Antimony-Zinc)**	**75 - 125**	**15**
Control Limits are static by EPA Method/EPD Lab default. Static Limits are generated for trend monitoring purposes.			