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

QA Manager Approval: Jeffrey Moore / 08/19/2021

TSP Lead – Federal Reference Method - 40CFR 50 Appendix G

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 The Federal Reference Method for the analysis of Lead on Total Suspended Particulates (PB TSP) (SOP reference 13.1) is used to determine the Lead concentration in air. A measured quantity of air is drawn through a quartz fiber filter of known weight and with a porosity of 10 µm. The filter is weighed to determine the weight of the collected particulates. A measured strip is cut from the filter, digested, and analyzed for Lead by inductively coupled plasma with mass spectrometry detection. Analytes are quantitated by standard calibration.

1.2 This method is restricted to analysts who have completed the requirements of the initial demonstration SOP. (See SOP reference 13.6)

2. Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Plan (see SOP reference 13.5) 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 other than 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 run at a level equal to that of a Laboratory Control Sample (LCS) or the mid-point of the calibration curve.

2.5 Low Level Calibration Verification (LLCV)- a standard prepared from a different source than the calibration curve. It must be prepared at a concentration not more than three times the lowest calibration standard and at a

concentration not used in the calibration curve. The LLCV is used to assess performance at the low end of the curve. This standard also serves as the Lower Level ICV and the Lower Level CCV.

2.6 Certified Reference Material (CRM) – An independently certified reference material purchased from an outside vendor, used for quality assurance monitoring.

2.7 Collocated Samples (Field Sample Duplicates) – Samples that are collected simultaneously using two separate sampling systems at the same location. The samples are analyzed and results compared. This approach monitors field collection quality.

2.8 Replicate Analyses –Duplicate analyses of two strips cut from one field sample filter. Each strip is digested following the same procedure as all other samples.

2.9 Reagent Blank (RB)/Method Blank (MB) – An aliquot of 5% Nitric Acid Extraction Blank Solution (see 6.4) 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 (see reference Method section 7.7.2., SOP reference 13.1). 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).

2.10 Filter Blank/Lab Blank (LB) – A clean 1" X 8" filter strip that is carried through the entire digestion process using 5% Nitric Acid Blank Extraction Solution. (see SOP section 6.4).

2.11 Reagent Spike Control (RSC) – An aliquot of 5% Nitric Acid Extraction Blank Solution (see SOP section 6.4.) 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.

2.12 Reagent Blank Spike (RBS) – An aliquot of 5% Nitric Acid Extraction Solution (see SOP section 6.4.) that is spiked with a known amount of the analyte or analytes and carried through the entire procedure using a clean filter strip. For purposes of this SOP, the RBS will be referred to as the Laboratory Control Spike (LCS). The RBS is equivalent to the Laboratory Control Sample (LCS) defined in the EPD Laboratory Quality Assurance Plan, chapter 3 (see SOP reference 13.5.).

2.13 Reagent Blank Spike Duplicate (RBSD) – A second (duplicate) RBS/LCS that is carried through the entire procedure, as described in 2.12, for the purpose of calculating laboratory precision. For purposes of this SOP, the RBSD will be referred to as the Laboratory Control Sample Duplicate (LCSD).

2.14 Method Detection Limit Standard- Cut a 1" X 8" strip from the same clean filter as the FB and spiked at a concentration equal to the lowest point on the calibration curve and carried through the entire process.

2.15 Initial Detection Limit Study (IDL)-Analyzed daily after calibration. 10 replicate readings of the 2% Nitric Acid Blank Solution. Acceptance criteria: Lead analyte concentration < RL.

2.16 Initial Calibration Blank (ICB)-A 2% Nitric Acid Solution (see 6.5) used as the 0 µg/L point on the calibration curve and to verify the instrument is continuously free from Lead contamination.

2.17 Continuing Calibration Blank (CCB)-A 2% Nitric Acid Solution (see 6.5) used to verify the instrument is continuously free from Lead contamination. Acceptance criteria: Lead analyte concentration <RL.

2.18 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.

2.19 Audit Strips: High (PBTSPGHI) and Low (PBTSPGLO) Audit strips used for quality control purposes.

3. Interferences

3.1 Isobaric elemental interferences: isotopes of different elements that 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. Lead is not subject to interference from common polyatomic ions.

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.

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

4.1 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 ICP-MS – Perkin Elmer Elan 9000, NexION 1000 or equivalent capable of providing resolution better or equal to 1.0 atomic mass units (amu) at 10% peak height. The system must have a mass range of at least 7 to 240 amu. The system must allow for the use of an internal standard.

5.2 High purity argon gas supply

5.3 Hot Block Digesters – Environmental Express models SC154, SC181 or equivalent capable of maintaining 95° C.

5.4 50ml HDPE digestion tubes – with threaded caps for extraction and storage

5.5 Disposable polypropylene ribbed watch glasses (for heated block extraction)

5.6 50ml HDPE centrifuge tubes, caps and other HPDE containers.

5.7 Various HDPE volumetric class A flask.

5.8 Electronic Balance – Mettler PB-303 or equivalent, with a weight range of 0 – 310 g or greater, and accurate to ± 0.001 g

5.9. Electronic Balance – Mettler PM-6 or equivalent, with a weight range of 0 – 6000 g or greater, and accurate to ± 1 g

5.10. Assortment of air displacement pipettes capable of delivering volumes between 0.001 ml and 10 ml with an assortment of disposable tips

5.10.1. Pipettes must be capable of ± 1% accuracy and within 1% precision (RSD)

5.11 Plastic tweezers

5.12 Disposable Syringes – 10 ml, with 0.45 µm filters (must be Lead free)

5.13 Non-Metallic Pizza Cutter

5.14 Lint free cleaning tissues.

6. Reagents and Standards

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

6.1 Reagent Water – Purified water which does not contain any measurable quantities of target analytes or interfering compounds for each compound of interest. (Deionized, HPLC, Milli-Q water or equivalent. Milli-Q water has a resistivity of 18.2 [MΩ·cm] @ 25° C and a TOC of 50 µg/L or less).

6.2 Concentrated Nitric Acid – 67 – 70 percent, trace metals grade, equivalent, or better

6.3 1% v/v Nitric Acid Solution

6.3.1 Inside a vented fume hood, add 1000 ml of 18.2 MΩ reagent water (see 6.1) to a 2 L HDPE container. Slowly add 20 ml of concentrated HNO_3 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. Cap and invert several times to mix the solution.

6.4 Extraction Solution – 1:19 v/v HNO_3 (concentrated reagent)

6.4.1 Note: *1:19 represents 1 part acid to 19 parts reagent water in this instance as is indicated by the reference method in the instructions for making the Extraction Solution (see reference method section 11.1.1). The EPD Laboratory standard for representing this ratio is 1:20, or 1 part acid diluted to a total of 20 parts with reagent water. This solution should not be represented as a 5% solution of Nitric acid as concentrated Nitric acid is only 67% – 70% HNO_3.*

6.4.1.1 Inside a vented fume hood, add 1000 ml of 18.2 MΩ reagent water (see 6.1) to a 2 L HDPE container. Slowly add 100 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. Cap, and invert several times to mix the solution. Extraction Solution must be prepared at least weekly.

6.5. 2 % v/v Nitric Acid Blank Solution.

6.5.1 Inside a vented fume hood, slowly 1000 ml of 18.2 MΩ reagent water (see 6.1) to a 2L HDPE container. Slowly add 40 ml of concentrated Nitric acid (see 6.2) with swirling to the flask. Solution will become warm.
Allow solution to cool to near room temperature, then dilute to 2000 ml with 18.2 MΩ reagent water. Cap and Invert several times to mix.

Note: Standards used for primary calibration and calibration verification may be single element (Lead only) or multi-element, ignoring elements other than Lead for this analysis.

6.6 Primary Source (PS) Standard Stock Solutions:

6.6.1 PS Vendor Calibration Stock Solution:

Table 0.1. – PS Vendor Calibration Stock Concentration

Analyte	Concentration (µg/ml)
Lead	1000

6.6.1.1 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.

6.6.2 *PS Intermediate Calibration Stock Solution*: Prepared weekly from vendor stock (see 0**)** in 2% Nitric Acid Blank Solultion (see 6.5). Concentration of Lead is 10 µg/ml as indicated in Table 6.6.2.1 below:

Table 6.6.2.1 – PS Intermediate Calibration Stock Solution in 2% Nitric Acid Blank Solution (see 6.5)

Analyte	**Initial Concentration (µg/ml)**	**Aliquot (ml)**	**Final Concentration**
Lead	1000	0.50	10.0**(µg\ml)** or 10,000 ug\L
Total Volume of Standard Aliquots			0.50 ml
Final Volume of PS Calibration Stock Solution in 2%Nitric Acid Blank Solution (see 6.5)			50 ml

6.7 Calibration Standards:

6.7.1 At minimum, this method must contain a blank and five Pb containing calibration standards.
The calibration standards are prepared weekly in **2%Nitric Acid Blank** Solution (see 6.5).

6.7.2 Level 0 of the calibration curve is **2%Nitric Acid Blank** Solution (see 6.5)

6.7.2.1 The calibration curve consists of standards at the following concentrations in µg/L:

Table 6.7.2.1 – TSP-Pb Calibration Levels Concentrations

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)**	**Level 8 (µg/L)**	**Level 9 (µg/L)**
Lead	0	1.00	5.00	10.0	25.0	50.0	100	200	500

6.7.2.2 Should alternate concentrations of vendor standards be required due to availability, adjust aliquots, or final concentrations as needed to meet the concentrations in Tables 6.7.2.1.

6.7.3 Calibration Levels Preparation:

6.7.3.1 Calibration standards are prepared weekly by the addition of aliquots PS from Intermediate Calibration Stock Solution (see 6.6.2) to the **2%Nitric Acid Blank** Solution (see 6.5) in a 50 ml volumetric flask and diluting to volume as follows:

Table 6.7.3.1 – Calibration Level Spike Volumes into 50 ml of 2%Nitric Acid Blank Solution

Calibration Level	1	2	3	4	5	6	7	8	9
Aliquot of PS Intermediate Calibration Stock Solution (see 6.6.2)	0 ml	1.00 ml (calibration level 6)	0.025 ml	0.050 ml	0.125 ml	0.250 ml	0.500 ml	1.00 ml	2.5 ml
Final Concentration	0 µg/L	1.00 µg/L	5.00 µg/L	10.0 µg/L	25.0 µg/L	50.0 µg/L	100 µg/L	200 µg/L	500 µg/L
	Bring all calibration levels up to 50 ml in class A volumetric flasks using 2% Nitric Acid Blank Solution (see 6.5)								

6.7.4 Secondary Stock Solution (SS):

6.7.4.1 SS Vendor Stock Solution

Table 6.7.4.1 – SS Vendor Stock Concentration

Analyte	Concentration (µg/ml)
Lead	1000

6.7.4.2 SS Intermediate Stock Solution: Prepared daily from a different Pb source than the calibration standards. This solution is prepared in **2%Nitric Acid Blank** Solution (see 6.5).

Table 6.7.4.2 – SS Intermediate Stock Solution in 2%Nitric Acid Blank Solution

Analyte	Initial Concentration (µg/ml)	SS Intermediate Stock Solution Aliquot (ml)	Final Concentration
Lead	1000	0.50 ml	10.0 ug/mL or 10,000 µg/L
Total Volume of Standard Aliquots			0.50 ml
Final Volume of SS Calibration Stock Solution in 2%Nitric Acid Blank Solution (see 6.5)			50ml

6.7.5 ICV, CCC and LLCV Solutions:

6.7.5.1 The ICV, CCC and LLCV solutions are prepared from a different Lead source than the calibration curve standards. The ICV and CCC are at a concentration that is either at or below the midpoint on the calibration curve, but within the calibration range. Note that the same solution may be used for ICV and CCC. See section 6.7.5.2 for LLCV preparation information. These solutions must be prepared fresh daily in **2%Nitric Acid Blank** Solution (see 6.5).

6.7.5.2 The ICV, CCC and LLCV are prepared at the following concentrations in ug\L:

Table 6.7.5.2.1. – ICV and CCC Solutions Concentrations

Standard	**SS Concentration of Standard Stock Solution (µg/ml)**	**Aliquot (ml)**	**Final Concentration**
ICV\CCC	10.0	0.50ml	0.1mg\L or 100 µg/L
Total Volume of Standard Aliquots			0.50 ml
Final Volume of SS Calibration Stock Solution in 2%Nitric Acid Blank Solution (see 6.5)			50ml

Table 6.7.5.2.2. – LLCV Solution Concentration

Standard	**SS Concentration of Standard Stock Solution µg/ml**	**Aliquot ml**	**Final Concentration**
LLCV	10.0 ug/ml	0.060ml	0.012mg\L or 12.0 µg/L
Total Volume of Standard Aliquots			0.06 ml
Final Volume of SS Stock Solution in 2%Nitric Acid Blank Solution (see 6.5)			50ml

6.7.6 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 6.3) to a concentration of 10 µg/ml: This solution is prepared every two months.

Table 6.7.6.1 – Tuning Intermediate Stock Solutions in 1% Nitric Acid Solution

Table Reference Number	Single Element Standard	Initial Vendor Stock Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)	Final Volume in 2% Nitric Acid Solution (ml)
6.7.6.1-01	Magnesium	1000	0.50	10	50
6.7.6.1-02	Barium	1000	0.50	10	50
6.7.6.1-03	Beryllium	1000	0.50	10	50
6.7.6.1-04	Cerium	1000	0.50	10	50
6.7.6.1-05	Cobalt	1000	0.50	10	50
6.7.6.1-06	Indium	1000	0.50	10	50
6.7.6.1-07	Lead	1000	0.50	10	50
6.7.6.1-08	Rhodium	1000	0.50	10	50
Total Volume of Standard Aliquots					4.0 ml
Final Volume of Tuning Solution in 1% HNO_3					50 ml

6.7.7 *Tuning Solution for ELAN 9000*: Prepared every two weeks from the individual element Tuning Intermediate Stock Solutions (see 6.7.6) in 1% Nitric Acid Solution (see 6.3):

Table 6.7.7.1 – Tuning Solution in 1% Nitric Acid Solution

Analyte (Table Reference Number)	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)
Magnesium (**6.7.7.1-01**)	10	0.050	0.010
Barium (**6.7.7.1-02**)	10		0.010
Beryllium (**6.7.7.1-03**)	10		0.010
Cerium (**6.7.7.1-04**)	10		0.010
Cobalt (**6.7.7.1-05**)	10		0.010
Indium (**6.7.7.1-06**)	10		0.010
Lead (**6.7.7.1-07**)	10		0.010

Table 6.7.7.1 – Tuning Solution in 1% Nitric Acid Solution

Analyte (Table Reference Number)	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)
Rhodium (**6.7.7.1-08)**	10		0.010
Total Volume of Standard Aliquots			0.050
Final Volume of Tuning Solution in 1% HNO_3			50 ml

6.7.8 *Tuning Solution for NexION 1000*: Prepared every two weeks from the individual element Tuning Intermediate Stock Solutions (see 6.7.6) in 1% Nitric Acid Solution (see 6.3):

Table 6.7.8.1 – Tuning Solution in 1% Nitric Acid Solution

Analyte (Table Reference Number)	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)
Magnesium (**6.7.7.1-01)**	10	0.050	0.0010
Barium (**6.7.7.1-02)**	10		0.0010
Beryllium (**6.7.7.1-03)**	10		0.0010
Cerium (**6.7.7.1-04)**	10		0.0010
Cobalt (**6.7.7.1-05)**	10		0.0010
Indium (**6.7.7.1-06)**	10		0.0010
Lead (**6.7.7.1-07)**	10		0.0010
Rhodium (**6.7.7.1-08)**	10		0.0010
Total Volume of Standard Aliquots			0.050
Final Volume of Tuning Solution in 1% HNO_3			500 ml

6.8 Stability Standard Solutions:

6.8.1 *Stability Intermediate Stock Solutions*: Single element intermediate standards for Cobalt, Indium, and Bismuth are prepared every two weeks from single element vendor stocks, usually at 1000 µg/ml, and diluted with 2% Nitric Acid Solution (see 6.3) to a concentration of 10 µg/ml.

Table 6.8.1.1 – Stability Intermediate Stock Solutions in 2% Nitric Acid Solution

Table Reference Number	Single Element Standard	Initial Vendor Stock Concentration	Aliquot (ml)	Final Concentration (µg/ml)	Final Volume in 2% Nitric Acid Solution

		(µg/ml)			(ml)
6.8.1.1.01	Bismuth	1000	0.50	10	50
6.8.1.1.02	Cobalt	1000	0.50	10	50
6.8.1.1.03	Indium	1000	0.50	10	50
Total Volume of Standard Aliquots					1.50
Final Volume of Tuning Solution in 2% HNO_3					50 ml

6.8.2 *Stability Check Solution*: Prepared every two weeks from 10µg/ml stability intermediate solutions (see table 6.8.1.1.) in 2% Nitric Acid Solution (see 6.3). Final concentration is 0.005µg/ml (***Note: Final volume is 100 ml***):

Table 6.8.2.1 – Stability Check Solution in 2% Nitric Acid Solution

Analyte (Table Reference Number)	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)
Bismuth (6.8.1.1.01)	10	0.050	0.005
Cobalt (6.8.1.1.02)	10		0.005
Indium (6.8.1.1.03)	10		0.005
Total Volume of Standard Aliquots			0.050 ml
Final Volume of Tuning Solution in 2% HNO_3			100 ml

6.9 Interference Check Standard (ICS) Solutions:
The reference method does not require interference checks for isobaric or polyatomic interferences for Lead as no such interferences occur in ambient air. See section 4.2 of the reference method Appendix G to Part 50 CFR (SOP reference 13.1).

6.10 Internal Standard (ISTD) Solutions:

6.10.1 *ISTD Intermediate Solution* #1: Prepared every two months from powdered 95 Lithium-6, Li2 carbonate, 95 atom% 6Li (6Li2CO3) in **2% Nitric Acid** Solution (see 6.5):

Table 6.10.1.1 – ISTD Intermediate Solution #1 in 2% Nitric Acid Solution

Analyte	Initial Concentration	Aliquot (g)	Final Concentration (µg/ml)
Lithium-6	Neat	0.25	2000

Table 6.10.1.1 – ISTD Intermediate Solution #1 in 2% Nitric Acid Solution

Analyte	Initial Concentration	Aliquot (g)	Final Concentration (µg/ml)

Total Solid of Standard Aliquots	0.25 g
Final Volume of ISTD Intermediate Solution #1 in 2% Nitric Acid Solution	20 ml

6.10.2 ISTD Intermediate solution #2: Prepared every two weeks from vendor stocks of Germanium, Indium, Lutetium, Scandium and Lithium-6 usually at 1000 ug\ml for Germanium, Indium, Lutetium and Scandium (2000 ug\ml for Lithium-6) in 1% nitric acid solution (see 6.5.):

Table 6.10.2.1– ISTD Intermediate Solution #2 in 2%Nitric Acid Solution

Analyte	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)
Germanium	1000	0.50	10
Indium	1000	0.50	10
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 #1 in 2% Nitric Acid Solution			50 ml

6.10.3 ISTD Solution: Prepared every two months from ISTD Intermediate Solution #2 (see 6.10.2) in 2% Nitric Acid Solution (see 6.5): Solution prepared in 2L HDPE container:

Table 6.10.3.1– ISTD Intermediate Solution #2 in 2%Nitric Acid Solution

Analyte	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)
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 Intermediate Solution #1 in 2% Nitric Acid Solution			2000 ml

6.10.4 *ISTD Solution*: For NexION- Prepared every two weeks in 2% Nitric Acid Solution (see 6.5):

Table 6.10.4.1– ISTD Intermediate Solution #2 in 2%Nitric Acid Solution

Analyte	Initial Concentration (µg/ml)	Aliquot (ml)	Final Concentration (µg/ml)
Germanium	10	0.125	0.250
Indium	10		0.250
Lutetium	10		0.250
Scandium	10	2.5	5.0
Lithium-6	20	0.0625	0.250
Total Volume of Standard Aliquots			2.0 ml
Final Volume of ISTD Intermediate Solution #1 in 2% Nitric Acid Solution			500 ml

6.11 Spiking Stock Solution: Spike straight from bottle

Vendor Stock Spiking Solution: See note 6.6.1.1 concerning coloration of standards. This stock is not colored.

Table 6.11.1 – Vendor Stock Spiking Solution Concentration

Analyte	Concentration (µg/ml)
Lead	50

6.12 Summary - Preparation Schedule for Standards:

Table 6.12.1 – Standard Solution Preparation Frequency

Solution	Fresh Daily	Weekly	Bi-Weekly	2 Months
PS Intermediate Calibration Stock Solution (6.6.2)		√		
Calibration Standards (6.7.3)		√		
SS Intermediate Stock Solution (6.7.4.2)	√			
ICV, CCC, and LLCV (6.7.5)	√			
Tuning Intermediate Stock Solutions (6.7.6)				√
Tuning Solution (6.7.7)			√	
Stability Intermediate Stock Solutions (6.8.1)			√	
Stability Check Solution (6.8.2)			√	
ISTD Intermediate Solution #1 (6.10.1)				√
ISTD Intermediate Solution #2 (6.10.2)				√
ISTD Solution (6.10.3)			√	

6.13 Calibration Blanks:

6.13.1 The Initial Calibration Blank (ICB) and the Continuing Calibration Blank (CCB): The ICB and the CCB are Calibration Standard Solution (see 6.4) analyzed as standards. Internal standards are added by the instrument.

7. Sample Collection:

7.1 Air samples are collected on 8" x 10" quartz fiber filters.

7.2 No preservation of the filters is required.

7.3 Sample filters are pre-logged into LIMS before field collection. Exposed sample filters are received and logged into the LIMS system by the EPD Air Laboratory where the samples are processed. Samples are then transferred to the EPD Metals Laboratory along with appropriate delivery and receipt acknowledgments on an internal custody sample transfer form, "TSP - PB – Filter Transfer Log." (See Figure 15.1)

8. Calibrations

8.1 Ignite the plasma flame and wait at least 30 minutes for the instrument to warm up and equilibrate before beginning calibration or analysis.

8.2 Aliquots of the tuning and calibration standards are transferred to 50 ml centrifuge tubes (see 5.6) for analysis on the instrument.

8.3 Mass Spectrometer Tuning:

8.3.1 Prior to calibration for analysis of samples, the mass spectrometer must be tuned. The Tuning Solution (see 6.7.7) is analyzed (5 replicates are run) and the instrument tuned as recommended by the instrument manufacturer. The tune must meet the criteria listed in Table 14.4 before calibration or analysis can continue.

8.3.2 No internal standards are added to the Tuning Solution.

8.3.3 After tuning, allow the sample probe to aspirate in 18Ω MilliQ water for at least 5 minutes before proceeding further with instrument stability check.

8.4 Instrument Stability:

8.4.1 After tuning and rinsing the system, stability of the sampling system must be checked. Aspirate the Stability Check Solution (see 6.8.2). The instrument must run 10 replicates of the solution.

8.4.2 The %RSD (see calculation 11.4) of the 10 replicates of each mass must be 3% or less.

8.4.3 If the %RSD of any mass is greater than 3%, check the sample introduction system, pump tubing, and the tune. Perform maintenance or other corrective action as needed. Reanalyze the tune following these actions.

8.4.4 After the stability check, allow the sample probe to aspirate in 18Ω Milli Q water for at least 5 minutes before proceeding further with calibration or analysis.

8.5 Initial Calibration:

8.5.1 A nine-point calibration curve is performed for Lead (see Table 6.7.2.1 for standard concentrations). The calibration system uses traceable, certified standards. The calibration is an internal standard calibration and must be prepared weekly. The calibration is performed using the same method parameters as used to analyze samples.

8.5.2 The calibration is a least squares, internal standard calibration with a correlation coefficient r of ≥ 0.998 ($r^2 \geq 0.996$) or greater. The correlation coefficient is calculated by the instrument software, as is the calibration itself.

8.5.3 The %Drift (see calculation 11.6) of the lowest Lead containing standard (Level 2) must be ≤ 15% from the expected value and the %Drift of the remaining standards must be ≤ 10% from the expected values.

8.6 Calibration Verification:

8.6.1 Immediately following initial calibration, the ICV standard (see 6.7.5) must be analyzed to confirm the calibration. The %Drift (see calculation 11.6) of the ICV must be ≤ 10% from the expected value.

8.6.2 Following the ICV, an ICB (see 2.16) must be analyzed. The Lead response of the ICB must be > 0.001 µg/ml (> 1 µg/L). The ICB is 2% acid solution (see 6.5.)

8.6.3 If either the ICV or ICB fail, rerun once. If it fails again, analysis is terminated, the problem identified and corrected and the analysis restarted.

8.7 Continuing Calibration Verification (CCC):

8.7.1 Following verification of the calibration, but prior to the analysis of samples, an LLCV (see 6.7.5.2), CCC (see 6.7.5.2), and a CCB (see 2.17) must be analyzed. It is recommended that the MDL (ML) spike standard, IDL standard, MB, LB, RSC, LCS, LCSD follow the LLCV, CCC and CCB. See section 6.5 for CCB and IDL solutions.

8.7.2 After no more than 10 samples, including QC samples such as MB, LB, RSC, LCS, LCSD, MS, MSD etc., a CCC and a CCB must be analyzed.

8.7.3 The analysis sequence must end with CCC, CCB, LLCV, CCC, and CCB.

8.7.4 A typical sequence of extracts (any field or QC samples carried through the extraction process), 30 extracts in this example, run on the instrument would be:

Ignite plasma flame and allow instrument to stabilize for at least 30 minutes
Tune – 5 replicates (followed with a 5 min. rinse)
Stability Check – 10 replicates (followed with a 5 min. rinse with Milli Q 18Ω water.)
Level 0, Level 1, …Level 9
ICV, ICB, LLCV, CCC, CCB, IDL, Audit Strips, CRM filters MDL(ML), MB, FB, RSC, LCS, LCSD
extract 1 … extract 10
CCC, CCB
extract 11 … extract 20
CCC, CCB
extract 21 … extract 30
CCC, CCB, LLCV, CCC, CCB

8.7.5 All LLCVs, CCCs, and CCBs must pass the following criteria:

8.7.5.1 The %Drift (see calculation 11.6) of each LLCV and CCC must be ≤ 10% from the expected values.

8.7.5.2 The Lead response of each ICB and CCB must be > 0.001 µg/ml (> 1 µg/L).

8.7.5.3 If a CCV, LLCV or CCB fails, rerun once. If it fails again, the sequence is terminated, the source of the problem found, corrected and the sequence restarted from the last passing CCV/LLCV/CCB inclusive.

8.8 Ongoing MDL study

8.8.1 A MDLs (low level mdl spike equivalent to the lowest spiked point on the calibration curve) must be analyzed with each analytical batch to perform an ongoing MDL study. All batch QC must be valid to report this result.

8.8.2 A MDLb (MDL blank) 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 Reporting Limits (RLs), Appendix B, Table B.1 for Quality Assurance criteria and Table 14.1 for the summary of Quality Control procedures associated with this method.

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 MDL studies are performed on a continuing basis with each analytical batch of samples. A report of this MDL data is generated annually. Alternately, an MDL study must be performed on a new instrument prior to results being reported and if instrument maintenance warrants a new MDL study. (See SOP reference 13.9).

9.2.2 A total of seven MDL_{blanks} and seven MDL_{spikes} must be digested and analyzed over 3 non-consecutive days. Please note: The digestion must include 3 non-consecutive days as well as the analysis.

9.2.3 MDL studies (see Appendix A Table A.1) are performed on a continuing basis with each analytical batch. The Filter Blank (LB\MB) will be entered in Labworks as the MDL_{blank} and the MDL_{sample} will be entered into Labworks using the $ML test code. The instrument used for 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 spiked at a concentration below the lowest point in the calibration curve for this method.

9.3 See SOP reference 13.7 for control charting procedures.

9.4 See SOP reference 13.6 for training and certification procedures.

9.4.1 For Initial Demonstrations of Capability (IDC), the EPD Laboratory has set a recovery range of 80% - 120% (the default LCS range, see below) and a 20% RSD is required for IDC replicates.

9.4.2 The EPD Laboratory uses the most current accuracy and precision control ranges in use for samples for Continuing Demonstrations of Capability (CDC).

If 4 replicates are performed (as opposed to two LCS/LCSD pairs) a 20% RSD is required (see calculation 11.4).

9.5 Control Limits:

9.5.1 Since not required by the EPA reference method, the GA EPD laboratory chooses to use the method default limits for sample validation. Control charts will be pulled annually for trend monitoring purposes.

9.5.2 The default recovery control limits for the TSP Lead reference method are 80% - 120% recovery.

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

9.5.4 The default recovery for matrix spikes (MS) and matrix spike duplicates (MSD) is 80% - 120%.

9.5.5 The default precision for the MS and MSD pair is 20% RPD (see calculation 11.5. The EPD Laboratory uses the MS/MSD precision to satisfy the reference method requirement of one sample and duplicate per batch with an RPD of ≤ 20%.

Note: For batched analyses, analysts must not exceed the method the default limits in Table 9.5.1

Table 9.5.1 – Default QC Limits

	Analyte	Default LCL % Recovery	Default UCL % Recovery	Default Precision % RPD
LCS/LCSD MS/MSD	TSP - Lead	80	120	20

9.6 Certified Reference Materia (CRM):

9.6.1 The reference method (see SOP reference 13.1) a CRM (see 2.6) for definition of a CRM) be included in each batch.

9.6.2 40 CFR 58, Appendix A (see SOP reference 13.1) and the QA Handbook Vol. II Table CRITICAL CRITERIA- Pb in TSP (see SOP reference 13.3) require audit strips to be analyzed as specified concentrations as a rate of three audit strip at each concentration per quarter.

9.6.3 The EPD Laboratory obtains certified filter strips from the EPA spiked with known concentrations of Lead. The strips are ordered and supplied once each

calendar year. These strips are provided in two concentrations as required by the Appendix A to Part 58 (see SOP reference 13.2).

9.6.3.1 *Low Range Strips*: 30% - 100% of NAAQS Limit (see SOP reference 13.2). The NAAQS limit is currently 0.15 µg/m^3 or 4 – 40 µg/strip.

9.6.3.2 *High Range Strips*: 200% - 300% of NAAQS Limit or 45 – 125 µg/strip.

9.6.3.3 The EPA allows for a slightly wider range when strips are supplied as µg/strip due to variations in collection flows and strip sizes used by laboratories. The above ranges reflect these allowances.

9.6.3.4 If EPA strips are not available, or if the EPD Laboratory chooses to make these strips in-house, standards and reagents of lots or sources other than those used for analysis must be used to prepare the strips.

9.6.4 The EPD Laboratory analyzes an audit strip for each concentration with each batch.

9.6.5 The result of the audit strip must be within ± 10% of the expected value.

9.6.5.1 If the audit strip result is not within ± 10% of the expected value, analysis must be halted and corrective action taken to correct the problem. The entire batch may be rerun or re-extracted and run as is appropriate.

9.7 5-Fold Dilution Interference Check, (5FDIC, Serial Diluted Sample or DD):

9.7.1 One MS extract from each batch must be diluted five-fold and analyzed. The result, after correction for dilution, must be within ± 10% of the undiluted result. The sample selected for dilution must have a Lead concentration 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 a Lead 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.

9.7.2 Analysts should use historical data to determine which samples are most likely to meet the requirements for the sample selected to be the 5FDIC and select a sample from amongst 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.

9.7.3 If the 5FDIC fails, chemical or physical interferences should be suspected.

9.7.3.1 Review instrumental reports and the extraction log for possible causes of the failure. Correct any problems.

9.7.3.2 If problems found would have impacted batch results, rerun the entire batch. If the problem was in the analysis of the sample or the 5FDIC (such as a bad reading from the triplicate readings) rerun the sample and 5FDIC.

9.7.3.3 If no obvious cause for the result is found, rerun the sample and the 5FDIC. If there is still more than ± 10% difference in the adjusted results, select another

sample and make a 5FDIC from that sample. If the second sample 5FDIC fails criteria, suspect a systemic problem. Determine and correct the problem and re-extract the batch.

If the second 5FDIC passes, there is likely matrix interference from in the original sample analyzed. Report that sample with the QA qualifier (see Table 6.10.3.1) "LJ".

9.8 Batching:

9.8.1 A batch consists of strips taken from 20 sample filters. Each batch must have a Filter Blank (LB\FB), RSC, MDL, LCS, LCSD, MS, MSD, 5FDIC, and a Method Blank (MB). Additionally, each batch must have audit strips (see 9.6) at both levels provided by the EPA and CRM filters at two levels also provided by EPA (see 9.6). Batch quality is validated by LCS recovery, LCS and LCSD precision, audit strip recoveries, CRM filters and the Method Blank. All samples in a batch, QA, audit, CRM and exposed field samples must be digested and analyzed in the same way.

9.9 Assessing the Internal Standard Response:

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

9.9.1.1 Internal standard responses for standards must be within 70% - 120% of the target response. The Internal Standard associated with Lead must pass this criteria. If that internal standard fails, analysis must be stopped, corrective action taken and at a minimum, all samples since the last passing CCC must be rerun. Samples must be bracketed by passing CCCs.

9.9.1.2 Internal standard responses for samples must be within 70% - 120% of the target response. The Internal Standard associated with Lead must pass this criteria. If the internal standard associated with lead fails for a given sample, that sample must be diluted at least 1:5 with 2% Nitric Acid Blank (see 6.5) and reanalyzed. Continue diluting until this internal standard passes. Adjust the reporting limit accordingly and with the LJ qualifier (see Table 6.10.3.1) and comment "Analyte identified; reported value estimated."

9.10 Data Qualifiers:

9.10.1 The Georgia EPD Ambient Air Monitoring Program (AMP) provides the EPD Laboratory with TSP Lead samples from non-NATTS sites. But in order to simplify reporting, the EPD Laboratory uses NATTS qualifiers when reporting all ambient air monitoring samples.

9.10.2 Null code qualifiers to be used by the Metals laboratory for TSP Lead samples are extracted from of the Technical Assistance Document for the National Ambient Air Toxics Trends and Assessment Program manual (the 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 Air laboratory; the qualifiers below are relevant to metals analyses only). Null qualifier flags listed in Table 9.10.2.1. below are applied to samples that are void. Null codes are entered in the result field as the two letter flags from Table 9.10.2.1. unless otherwise noted for a specific flag. Only one null flag is to be applied to a given voided sample or individual analyte.

Table 9.10.2.1. - Null Qualifier Flags

Qualifier Flags	Description
ND or "Not Detected"	No value detected ("Not Detected" is considered to be a null qualifier for the purposes of NATTS reporting and reported as 0). Result reported value is ≤ 0 (Manually enter "ZD" for "ND" due to the use of ND in Labworks for Not Detected).
AJ	Filter Damage
AM	Miscellaneous void (comment required)
AR	General lab error

9.10.3 Quality Control and Detection Flags to be used for TSP Lead results are extracted from of the TAD, Section 3.3.1.3.15: Table 3.3-2 (SOP reference 13.4). If a Null qualifier from Table 9.10.2.1 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 Lead result.

Table 9.10.3.1 - 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

Table 9.10.3.1 - Quality Control and Detection Flags + Laboratory Generated Flags

Qualifier Flags	Description
LL	Analyte identified; reported value may be biased low

9.10.4 A sample may be reported with up to six QA qualifiers (the maximum that the EPA reporting system, AQS, can handle) if and only if there are no null qualifiers attached to the result. QA qualifiers must be reported in the qualifier field of Labworks and separated by spaces only (***NO Commas!***). Qualifiers in the Labworks qualifier field with be combined with the data point 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 in and assigned 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.

10.1 The filters are transferred to the Metals Laboratory from the Air Laboratory. This transfer is documented with the "TSP-Pb Filter Transfer Log" form (see Figure 15.1).

10.2 TSP Lead extractions are recorded on the "Pb TSP Air Filter Extraction Log Sheet."

10.3 Prior to use, the calibrations of all air displacement (auto) pipettes must be verified.

10.3.1 Verify each auto pipette by dispensing the volume to be used into a tared pan on the balance (see 5.9) and determining 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 the three values must be ≤ 1%. Record the results on the Pb TSP Extraction Sheet in the designated fields on the second page of the form.

10.4 Sample Preparation:

10.4.1 Filters must be handled carefully to prevent collected particulates from being dislodged.

10.4.2 Samples are extracted in batches of up to 20 field samples plus a Method Blank (MB), Filter Blank (FB\LB), MDL(ML),IDL, RBC, LCS, LCSD, MS, MSD, Duplicate Sample, Audit Strips, CRM filters and a 5FDIC.

10.4.3 A QC sample is selected for the MS and MSD. Three strips are also cut from this filter.

10.5 For each filter to be analyzed, cut a 1" by 8" strip from the center of the air filter (one cut should be along the fold crease) using a non-metallic paper cutter. Second and third strips can be cut, as needed, one each from the remaining 2 pieces of the filter.

10.5.1 Using plastic tweezers roll each strip into a coil and place in the bottom of a labeled 50 ml extraction tube. Add 20 ml (± 0.15 ml) of Extraction Solution (see 6.4) to the tube, making sure that the filter strip is entirely covered by the fluid.

10.5.2 The Extraction Solution is added to the tube in two 10 ml increments using a calibrated and verified auto pipette (see 10.3).

10.5.3 The Filter Blank (LB) is prepared by cutting a 1" X 8" strip from a clean filter with a non-metallic paper cutter from the center of an unexposed filter. Two more 1" X 8" strips are cut from this same filter and used for the LCS and LCSD. See section 10.5. The LB is taken through the digestion process.

10.5.4 The LCS and LCSD are prepared from the same filter as the Lab Blank (LB). Using a non-metallic paper cutter, cut two 1" X 8" strips from the center of the filter, one for LCS and one for LCSD. Using plastic tweezers, roll each strip into a coil and place in the bottom of a labeled 50 ml digestion tube. To the middle of the spiked filter, add 20 ml of 5% Extraction Solution (see 6.4) to the digestion tubes. The resultant expected concentration for the LCS and LCSD is 5.0 µg/Strip of Lead (45 µg/Filter or 0.10 µg/ml (100ug\L) in the extract, for a 50 ml final volume after digestion is complete and samples have been allowed to cool to room temperature.

10.5.5 The MS and MSD are prepared from the extra strips cut from the selected QC filter (see 10.4.3). Add 20 ml of 5% Extraction Solution (see 6.4) to the middle of each strip in extraction tubes. Bring to final volume of 50ml with extraction solution after digestion is complete and samples have been allowed to cool to room temperature. The MS and MSD spike recoveries and precision (%RPD) are determined per calculations 11.11.2 and 11.5 respectively.

10.6 Sample Extraction:

10.6.1 A block digester (see 5.3) is pre-heated to a temperature of 95 ± 5° C. (See reference method section 11.1.4)

10.6.2 One extraction tube with 50 ml of water with a temperature probe inserted inside a digestion tube is placed in a random well of the block. The well position is recorded on the filter extraction log. The temperature should stabilize at 95 ± 5° C prior to sample extraction. Over time, the temperature should be measured in every well of the block by rotating which well is used for each sample batch.

10.6.3 Prepared digestion tubes are placed in a heated block digester and covered with disposable ribbed watch glasses (see 5.5). Samples are digested for 1 hour. Monitor the digestion to assure that samples to not evaporate to dryness.

10.6.4 The LCS sample is placed in a different random well with each batch digested and the well position recorded on the filter extraction log. Over time, the LCS should be digested in every well in the block.

10.6.5 After digesting for 1 hour, remove the samples from the hot block and allow them to equilibrate to room temperature.

10.6.6 Bring the samples to 50 ml final volume with reagent water (see 6.1). Tightly cap the tubes and shake each tube vigorously for at least 5 seconds.

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

10.6.8 Shake each tube vigorously and allow settling for at least one hour.

10.6.9 Using a disposable, Lead free, plastic Luer-lock syringe fitted with a 45 µm filter (see 5.12) transfer an aliquot of digestate to a clean, labeled extraction tube for analysis on the ICP-MS.

10.7 Instrumental Analysis:

10.7.1 Prior to sample analysis, warm, tune, test stability, calibrate, and verify the calibration of the instrument. Once the instrument passes all calibration criteria, analysis of samples may begin. Appropriate continuing and ending calibration verifications must be performed.

10.7.2 Below is a typical instrument sequence. For extracts 1 through 10, the following sample order is suggested:

Extract #	Sample
1	Calibration Curve Standards
2	ICV
3	ICB
4	LLCV
5	CCC
6	CCB
7	IDL Standard
8	MDL (ML) Spike Standard
9	Method Blank
10	Filter Blank (LB)
11	RSC
12	LCS
13	LCSD
14	QC Sample
15	MS

Extract #	Sample
16	MSD
16	Sample for 5FDIC
17	5FDIC
18	CCC
19	CCB
20	Pb Audit High (dilution required)*
21	Pb Audit Low (dilution required)*
22	CRM high*(dilution required)*
23	CRM low*(dilution required)*
24	Duplicate Sample
25	CCC
26	CCB
27	LLCV
28	CCC
28	CCB

*The concentrations of the Lead audit are known to be above the top of the calibration curve, and are therefore diluted prior to analysis.

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

10.8 Dilutions:

10.8.1 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.)

10.8.2 Dilutions are prepared by dilution of an aliquot of extract with the 2% HNO_3 Blank Solution (see 6.5) to achieve an acid matched matrix.

10.8.3 Any air displacement pipette used to measure the aliquot must have the pipette volume verified per section 10.3.

10.9 Data Review, Reporting and Validation:

10.9.1 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 submit the completed data package to the supervisor overseeing the method or to the laboratory manager if no supervisor has been assigned to this analysis.

10.9.2 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 the Lead part of the analysis are to be validated. The reviewer then must initial and date the Metals Data Check List. The filters are then transferred back to the air lab, documenting the transfer on the filter transfer form (Figure 15.1)

11. Calculations

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

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

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}):

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

11.3.1 Where:

$\overline{X}$ = Mean of the values

X_i = Individual values 1 through i

n = Number of values

11.4 Percent Relative Standard Deviation (%RSD):

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

11.4.1 Where:

σ_{n-1} = Sample Standard Deviation

$\overline{X}$ = Mean of the values

11.5 Relative Percent Difference (%RPD or RPD):

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

11.5.1 Where:

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

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

11.6 Percent Drift, %Drift:

$$\%\text{Drift} = \frac{(\text{Concentration}_{\text{Calculated}} - \text{Concentration}_{\text{Expected}})}{\text{Concentration}_{\text{Expected}}} * 100$$

11.6.1 Where:

Concentration $_{\text{Calculated}}$ = Concentration calculated from result

Concentration $_{\text{Expected}}$ = Theoretical concentration of the standard

11.7 Extract Concentration:

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

11.8 Sample Concentration per strip (µg/Strip):

11.8.1 The instrument reports extract concentrations as µg/ml. The typical final volume of an extract is 50 ml for a 1" x 8" strip of filter. Therefore the concentration in µg/Strip is calculated as:

$$\mu g/_{\text{Strip}} = \text{Conc}_{\text{extract}} \left(\mu g/_{\text{ml}}\right) * 50 \ \text{ml}/_{\text{Strip}}$$

11.9 Where:

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

11.10 Sample Concentration per filter (µg/Filter):

11.10.1 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:

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

following the calculation in 11.8, or

$$\mu g/_{\text{Filter}} = \text{Conc}_{\text{extract}} \left(\mu g/_{\text{ml}}\right) * 50 \ \text{ml}/_{\text{Strip}_{\text{in}^2}} * 9 \ \text{Filter}_{\text{in}^2}/_{\text{Strip}_{\text{in}^2}}$$

calculated directly from the extract concentration

11.10.2 Where:

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

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

11.11 Percent Recovery:

11.11.1 *LCS/LCSD*:

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

11.11.1.1 Where:

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

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

11.11.2 *MS/MSD*:

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

11.11.2.1 Where:

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

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

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

11.11.2.2

12. Waste Management

12.1 See GA EPD Laboratory DOP – EPD Laboratory Waste Management Standard Operating Procedures, SOP 6-015, online revision.

13. References

13.1 Appendix G to Part 50 - Reference Method for the Determination of Lead in Total Suspended Particulate Matter, CFR Title 40 – Protection of the Environment, Part 50 – National Primary and Secondary Ambient Air Quality Standards, Sept. 1, 2015 or later.

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 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. Practical Reporting Limits (RLs) See Appendix A, Precision and Accuracy Criteria, and Quality Control Approach

14.1 Tables:

Table 14.1 – Acceptance Criteria for PBTSPG

	Analyte	Default LCL % Recovery	Default UCL % Recovery	Default Precision % RPD
LCS/LCSD MS/MSD	TSP - Lead	80	120	20

Table 14.2 Summary of Calibration and QC Procedures for TSP Lead

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
TSP Lead	Lead	Lot Blank Background Determination	Once per lot of filters	Five filter strips each cut from a separate filter from a given lot of filters.		
		Initial Demonstration of Capability (IDC)	Once per analyst	Method Blank < RL, Filter Blank\Lab Blank <RL. 4 LCSs and Unknown recoveries within default QC limits (see Table 9.5.1)	Correct problem and rerun initial demonstration	
		Continuing Demonstration of Capability	Every 6 Months	Method Blank <RL, Filter Blank\Lab Blank <RL. 2 acceptable LCS pairs or 4 LCSs or an unknown sample. See Appendix B, Table B.1 for acceptable LCS and unknown recoveries.	Correct problem and rerun continuing demonstration.	

TSP Lead	Lead	MDL Study Initial	New instrument start-up, annually or whenever major maintenance is performed on the instrument.	See SOP 13.9	.	
		MDL Study continuous	Generated yearly over a two-year period			
		MDLspike	Once oer 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 be a value greater than zero.	Rerun the MDL once and initiate a corrective action. If the MDL fails a second time, do not use the MDL data. Initiate corrective action and use associated sample data.	None
		MDLblank (FB\LB)	Once per analytical batch or as needed to acquire data points per SOPMDL6-007, online version	All batch QC must meet established criteria. All MDLblanks 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 barch if MDLblank is matrix blank	
		Linear Dynamic Range	Every 12 months	Consecutive levels of increasing concentration must be within 10% of expected values.	Dilute any sample result outside of LDR criteria and comment report for dilution and elevated reporting limit.	
		MS Tune	Each analysis day prior to initial calibration	See Table 14.2	Correct problem and re-tune instrument	

TSP Lead	Lead	Stability Check	10 replicates of the Stability Check Solution following the tune and prior to initial calibration	≤ 3% RSD for the 10 replicates.	Correct the problem, rerun once. If still outside of acceptance criteria, re-initiate calibration after the tune.	
		9- point initial calibration (including a blank level)	Run daily prior to the analysis of samples.	Correlation coefficient r ≥0.998 (r^2 ≥0.996) Level 2 cal standard must have %Drift of < 15% from the curve. Levels 3 and up of the cal standards must have a %Drift of < 10% from the curve.	Correct problem and recalibrate	
		Initial Calibration Verification (ICV)	Daily after initial calibration	Recovery ≤ 10% Drift from expected value.	May be rerun once. If ICV fails 2nd run, determine problem, correct and recalibrate	
		Initial Calibration Blank (ICB)	Immediately after ICV.	Lead < 0.001µg/ml	Correct problem and recalibrate	
		Low Level Calibration Verification (LLCV)	Immediately after ICB and at the end of sample analysis	Recovery ≤ 10% Drift from expected value.	May be rerun once. If LLCV fails 2nd run, determine problem, correct and recalibrate	
		Continuing Calibration Verification (CCC)	Immediately after LLCV, after every 10 samples and at the end of sample analysis.	Recovery ≤ 10% Drift from expected value.	May be rerun once. If CCV fails 2nd run, determine problem, correct and rerun all samples analyzed since the last passing CCC.	
		Continuing Calibration Blank (CCB)	Immediately after each CCV.	Lead < 0.001µg/ml	May be rerun once. If CCB fails 2nd run, determine problem, correct and rerun all samples analyzed since the last passing CB.	
		Field Blanks (FB)-Flag	1 per quarter minimum.	Lead <MDL		"FB" qualifier added to Field Blank and all associated field samples.

TSP Lead	Lead	Method Blank (MB)	Once per batch	Lead < RL	Rerun once. If still outside of acceptance criteria, recalibrate. If the MB continues to fail, re-extract batch. If re-extraction fails, find and eliminate lab contamination	"LB" qualifier added to Method Blank and all samples in the batch if re-extraction fails.
		Filter Blank\Lab Blank (LB)	Once per batch	Lead <MDL(ML)	Rerun once, is still outside of acceptance criteria, flag data.	"LB" qualifier added to Method Blank and all samples in batch.
		LCS\Reagent Blank Spike (RBS)	Once per batch	Recovery must be ≤ 20% drift from expected value.	Rerun once if still outside of acceptance criteria, recalibrate. If the LCS continues to fail, re-extract the batch. If re-extraction fails comment and qualify sample. Determine source of problem and correct	Use "LL" or "LK" qualifier as is appropriate.
		Laboratory Control Sample (LCS)	Once per batch	See App. B, Table B.1 for recovery and precision criteria	Rerun once. If still outside of acceptance criteria, recalibrate. If LCS continues to fail, re-extract the batch. If re-extraction fails, comment and qualify sample. Determine source of problem and correct.	Use "LL" or "LK" qualifier as is appropriate.

TSP Lead	Lead	Laboratory Control Sample Duplicate (LCSD)	Once per batch	See App. B, Table B.1 for recovery and precision criteria.	Rerun once. If the LCSD recovery or precision is still outside of acceptance criteria, recalibrate. If the LCSD recovery or precision continues to fail, re-extract the batch. If re-extraction fails, comment and qualify sample. Determine source of problem and correct.	Use "LL" or "LK" qualifier as is appropriate.
		Matrix Spike (MS)	Once per batch	See App. B, Table B.1 for recovery and precision criteria.	If MS recovery fails, matrix interference is suspected and comment report.	Use "LL" or "LK" qualifier as is appropriate.
		Matrix Spike Duplicate (MSD)	Once per batch	See App. B, Table B.1 for recovery and precision criteria.	If MSD recovery fails or the MS/MSD precision fails, matrix interference is suspected and comment report.	Use "LL" or "LK" qualifier as is appropriate.
		Duplicate Sample (DS)	Once 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.

TSP Lead	Lead	Replicate Sample (RS)	Once 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.
		5-Fold Dilution Interference Check (5FDIC)	Once per batch	Sample must have a concentration 10X the low standard. Dilution result (adjusted for dilution) must be ± 10% of undiluted result.	Rerun sample and dilution once. If the 5FDIC still fails, select another sample for dilution.	If not a systemic problem and the 2nd sample passes, flag the first, failing sample as "LJ" for estimated and comment the results.
		Audit Strips (High/Low)	One high and on low audit strip per batch	Results must be within ± 10% of the expected values. ***Note: Extracts must be diluted prior to analysis as is appropriate for the expected value of each strip.***	Rerun once. If the audit strip(s) continue to be outside of acceptance criteria recalibrate. If the audit strips continue to fail, determine the problem and re-extract the batch.	Use "LL" or "LK" qualifier as is appropriate.
		CRM (high and low 47mm filters)	One high and one low per batch	Range varies per ERA lot number	Rerun once. If the CRM is still outside of acceptable criteria, recalibrate. If the CRM continues to fail, determine the problem and re-extract if sample volume allows.	Use "LL" or "LK" qualifier as is appropriate.
		Sample Dilution	Samples over the calibration range must be diluted a minimum of 1:5 (1 part diluted to a final volume of 5 parts) and re-analyzed.	All samples (both QC and field samples) must be analyzed within the calibration range. If the first dilution does not result in a response within the calibration range, adjust dilution accordingly and re-analyze.		

TSP Lead	Lead	IDL standard	Once per batch	Lead concentration < RL	Rerun once. If still outside of acceptance criteria, correct the problem and recalibrate.	
		MDL Standard (ML)	Once per batch	ML standard equal to concentration of lowest calibration curve standard.		
		Internal Standard	Every sample and standard except for tuning.	All internal standard recoveries must be between 70-120% of target response.	Dilute at least 1:5 with 2% Nitric Acid Blank and reanalyze. Continue diluting until the internal standard response meets criteria. Adjust reporting limit accordingly.	Flag with LJ qualifier and comment report "Analyte identified; reported value estimated.

Table 14.2 Tuning Criteria ElAN 9000 Method TSP Lead

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 $^{206, 207, 208}Pb$, ^{115}In	Between 0.6 and 0.8 AMU at 10% peak height.

Table 14.2 Tuning Criteria NexION 1000 Method TSP Lead

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 1.0 ug/L solution of ^{9}Be, ^{24}Mg, ^{59}Co, ^{115}In, and ^{208}Pb	< 5
^{9}Be counts of a 1.0ug\L	>4,500 CPS
^{24}Mg counts of a 1.0 ug/L solution	>5,000 CPS
^{115}In counts of a 1.0 ug/L solution	>80,000 CPS
^{208}Pb counts of a 1.0 ug/L solution	>7,500 CPS
Peak width of $^{24, 25, 26}Mg$ and $^{206, 207, 208}Pb$, ^{115}In	Between 0.6 and 0.8 AMU at 10% peak height.

Appendix A- MDLs and RLs for TSP Lead – Federal Reference Method – 40CFR 50 Appendix G

Table A.1 MDLs and RLs

Parameter/Method	Analyte	MDL (µg/Filter)	*RL (µg/Filter)
TSP-Lead	**Lead**	**0.753**	**2.39**
MDLs are based on MDL baseline studies from 05/03/2021-05/11//2021			

**Note: RL is determined by multiplying the calculated MDL value by 3.18.*

Appendix B for TSP Lead Federal Reference Method- 40CFR 50 Appendix G

Table B.1 Acceptance Criteria for PbTSP (PBTSPG)

QC Type	Analyte	Accuracy (%R)		Precision
		LCL	UCL	(%RPD)
LCS/LCSD	TSP Lead	80	120	20
MS/MSD	TSP Lead	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.
Appendix A & B added.
ICN for SOP included.