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Method IO-3.5 Determination of Metals in Ambient Particulate Matter Using ICP-MS

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1 Scope and Application

1.1 Method IO 3.5 is used to determine the elemental metal components in ambient air particulate matter. Filters are numbered, field deployed, sampled and returned to the laboratory for analysis by inductively coupled plasma mass spectrometry (ICP-MS). The extraction procedure is accomplished by following Inorganic Compendium Method IO.3.1. In the procedure, a measured strip is cut from the filter, digested and analyzed. Analytes are quantitated by standard calibration.

1.2 This procedure is restricted to use by an analysts experienced in the operation of Inductively Coupled Plasma Mass Spectrometers and who have completed the requirements of the initial demonstration SOP (See SOP reference 13.6) prior to analyzing samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GA EPD Chemical Hygiene Plan for additional information regarding chemicals required by this method. (See SOP reference 13.8)

Compound	CAS No.
Antimony	7440-36-0
Arsenic	7440-38-2
Beryllium	7440-41-7
Cadmium	7440-43-9
Chromium	7440-47-3
Cobalt	7440-48-4
Lead	7439-92-1
Manganese	7439-96-5
Nickel	7440-02-0
Selenium	7782-49-2

2 Definitions

2.1 Refer to Chapter 3 and 4 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions.

2.2 Primary Source (PS) - A standard that is used to make up the calibration points of a curve.

2.3 Secondary Source (SS) - A standard made from a manufacturer with a different lot number from that of the primary source.

2.4 Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the correctness of the primary source calibration curve. The ICV is usually run at a level equal to the Laboratory Control Sample (LCS) or the mid-point of the calibration curve.

2.5 Reagent Blank (RB)/Method Blank (MB)- An aliquot of 3% HNO_3 and 1.5% HCL (see 6.6) that is carried through the entire procedure, with the exception that a filter strip from a clean filter is not required per the reference method. For purposes of this SOP, the RB will be referred to as the Method Blank (MB). The RB is equivalent to the MB defined in the EPD Laboratory Quality Assurance Plan, Section 3 (see SOP reference 13.5).

2.6 Lab Blank (LB)/Filter Blank (FB) - A clean 1" X 8" filter strip that is carried through the entire digestion process using the calibration blank solution (see 6.6). For the purposes of this SOP, the LB will be referred to as the FB.

2.7 Reagent Blank Spike (RBS)- The RBS as defined in the October 2016 Technical Assistance Document (TAD), will be referred to as the Reagent Spike Control (RSC) for the purposes of this SOP. An aliquot of calibration blank solution (see 6.6) that is spiked with a known amount of the analytes and carried through the entire procedure, with the exception that a filter strip from a clean filter is not required.

2.8 Laboratory Control Sample (LCS)- An aliquot of calibration blank solution (see 6.6) that is spiked with a known amount of the analytes and carried through the entire procedure using the same clean 1" X 8" strip from the same filter as the FB.

2.9 Laboratory Control Sample Duplicate (LCSD)- For the purposes of calculating laboratory precision, an LCS duplicate is carried through the entire procedure as described in 2.8.

2.10 Method Detection Limit Standard (MDLs or ML)- A 1" X 8" strip from the same clean filter as the FB and spiked at a concentration below the lowest point of the calibration curve for that analyte, and carried through the entire procedure using an aliquot of calibration blank solution (see 6.6).

2.11 Initial Detection Limit Study (IDL)- Analyzed daily after calibration. Ten replicate readings of the calibration blank solution (see 6.6). Acceptance criteria: Analyte concentration <MDL.

2.12 Initial Calibration Blank (ICB)-An aliquot of calibration blank solution (see 6.6) also used as the 0 point on the calibration curve and to verify the instrument is continuously free from contamination.

2.13 Continuing Calibration Blank (CCB)-An aliquot of calibration blank solution (see 6.6) used to verify the instrument is continuously free from contamination.

2.14 Internal Standard (ISTD)-Equal Amounts of non-target elements added prior to analysis to blanks, standards and samples at a known concentration. The instrument responses to the internal standard are monitored to assess overall instrument performance.

2.15 Continuing Calibration Check (CCC)-A standard usually at mid-curve used to verify the accuracy during the course of the analytical run.

2.16 High Standard (HS)-A standard at the highest point on the calibration curve used to verify the accuracy at the top end of the calibration curve.

2.17 Duplicate Sample (DS)-A duplicate strip cut from a collected field sample and carried through the entire digestion process (evaluates precision of the sample result and digestion process).

2.18 Duplicate Sample Collection- Samples collected simultaneously using a collection system (i.e., two separate samples through the same sampling system at the same time), and then analyzing the samples and comparing the results obtained.

2.19 Linear Dynamic Range (LDR) - The concentration range over which the analytical working curve remains linear.

2.20 Interference Check Standards (ICS) - Standards analyzed to show the instrument is free of interferences.

2.21 Field Sample- A filter collected outside of the laboratory for analysis.

2.22 Collocated (Field Sample Duplicates) - Samples that are collected simultaneously using two separate sampling systems, and then analyzing the samples and comparing the results obtained. This approach provides information on "Inter-system" variability and field collection quality. The EPD will designate the first of these samples as the "Primary Sample" and the second as the "Collocated Sample (QA) or Duplicate." The samples are analyzed by the Metals Laboratory and results compared. This approach monitors field collection quality.

2.23 Replicate analysis- The analysis of one discrete sample multiple times. This approach provides information on "Analytical" variability.

2.23.1 Replicate Sample (RS) - One field sample analyzed multiple times.

2.24 Temperature Blank- A digestion tube filled with water to monitor the temperature of the wells inside the hotblock.

2.25 Quartz Fiber Filter (QFF)- 8inch X 10inch high volume filter with a total collection volume of flow at $1627m^3$.

2.26 Teflon Filter- 47mm low volume filter with a total collection volume of flow at $24.05m^3$.

3 Interferences

3.1 Isobaric elemental interferences: isotopes of different elements which form singly or doubly charged 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.

3.1.1 The EPD Laboratory uses multi-element standards for calibration, verification and quality assurance solutions, and samples so as to continually monitor 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's 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. Rinse and analysis delay times are used to eliminate these interferences. Continuing calibration blanks are used to document the absence of memory effects throughout the run.

4 Safety

Refer to the EPD Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision. (See SOP reference 13.10).

5 Apparatus and Equipment

5.1 ICPMS- Perkin Elmer ELAN 9000, NexION 1000 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 7 to 240 AMU and must allow for the use of internal standard.
5.2 High purity argon gas supply
5.3 50 ml HDPE digestion tubes- with threaded caps for extraction and storage.
5.4 Assorted HDPE centrifuge tubes
5.5 Electronic Balance- Mettler PB-303 or equivalent, with a weight range of 0-310g or greater, and accurate to ± 0.001g
5.6 Electronic Balance-Mettler PM-6 or equivalent, with a weight range of 0-6000g or greater, and accurate to ±1g.
5.7 Air Displacement Pipettes capable of delivering volumes between 0.001 mL and 1 mL with an assortment of tips. Air displacement pipettes must be professionally calibrated every six months. Air displacement pipettes and auto-pipettes 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, 1ml of water is equal to 1g. Pipettes must be capable of ± 2.5% accuracy and with 2.5% precision Relative Standard Deviation (RSD).
5.7.1.2 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.
5.8 Assorted HDPE certified labware items.
5.9 Assorted certified volumetric labware.
5.10 Non-metallic paper or pizza cutter.
5.11 Plastic template for cutting
5.12 Hot Block Digesters- Environmental Express modes SC154, SC181 or equivalent capable of maintaining a temperature of at least 95℃.
5.13 Disposable polypropylene ribbed watch glasses (for heated block extraction)
5.14 Plastic tweezers.
5.15 Disposable Syringes (available from Environmental Express)
5.16 Disposable10 ml 0.45µm Syringe Filters (must be lead free)
5.17 Lint Free cleaning tissues.
5.18 Rubber Gloves- Latex and powder free.
5.19 Plastic Digestion Rack.

6 Reagents and Standards

All reagents and standards that are prepared must be logged into the standard log notebook, the standard number must be written on the sample prep log, and the container must be labeled with the standard number and the expiration date.

6.1 Reagent water: 18MΩ water. Purified water does not contain any measurable quantities of target elements or interfering elements for each element of interest. Milli-Q water has a resistivity of 18.2 [MΩ.cm] @ 25°C and TOC of 50 µg/L or less. The resistivity and TOC must be checked and recorded in the Milli-Q water log prior to use.

6.2 Concentrated Nitric Acid (HNO_3) - 67-70% trace metals grade equivalent or better.

6.3 Concentrated Hydrochloric Acid (HCL) - Trace metals grade equivalent or better.

6.4 Extraction solution (5.55% Nitric Acid, 3% Hydrochloric Acid): Inside a vented fume hood, add 500 ml of 18.2 MΩ reagent (see 6.1) to a 2 L HDPE container. Slowly add 55.5 ml of concentrated Nitric Acid (see 6.2) and 30 ml concentrated Hydrochloric Acid (see 6.3) with swirling (caution: solution will get very warm). Allow solution to cool to room temperature, then dilute to 1000ml with 18.2 MΩ water (see 6.1). Cap tightly and invert several times to mix solution.

6.5 1% v/v Nitric Acid Solution - Inside a vented fume hood, add 1000ml of 18.2 MΩ reagent water (see 6.1) to a 2 L HDPE container. Slowly add 20 ml of concentrated HNO_3 (see 6.2) with swirling (caution: solution will get very warm). Allow solution to cool to room temperature, then dilute to 2000ml with 18.2 MΩ reagent water (see 6.1). Cap tightly and invert several times to mix solution.

6.6 Calibration Blank Solution (3% HNO_3 and 1.5% HCL) - Inside a vented fume hood, add 500 ml of 18.2 MΩ reagent water (see 6.1) to a 2 L HDPE container. Slowly add 30ml of concentrated Nitric Acid (see 6.2) and 15ml of concentrated Hydrochloric Acid (see 6.3) with swirling (caution: solution will get very warm). Allow solution to cool to room temperature, then dilute to 1000 ml with 18.2 MΩ water (see 6.1). Cap tightly and invert several times to mix solution.

6.7 10% Nitric Acid Solution- Inside a vented fume hood, add 1000ml of 18.2 MΩ reagent water (see 6.1) to a 2L HDPE container. Slowly add 200 ml of concentrated HNO_3 (see 6.2) with swirling (caution: solution will get very warm). Allow solution to cool to room temperature, then dilute to 2000ml with 18.2 MΩ water (see 6.1). Cap and invert several times to mix the solution. This solution is used for cleaning labware if not disposable.

6.8 Primary Source (PS) Standard Stock Solutions:

6.8.1 PS Vendor Calibration Stock Solutions: Table 6.8.1.1 and Table 6.8.1.2

Table 6.8.1.1 – PS Vendor Calibration Stock A Concentration

Analyte	**Concentration (µg/ml)**
Antimony	**1000**
Arsenic	**1000**
Beryllium	**1000**
Cadmium	**1000**
Chromium	**1000**
Cobalt	**1000**
Lead	**1000**
Manganese	**1000**
Nickel	**1000**

Table 6.8.1.2- PS Vendor Calibration Stock B Concentration	
Analyte	**Concentration (µg/ml)**
Selenium	**5000**

6.8.1.3 *Note: To distinguish between standard stocks used for calibration and those used for spiking, vendor standards used by the EPD Laboratory for this analysis typically have dyes added to primary calibration stocks. Stocks intended for spiking are typically not colorized.*

6.8.2 PS Intermediate Calibration Stock Solution: Prepared every two months from vendor calibration stock solution A and B in calibration blank solution (see 6.6).

Table 6.8.2.1- PS Intermediate Calibration Stock Solution in Calibration Blank Solution. (see 6.6)			
Analyte	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration
Antimony	1000	0.50 Solution A	10 µg/ml
Arsenic	1000		
Beryllium	1000		
Cadmium	1000		
Chromium	1000		
Cobalt	1000		
Lead	1000		
Manganese	1000		
Nickel	1000		
Selenium	5000	0.50 solution B	50µg/ml
Total volume of Standard Aliquots			1.0 ml
Final Volume of PS Calibration Stock Solution A and B in calibration blank Solution (see 6.6)			50 ml

6.9 Calibration Standards:

6.9.1 The ICP-MS is calibrated daily using a multipoint calibration curve with a minimum of one blank and six standards. The calibration curve is prepared bi-weekly in calibration blank solution (see 6.6). Refer to table 6.8.1.1 for calibration stock standard concentration levels. Minimum acceptable correlation coefficient is 0.995 using linear regression.

Table 6.9.1.1- IO-3.5 Calibration Curve Standard Concentration Level							
Analyte	**Level 1 (µg/L)**	**Level 2 (µg/L)**	**Level 3 (µg/L)**	**Level 4 (µg/L)**	**Level 5 (µg/L)**	**Level 6 (µg/L)**	**Level 7 (µg/L)**
Antimony	0	5.00	10.0	25.0	50.0	100	200
Arsenic	0	5.00	10.0	25.0	50.0	100	200

Table 6.9.1.1- IO-3.5 Calibration Curve Standard Concentration Level

Analyte	Level 1 (µg/L)	Level 2 (µg/L)	Level 3 (µg/L)	Level 4 (µg/L)	Level 5 (µg/L)	Level 6 (µg/L)	Level 7 (µg/L)
Beryllium	0	5.00	10.0	25.0	50.0	100	200
Cadmium	0	5.00	10.0	25.0	50.0	100	200
Chromium	0	5.00	10.0	25.0	50.0	100	200
Cobalt	0	5.00	10.0	25.0	50.0	100	200
Lead	0	5.00	10.0	25.0	50.0	100	200
Manganese	0	5.00	10.0	25.0	50.0	100	200
Nickel	0	5.00	10.0	25.0	50.0	100	200
Selenium	0	25	50	125	250	500	1000

6.9.1.2 Should alternate concentrations of vendor standards be required due to availability, adjust aliquots or final concentrations as needed to meet the concentrations in table 6.9.1.1.

6.9.2 Calibration Levels Preparation:

6.9.2.1 Calibration standards are prepared bi-weekly using the addition of aliquots from PS Intermediate Stock Solution (see 6.9.2.1.1) in calibration blank solution (see 6.6). The final volume is 50 ml and diluted to volume as follows:

Table 6.9.2.1.1 – Calibration Level Spike Volumes into 50 ml of calibration blank solution (see 6.6)

Calibration Level	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Aliquot of PS Intermediate Calibration Stock Solution (see 6.8.2.1)	**0 ml**	**0.025 ml**	**0.050 ml**	**0.125 ml**	**0.250 ml**	**0.500 ml**	**1.00 ml**
Final Concentration	**0 µg/L**	**5.00 µg/L**	**10.0 µg/L**	**25.0 µg/L**	**50.0 µg/L**	**100 µg/L**	**200 µg/L**
Bring all calibration levels up to 50 ml using Calibration Blank Solution (see 6.6)							

6.9.2.2 Note, higher level calibration standards at levels 5, 6 and 7 maybe used to prepare lower level calibration standards 2, 3 and 4.

6.10 <u>Secondary stock Solution (SS):</u> (Combination of Tables 6.10.1 and 6.10.2)

Table 6.10.1 SS Vendor Stock Solution A Concentration	
Analyte	**Concentration (µg/ml)**
Antimony	**1000**
Arsenic	**1000**
Beryllium	**1000**
Cadmium	**1000**
Chromium	**1000**
Cobalt	**1000**
Lead	**1000**
Manganese	**1000**
Nickel	**1000**

Table 6.10.2- SS Vendor Stock Solution B Concentration	
Analyte	**Concentration (µg/ml)**
Selenium	**5000**

6.10.3 *Note: To distinguish between standard stocks used for calibration and those used for spiking, vendor standards used by the EPD Laboratory for this analysis typically have dyes added to primary calibration stocks. Stocks intended for spiking are typically not colorized.*

6.10.4 SS Intermediate Stock Solution: Prepared every two months from vendor calibration stock solution A and B in calibration blank solution (see 6.6).

Table 6.10.4.1- SS Intermediate Stock Solution in Calibration Blank Solution. (see 6.6)			
Analyte	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration
Antimony	1000	0.50 ml Solution A	10 µg/ml
Arsenic	1000		
Beryllium	1000		
Cadmium	1000		
Chromium	1000		
Cobalt	1000		
Lead	1000		
Manganese	1000		
Nickel	1000		
Selenium	5000	0.50 ml Solution B	50µg/ml

Total volume of Standard Aliquots	1.0 ml
Final Volume of SS Stock Solution A and B	50 ml

6.10.4.1.1 The ICV is prepared at the following concentrations in ug/L every two weeks.

Table 6.10.4.1.2 – SS ICV Standard Solution in Calibration Blank Solution (see 6.6)

Analyte	**Initial Concentration (µg/ml)**	**Aliquot (ml)**	**Final Concentration µg/L**
Antimony	10	**0.50 ml**	100
Arsenic	10		100
Beryllium	10		100
Cadmium	10		**100**
Chromium	10		100
Cobalt	10		100
Lead	10		100
Manganese	10		100
Nickel	10		100
Selenium	50		500
Total Volume of Standard Aliquots			**0.5 ml**
Final Volume of SS Intermediate Stock Solution in Calibration Blank Solution (see 6.6)			**50 ml**

6.11 Tuning Standard Solutions: Tuning Intermediate Stock Solutions: Single element intermediate standards for Magnesium, Barium, Beryllium, Cerium, Cobalt, Indium, Lead and Rhodium are prepared every two months from single element vendor stocks, usually at 1000 µg/ml and diluted with 1% Nitric Acid Solution (see 6.5) to a concentration of 10 µg/ml.

Table 6.11.1. – Tuning Intermediate Stock Solutions in 1% Nitric Acid Solution (see 6.5)

Single Element Standard	**Initial Vendor Stock Concentration (µg/ml)**	**Aliquot (ml)**	**Final Concentration (µg/ml)**	**Final Volume in 1% Nitric Acid Solution (ml)**
Magnesium	1000	0.50	10	50
Barium	1000	0.50	10	50
Beryllium	1000	0.50	10	50
Cerium	1000	0.50	10	50
Cobalt	1000	0.50	10	50
Indium	1000	0.50	10	50
Lead	1000	0.50	10	50

Table 6.11.1. – Tuning Intermediate Stock Solutions in 1% Nitric Acid Solution (see 6.5)					
Single Element Standard	**Initial Vendor Stock Concentration (µg/ml)**	**Aliquot (ml)**	**Final Concentration (µg/ml)**	**Final Volume in 1% Nitric Acid Solution (ml)**	
Rhodium	1000	0.50	10	50	
Total Volume of Standard Aliquots					4.0 ml
Final Volume of Tuning Solution in 1% Nitric Acid Solution					50 ml

6.11.2 Tuning Solution: Prepared every two weeks from the individual element Tuning Intermediate Stock Solution (see 6.11.1) in 1%Nitric acid solution (see 6.5)

Table 6.11.2.1. – Tuning Solution in 1% Nitric Acid Solution for Elan 9000 ICPMS			
Analyte	**Initial Concentration (µg/ml)**	**Aliquot (ml)**	**Final Concentration (µg/ml)**
Magnesium	10	0.050 ml	0.010
Barium	10		0.010
Beryllium	10		0.010
Cerium	10		0.010
Cobalt	10		0.010
Indium	10		0.010
Lead	10		0.010
Rhodium	10		0.010
Total Volume of Standard Aliquots			0.050 ml
Final Volume of Tuning Solution in 1% Nitric Acid Solution (see 6.5)			50 ml

Table 6.11.2.2. – Tuning Solution in 1% Nitric Acid Solution for NexION 1000 ICPMS			
Analyte	**Initial Concentration (µg/ml)**	**Aliquot (ml)**	**Final Concentration (µg/ml)**
Magnesium	10	0.050 ml	0.0010
Barium	10		0.0010
Beryllium	10		0.0010
Cerium	10		0.0010
Cobalt	10		0.0010

Table 6.11.2.2. – Tuning Solution in 1% Nitric Acid Solution for NexION 1000 ICPMS

Analyte	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)
Indium	10		0.0010
Lead	10		0.0010
Rhodium	10		0.0010
Total Volume of Standard Aliquots			0.050 ml
Final Volume of Tuning Solution in 1% Nitric Acid Solution (see 6.5)			500 ml

6.12 Internal Standard (ISTD) Solutions:

6.12.1 ISTD Intermediate Solution #1: Prepared every two months from powdered Lithium-$^{6}Li_2$ carbonate, 95 atom %^{6}Li ($^{6}Li_2CO_3$) in 1% Nitric Acid Solution (see 6.5).

Table 6.12.1.1 – ISTD Intermediate Solution #1 in 1% Nitric Acid

Analyte	Initial Concentration	Aliquot (g)	Final Concentration (µg/ml)
Lithium-6	Neat	0.25	2000
Total Volume of Standard Aliquots			0.25 g
Final Volume of ISTD Intermediate Solution #1 in 1% Nitric Acid Solution (see 6.5)			20 ml

6.12.1.2 Note: Invert several times to mix until solution is completely dissolved. This may take several minutes.

6.12.2 ISTD Intermediate Solution #2: Prepared every two months from Lithium-6 (see table 6.12.1.1) and 1000 **µg/ml** vendor stock solutions of Germanium, Indium, Lutetium and Scandium in 1% nitric acid solution (see 6.5).

Table 6.12.2.1 – ISTD Intermediate Solution #2 in 1% Nitric Acid Solution

Analyte	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)
Germanium	1000	0.50	10
Indium	1000	0.50	10

Table 6.12.2.1 – ISTD Intermediate Solution #2 in 1% Nitric Acid Solution

Analyte	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)
Lutetium	1000	0.50	10
Scandium	1000	0.50	10
Lithium-6	2000	0.50	20
Total Volume of Standard Aliquots			2.5 ml
Final Volume of ISTD Intermediate Solution #2 in 1% Nitric Acid solution (see 6.5)			50 ml

6.12.3 ISTD Solution: Prepared every two weeks from ISTD Intermediate Solution #2 (see 6.12.2.1) in 1% Nitric Acid Solution (see 6.5).

Table 6.12.3.1 – ISTD Solution #2 in 1% Nitric Acid Solution

Analyte	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/L)
Germanium	10	2.0	10
Indium	10		10
Lutetium	10		10
Scandium	10		10
Lithium-6	20		20
Total Volume of Standard Aliquots			2.0 ml
Final Volume of ISTD Solution #2 in 1% Nitric Acid Solution (see 6.5)			2000 ml

6.12.4 Internal Standard Solution for NexION 1000: To a 500ml clean Teflon volumetric class A flask, add 0.125ml of 1000µg/ml single element vendor stock standards of Germanium (Ge), Indium (In), Lutetium (Lu) to 1% Nitric Acid Solution. In addition, add 2.50ml of 1000µg/ml Scandium (Sc) and 0.0625ml of Lithium^6 (See 6.6.1). Bring to volume with 1% Nitric Acid Blank Solution. The final concentration of Ge, In, Lu and Li is 0.0250µg/ml. The final concentration of Sc is 5.0µg/ml.

6.13 Vendor Stock Spiking Solution: (Bottles A and B) Spike straight from bottle.
The stock solutions are not colored (see 6.8.1.3).

Table 6.13 Vendor Stock Spiking Solution Concentration	
Analyte	**Concentration (µg/ml)**
Antimony	50
Arsenic	50
Beryllium	50
Cadmium	50
Cobalt	50
Lead	50
Manganese	50
Nickel	50
Selenium	50

6.14 Interference Check Solution Standards: Prepared every two weeks from vendor purchased multi-element stock standards.

6.14.1 Interference Check Solution #1 (Purchased Solution)

Table 6.14.1.1 – Interference Check Solution #1	
Analyte	**Concentration (µg/ml)**
Aluminum	1000
Calcium	1000
Iron	1000
Potassium	1000
Magnesium	1000
Sodium	1000
Phosphorus	1000
Sulfur	1000
Molybdenum	20
Titanium	20
Carbon	2000
Chlorine	10000

6.14.2 Interference Check Solution #2 (Purchased Solution)

Table 6.14.2.1 Interference Check Solution #2	
Analyte	**Concentration (µg/ml)**
Silver	10

Table 6.14.2.1 Interference Check Solution #2	
Analyte	**Concentration (µg/ml)**
Arsenic	10
Cadmium	10
Cobalt	10
Chromium	10
Copper	10
Manganese	10
Nickel	10
Zinc	10

6.14.3 Interference Check Solution (ICS #1) Standard: This solution is prepared every two weeks from Interference Check Solution #1 (see 6.14.1) in calibration blank solution (see 6.6)

Table 6.14.3.1 ICS #1 Standard			
Analyte	**Initial Concentration (µg/ml)**	**Aliquot (ml)**	**Final Concentration (µg/L)**
Aluminum	1000	2.5	50,000
Calcium	1000		50,000
Iron	1000		50,000
Potassium	1000		50,000
Magnesium	1000		50,000
Sodium	1000		50,000
Phosphorus	1000		50,000
Sulfur	1000		50,000
Molybdenum	20		1000
Titanium	**20**		1000
Carbon	**2000**		100,000
Chlorine	**10,000**		500,000
Total Volume of Standard Aliquots			2.5 ml
Final Volume of ICS #1 Standard in calibration blank solution			50 ml

6.14.3.1.1 Note: Molybdenum is the only analyte monitored for ICS #1

6.14.4 Interference Check Solution (ICS #1-2) Standard: This solution is prepared every two weeks from Interference Check Solution #1 (see 6.14.1) and Interference Check Solution #2 (see 6.14.2) in calibration blank solution (see 6.6) by adding 2.5ml of Interference Check Solution 1 and 0.1ml of Interference Check Solution 2. The final volume is 50ml.

6.14.4.1.1 Note: The following analytes are monitored for standard ICS #1-2: Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Lead Manganese, Nickel, Selenium and Molybdenum.

6.15 Calibration Blanks

6.15.1 The Initial calibration Blank (ICB) and the Continuing Calibration Blank (CCB): The ICB and the CCB are Calibration Blank Solution (see 6.6) analyzed as standards. Internal Standards are added by the instrument.

6.15.2 Rinse Blank: 18.2 MΩ water combined with internal standard solution (see 6.12.3.1).

6.15.2.1 Note: The instrument performs a 1 to 2 minute rinse cycle after each reading using Rinse Blank (see 6.15.2).

6.16 Continuing Calibration Check (CCC):

6.16.1 Use 100 µg/L standard (level 6). See Table 6.9.2.1.1

7 Sample Collection

7.1 Quartz Fiber Filter

7.1.1 Air samples are collected on 8" X 10" quartz fiber filters (QFF), folded lengthwise in half with the particulate matter inward and placed into a protective manila envelope or folder.

7.2 Teflon Filter

7.2.1 Air samples are collected on a Teflon Filter and placed in protective non-metallic cassettes.

7.3 No preservation of the filters is required. Following collection, filters should be stored at ambient conditions and must be digested and analyzed within 180 days.

7.4 Sample filters are pre-logged into LIMS prior to field collection. Exposed sample filters are received by the EPD Shipping and Receiving Dept. Appropriate field data and test codes are added into the LIMS system. Samples are then transferred to the EPD Metals Laboratory along with the appropriate paperwork.

8 Calibrations

8.1 Ignite the plasma flame and wait at least one 30 minutes for the instrument to warm up and equilibrate before tuning.

8.2 Inspect tubing, sample introduction system and check oil levels.

8.3 A waste carboy should be labeled correctly with a hazardous waste sticker that includes the name and address of the laboratory, room number, EPA Identification Number/Manifest Document Number (GA D981264237), accumulation start date and EPA waste Numbers. The type of waste should also be entered on this sticker (for example, dilute nitric and hydrochloric acid along with standards). If the carboy is more than half full it should be replaced before calibration and analysis begins.

8.4 Aliquots of tuning and calibration standards are transferred to 50 ml centrifuge tubes (see 5.4) before analysis on the instrument.

8.5 Daily Tuning of the instrument:

8.5.1 Print Mass Calibration report. Criteria: Between 0.6 and 0.8 Measured Peak Width.

8.5.2 Daily, prior to calibration for analysis of samples, the mass spectrometer must be tuned. The Tuning Solution (see table 6.11.2.1) is analyzed (5 replicates) and the instrument tuned as recommended by the instrument manufacturer. The tune must meet the criteria listed in Table 14.3 before calibration or analysis can begin.

8.5.2.1 No internal standards are added to the Tuning Solution.

8.6 After tuning allow the instrument to rinse for 5 minutes using 18MΩ (see 6.1) water before proceeding.

8.7 Initial Calibration:

8.7.1 Calibration Curve- A seven point calibration curve is performed for (see Table 6.9.2.1.1 for standard concentrations). The calibration system uses traceable, certified standards. The calibration is an internal standard calibration and must be prepared bi- weekly. The calibration is performed using the same method parameters as used to analyze samples.

8.7.1.2 The correlation coefficient is a least squares, internal standard calibration with a correlation coefficient r of ≥ 0.995 ($r^2 \geq 0.990$) or greater. The correlation coefficient is calculated by the instrument software, as is the calibration itself.

8.8 Calibration Verification:

8.8.1 Immediately following initial calibration, the ICV standard (see 6.10.4.1.2) must be analyzed to confirm the calibration. If the ICV fails, rerun once. If fails again, terminate analysis, correct the problem and restart analysis with calibration.

8.8.2 Following the ICV is the ICB (see 6.15.1). The ICB is Calibration Blank Solution (see 6.6.) If the ICB fails, rerun once. If fails again, terminate analysis, correct the problem and restart analysis with calibration.

8.9 High Standard Verification (HS) Check:

8.9.1 Immediately following the ICB, the HS is verified using calibration standard level 7 (see table 6.9.2.1.1). See Table 14.2 for acceptance criteria.

8.10 Continuing Calibration Verification (CCC and CCB):

8.10.1 Following the Interference check standards, the CCC and CCB are verified. It is recommended that the IDL standard (see 2.11) and MDL (ML) (see 2.10) standard follow. The CCC and CCB must also be verified after every tenth sample and at the end of every analytical batch.

8.10.1.1 Note: The ending CCC must be analyzed following the CCB.

8.11 Ongoing MDL Study (Continuous):

8.11.1 An MDLs (ML) Spike (spiked below the lowest point on the calibration curve) must be analyzed with each analytical batch to perform and ongoing MDL study. All batch QC must be valid to report this result.

8.11.2 An MDL_b (MDL blank which is equivalent to the MB) must be analyzed once per analytical batch to perform an ongoing MDL study. All batch QC must be valid to report this result.

9 Quality Control

9.1 Refer to Appendix A Table A.1 for MDLs and Reporting Limits (RL). For Quality Assurance criteria and Quality Control procedures associated with this method, refer to Appendix B Table B.1.

9.2 MDL studies: An MDL study is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

9.2.1 An MDL study must be determined initially on a new instrument prior to results being reported. A total of seven MDL_{blanks} and seven MDL_{spikes} must be digested and analyzed over three non-consecutive days. Please note: the digestion must include 3 non-consecutive days as well as the analysis.

9.2.2 MDL Studies (see Appendix A Table A.1) are performed on a continuing basis with each analytical batch of samples. The Filter Blank (FB) will be entered in Labworks and the MDL_{sample} will be entered into Labworks using the $ML test code. The instrument used for the MDL_{blank} and MDL_{sample}

will be selected using the prefix INSTR followed by the instrument number. This report is generated annually. Please note: the MDL_{sample} is below the lowest point in the calibration curve for this method.

9.2.2.1 Tier 1 NATTS analytes not meeting Cancer Risk MDLs (See Table 9.2.2.1.1) must include on the corrective action report for those analytes.

Table 9.2.2.1.1 Tier 1 NATTS MDL Cancer Risk

Method	Analyte	Cancer Risk 10^{-6} µg/m^3 (As of 12/2017)	Non-cancer Risk µg/m^3 (As of 12/2017)	MDL µg/Filter
IO-3.5	Arsenic	0.00023		See Appendix A
	Beryllium	0.00042		See Appendix A
	Cadmium	0.00056		See Appendix A
	*Lead	_	0.015	See Appendix A
	*Manganese	_	0.03	See Appendix A
	Nickel	0.0021		See Appendix A
***No cancer risk required for these Tier 1 analytes, use non-cancer risk for requirement**				

9.2.2.2 Alternately, an MDL study must be performed annually or if the instrument maintenance warrants a new MDL study (See SOP reference 13.9). In this case, refer to section 9.2.1.

9.3 See SOP reference 13.6 for training and certifications.

9.3.1 For Initial Demonstrations of Capability (IDC), the EPD Laboratory has set a recovery range of 80-120% (Antimony 75-125%) and a 20% RSD is required for RSD replicates.

9.3.2 The EPD laboratory uses the most current accuracy and precision control ranges in use for Continuing Demonstrations of capability (CDC). If 4 replicates are performed (as opposed to two LCS/LCSD pairs) a 20% RSDs is required.

9.4 Record all reagents used, volumes, standards or lot numbers, times and sample IDs on the digestion log sheet (see figure 2). 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.

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

9.6 <u>Linear Dynamic Range (LDR) study:</u>

9.6.1 Performed on an annual basis or whenever a significant change in the instrument response is expected (e.g. detector change).

9.7 <u>Control Limits:</u> (See SOP reference 13.7 for control charting procedures)

9.7.1 Since not required by the EPA method IO-3.5, the GA EPD Laboratory chooses to use the method default limits for sample validation. Control charts will be pulled annually for trend monitoring purposes.

9.7.2 The LCS default recovery control limits for EPA Method IO-3.5 are 75-125% for Antimony and for all other analytes 80-120%. 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.

9.7.3 The default precision for LCS and LCSD pairs is 20%.

9.7.4 The default recovery for Matrix spike (MS) and Matrix Spike Duplicates (MSD) is 80-120%.

9.7.5 The default precision for the MS and MSD pair is 20% RPD. The EPD Laboratory uses the MS/MSD precision to satisfy the reference method and requirement of one sample and duplicate per batch with and RPD of ≤ 20%.

Table 9.7.5.1 – Default QC Limits

	Analyte	Default LCL % Recovery	Default UCL % Recovery	Default Precision % RPD
LCS/LCSD MS/MSD	**IO-3.5**	**80**	**120**	**20**
LCS/LCSD MS/MSD	**IO-3.5 (Antimony)**	**75**	**125**	**20**

9.8 <u>Five-Fold Dilution Interference Check (5FDIC, Serial Diluted Sample or DD):</u>

9.8.1 Usually one MS extract from each batch must be diluted five-fold and analyzed. The result after correction for dilution, must be with ± 10% of the undiluted expected value for analytes ≥ 25x MDL. The sample selected for dilution must have analyte concentrations in the undiluted extract at least 10X the concentration of the lowest standard in the curve to assure that the dilution response will be within the calibration range. If no sample has an analyte concentration of at least 10X the concentration of the lowest standard, the sample with the highest extract concentration should be chosen and diluted so that the response of the dilution is within the calibration range.

9.8.2 Analysts should use historical data to determine which samples are most likely to meet requirements for the sample selected to be the 5FDIC and select a sample from those samples for dilution prior to sample analysis to save time. If the sample fails to meet the selection criteria, another 5FDIC can be selected using the analysis data if necessary.

9.9 <u>RS:</u> One per batch of 20 or fewer field collected samples with precision ≤ 20% RPD for analytes ≥ 5x MDL.

9.10 <u>DS:</u> One per batch of 20 or fewer field collected samples with precision ≤ 20% RPD for elements ≥ 5x MDL.

9.11 <u>Assessing the Internal Standard Response:</u>

9.11.1 The response of the internal standard must be monitored for all samples and standards analyzed by this method.

9.11.2 Internal standard responses for standards must be within 60-125% of the target response. If the internal standard associated with that analyte fails for a given sample, the sample must be diluted at least 1:5 with calibration blank solution (see 6.6) and reanalyzed. Continue diluting until the internal standard passes. Adjust the RL and MDL accordingly and with the LJ and DI qualifiers (see 9.13.2.1) and comment “Analyte identified”; reporting limit elevated.

9.12 Batching:

9.12.1 A batch consists of strips taken from 20 or fewer sample filters and QC. Each batch must have the following: MB, FB (LB), ICB, ICV, HS, IDL, MDLs(ML), ICS 1, ICS 1-2, RSC, LCS, LCSD, MS, MSD, DD, DS and Replicate sample. CCC's and CCB's are analyzed after calibration, after 10th sample in batch and at the end of the analytical sequence.

9.13 Data Qualifiers:

9.13.1 Null code qualifiers to be used by the Metals Laboratory are extracted from the Technical Assistance Document for the national Ambient Air Toxics Trends and Assessment Program manual (TAD), Revision 3 October 2016, Section 3.3.1.3.15: Table 3.3.2 AQS Qualifier Codes Appropriate for NATTS Data Qualification (SOP reference 13.4). Other qualifiers may be used by the EPD Air Branch before export to AQS. Null qualifier flags listed in Table 9.13.1.1 below are applied to samples that are void. Null codes are entered in the result field as the two letter flags from Table 9.13.1.1, unless otherwise noted for a specific flag. Only one null flag is to be applied to a given void sample or individual analyte.

Table 9.13.1.1. - Null Qualifier Flags

Qualifier Flags	Description
AF	Scheduled but not collected
AG	Sample time out of limits
AH	Sample flow rate out of limits
AJ	Filter Damage
AL	Voided by operator
AM	Miscellaneous void (comment required)
AN	Machine malfunction
AO	Bad weather
AP	Vandalism
AQ	Collection Error
AV	Power failure
BA	Maintenance / routine repairs
BB	Unable to reach site
BE	Building site repair
BJ	Operator error
TS	Holding time or transport temperature is out of specs.

9.13.2 Quality Control and Detection Flags are extracted from the TAD, section 3.3.1.3.15: Table 3.3.2 (SOP reference 13.4). If a Null Qualifier from Table 9.13.1.1 above is entered, no Quality Control or Detection Flags are to be entered. If no Null Flags are entered, up to six Quality Control or Detection Flags may be entered for a single result.

Table 9.13.2.1 - Quality Control and Detection Flags + Laboratory Generated Flags

Qualifier Flags	**Description**
SQ	Result reported is between PQL and MDL
MD	Less than or equal to MDL
AR	General lab error
AS	Poor quality assurance results
FB	Field blank value above acceptable limit
TB	Trip blank value above acceptable limit
LB	Lab blank value above MDL
LJ	Identification of analyte is acceptable; reported value is an estimate
LK	Analyte identified; reported value may be biased high
LL	Analyte identified; reported value may be biased low
DI	Sample was diluted for analysis
ND	Result reported value is ≤0 (Manually enter "ZD" for "ND" because of the use of ND in Labworks for Not Detected)

9.13.3 A sample may be reported with up to six Qualifier Flags (the maximum that the EPA reporting system, AQS can handle) if and only if there are no null qualifiers attached to the result. Qualifiers must be reported in the qualifier field of Labworks and separated by spaces only (NO COMMAS). Qualifiers in the Labworks qualifier field will be combined with data during the creation of the extract.

10 Procedure

Note: For each lot of filters, the concentration of metals in the lot background must be determined by digesting and analyzing five filter strips, each cut from a separate filter from a given lot of filters. Each strip must be logged and assign a sample identification number. While there is no prescribed threshold for the lot background concentration for each element, the lot blank concentrations must be reported.

Note: These samples should be prepped in a clean hood so protect the safety of the analyst while using acid solutions.

10.1 The filters are transferred to the Metals Laboratory from the laboratory Receiving Department.

10.2 <u>IO-3.1 Digestion Log Sheet with Hot Block Well:</u>

10.2.1 IO-3.5 digestions are recorded on the IO-3.1 Digestion Log Sheet with hot block form (See figure 15.1). Please note, the digestion sheet log is located in the folder S:\MetalsForms\ and must be included with the associated data package.

10.2.1.1 Verify each auto pipette by dispensing the volume to be used into a tared pan on the balance (see section 5.6) and determine if the volume dispensed is within the acceptable range of ± 1% assuming a 1:1 correlation between µg and µl (or mg and ml, etc.) for reagent water (see 6.1).

Three measurements are taken. The %RSD (see calculation 11.4) of three values must be ≤ 1%. Record the results on the IO-3.1 Digestion Log Sheet.

10.2.1.2 Record all other entries as required by IO-3.1 Digestion Log Sheet with hot block form.

10.3 Sample Preparation:

10.3.1 Use Rubber Latex and Powder Free Gloves to prepare filters for digestion

10.3.2 Filters must be handled carefully in order to prevent collected particulates from being dislodged.

10.3.3 Carefully inspect filters. Consult with the Metals Laboratory Manager if filters contain pinholes, discolorations, creases, thin spots, tares and other defects for QFF filters. For Teflon filters, inspect for separation of the support ring. All filters will be digested but notation will be made of flaws and a comment will be added to the sample report.

10.3.4 Clean sample preparation area with 18MΩ water (see 6.1) and lint free cleaning tissues. Labware that is not single use should be cleaned by rinsing with 18MΩ water (see 6.1) to remove as much of the previous contents as possible. Following the 18MΩ water (see 6.1) rinse, labware should be soaked minimally overnight in a 10% aqueous acid solution (see 6.7). Soaking should be followed by a minimum of three rinses with 18MΩ water (see 6.1) and air drying. Clean labware should be stored in a contaminant-free area, upside down or capped to minimize introduction of contamination. Additional cleaning and acid rinsing steps should be considered when blanks exceed the specified acceptance criteria.

10.4 Samples are extracted in batches of 20 or fewer field samples plus blanks and all required QC.

10.4.1 Prepare a Method Blank (MB) by adding 10ml of extraction solution (see 6.4) to a labeled digestion tube and carry through the entire digestion procedure with the exception that a filter strip is not required.

10.4.2 Prepare a Regent Spike Control (RSC) by adding 10ml of extraction solution (see 6.4) to a labeled digestion tube. Add 40µL of spiking solution (see 6.13) and carry through the entire digestion procedure with the exception that no filter strip is needed. The result expected concentration is 100µg\L.

10.4.3 For QFF, select a QC sample for MS and MSD. Three strips are cut from this filter. Two of the three tubes are labeled MS and MSD and spiked with 40µL of spiking solution (see 6.13) and carried through the entire digestion procedure. Not a requirement for Teflon filters.

10.4.4 A DS is selected for QFF and two strips are cut from this filter and carried through the entire digestion process. Not a requirement for Teflon filters.

10.4.5 A Replicate reading of one field sample is required (see 2.24).

10.5 For each filter to be analyzed for QFF, cut a 1"X8" strip from the center of the air filter (one cut should be along the fold crease) using a non-metallic pizza cutter. For Teflon filters, the whole filter is digested.

10.6 Using plastic tweezer for QFF, roll each strip into a coil and place in the bottom of a labeled digestion tube. Add 10 ml (± 0.15 ml) of extraction solution (see 6.4) to each tube, making sure that the filter strip is entirely covered by the fluid. The Extraction Solution is added to the tube using a calibrated and verified auto pipette. For Teflon filters, using plastic tweezers carefully remove the filter from a new cassette and place in the bottom of a labeled digestion tube. Add 10 ml (± 0.15 ml) of extraction solution (see 6.4) to each tube, making sure that the filter strip is entirely covered by the fluid. The Extraction Solution is added to the tube using a calibrated and verified auto pipette.

10.7 Lab Blank (LB)/Filter Blank (FB)- is prepared by cutting a 1" X 8"strip from a clean filter with a non-metallic pizza cutter from the center of an unexposed QFF. For the Teflon filter, remove one new filter from the cassette for the Teflon filter LB/FB. The LB/FB is taken through the entire digestion process.

10.8 The LCS and LCSD are prepared by cutting two 1" X 8" strip from the same clean filter as the FB for the QFF. Please note: (For Teflon filters, using plastic tweezer remove one filter from the cassette for LCS and remove one filter from another cassette for the LCSD). To the middle of tube containing the filter add at least10 ml of extraction solution and 0.040 ml (40 µL) of spiking solution (see 6.13) for the LCS and LCSD. The result expected concentration is 2µg/Strip (18µg/Filter or 0.10µg/ml which is equivalent to 100µg/L) in extract for QFF. The result expectant factor for Teflon filters is 4µg/Filter or 0.10µg/ml which is equivalent to 100µg/L in extract. The final volume is 20 ml after digestion is complete and samples have been allowed to cool to room temperature for QFF. The final volume for Teflon filters is 40 ml after digestion is complete and samples have been allowed to cool to room temperature

10.9 The MDL (ML) is also prepared from the same strip as the FB, LCS and LCSD for QFF. Please note: (For Teflon filters, using plastic tweezers, remove the filter from a new cassette). To the middle of the tube containing the filter add at least10 ml of extraction solution, and 1.8 ml (1800µL) of 50µg/L standard (level 5 calibration standard, see 6.9.1.1). The result expected concentration is 0.5 µg/Strip (4.5µg/Filter or 0.025µg/ml (25µg/L)) in extract for the QFF. The result expected concentration is 0.5 µg/Filter or 0.020µg/ml which is equivalent to 20µg/L in extract for Teflon filters. The final volume for QFF is 20 ml and for Teflon 40 ml after digestion is complete and samples have been allowed to cool to room temperature.

10.10 The MS and MSD are prepared from the extra strips cut from the selected QC filter (see 10.4.3). To the middle of the tube containing the filter and 10 ml of extraction solution, add 0.040 ml (40 ul) of spiking solution (see 6.13) for the MS and MSD. The result expected concentration is 2µg/Strip (18µg/Filter or 0.10 µg/ml (100µg/L)) in extract. The final volume is 20 ml after digestion is complete and samples have been allowed to cool to room temperature. No MS and MSD required for Teflon filters.

10.11 Collocated Samples:

10.11.1 If available, the primary and collocated samples are prepared with a batch of 20 samples or fewer. The primary and collocated samples are analyzed in replicate and the results are recorded using the NATTS $IMSAR Primary and Collocated Pair mean and %RPD form (see figure15.3). Please note, this form is located on the S:Drive and should be included with the associated data package.

10.11.2 If the primary and collocated samples are not available, analyze a NATTS sample in replicate.

10.12 Sample Digestion:

10.12.1 Preheat block digester (see 5.12) to a temperature of 95°C ±5°C

10.12.2 A temperature probe is inserted inside the Temperature Blank and is placed in a random well of the hotblock. The temperature should stabilize at 95° C ±5 C prior to sample digestion. Over time, the temperature should be measured in every well of the block by rotating which well is used for each sample batch.

10.12.3 Prepared digestion tubes are placed inside a plastic digestion rack (see 5.19) and placed in a heated block digester and covered with disposable ribbed watch glasses (see 5.13). Samples are heated for for a minimum of 30 minutes but no longer than 2 hours. Monitor the digestion process to assure that samples do not evaporate to dryness. *(If evaporation occurs, the digestion procedure must be stopped.)*

10.12.4 The MB, LCS, LCSD and MDL(ML) must be placed in a different random well with each batch digested and the well position recorded on the Hot Block Well Form (see figure 15.5). Over time, the MB, LCS, LCSD and MDL(ML) should be digested in every well in the hotblock.

10.12.5 After digesting for a minimum of 30 minutes but no longer than 2 hours, remove tubes from the hotblock and allow them to equilibrate to room temperature.

10.12.6 Bring the samples to 20 ml for QFF and 40 ml for Teflon filters with 18.2 MΩ water (see 6.1). Tightly cap to tubes and mix each tube by inverting several times.

10.12.7 Allow samples to sit for at least 30 minutes to allow HNO_3 in the filter material to diffuse into the extraction solution.

10.12.8 Carefully filter samples directly inside the tube by using a disposable syringe fitted with a disposable lead free 0.45 µm filter (see 5.15 and 5.16). The samples are now ready for analysis using the ICP-MS. Note, leave the 0.45µm filter in the sample during analysis. (*Assure the probe remains suspended and does not touch the filter during analysis.)*

10.13 Instrument Analysis:

10.13.1 Each day the analysis is performed, inspect tubing (replace if needed), check oil levels and assure waste tubing is inside a properly labeled waste container (see 8.3) prior to warming the instrument. Once instrument has warmed up, tune the instrument (internal standards are not adding to the tuning solution), calibrate and verify the calibration against the initial calibration verification standard (ICV).

10.13.2 Analyze the ICB.

10.13.3 Analyze the High Standard (HS) after the ICB.

10.13.4 Analyze the Interference Check Solutions Standards (ICS 1 and ICS 1-2) after the HS and at the end of the analytical run and every 8 hours of continuous operation.

10.13.5 Analyze a CCC and CCB after the ICS standards and after every ten samples and at the end of the run.

10.13.6 Analyze an IDL for each batch. Change replicates to 10 and analyze using calibration blank solution. (See 6.6).Once the instrument meets all calibration criteria, analysis of sample batch can begin. Appropriate continuing and ending calibration verifications must be performed.

10.13.7 Change replicates back to 3 and analyze MDL (ML) spike sample for each batch.

10.13.8 Once the instrument meets all calibration criteria, analysis of sample batch can begin. Appropriate continuing and ending calibration verifications must be performed.

10.13.9 Analyze the Matrix Blank (MB) for each batch.

10.13.10 Analyze the Reagent Spike Control (RSC) Sample with each batch. Note, the RSC is made up in calibration blank solution (see 6.6) and no filter is required.

10.13.11 Analyze the Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD) with each batch.

10.13.12 Analyze a Matrix Spike (MS) and Matrix Spike Duplicate (MSD) with each batch.

10.13.13 Analyze the serial diluted duplicate (DD) by preparing a 5X dilution of the MS.

10.13.14 Internal Standard responses must be within 60-125% of the original response in the calibration blank. If not, prepare a dilution of a fresh aliquot and reanalyze.

10.13.15 Any analyte concentration above the highest point on the calibration curve must diluted to bring the result between the MDL and PQL.

10.13.16 Samples with analyte concentrations within 10% of the expected value of the Linear Dynamic Range (LDR) must be diluted to bring the result within LDR range and reanalyzed. Also, samples above the highest point of the calibration curve must be diluted and reanalyzed to bring results within calibration range.

10.13.17 The instrument software is set-up to rinse 1 to 2 minutes after each sample reading.

10.13.18 Below is a typical instrument sequence (SEQ). For samples 1 through 10, the following sample order is suggested. Please note: The sequence for Teflon filters will not include MS, MSD and sample duplicates.

Table 10.13.18.1 – Instrument Sequence

SEQ. #	Solution Analyzed
1	TUNING
2	CALIBRATION STANDARDS
3	ICV
4	ICB
5	HS
6	ICS1-2
7	ICS1
8	CCC
9	CCB
10	IDL
11	MDL(ML)
12	MB
13	FB
14	RSC
15	LCS
16	LCSD
17	FIELD SAMPLE 1
18	FIELD SAMPLE 1 MS
19	FIELD SAMPLE 1 MSD
20	CCC
21	CCB
22	FIELD SAMPLE 1 DD
23	FIELD SAMPLE 2

Table 10.13.18.1 – Instrument Sequence

SEQ. #	Solution Analyzed
24	FIELD SAMPLE DUPLICATE
25	FIELD SAMPLE 3
26	FIELD SAMPLE 3 REPLICATE ANALYSIS
27	FIELD SAMPLE 4
28	FIELD SAMPLE 5
29	FIELD SAMPLE 6
30	FIELD SAMPLE 7
31	FIELD SAMPLE 8
32	CCC
33	CCB
34	FIELD SAMPLE 9
35	FIELD SAMPLE 10
36	ICS1-2
37	ICS1
38	CCC
39	CCB

10.13.18.2 The remaining extracts are analyzed in an appropriate order with appropriate continuing and ending calibration verifications.

10.13.19 If available, analyze a primary sample and replicate of the primary sample as well as a collocated sample and a replicate of the collocated sample with each batch of 20 or fewer.

10.13.19.1 If the primary and collocated samples are not available, analyze a NATTS sample in replicate.

10.14 Dilutions:

10.14.1 Any extract with a response over the calibration curve must be diluted a minimum of 1:5 (1 part diluted to a final volume of 5 parts).

10.14.2 Dilute any response within 10% of the Liner Dynamic Range (LDR).

10.14.3 Dilutions are prepared by dilution of an aliquot of extract with calibration blank solution (see 6.6) to achieve an acid matched matrix.

10.14.4 Any air displacement pipette used to measure the aliquot must have the pipette volume verified per section 5.7.

10.15 Data Review, Reporting and Validation:

10.15.1 Upon completion of analysis, the analyst should complete all appropriate paperwork and enter data into Labworks. After reviewing all data, calculations, forms and Labworks entries for completeness and accuracy, the analyst must complete the Metals Data Check List. The analyst should then summit the completed data package to the supervisor overseeing the method or the laboratory manager if no supervisor has been assigned to that analysis.

10.15.2 The responsible supervisor or manager will review the data package for completeness and correctness, including reviewing Labworks entries. Corrective actions should be initiated to address any quality assurance issues found. Errors and incomplete data should be addressed with the analyst. When the reviewer is satisfied that the data is complete and correct, all Labworks test codes associated with analysis are to be validated. The reviewer then must initial and date the Metals Data Check List.

10.15.3 Analyzed filters will be retained by the Metals Lab until whatever time the Air Branch determines disposal can occur.

11 Calculations

11.1 Mean ($\bar{X}$):

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

11.1.1 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

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

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

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

11.3.1 Where:

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

11.4 Percent Relative Standard Deviation (%RSD):

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

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 Extract Concentration:

11.6.1 The extract concentration is calculated relative to the calibration curve by the instrument software.

11.7 Sample Concentration per strip (µg/Strip):

11.7.1 The instrument reports extract concentrations as µg/ml. The typical final volume of an extract is 20 ml for a 1" x 8" strip of filter. Therefore the concentration in µg/Strip is calculated as:

$$^{\mu g}/_{Strip} = Conc_{extract}\left(^{\mu g}/_{ml}\right) * 20\ ^{ml}/_{Strip}$$

11.8 Where:

$Conc_{extract}\left(^{\mu g}/_{ml}\right)$ = Extract concentration in µg/ml

11.9 Sample Concentration per filter (µg/Filter):

11.9.1 Filters are 8" x 10" and the strips cut from them are 1" x 8". However, not all of the surface area of a filter is exposed. A ½" border around the filter is blocked by the support frame. Therefore the actual exposed surface is 7" x 9" or 63 sq. in. The exposed area of a strip (cut from the middle of the filter so only the ends of the strip are from the covered portion) is 1" x 7" or 7 sq. in. As a result, the *exposed area* of a strip represents one ninth (7/63) of the total exposed area or a ratio of 9:1 exposed filter area to exposed strip area. The sample concentration per filter in µg/Filter is calculated as:

$$^{\mu g}/_{Filter} = {}^{\mu g}/_{Strip} * 9$$

following the calculation in 11.7, or

$$^{\mu g}/_{\mathrm{Filter}} = \mathrm{Conc}_{\mathrm{extract}} \left(^{\mu g}/_{\mathrm{ml}}\right) * 20\ ^{\mathrm{ml}}/_{\mathrm{Strip}_{\mathrm{in}^2}} * 9\ ^{\mathrm{Filter}_{\mathrm{in}^2}}/_{\mathrm{Strip}_{\mathrm{in}^2}}$$

calculated directly from the extract concentration

11.9.2 Where:

$\mathrm{Conc}_{\mathrm{extract}} \left(^{\mu g}/_{\mathrm{ml}}\right)$ = Measured concentration of the sample extract

$9\ ^{\mathrm{Strip}_{\mathrm{in}^2}}/_{\mathrm{Filter}_{\mathrm{in}^2}}$ = Ratio of exposed area on filter to exposed area on strip

11.9.3 For Teflon Filters the whole strip is used:

11.9.4 µg/ml (Measured concentration of sample extract) *20ml/strip

11.10 Percent Recovery:

11.10.1 *LCS/LCSD*:

$$\%\mathrm{Recovery} = \frac{\mathrm{Conc}_{\mathrm{spiked}}}{\mathrm{Conc}_{\mathrm{expected}}} * 100$$

11.10.1.1 Where:

$\mathrm{Conc}_{\mathrm{spiked}}$ = Concentration found in the spiked sample

$\mathrm{Conc}_{\mathrm{expected}}$ = Expected concentration

11.10.2 *MS/MSD*:

$$\%\mathrm{Recovery} = \frac{\mathrm{Conc}_{\mathrm{spiked}} - \mathrm{Conc}_{\mathrm{unspiked}}}{\mathrm{Conc}_{\mathrm{expected}}} * 100$$

11.10.2.1 Where:

$\mathrm{Conc}_{\mathrm{spiked}}$ = Concentration found in the spiked sample

$\mathrm{Conc}_{\mathrm{unspiked}}$ = Concentration found in unspiked sample

$\mathrm{Conc}_{\mathrm{expected}}$ = Expected concentration

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 Methods for the Determination of Metals in Environmental Samples, Supplement I, Compendium Method IO-3.5, Compendium Method IO-3.1, Environmental monitoring Systems Laboratory, Office of Research and Development, USEPA Cincinnati, Ohio, 45268, June 1999-EPA/625/R-96/010a
13.2 Appendix A to Part 58—Quality Assurance Requirements for Slams, SPMs and PSD Air Monitoring, CFR Title 40 – Protection of the Environment, Part58 – Ambient Air Quality Surveillance, Sept. 1, 2015 or later.
13.3 EPA Quality Assurance Handbook for Air Pollution Measurement Systems Volume II, Ambient Air Quality Monitoring Program, EPA-454/B-13-003 May, 2013
13.4 EPA Technical Assistance Document (TAD) for the National Ambient Air Toxics Trends and Assessment Program manual, Revision 3, October, 2016
13.5 EPD Laboratory Quality Assurance Plan, online revision.
13.6 GA EPD Laboratory SOPs – Initial Demonstration of Capability, SOP 6-001, online revision, and Continuing Demonstration of Capability, SOP 6-002, online revision.
13.7 GA EPD Laboratory SOP – EPD Laboratory Procedures for Control Charting and Control and Control Limits, SOP 6-025, online revision.
13.8 GA EPD Laboratory SOP – EPD Laboratory Waste Management SOP, SOP 6-015, online revision.
13.9 GA EPD Laboratory SOP – Determination of Method Detection Limit, SOP 6-007, online revision.
13.10 GA EPD Laboratory Safety Plan – EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision.

14 Reporting Limits and MDLs, Precision and Accuracy Criteria, and Quality Control Approach

Table 14.1 MDL and RL for EPA Method IO-3.5

Parameter/Method	Analyte	MDL	RL	Units
IO-3.5	Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Nickel, Selenium	See Appendix A for current MDL	See Appendix A for current RL	µg/Filter

Note: RL is determined by multiplying the calculated MDL value for each analyte by 3.18.

Table 14.2.1 – LCS/LCSD & MS/MSD* Acceptance Criteria for EPA Method IO3.5

Method	Analyte	Accuracy (%R)	Precision (RPD)
IO3.5 Metals	Antimony	75 - 125	20
	Arsenic	80 - 120	20
	Beryllium	80 - 120	20
	Cadmium	80 - 120	20
	Cobalt	80 - 120	20
	Lead	80 - 120	20
	Manganese	80 - 120	20
	Nickel	80 - 120	20
	Selenium	80 - 120	20

*LCS/LCSD and MS/MSD recovery and precision limits are static based on the default limits in the Technical Assistance Document for the National Air Toxics Trends Stations Program, Rev. 3, Oct. 2016. Annual Control Charts will be generated for this method. They will be used for trend monitoring of analytical systems.

Table 14.2.2 – Acceptance Criteria for EPA Method IO3.5 Primary/Co-Location and Replicates*

Method	Analyte	Primary/Collocation + Primary/Replicate Precision (RPD)	Collocation/Replicate Precision (RPD)
IO3.5 Metals	Antimony	20	10
	Arsenic	20	10
	Beryllium	20	10
	Cadmium	20	10
	Cobalt	20	10
	Lead	20	10
	Manganese	20	10
	Nickel	20	10
	Selenium	20	10

*Precision limits are static based on the default limits in the Technical Assistance Document for the National Air Toxics Trends Stations Program, Rev. 3, Oct. 2016.

Table 14.3 Summary of Calibration and QC Procedures for Method IO 3.5

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
IO 3.5	Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Nickel, Selenium	Lot Blank Background Determination	Once per lot of filters	Five filter strips each cut from a separate filter from a given lot of filters.		
		Analyst Initial Demonstration (IDC).	Once per analyst	1 MB <RL. 1 FB <MDL Average of 4 LCS recoveries and unknown sample recoveries between 80-120% .Sb recoveries between 75%-125%. (See Table 14.2.1 for acceptable limits)	Rerun once, correct the problem, then rerun the initial demonstration for those analytes that did not meet criteria.	
		Continuing Demonstration (CDC).	Every 6 months.	1 MB <RL. 1 FB <MDL Average of 4 LCS recoveries or 2 LCS pairs or unknown. (See Table 14.2.1 for acceptable limits)	Rerun once, correct problem, then rerun the continuing demonstration for those analytes that did not meet criteria.	
		MDL study Initial	New instrument start-up, annually or whenever major maintenance is performed on the instrument.	Required MDLs for all Tier 1 analytes are set by the Technical Assistance Document (TAD).		
		MDLstudy continuous	Generated yearly over a two year period			

Table 14.3 Summary of Calibration and QC Procedures for Method IO 3.5

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
IO-3.5	Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Nickel, Selenium	MDLspike	Once per analytical batch or as needed to acquire data points per SOPMDL6-007, online version	All batch QC must meet established criteria. All spiked MDLs must have a value greater than 0.	Rerun the MDL once and initiate a corrective action. If the MDL fails a second time, do not use the MDL data. Update corrective action and use associated sample data.	None
		MDLblank (FB) Can be combined with Martrix Blank (FB)	Once per analytical batch or as needed to acquire data pointers per SOPMDL6-007, online version	All batch QC must meet established criteria. All MDL blanks (FB) must be <MDL. Any result without a positive or negative response, must be entered as "ND"	Reanalyze once, if still out of control limits, correct the problem and reanalyze affected batch if MDL blank(FB) is matrix blank (FB)	
		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.	Dilute any sample result outside of LDR criteria and comment report for dilution and elevated reporting limit.	
		Analysis of PT sample.	Twice every 12 months, as provided by EPA PT contractor.	All analyte results acceptable per the auditing agency.	Investigation to find Root Clause of 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 re-tune instrument.	Criteria must be met before calibration can begin.
		Initial Calibration. Using 7 standards including level 1 blank.	Daily initial calibration prior to sample analysis.	Correlation Coefficient r of ≥ 0.995/ (r^2≥0.990).	Correct the problem and recalibrate	
		IDL Calculation.	Daily after calibration.	10 replicate readings for analytes <MDL	Rerun once, correct the problem, recalibrate.	

Table 14.3 Summary of Calibration and QC Procedures for Method IO 3.5

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
IO-3.5	Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Nickel, Selenium	Initial Calibration Verification (ICV)	Daily after calibration.	All analyte recoveries between 90%-110%.	Rerun once, correct the problem and recalibrate.	
		Intial Calibration Blank. (ICB)	Immediately after ICV	All analyte concentrations <MDL.	Rerun once, correct the problem and recalibrate.	
		High Standard Verification (HSV)	Immediately after ICB.	All analyte recoveries between 95% and 105%.	Rerun once, correct the problem and recalibrate.	
		Interference Check Samples (ICS 1) (ICS 1-2)	Daily after calibration, every 8 hours, at end of run.	Spiked elements required for IO-3.5 recoveries between 80-120%. The absolute value of unspiked element required for IO-3.5< 3x MDLsp. Background subtraction of these levels may be necessary if observed concentrations exceed the acceptance criterion. Concentrations of target analytes in samples which exceed the concentrations in ICS 1-2, should be diluted and reanayzed.	Rerun once, correct the problem and recalibrate.	
		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 reanalyze 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<MDL.	Rerun once, if still out of control, correct the problem, recalibrate, and reanalyze all samples since the last acceptable CCB.	

Table 14.3 Summary of Calibration and QC Procedures for Method IO 3.5

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
IO-3.5	Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Nickel, Selenium	Lab Blank (FB)	Once per batch.	Results must be below MDL.	Rerun once, if still outside of acceptance, recalibrate. If continues to fail, re-extract batch. If re-extraction fails and insufficient sample amount to extract again, eliminate lab contamination and flag data.	"LB" qualifier added to FB and all samples in the batch.
		Reagent Spike Control (RSC)	Once per batch	Recoveries between 80-120%.	Rerun once, if still outside of acceptance, recalibrate. If continues to fail, re-extract batch. If re-extraction fails and insufficient sample amount to extract again, eliminate lab contamination and flag data.	Use "LL" or "LK" qualifier as is appropriate.
		Laboratory Control Sample (LCS).	Once per batch.	See Table 14.2.1 for acceptable recovery criteria.	Rerun once, if still outside of acceptance, recalibrate. If continues to fail, re-extract batch. If re-extraction fails and insufficient sample amount to extract again, eliminate lab contamination and flag data.	Use "LL" or "LK" qualifier as is appropriate.

Table 14.3 Summary of Calibration and QC Procedures for Method IO 3.5

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
IO-3.5	Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Nickel, Selenium	Laboratory Control Sample Duplicate (LCSD).	Once per batch.	See Table 14.2.1 for acceptable recovery and precision criteria.	Rerun once, if still outside of acceptance, recalibrate. If continues to fail, re-extract batch. If re-extraction fails and insufficient sample amount to extract again, eliminate lab contamination and flag data.	Use "LL" or "LK" qualifier as is appropriate.
		Matrix Blank (MB).	Once per batch.	All analyte concentrations <MDL.	Rerun once, if still outside of acceptance, recalibrate. If continues to fail, re-extract batch. If re-extraction fails and insufficient sample amount to extract again, eliminate lab contamination and flag data	LB" qualifier added to MB and all samples in the batch.
		Matrix Spike (MS).	Every 10 samples.	See Table 14.2.1 for acceptable recovery criteria.	Rerun once. If recovery exceeds QC limits but CCC, CCB, LCS, and LCSD are acceptable, matrix effect is suspected.	Comment report.
		Matrix Spike Duplicate (MSD).	Every 10 samples.	See Table 14.2.1 for acceptable recovery and precision criteria.	Rerun once. If recovery exceeds QC limits but CCC, CCB, LCS, and LCSD are acceptable, matrix effect is suspected.	Comment Report.
		Serial dilution. (DD)	Prepare and analyze a 5X dilution of one sample spike per batch.	Diluted concentrations must be within 90% and 110% of the undiluted concentration for elements ≥ 25x MDL.	Rerun once if a problem was suspected with initial run. If still outside of acceptable control range comment report.	Comment Report.

Table 14.3 Summary of Calibration and QC Procedures for Method IO 3.5

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
IO-3.5	Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Lead, Manganese, Nickel, Selenium	Duplicate Sample (DS).	One per batch.	Precision ≤ 20% RPD for analytes ≥5x MDL.	Rerun once if a problem was suspected with initial run. If still outside of acceptable control range comment report.	Comment Report.
		Replicate Sample (RS).	One per batch.	Precision ≤ 10% RPD for analytes ≥5x MDL.	Rerun once if a problem was suspected with initial run. If still outside of acceptable control range comment report.	Comment Report.
		Field Blanks.	Minimum once per quarter (These are provided by Air Branch. We analyze all that are provided.)	Analyte concentration <MDL.		"FB" qualifier added to Field Blank and all associated field samples.
		Collocated Precision (Primary Sample and Collocated Sample %RPD)	Once every batch of 20 samples or fewer, if available.	Precision ≤20% RPD for primary and collocated results for analytes ≥ 5x MDL. (See Table 14.2.2)	Re-run Primary and Collocated samples.	
		Replicate Precision (Collocated Sample and Replicate %RPD).	Once every batch of 20 samples or fewer , if available.	Precision ≤10% RPD of Collocated and replicate results for analytes ≥ 5xMDL. (See Table 14.2.2)	Re-run Primary and Collocated samples.	
		Internal Standards.	Every sample and standard except for tuning	All internal standard recoveries must be between 60% and 125% of the original response of the calibration blank.	Dilute and reanalyze to bring internal standard results within acceptance range.	Comment results for elevated reporting limited.
		Flags.	All Field Samples and LB.	See section 9.14.		Flag data with appropriate data qualifiers.

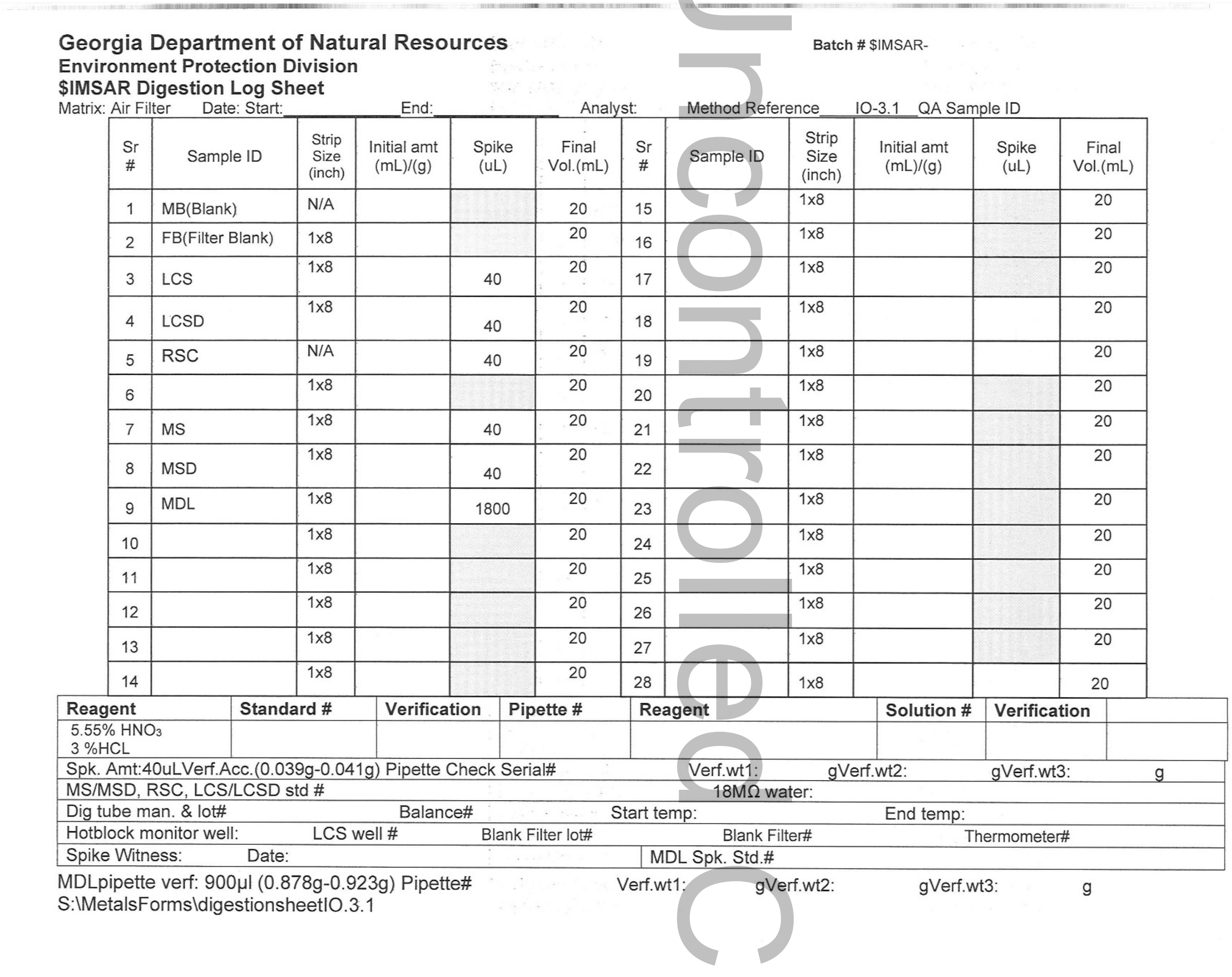
Table 14.4 ELAN 9000 Tuning Criteria Method IO3.5

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
^{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.

Table 14.4 NexION 1000 Tuning Criteria Method IO3.5

Mass 220 counts	≤3
Cerium Oxide ratio	≤3%
Ce^{++} 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
$_{9}$Be counts of a 1.0 ug\L solution	>4500 CPS
^{24}Mg counts of a 10 ug/L solution	>5,000 CPS
^{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.

Figure 1 - $IMSAR Digestion Log Sheet with Hot Block Well Form
(Located on S:\Metalsforms2\digestionsheetIO.3.1with hot block form after Figure 2)



Georgia Department of Natural Resources
Environment Protection Division
$IMSAR Digestion Log Sheet

Batch # $IMSAR-

Matrix: Air Filter Date: Start:______________End:______________ Analyst: Method Reference____IO-3.1__QA Sample ID

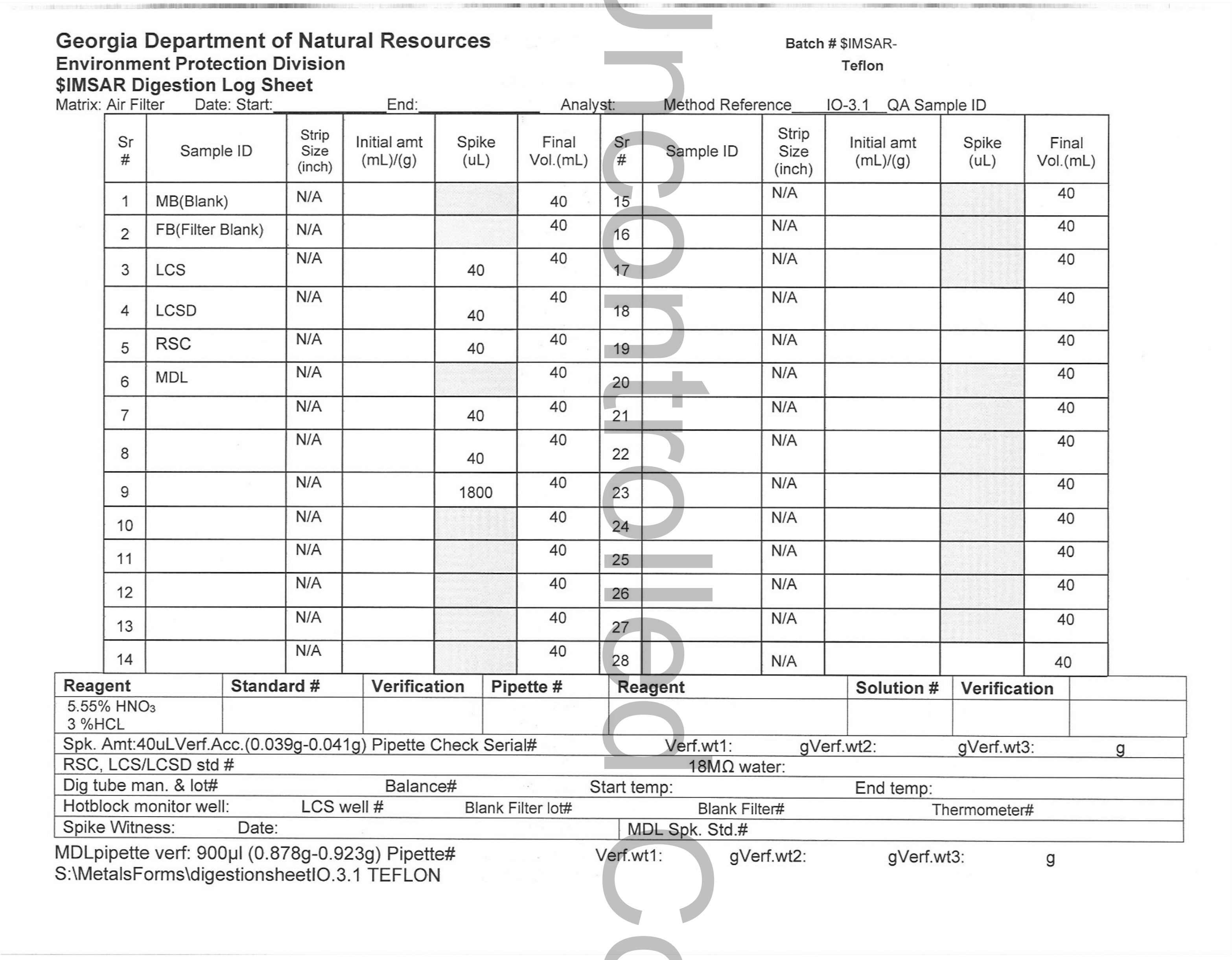
Sr #	Sample ID	Strip Size (inch)	Initial amt (mL)/(g)	Spike (uL)	Final Vol.(mL)	Sr #	Sample ID	Strip Size (inch)	Initial amt (mL)/(g)	Spike (uL)	Final Vol.(mL)
1	MB(Blank)	N/A			20	15		1x8			20
2	FB(Filter Blank)	1x8			20	16		1x8			20
3	LCS	1x8		40	20	17		1x8			20
4	LCSD	1x8		40	20	18		1x8			20
5	RSC	N/A		40	20	19		1x8			20
6		1x8			20	20		1x8			20
7	MS	1x8		40	20	21		1x8			20
8	MSD	1x8		40	20	22		1x8			20
9	MDL	1x8		1800	20	23		1x8			20
10		1x8			20	24		1x8			20
11		1x8			20	25		1x8			20
12		1x8			20	26		1x8			20
13		1x8			20	27		1x8			20
14		1x8			20	28		1x8			20

Reagent	**Standard #**	**Verification**	**Pipette #**	**Reagent**	**Solution #**	**Verification**	
5.55% HNO_3 3 %HCL							

Spk. Amt:40uLVerf.Acc.(0.039g-0.041g) Pipette Check Serial# Verf.wt1: gVerf.wt2: gVerf.wt3: g
MS/MSD, RSC, LCS/LCSD std # 18MΩ water:
Dig tube man. & lot# Balance# Start temp: End temp:
Hotblock monitor well: LCS well # Blank Filter lot# Blank Filter# Thermometer#
Spike Witness: Date: MDL Spk. Std.#

MDLpipette verf: 900µl (0.878g-0.923g) Pipette# Verf.wt1: gVerf.wt2: gVerf.wt3: g
S:\MetalsForms\digestionsheetIO.3.1

Figure 2 - $IMSAR Digestion Log Sheet with Hot Block Well Form
(Located on S:\Metalsforms2\digestionsheetIO.3.1with hot block form)



Georgia Department of Natural Resources
Environment Protection Division
$IMSAR Digestion Log Sheet

Batch # $IMSAR-
Teflon

Matrix: Air Filter Date: Start:__________ End:__________ Analyst: Method Reference___IO-3.1__QA Sample ID

Sr #	Sample ID	Strip Size (inch)	Initial amt (mL)/(g)	Spike (uL)	Final Vol.(mL)	Sr #	Sample ID	Strip Size (inch)	Initial amt (mL)/(g)	Spike (uL)	Final Vol.(mL)
1	MB(Blank)	N/A		▨	40	15		N/A		▨	40
2	FB(Filter Blank)	N/A		▨	40	16		N/A		▨	40
3	LCS	N/A		40	40	17		N/A		▨	40
4	LCSD	N/A		40	40	18		N/A			40
5	RSC	N/A		40	40	19		N/A			40
6	MDL	N/A		▨	40	20		N/A		▨	40
7		N/A		40	40	21		N/A		▨	40
8		N/A		40	40	22		N/A		▨	40
9		N/A		1800	40	23		N/A		▨	40
10		N/A		▨	40	24		N/A		▨	40
11		N/A		▨	40	25		N/A		▨	40
12		N/A		▨	40	26		N/A		▨	40
13		N/A		▨	40	27		N/A		▨	40
14		N/A		▨	40	28		N/A			40

Reagent	Standard #	Verification	Pipette #	Reagent	Solution #	Verification	
5.55% HNO_3 3 %HCL							

Spk. Amt:40uLVerf.Acc.(0.039g-0.041g) Pipette Check Serial# Verf.wt1: gVerf.wt2: gVerf.wt3: g
RSC, LCS/LCSD std # 18MΩ water:
Dig tube man. & lot# Balance# Start temp: End temp:
Hotblock monitor well: LCS well # Blank Filter lot# Blank Filter# Thermometer#
Spike Witness: Date: MDL Spk. Std.#

MDLpipette verf: 900µl (0.878g-0.923g) Pipette# Verf.wt1: gVerf.wt2: gVerf.wt3: g
S:\MetalsForms\digestionsheetIO.3.1 TEFLON

Georgia Department of Natural Resources
Environment Protection Division

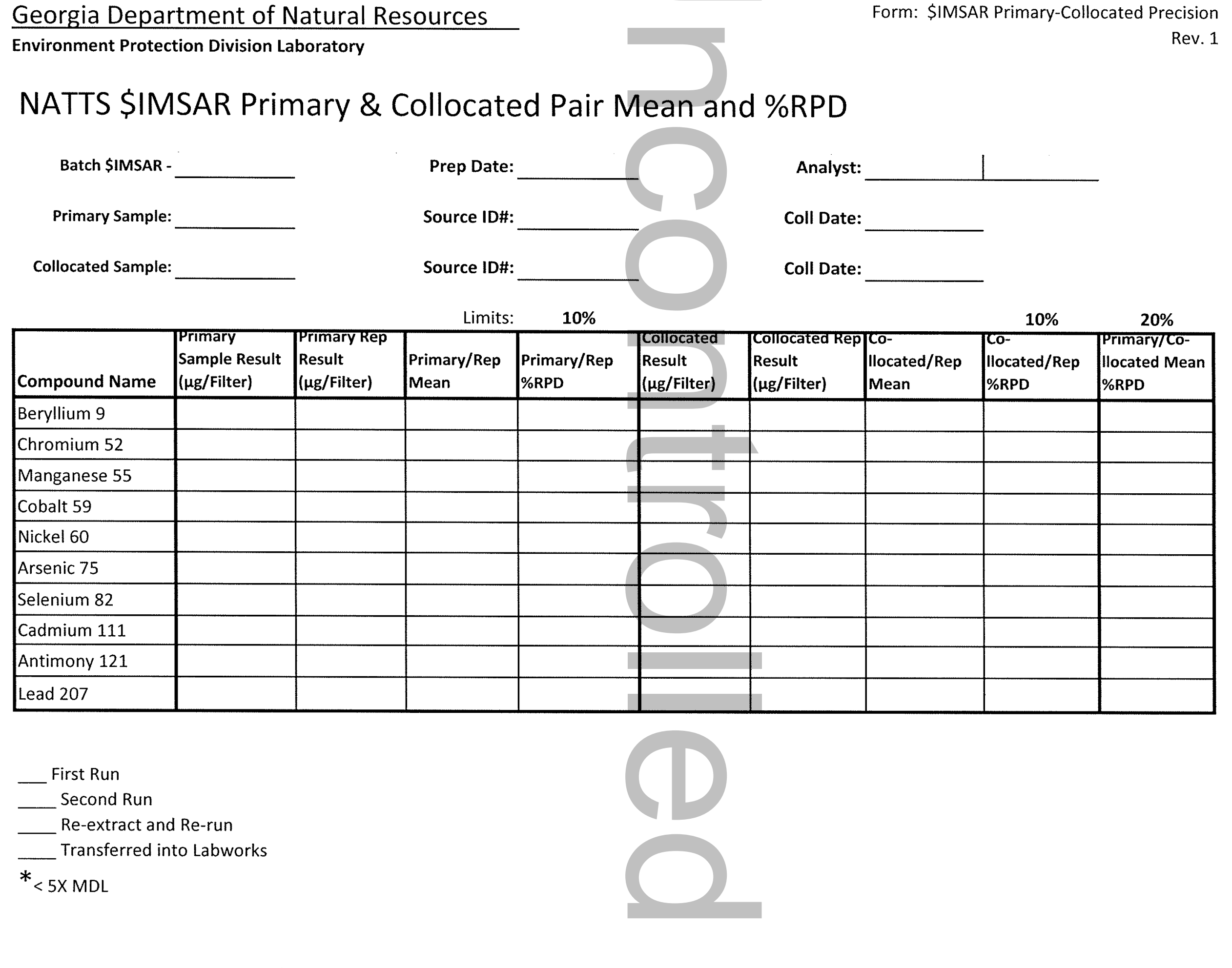
Batch # 2-_$IMSAR-________________.

HOT BLOCK WELL FORM

	1	2	3	4	5	6	7	8	9
A									
B									
C									
D									
E									
F									

S:\MetalsForms2\digestionsheetIO.3.1 with hot block form

Figure 3 - NATTS $IMSAR Primary & Collocated Pair Mean and %RPD Form
(Located on S:\Metals Collocated Spreadsheets\NATTS $IMSAR Primary Collocated Pair Mean and %RPD.xlsx)



Georgia Department of Natural Resources
Environment Protection Division Laboratory

Form: $IMSAR Primary-Collocated Precision
Rev. 1

NATTS $IMSAR Primary & Collocated Pair Mean and %RPD

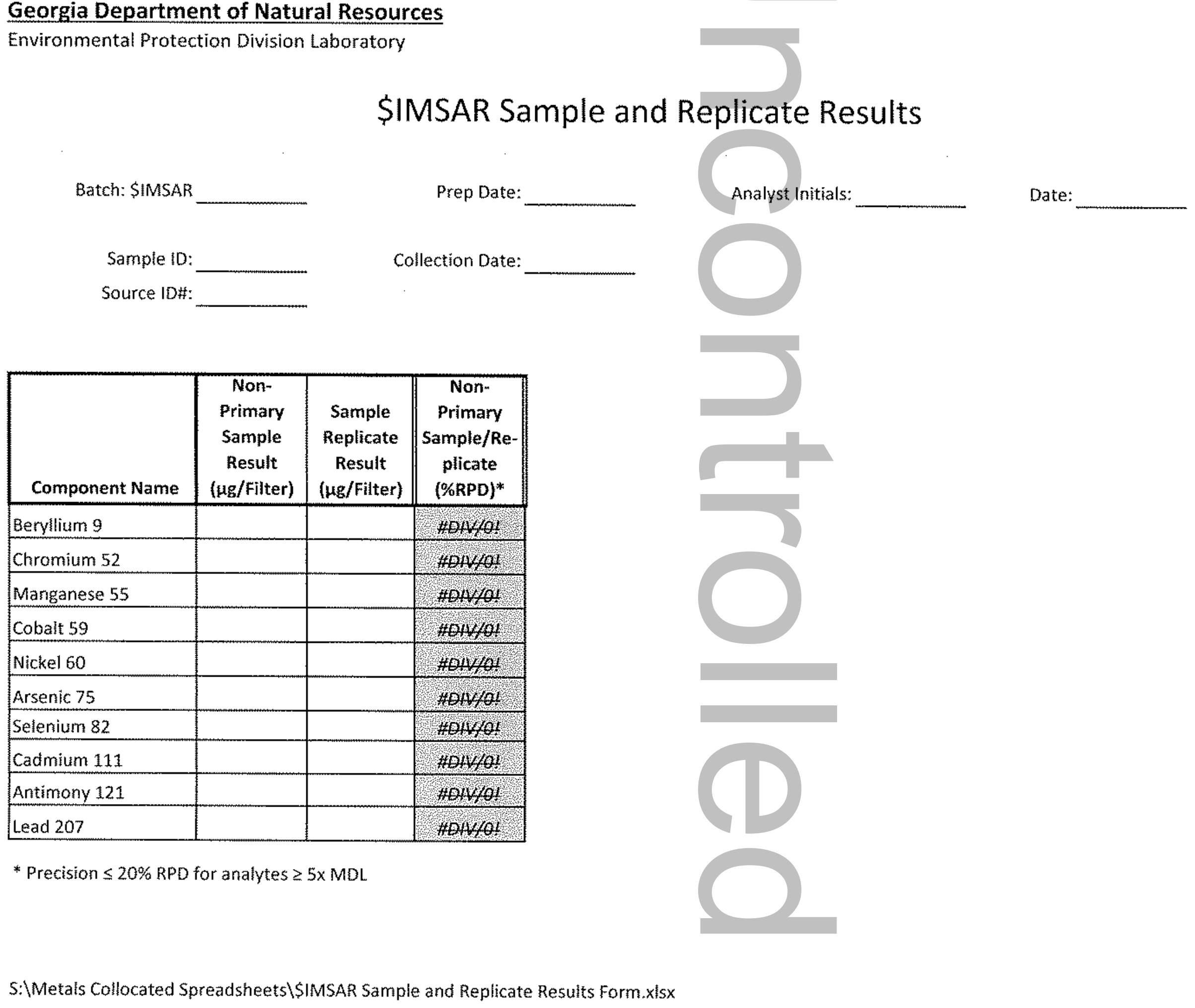
Batch $IMSAR - ____________
Prep Date: ____________
Analyst: ____________
Primary Sample: ____________
Source ID#: ____________
Coll Date: ____________
Collocated Sample: ____________
Source ID#: ____________
Coll Date: ____________

Limits:				10%				10%	20%
Compound Name	**Primary Sample Result (µg/Filter)**	**Primary Rep Result (µg/Filter)**	**Primary/Rep Mean**	**Primary/Rep %RPD**	**Collocated Result (µg/Filter)**	**Collocated Rep Result (µg/Filter)**	**Co-llocated/Rep Mean**	**Co-llocated/Rep %RPD**	**Primary/Co-llocated Mean %RPD**
Beryllium 9									
Chromium 52									
Manganese 55									
Cobalt 59									
Nickel 60									
Arsenic 75									
Selenium 82									
Cadmium 111									
Antimony 121									
Lead 207									

___ First Run
____ Second Run
____ Re-extract and Re-run
____ Transferred into Labworks
*< 5X MDL

S:Metals\Metals Collocated Spreadsheets\NATTS $IMSAR Primary Collocated Pair Mean and %RPD.xlsx

Figure 4 - $IMSAR Sample and Replicate Results
(Located on S:\Metals Collocated Spreadsheets\$IMSAR Sample and Replicate Results Form.xlsx)



Georgia Department of Natural Resources
Environmental Protection Division Laboratory

$IMSAR Sample and Replicate Results

Batch: $IMSAR ___________
Prep Date: ___________
Analyst Initials: ___________
Date: ___________

Sample ID: ___________
Collection Date: ___________
Source ID#: ___________

Component Name	Non-Primary Sample Result (µg/Filter)	Sample Replicate Result (µg/Filter)	Non-Primary Sample/Replicate (%RPD)*
Beryllium 9			#DIV/0!
Chromium 52			#DIV/0!
Manganese 55			#DIV/0!
Cobalt 59			#DIV/0!
Nickel 60			#DIV/0!
Arsenic 75			#DIV/0!
Selenium 82			#DIV/0!
Cadmium 111			#DIV/0!
Antimony 121			#DIV/0!
Lead 207			#DIV/0!

* Precision ≤ 20% RPD for analytes ≥ 5x MDL

S:\Metals Collocated Spreadsheets\$IMSAR Sample and Replicate Results Form.xlsx

Appendix A- MDLs and RLs for EPA Method IO-3.5

Table A.1 MDLs and RLs

Parameter/Method	Analyte	MDL (µg/Filter)	*RL (µg/Filter)
IO-3.5	Beryllium	0.242	0.770
	Chromium	2.51	7.98
	Manganese	0.544	1.73
	Cobalt	0.338	1.07
	Nickel	1.13	3.59
	Arsenic	0.445	1.42
	Selenium	1.24	3.94
	Cadmium	0.279	0.887
	Antimony	0.334	1.06
	Lead	0.390	1.24
MDLs are based on MDL baseline study from 3/28/2019-3/28/2021			

**Note: RL is determined by multiplying the calculated MDL value by 3.18.*
See Corrective Action 2-111819-497 & 2-032821-094

Appendix B for Method IO-3.5 Determination of Metals in Ambient Particulate Matter Using ICP-MS

Table B.1 Acceptance Criteria for IO-3.5 ($IMSAR)

QC Type	Analyte	Accuracy (%R) LCL	UCL	Precision (%RPD)
LCS/LCSD	Antimony	75	125	20
	Arsenic	80	120	20
	Beryllium	80	120	20
	Cadmium	80	120	20
	Chromium	80	120	20
	Cobalt	80	120	20
	Lead	80	120	20
	Manganese	80	120	20
	Nickel	80	120	20
	Selenium	80	120	20
MS/MSD	Metals (Antimony)	75	120	20
MS/MSD	Metals (Arsenic-Selenium)	80	120	20

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

Updates:

Updated for online revision.