

**Standard Operating Procedure for Determination of Lead in TSP by  
Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Hot  
Block Dilute Acid and Hydrogen Peroxide Filter Extraction**

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## 1.0 SCOPE AND APPLICATION

This procedure details the acid extraction and trace elemental lead (Pb) analysis of ambient air samples using an inductively coupled plasma-mass spectrometer (ICP-MS). The extraction procedures are suitable for high-volume Total Suspended Particulate (TSP) ambient air samples collected, as described in 40 CFR Appendix G to part 50, *Reference Method for the Determination of Lead in Suspended Particulate Matter Collected From Ambient Air*, on quartz membrane filters, sized 8" x 10".

This procedure is applicable to the analysis of suspended particulate matter collected with quartz filters. Acid digestion and filtration is required prior to analysis of quartz filter extracts.

## 2.0 METHOD SUMMARY

This procedure describes the determination of Pb by ICP-MS in ambient air samples collected on quartz filters. The 8" x 1" portion is cut from the exposed filter. The filter is digested in a HotBlock™ set to 95°C for 2.5 hours using an extraction fluid containing 1.5% hydrochloric acid (HCl) and 5.55% nitric acid (HNO<sub>3</sub>). Two aliquots of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) are added after 1.5 hours and 2.0 hours of extraction and are allowed to effervesce. After extraction, the samples are filtered and diluted to a final volume of 50 mL. The extract is analyzed by ICP-MS and the data are collected using the manufacturer's software. The Method Detection Limit (MDL) was determined to be 0.000027 µg/m<sup>3</sup> using spiked filter strips analyzed in accordance to 40 CFR Part 136, Appendix B with an assumed filter volume of 2000 m<sup>3</sup> (see Table 21-1). This method is derived from the requirements of EPA Compendium Method IO- 3.5 and SW-846 Method 6020A.

## 3.0 DEFINITIONS AND ABBREVIATIONS

### 3.1 Definitions

- 3.1.1 Blank (BLK) – An analytical sample designed to assess specific sources of contamination.
- 3.1.2 Blank Spike (BS) – A quality control sample (QCS) that contains a quartz filter strip spiked with a known quantity of Pb that is carried through the entire extraction process. This sample is synonymous with the Laboratory Control Sample (LCS).
- 3.1.3 Calibration Blank – A blank solution containing all of the reagents in the same concentration as those used in the analytical sample preparation. This blank is not subject to the preparation method.
- 3.1.4 Calibration Standards – A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions are not subject to the preparation method but contain the same matrix (i.e., the same amount of reagents and/or preservatives) as

the sample preparations to be analyzed.

- 3.1.5 Continuing Calibration Blank (CCB) - A volume of ASTM Type I water acidified with the same acid matrix as is present in the calibration standards used to verify after every continuing calibration verification (CCV) that the instrument blank checks are reading ~ MDL.
- 3.1.6 Continuing Calibration Verification (CCV) – A Pb standard solution prepared by the analyst and used to verify the stability of the instrument calibration with time, and the instrument performance during the analysis of samples. The CCV is the original calibration standard whose concentration is at the midpoint of the calibration curve that is re-analyzed as a sample.
- 3.1.7 Duplicate (DUP) – A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method. The DUP in this method is performed by preparing and analyzing a second quartz filter strip from the parent sample. See Section 13.4 for further elaboration on duplicates.
- 3.1.8 Field Blank (FB) – This is any sample that is submitted from the field and is identified as a blank. This also includes trip blanks.
- 3.1.9 High Standard Verification (HSV) – The HSV is the highest calibration standard that is reanalyzed to verify the accuracy of the calibration curve at that concentration at the beginning of the analytical run.
- 3.1.10 Initial Calibration Blank (ICB) – A volume of ASTM Type I water acidified with the same acid matrix as is present in the calibration standards, which is analyzed after the initial calibration verification (ICV) and used to verify that the instrument blank checks are ~ MDL.
- 3.1.11 Initial Calibration Verification (ICV) – A solution prepared from a stock standard solution obtained from a source separate from that utilized to prepare the calibration standards. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration.
- 3.1.12 Interferents – Substances (atoms, ions, polyatomic ions, etc.) which may affect the analytical result for the element of interest.
- 3.1.13 Internal Standard (ISTD) – A non-target element added to a sample at a known concentration after preparation but prior to analysis. Instrument responses to internal standards are monitored as a means of assessing overall instrument performance.
- 3.1.14 Laboratory Control Sample (LCS) – A spiked aliquot of laboratory reagent blank (LRB) with a blank quartz filter used as a QCS that is prepared and brought through the entire digestion/extraction and analytical process to

demonstrate spike recoveries.

- 3.1.15 Lower Limit of Quantitation Check (LLQC) – The check sample is used to both establish and confirm the lower limit of quantitation and is prepared by spiking a low concentration of analyte into reagent water and carrying the solution through the entire preparation and analytical procedure.
- 3.1.16 Lower Limit of Quantitation (LLQL) – The lower limit of quantitation is considered the lowest reliable laboratory reporting concentrations and should be established from the lower limit of quantitation check sample and then confirmed using either the lowest calibration point or from a low level calibration check standard.
- 3.1.17 Low Level Calibration Verification (LCV) – A stock standard solution prepared using the same source as the calibration standards that is analyzed to verify the LLQL. The standard is prepared at the same concentration as the LLQL and must meet an acceptance criteria of  $\pm 30\%$ . An LCV is analyzed at the beginning and end of every analysis.
- 3.1.18 Limit of Quantification (LOQ) – The lowest concentration of an analyte that produces a signal/response that is sufficiently greater than the signal/response of lab reagent blanks to enable reliable detection and quantification during routine lab operating conditions. Statistically defined, this is the concentration of analyte in sample matrix that produces an instrument signal/response that is 10 times the standard deviation above the LRB (at 99% confidence, n-1 degree freedom).
- 3.1.19 Laboratory Reagent Blank (LRB) – An aliquot of ASTM Type I water that is treated exactly as a sample including exposure to all labware, equipment, solvents, reagents and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus.
- 3.1.20 Linear Dynamic Range (LDR) – The concentration range over which the analytical working curve generated from the calibration standards remains linear.
- 3.1.21 Matrix Interference/Effect – In general, the interference and/or effect that particular matrix constituents may cause during sample processing and/or analysis. Matrix effects may be determined to exist from the careful interpretation of quality control (QC) samples and criteria. Examples of observed effects include but are not limited to poor recoveries of spikes/ISTD and poor percent differences.
- 3.1.22 Matrix Spike and Matrix Spike Duplicate (MS/MSD) – A sample chosen in a batch where additional filter strips are spiked prior to digestion/extraction with known quantities of Pb and carried through the

entire analytical process to demonstrate their spike recoveries and precision.

- 3.1.23 Method Blank (MB) – An aliquot of LRB with a blank quartz filter strip that is carried through the entire preparation and extraction process to demonstrate background contamination contribution from the filter and process.
- 3.1.24 Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.
- 3.1.25 Performance Evaluation (PE) Sample – A sample of known composition provided by a source outside the laboratory for analysis that evaluates the laboratory's analytical performance.
- 3.1.26 Quality Control Sample (QCS) – A solution containing known concentrations of Pb that is used to fortify an aliquot of LRB matrix. The QCS is prepared from a source(s) external to the laboratory and is used to verify the laboratory's analytical performance.
- 3.1.27 Serial Dilution (SRD) – The dilution of a sample by a factor of five. If the undiluted parent sample concentration is minimally a factor of 50 above the MDL, the diluted sample should agree with the parent sample concentration within  $\pm 10\%$  when corrected by the dilution factor. The SRD may indicate the influence of interferences.
- 3.1.28 Standard Reference Material (SRM) – A prepared standard material that has certified metals concentrations, for example, the NIST 1648a (Urban particulate matter with certified concentrations of lead at  $0.655 \pm 0.033$  mass fraction (in %)). The SRM is used to verify the extraction procedure.
- 3.1.29 Stock Standard Solution – A commercially prepared standard solution (traceable to NIST or other certified standard sources), which can be diluted to derive other standards.
- 3.1.30 Tuning Solution – A solution used to determine acceptable instrument performance prior to calibration and sample analyses. This solution is used for mass calibration, nebulizer optimization, auto lens optimization, and daily performance reports. Acceptable instrument performance is demonstrated by the analysis of the tuning solution in accordance with the instrument manufacturer.

## 3.2 Abbreviations

amu	Atomic Mass Units
ASTM	American Society for Testing and Materials
COC	Chain of Custody

cps	Counts Per Second
DI	Deionized
L	Liter(s)
LDPE	Low Density Polyethelyene
LIMS	Laboratory Information Management System
M~	Megohm
m	Meter(s)
m <sup>3</sup>	Cubic Meter(s)
mg	Milligram
mg/L	Milligram(s) per Liter(s)
min	Minute(s)
mL	Milliliter(s)
ng	Nanogram(s)
ng/mL	Nanogram(s) per milliliter(s)
NIST	National Institute of Standards and Technology
µg/L	Microgram(s) per liter
µg/m <sup>3</sup>	Microgram(s) per cubic meter
µL	Microliter (s)
µm	Micrometer(s)
v/v	volume to volume ratio

## 4.0 INTERFERENCES

**Note:** The background level of Pb on a given lot of quartz filters can vary. Any background levels found on blanks should be documented for all the filters from the corresponding lot. It is recommended to consult 40 CFR Appendix G to part 50, Section 6.1 for guidance.

### 4.1 Laboratory Interferences

4.1.1 Wear powder-free nitrile gloves when handling unexposed or exposed filters.

4.1.2 Clean all equipment used in the sample preparation and analysis in a manner consistent with good laboratory practices for metals analysis (See Sections 13.9).

4.1.3 Use ASTM Type I DI water or equivalent, with a resistivity greater than 17.3 MΩ·cm, for sample extraction and standard preparation. Record the water resistivity prior to use.

### 4.2 Chemical Interferences

Pay close attention to the nature of solutions introduced to the ICP-MS.

4.2.1 Nitric acid must be less than 2% (v/v) for ICP-MS analysis to minimize the damage to the interface and to minimize isobaric molecular interferences.

The use of platinum cones and other acid-resistant sample introduction components can be used for more aggressive acid matrices.

- 4.2.2 The final dilutions of sample extracts must match the acid content of the calibration standards in order to match potential interferences.
- 4.2.3 The concentrations of dissolved solids in analysis solutions should be less than 2% to protect the sample interface on the instrument and prevent signal suppression. Higher concentrations may plug the sample and/or skimmer cone orifices.

**Note:** Protect the channel electron multiplier from high chemical concentrations (high ion currents). The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this period, response factors are constantly changing, which causes instrument instability that invalidates the calibration curve, and thereby, invalidates all associated sample results. A sodium bicarbonate ( $\text{NaHCO}_3$ ) sample matrix is known to cause this problem.

### 4.3 Instrument Interferences

- 4.3.1 Isobaric molecular and doubly charged ion interferences are caused by polyatomic ions or more than one charge.
- 4.3.2 Spectral interferences result from the presence of other isotopes or ions that have the same atomic weight or mass number as the analyte.

Pb isotopes 206, 207 and 208 do have interferences of Platinum (190) + Oxygen (16), Iridium (191) + Oxygen (16) and Platinum (192) + Oxygen (16) respectively; however, Platinum and Iridium should not have significant concentrations in ambient air to warrant correction.

- 4.3.3 Transport interferences are a specific physical interference associated with the sample nebulization and transport process through the instrument. These usually result from sample matrix components that influence the aerosol formation or cause a change in the surface tension or viscosity. Changes in the matrix composition can cause observed signal suppression or enhancement.
- 4.3.4 Matrix interferences may be caused by elemental chemical and physical properties in the samples. For matrices of known composition, match the composition of the calibration and QC standards to that of the samples. For matrices of unknown composition, use an ISTD that has been matched to the analytes' chemical and physical properties (i.e., ionization potential,  $\pm 50$  amu) so that the ISTD and element of interest behave similarly during the analytical process.
- 4.3.5 Memory interferences can occur when there are large concentration

differences between samples or standards that are analyzed sequentially. Sample deposition on the sample and skimmer cones, spray chamber, peristaltic pump tubing and the type of nebulizer all affect the extent of the memory interferences that are observed. The rinse period between samples must be long enough to eliminate significant memory interferences.

- 4.3.6 Lead values are reported from isotope 208; however, all three isotopes must be used to quantitate lead to allow for the variability of lead isotopes in nature. The following correction equation must be applied to isotope 208:

$$(1.000) (^{206}\text{Pb}) + (1.000) (^{207}\text{Pb}) + (1.000) (^{208}\text{Pb})$$

## 5.0 SAFETY

- 5.1 Personal protection should be used for all work performed in the inorganic laboratory, (e.g., gloves, safety glasses, laboratory coats, etc.).
- 5.2 The compressed gas cylinders must be stored and handled according to relevant safety codes outlined in the corporate health and safety manual. In use, the cylinders must be secured to an immovable structure and moved using a gas cylinder cart.
- 5.3 Make sure that sample vials are kept capped and in racks to prevent spills.
- 5.4 All personnel should be trained in the handling, extraction and analysis of acid samples for inorganic analysis.
- 5.5 Strong acids must not be stored with organic solvents or samples.

## 6.0 EQUIPMENT

### 6.1 ICP-MS

This method uses the PerkinElmer SCIEX™ ELAN® 9000 ICP-MS, or equivalent. The system must consist of an inductively coupled plasma source, ion optics, a quadrupole mass spectrometer, a computer that controls the instrument, data acquisition and data handling software, a printer, an autosampler and a recirculator. The quadrupole mass spectrometer has a mass range of 2 to 270 amu. The ICP-MS should be maintained appropriately according to manufacturer recommendations.

### 6.2 Digestion System

Environmental Express HotBlock™ Digestion System or equivalent system capable of maintaining a temperature of 95°C within ± 2°C. This temperature will heat the samples to a temperature of ~85°C (±5°C).



## 7.0 MATERIALS

- 7.1 Graduated polypropylene sample vials with screw caps, 50 mL volume (certified to be within  $\pm 0.2$  mL).
- 7.2 Pipetters with adjustable volumes ranging from 0.5  $\mu\text{L}$  to 10 mL and disposable tips. Mechanical pipettes must be verified for accuracy quarterly (or every three months). Repeatable, mechanical pipettes, such as Eppendorf Research<sup>®</sup>, may be used and their accuracy should be verified on a quarterly basis to be within the manufacturer's specifications. If a pipette's accuracy exceeds the manufacturer's specifications its use should be discontinued and it should be replaced or sent in for repair.
- 7.3 Reflux caps and FilterMate<sup>™</sup> 2  $\mu\text{m}$  Teflon<sup>®</sup> filters with plungers.
- 7.4 Miscellaneous: powder-free nitrile gloves; disposable laboratory wipes; self adhesive labels.
- 7.5 Volumetric flasks. Teflon<sup>®</sup>, Class A, 100, 250, 500 and 1,000 mL capacities.
- 7.6 Storage bottles. Wide and narrow mouth, Teflon<sup>®</sup> FEP (fluorinated ethylene propylene) with Tefzel ETFE (ethylene tetrafluorethylene) screw closure, 100, 250 500, 1,000 and 2,000 mL capacities.
- 7.7 Wash bottles made of LDPE and Teflon<sup>®</sup> having 500 mL and 1 L capacities.
- 7.8 Plastic or Teflon<sup>®</sup> coated tweezers.
- 7.9 Filter cutting apparatus with 2 part Plexiglas board and plastic rotary cutter.

## 8.0 CHEMICALS, REAGENTS, STANDARDS AND THEIR PREPARATION

**Note:** In general, chemicals, reagents and commercial stock standards expire when specified by the manufacturer. If the manufacturer does not provide an expiration date then they shall expire one year from the opened date. Standards and other solutions prepared in-house expire as specified throughout the procedure.

- 8.1 High Purity Acids –Concentrated ultrapure acids stored in Teflon<sup>®</sup> Bottles. These reagents are used for the preparation of sample extraction fluid and all standards.
  - 8.1.1 60-70% Nitric Acid ( $\text{HNO}_3$ )
  - 8.1.2 32-35% Hydrochloric Acid ( $\text{HCl}$ )
  - 8.1.3 Extraction fluid (1.5%  $\text{HCl}$  and 5.55%  $\text{HNO}_3$ )

Preparation: The extraction fluid is prepared in a 1,000 mL volumetric flask by adding 15 mL of  $\text{HCl}$  and 55.5 mL of  $\text{HNO}_3$  to ~900 mL ASTM Type I

DI water. Dilute to 1000 mL with DI water and mix thoroughly.

8.1.4 Standard solvent (0.3% HCl and 1.11% HNO<sub>3</sub>)

Preparation: The standard solvent is prepared in a 1,000 mL volumetric flask by adding 3 mL of HCl and 11.1 mL of HNO<sub>3</sub> to ~900 mL ASTM Type I DI water. Dilute to 1,000 mL with DI water and mix thoroughly.

8.2 30-32% Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) – Concentrated ultrapure stored in Teflon<sup>®</sup> bottles. This reagent is used in the extraction procedure.

8.3 Nitric Acid – Concentrated Trace Metal Grade in 2.5 L glass for rinse blank and labware cleaning.

8.3.1 Rinse blank (2% HNO<sub>3</sub> and 0.5% HCl)

Preparation: The rinse blank is prepared in a 1,000 mL volumetric flask by adding 20 mL of trace metal grade HNO<sub>3</sub> and 5 mL of HCl to ~900 mL ASTM Type I DI water. Dilute to 1,000 mL with DI water and mix thoroughly.

8.3.2 10% HNO<sub>3</sub> acid bath for labware cleaning.

Preparation: The acid bath solution is prepared by adding 2.5 L of trace metal grade HNO<sub>3</sub> to 22.5 L ASTM Type I DI water.

8.4 ASTM Type I deionized water - With a resistivity greater than 17.3 MΩ·cm.

8.5 Argon gas – Purity > 99.996%, Oxygen < 5 mg/L, Hydrogen < 1 mg/L, Nitrogen < 20 mg/L and Water < 4 mg/L.

8.6 Calibration Working Standard – Prepared standard used to create the calibration standards.

Preparation: The calibration working standard is prepared at a lead concentration of 0.2 µg/mL by diluting 0.02 mL of a 1,000 µg/mL Pb standard to 100 mL with standard solvent as described in Section 8.1.4.

8.7 Secondary Source Control Standard – A commercially prepared Pb element secondary source (different manufacturer from the calibration standard) NIST traceable calibration standard utilized to produce the ICV is run as a verification of the instrument's calibration for accuracy and precision (99.99 – 99.999% pure).

8.8 Single-Element Stock Standard Solutions – Commercially prepared NIST traceable standards from ultra high-purity grade Pb (99.99 – 99.999% pure) with a concentration of 1,000 µg/mL designed for use with ICP-MS instruments.

8.9 Smart Tune Solution – Although custom tuning solutions may be used, the tuning solution for this procedure may be purchased through the manufacturer or prepared

in-house using single-element standards. Solutions prepared in-house should follow the manufacturer's recommendations for added elements and concentrations.

8.10 Dual Detector Cross Calibration Solution – Refer to Section 10.3 for the purpose of this solution. Although custom cross calibration solutions can be used, it may be purchased through the manufacturer or prepared in-house using single-element standards.

8.11 ISTD stock standard – A commercially prepared 1,000 µg/mL bismuth standard (99.9998% pure) is used to prepare the internal standard, which can be purchased from vendors such as High-Purity™ Standards.

8.12 Internal Standard Spike Solution – Prepared standard used to manually spike all calibration and QC standards as well as all samples that are analyzed by the ICP-MS.

Preparation: The internal standard solution is prepared at a Bi concentration of 35 µg/mL by diluting 3.5 mL of a 1,000 µg/mL Bi standard to 100 mL with standard solvent. For every 10 mL of sample, 20 µL of ISTD spike solution should be added prior to instrument analysis.

8.13 Matrix Spike (MS) Standard – The MS standard is used to spike the BS/LCS and MS/MSD (See Section 13.3.1 and 13.3.2).

Preparation: The matrix spike standard is prepared at a lead concentration of 0.5 µg/mL by diluting 0.025 mL of a 1,000 µg/mL Pb standard to 50 mL with standard solvent. Information on how to prepare the spiked sample can be found in Section 11.1.5.

8.14 Second Source Working Standard – The second source working standard is used to create the ICV.

Preparation: The second source working standard is prepared at a lead concentration of 0.005 µg/mL by diluting 0.10 mL of a 1,000 µg/mL Pb secondary source control standard to 100 mL with standard solvent. The ICV is then prepared by diluting 0.50 mL of the second source working standard to 100 mL with standard solvent.

8.15 Citranox® Acid Cleaner and Detergent, or equivalent - Prepare a 5% solution for labware cleaning and decontamination. This detergent bath should be changed about once every month, depending on use.

8.16 Standard Reference Material (SRM) – The standard reference material used to prepare the SRM samples. NIST SRM 1648a (Urban particulate matter with certified concentrations of lead at  $0.655 \pm 0.033$  mass fraction (in %)) is used to verify the extraction procedure.

Preparation: The SRM sample is prepared for extraction by adding a blank 8x1” filter strip to a clean sample vial as described in Section 11.1.4. The loaded vial is then placed on an analytical 5-place balance and zeroed. Add no less than 5.0 mg of NIST SRM 1648a to the sample vial, but do not exceed 7.0 mg. The SRM is then ready for extraction as described in Section 11.1.

- 8.17 Lower Limit of Quantitation Check (LLQC) – This quality control sample is used to determine the LLQL, and is prepared by creating a spike solution that will create a final concentration of analyte in the sample matrix that produces an instrument signal/response that is 10x the standard deviation above the lab reagent blank (at 99% confidence; n-1 degrees of freedom). Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within  $\pm 30\%$  of their true value.

Preparation: This quality control check is prepared by spiking an aliquot of prepared spiking standard into 10mL of extraction fluid (Section 8.1.4) and bring to a final volume 50mL with DI water. When brought to volume, the final solution is representative of the standard solvent (Section 8.1.4).

## **9.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE**

### 9.1 Collection and Handling of Filters

Whenever the filter is handled use clean disposable nitrile gloves and if necessary clean Teflon<sup>®</sup> coated (no exposed metal surfaces) or plastic tweezers. Never touch the particulate laden surface of the filter and take care not to puncture or damage the filter with the tweezers. See also Section 13.1.

### 9.2 Preservation and Storage of Filters

Samples do not have a preservative and can be stored for up to 180 days in ambient conditions. Upon retrieval from field sampling during humid or rainy conditions be certain the filter is not moisture-laden. Damp filters may stick to the sample transport container causing damage and thereby invalidating the sample. If the sample is found to be moisture-laden allow the membrane to dry before enclosing in the transport container. Once the filter arrives at the laboratory, a unique laboratory identification number is assigned and placed on the outside of the COC, sample envelope and/or container for tracking and storage purposes. All samples must be extracted within 180 days of the sample date.

After a filter strip has been removed, the remaining filter is stored in the original envelope with the applicable bench sheet and associated filters in the laboratory. Once the associated data has been reported to the client, the filter may be moved to storage. All non-extracted filter media is retained as determined by the site operating agency.

### 9.3 Shipment of Filters

When filters are shipped to or from the laboratory follow proper handling instructions in Section 9.1 and take proper precautions when packing so filters are not exposed to contaminants or damage during shipment.

## 10.0 CALIBRATION AND STANDARDIZATION

### 10.1 Daily Optimization Procedures

Daily optimization is performed according to instrument manufacturer recommendations. Refer to the instrument user manual for specific information on how to perform optimizations.

### 10.2 Mass Calibration and Resolution

Before performing any kind of calibration or optimization, allow a period of not less than 30 minutes (preferably 1 hour) for instrument warm-up. After the warm-up, the mass calibration and resolution may be optimized using the tuning solution by running a mass calibration and resolution optimization. Resolution at low mass is indicated by magnesium isotopes 24, 25, and 26. Resolution at high mass is indicated by lead isotopes 206, 207, and 208. For optimal performance, adjust spectrometer mass calibration to  $\pm 0.05$  amu and the resolution to produce a peak width of  $0.70 \pm 0.1$  amu at 5% peak height. Repeat mass calibration and resolution optimization if it has shifted by more than  $\pm 0.05$  or  $\pm 0.1$  amu respectively.

### 10.3 Dual Detector Cross Calibration

The dual detector cross calibration is used to provide a smooth transition from the pulse counting mode to the analog mode, which extends the linear dynamic range of the detector. This calibration should be performed daily or when instrument maintenance to the sample introduction system generates unsatisfactory performance reports.

### 10.4 Daily Performance

10.4.1 The daily performance report must be generated before each analysis.

10.4.2 Instrument stability must be demonstrated by running a daily performance check using the tuning solution. A minimum of five replicates with resulting relative standard deviations of absolute signals for all analytes of less than 5% is required prior to calibration. Consult the instrument manufacturer's manual for specific daily performance criteria.

## 10.5 Calibration

10.5.1 Prior to initial calibration, set up proper instrument software routines for quantitative analysis (i.e., autosampler table, QC sample names etc.). The instrument must be calibrated using a minimum of a calibration blank and four Pb calibration standards. Consideration should be given to have lower concentrations in order to better define the LDR and LOQ. A typical range for calibration standards is 0.0005 to 0.010  $\mu\text{g/mL}$ . A minimum of 3 replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

For a linear calibration to be considered acceptable, the calibration curve should have a correlation coefficient  $\geq 0.998$ . The resulting curve should then be verified with mid-level and low-level calibration standards as described in Section 13.6.

**Note:** For non-linear calibration curves, please see SW-846 Method 6020A, Section 10.6 for acceptance criteria.

Preparation: Non-blank calibration standards are prepared by diluting the calibration working standard (0.20  $\mu\text{g/mL}$ ) to appropriate levels using the standard solvent. The following is an example of how to prepare four calibrations standards using the calibration working standard:

	Amt. of Calibration Working Standard (mL)	Final Volume (mL)	Final Concentration ( $\mu\text{g/mL}$ )
Cal Standard 1	0.25	100	0.0005
Cal Standard 2	0.5	100	0.001
Cal Standard 3	12.5	500	0.005
Cal Standard 4	12.5	250	0.010

10.5.2 For matrices of known composition, match the composition of the calibration and QC standards to that of the samples. For matrices of unknown composition, use an ISTD that has been matched to the analytes chemical and physical properties (i.e., ionization potential,  $\pm 50$  amu) so that the ISTD and element of interest behave similarly during the analytical process.

10.5.3 The rinse blank should flush the system between solution changes for blanks, standards, and samples. Allow sufficient rinse time ( $\sim 1$  min) to remove traces of the previous sample. Solutions should aspirate for at least 30 seconds prior to the acquisition of data to establish equilibrium.

10.5.4 Refer to Section 8.1.4 for the acid concentration at which to prepare the

standard solvent. Once prepared, all calibration standards must be stored in Teflon<sup>®</sup> bottles/flasks.

**Note:** Commercial stock standards used to prepare calibration standards and other quality control standards must be used within their expiration date. Calibration blanks/standards and other QC standards made from the stock standards may be set to expire no later than any reagent's or standard's expiration date used for preparation.

10.5.5 Refer to the quality control requirements presented in Table 21-2 for calibration acceptance criteria.

## 10.6 Internal Standardization

10.6.1 Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. ISTD quality control requirements as described in Section 13.7 must be followed.

10.6.2 The ISTD for this method is <sup>209</sup>Bi, or another element suitable for internal standardization of high mass elements (<sup>165</sup>Ho may be used but is not ideal). The internal standard must be manually added to each calibration standard **after** they are brought to volume.

10.6.3 Concentrations of the internal standards for this method are determined by the concentration of each element that will produce an intensity that is sufficiently stable. Typical intensities are between 200,000 and 500,000 cps; however, ideal intensities may be as high as 1,000,000 cps.

10.6.4 The concentration of the internal standard must be added equally and in the same manner to the calibration blank/standards, QC standards and samples. For each 10 mL of blank, standard, or sample to be loaded onto the autosampler, 0.02 mL of ISTD solution must be added with a mechanical pipette prior to analysis. For example, after pipetting 0.02 mL of ISTD solution into an autosampler tube add 10 mL of sample and mix with pipettor. If a 50 mL tube was used instead, then 0.10 mL of ISTD would be added.

## 10.7 Instrument Performance

10.7.1 After instrument calibration, an ICV and ICB must be analyzed for initial verification of the calibration curve. Refer to Sections 13.6.1 and 13.2.2 and Table 21-2 for specific QC criteria.

10.7.2 To verify that the instrument is properly calibrated on a continuing basis, analyze a CCV and CCB after every 10 samples.

## 10.8 Linear Dynamic Range (LDR)

The LDR study is performed every 6 months to determine the maximum concentration level at which the initial calibration is linear. The recovery criterion for the LDR is 90-110%. Dilutions must be performed for Pb concentrations over 90% of the established LDR. If an LDR study has not been performed within 6 months, any Pb concentrations over the highest calibration concentration must be diluted.

## 10.9 Lower Limit of Quantitation Limit (LLQL)

The LLQL study is performed every 6 months to determine the lowest concentration level at which data may be reported. This is done by extracting and analyzing a lower limit quantitation check (LLQC). The recovery criterion for the LLQC is 70-130%. Any results reported below the LLQL must be qualified as an estimated value.

## **11.0 PROCEDURE**

### 11.1 Filter Extraction Procedure

- 11.1.1 Prior to sample processing, be sure to turn on the HotBlock™ and start the appropriate program to allow it to warm to extraction temperature.
- 11.1.2 Wipe the filter-cutting apparatus and Teflon® rotary-cutter with a Kimwipe® prior to use.
- 11.1.3 If the filter is not already folded in half, carefully fold the filter in half along the 10" length with the side containing the particulates facing on the inside of the fold. Using the filter-cutting apparatus, align the 10" folded edge of the filter along the dashed line. Cut a 4" by 1" section of the folded filter using the Teflon® rotary-cutter.
- 11.1.4 Carefully fold the 4" by 1" section end over end into a size just larger than the mouth of the extraction vial. Place the folded filter into the labeled extraction vial and push all the way to the bottom using a pre-cleaned Teflon® stirring rod for each sample to be sure the filter is below the 10 mL line.
- 11.1.5 Add 0.5 mL of Matrix Spike Solution to LCS, MS/MSD samples. Add 10 mL of extraction fluid (1.5% HCl, 5.55% HNO<sub>3</sub>) to the extraction tube with the cut filter. See Section 8.1.3 for information about how to prepare the extraction fluid.
- 11.1.6 The SRM sample is prepared for extraction by adding a blank 8x1" filter strip to a clean sample vial as described in Section 11.1.4. The loaded



vial is then weighed, as described in Section 8.16 using NIST SRM 1648a. Add 10 mL extraction fluid to the extraction tube.

11.1.7 Place all samples in a plastic HotBlock™ rack and add a reflux cap to each sample tube and place in HotBlock™. Samples will be extracted for a total time of 2.5 hours with the HotBlock™ temperature set to 95°C (± 2°C). This temperature will heat the samples to a temperature of ~85°C (± 5°C).

**Note:** Monitor sample temperature with a thermometer in an extraction tube with a reflux cap and 10 mL of extraction fluid.

11.1.8 After 1.5 hours of extraction, add 1.8 mL of H<sub>2</sub>O<sub>2</sub> and allow to effervesce for 0.5 hours. Add an additional 1.8 mL of H<sub>2</sub>O<sub>2</sub> after 2 hours of extraction and allow to effervesce again for 0.5 hours. This completes the extraction process.

11.1.9 After extraction is complete, remove the rack of samples and allow them to cool to room temperature. Add 20 mL of DI water and allow to stand for 0.5 hours. This critical step must not be omitted; it allows the acid to diffuse from the filter into the rinse.

11.1.10 After this time period, bring the sample volume to the 50 mL line on the vial (certified Class A vessel with a tolerance of 0.5% or 0.25 mL for a 50 mL vial) with a wash bottle filled with ASTM Type I DI water prior to filtering.

**Note:** If the final volume exceeds 50 mL, ± 0.25 mL, measure the amount exceeded using an appropriate pipette (usually the 1 or 5 mL) and record the final sample volume. Using the pipettor, pull sample from the vial in varying increments until enough liquid is removed so that the sample line is level with the 50 mL line on the vial. Add the amount of liquid removed to 50 mL and record that as the final volume. This information must be entered into the LIMS so that the final sample concentration is calculated and reported correctly. Overfilling may be avoided by using fine streamed wash bottles to add the D.I. water.

11.1.11 Carefully filter the sample extract with a 2 µm FilterMate™ filter.

**Note:** When using a FilterMate™, slowly plunge the filter through the sample and be sure to get the filter all the way to the bottom. Do not force the filter or you will rupture the FilterMate™ filter. Ruptured filters that caused a loss of sample extract result in the re-extraction of that sample.

11.1.12 Homogenize the sample by inverting three times and then the extract is ready to be analyzed. The extracted filter and FilterMate™ remain in

the sample vial with the extract to be analyzed. This does not interfere with sample recoveries or analysis.

## 11.2 Filter Analysis Procedure

11.2.1 Prior to analyzing samples, check the instrument performance as described in Sections 10.1, 10.2 and 10.3. Refer to the instrument manual for manufacturer recommended performance specifications. If the performance check fails, follow the optimization procedures recommended by the instrument manufacturer.

11.2.2 Before starting the calibration adequately flush the sample introduction system with rinse blank and be certain the rinse blank bottle has enough solution for the analysis.

11.2.3 Pour off the calibration blank/standards and initial/continuing QC standards (ICV, ICB, HSV, CCV, LCV, CCB) into autosampler tubes and add the appropriate amount of ISTD. Place the tubes in the appropriate autosampler positions. See SOP Section 10.6.4 for specific instruction on how to add ISTD to standards.

11.2.4 Start the analysis. Once the calibration has been completed and reviewed, save the calibration file and print a calibration report to be included with the sequence files.

11.2.5 Label autosampler tubes with the correct QCS or sample ID and spike 20 µl of ISTD into the bottom of each empty tube if using 10 mL of sample. Carefully pipette 10 mL of the sample for analysis and add to the appropriate tube. Once the sample has been dispensed into the tube it may be re-pipetted with the same pipette tip to mix 2 times. Then place the samples in the appropriate autosampler location for analysis. See SOP Section 10.6.4 for specific instruction on how to add ISTD to QCS and samples.

11.2.6 Samples with Pb concentrations greater than 90% of the current LDR must be diluted and re-analyzed.

## 11.3 Data Review

All instrument data should be first reviewed by the analyst and then a secondary reviewer.

### 11.3.1 Initial Calibration

In addition to the requirements outlined in Table 21-2, the analyst and reviewer must also verify that the intensities measured for reportable

analytes in the calibration blank are acceptable and will not interfere with the sensitivity. A review of previously analyzed calibration blanks can demonstrate acceptable intensity values. The intensities of the internal standards in the calibration standard should be monitored relative to the intensities seen in the calibration blank.

#### 11.3.2 Internal Standards

Internal standards must be monitored for each sample throughout a sequence; the measured intensities must stay between 60 and 125% of the measured intensity of the calibration blank. See Section 13.7 for corrective actions to remedy internal standard intensities that are measured outside of this range.

#### 11.3.3 Relative Standard Deviation (RSD)

Follow the prescribed acceptance criteria for RSDs for calibration standards as listed in Table 21-2. Sample RSDs should also be monitored throughout analysis, especially for analyte concentrations greater than the LOQ. High RSDs (greater than 20%) can indicate memory interference from previous samples, as well as other instrumentation issues that may need to be corrected before analysis can be continued.

#### 11.3.4 Multiple Isotopes

Pb must be monitored for all three isotopes (206, 207, and 208). Examine the concentration calculated for each isotope, or isotope ratios, to detect a possible spectral interference. Consider both primary and secondary isotopes when evaluating the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes (208); therefore, differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

#### 11.3.5 Reprocessing Data

Reprocessed data must include reprocessing of all calibration standards and QC samples associated with the reprocessed sample results. Original data shall be kept with the reprocessed data and annotated with the reason for reprocessing. It is imperative that the reprocessed calibration file be saved as a separate file from the original calibration file.

## 12.0 CALCULATIONS

### 12.1 Analyte Concentration

Metal concentration in the air sample should be calculated as follows:

$$C = \frac{[C_i \times V_f \times 9]}{V_{std}}$$

Where:

C = concentration,  $\mu\text{g metal}/\text{m}^3$

$C_i$  = metal concentration determined from Section 11.2,  $\mu\text{g metal}/\text{L}$ .

$V_f$  = total sample extraction volume from extraction procedure (i.e., 0.05 L).

9 = [Usable filter area (8"×9")] / [Exposed area of one strip ((4"×1") × 2) representing a strip that has been folded]

$V_{std}$  = standard air volume pulled through the filter,  $\text{m}^3$

### 12.2 Relative Percent Difference (RPD) The RPD is calculated as follows:

$$\text{RPD} = (R_1 - R_2) / [(R_1 + R_2)/2] \times 100$$

Where:

$R_1, R_2$  = values that are being compared (i.e., response factors in calibration verification)

### 12.3 Percent Recovery

Percent Recovery is calculated as follows:

$$\text{Percent Recovery} = (\text{Analytical result}/\text{Theoretical result}) \times 100$$

### 12.4 Relative Standard Deviation (RSD)

RSD is calculated as follows:

$$\text{RSD} = (\text{Standard Deviation}/\text{Average}) \times 100$$

## 13.0 QUALITY CONTROL

The analyst must perform the quality control checks listed in Table 21-2 and meet the requirements in this section. Method Quality Objectives (MQO) and data assessment criteria are determined from the results of the quality control samples. The MQO criteria are summarized in Table 21-2.

### 13.1 Sample Collection Quality Control

- 13.1.1 Filters which are dropped or become contaminated with any foreign matter (i.e., dirt, finger marks, ink, liquids, etc.) are invalid.
- 13.1.2 Filters with tears or pinholes, which occurred before, during or after sampling, are invalid.
- 13.1.3 A power failure during a field sample collection event invalidates the sample collection during that event.

### 13.2 Blanks

- 13.2.1 The Rinse Blank must be used to flush the system between standards and samples. Refer to Section 8.3.1 for preparation details.
- 13.2.2 Initial Calibration Blank (ICB) is analyzed immediately following the initial calibration verification. The absolute value of the instrument response should be less than the method detection limit. If the ICB fails it may be re-analyzed twice. If the ICB still does not pass, the analysis should be terminated, the problem corrected and, if appropriate, the ICV and ICB must be verified again before the analysis can continue. If the ICV or ICB still fail, recalibrate the instrument and verify the ICV and ICB again before continuing. If recalibration fails to correct the problem, all QC and samples included in the sequence must be flagged.
- 13.2.3 Continuing Calibration Blanks (CCB) are analyzed following each continuing calibration verification sample. The acceptance criteria are the same as the ICB. If the first CCB analyzed fails, it may be reanalyzed once. If it fails again the analysis should be terminated, the instrument recalibrated and the initial QC repeated. If the CCB fails later, in the analysis it may also be reanalyzed once but if it fails again any samples between the last valid and failing CCB must be either reanalyzed or the affected samples and Pb concentrations must be flagged.
- 13.2.4 Laboratory Reagent Blank (LRB) consists of all reagents (extraction fluid) used to process samples and is carried through the entire preparation and extraction process to determine the background levels, if any, from the extraction fluid and process. If the absolute value of the Pb concentration of the LRB is less than or equal to the MDL, no further action is required. If the resulting concentration is greater than the MDL, but less than 5 times the MDL, all associated samples must be flagged. If the concentration of a reported Pb concentration is greater than 5 times the MDL all associated samples must have the results blank subtracted with the LRB value.
- 13.2.5 The Method Blank (MB) is prepared as an LRB but with the addition of a

blank quartz filter strip and analyzed as a sample to determine the background levels, if any, from the blank filter and extraction process. While the absolute value of resulting concentrations should be less than the established MDL, there is no corrective action procedure should the blank fail.

### 13.3 Spikes

13.3.1 Laboratory Control Sample (LCS) is prepared and carried through the entire sample digestion process. At least one LCS is analyzed with each sample batch. The LCS is a spiked MB and can be referred to as a BS. The results of the spike recovery must be within 80 -120% of actual value. If not, the sample may be reanalyzed once.

13.3.2 Matrix Spike and Matrix Spike Duplicate (MS/MSD): A sample is chosen for the MS/MSD sample and extra filter strips are cut for this purpose. They are prepared by spiking the extra filter strips and carrying them through the entire preparation and extraction procedure. These samples should recover within 75% to 125% of the true value. If not, the MS and/or MSD may be reanalyzed once each. If they still do not pass, the batch of samples associated with the MS/MSD must be flagged for any analytes that failed in either or both. The parent sample used to prepare the MS/MSD should also have a SRD sample prepared and analyzed to determine if the poor recoveries are from matrix interference. If the SRD is within acceptance criteria a re-extraction of the samples should be considered.

**Note:** If the parent sample concentration is greater than 4 times the spike concentration, the recovery criteria does not apply and the sample should be flagged appropriately.

13.3.3 Standard Reference Material (SRM) is prepared and carried through the entire sample digestion process. At least one SRM is analyzed with each batch. The SRM is a NIST Urban dust that is prepared with a blank filter and can be referred to as a SRM in the LIMS. The results of the SRM recovery must be within 80 – 120% of the certified value. If not, the sample may be reanalyzed once. If the SRM still fails to meet criteria, all associated samples must be flagged.

### 13.4 Duplicates

There are three types of duplicates found in this method. There is a MSD which is a true spiked laboratory duplicate of a separate strip of the parent sample filter. Additionally, there is a true laboratory duplicate also prepared of an additional strip of filter material from the original sample and an analytical duplicate which is a second aliquot of an extracted sample analyzed twice. The RPD for any of these DUPs shall be 20% for values greater than or equal to 10 times the MDL. If the

sample analyte value is greater than 10 times the MDL and the RPD exceeds 20% it should be flagged. In the case of the analytical duplicate, it is appropriate to re-analyze the samples if a poor sample replicate is suspected.

### 13.5 Performance Evaluation (PE) Samples

Performance evaluation samples should be obtained from independent sources and analyzed as a routine sample. PE samples are prepared and analyzed like field samples and should be analyzed in duplicate to verify results.

### 13.6 Standard Checks

13.6.1 Immediately after the initial calibration, the ICV is analyzed. The measured concentrations should be  $\pm 10\%$  or within 90-110% of the actual concentration. If the criteria are not met, reanalyze the standard. If the criteria are still not met, repeat the initial calibration and ICV.

13.6.2 The HSV must be analyzed after the ICB and prior to analysis of samples. The measured concentration should be within 95% to 105% of the actual concentration. If the HSV fails it may be reanalyzed once. If the HSV still fails, recalibrate.

13.6.3 Before the analysis of samples and after every 10 samples during a batch analysis, the calibration must be verified using a CCV. Results must be within  $\pm 10\%$ , or 90% - 110%, of the target value for Pb to verify that the calibration is valid. If a standard check exceeds the limit, the analysis must be stopped and the check standard must be reanalyzed. If the target value exceeds the limit again, the instrument must be recalibrated and any samples between the last valid and failing CCV must be reanalyzed.

13.6.4 Following the first and last CCV of each analysis an LCV must be analyzed. The measured concentration should be  $\pm 30\%$  of the true concentration. If the criteria are not met, reanalyze the standard once. If criteria still are not met, terminate the analysis, correct any issues, and repeat the initial calibration.

**Note:** The intended use of this SOP is determination of lead. If additional elements are to be analyzed by ICP-MS using this SOP, an interference check solution (ICS) shall be prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. See EPA Method 6020A for additional details on recommended ICS solution concentrations and potential interferences.

### 13.7 Internal Standards

The intensities of all ISTDs must be monitored for every analysis (see Table 21-3 for isotopes). When the intensity of any ISTD fails to register between 60 to 125% of the intensity of that ISTD in the calibration blank, the following procedure is implemented:

- 13.7.1 Check that the intensity levels of the ISTD for the calibration blank and sample(s) of interest are within 60% - 125% of the intensity level of the ISTD of the original calibration blank. If the intensities are too high as a result of the ISTD being present in the sample, the sample must be diluted and reanalyzed with the addition of appropriate amounts of ISTD.
- 13.7.2 Repeat and increase the dilution until the ISTD intensities fall within the prescribed window.
- 13.7.3 If the intensities are determined to be a result of instrument drift, stop the analysis, find and correct the problem, recalibrate if needed and reanalyze the affected samples since the last acceptable ISTD recoveries.

### 13.8 Dilutions

#### 13.8.1 Serial Dilution

The SRD analysis must be performed on one sample per batch, preferably on the parent sample chosen for the MS/MSD as guidance for poor recoveries in the spiked samples, which may be due to matrix interference. The same sample matrix used to extract the parent sample must be used as the diluent. After the dilution is applied to the SRD results, the analyte concentration should be within 90% and 110% of the undiluted sample results if the parent Pb concentration is minimally a factor of 50 above the MDL in the original sample. If the SRD fails and the MS/MSD also fail for the same analyte, this may indicate a matrix interference. A matrix effect must be suspected and the data flagged for this sample.

#### 13.8.2 Sample Dilution

Any samples needing dilution due to concentrations exceeding the LDR or the presence of ISTD in the sample causing ISTD recoveries to fail shall be diluted in an appropriate manner to bring the diluted concentration within the calibration curve and preferably near the mid-point. If the SRD was performed on the parent sample of a DUP, the results from the SRD may be used to report values of that parent sample if the 5 times dilution was appropriate.



### 13.9 Decontaminating/Cleaning Labware

13.9.1 Soak labware using tap water and detergent (preferably a 1-2% Citranox® solution, but Liquinox or other lab detergents may be used in same concentrations) for a minimum of one hour, but preferably overnight.

13.9.2 Rinse labware with hot tap water to remove detergent completely. Place labware in DI water bath for transporting “to acid bath.”

13.9.3 Place in a 10% nitric acid bath overnight. Remove labware from acid bath and place in DI bath “from acid bath.”

13.9.4 Rinse labware three times with DI water. Allow glassware to air dry. Place labware such that open orifices are facing down.

13.9.5 The nitric bath is monitored for contamination by analyzing the bath solution. The nitric acid bath is changed at least every 6 months or when contamination levels are significantly elevated. The nitric bath solution is disposed of by placing in the appropriate drum in the hazardous waste room by qualified personnel.

## 14.0 PREVENTION

When possible, minimize the amount of chemicals used in the preparation and analysis of the metals filters to reduce waste.

## 15.0 DATA REVIEW AND CORRECTIVE ACTION

### 15.1 Data Review Documentation

Project files including at a minimum the information required in Section 19 are assembled and maintained by the performing analyst. Documentation for Pb analysis by ICP/MS will be reviewed for completeness and meeting acceptance criteria by a secondary reviewer as described in this section. Corrections and flags are added to the data consistent with the corrective action required for each review finding.

## 16.0 WASTE MANAGEMENT

Hazardous waste disposal should be handled according to laboratory guidelines. Sample digestate, including the extracted filter and FilterMate™ filter, is retained in its original tube for a period of at least 6 months from the sample date. After this time, sample digestate is disposed of by pouring it off in the satellite waste containers located in the laboratory. Used sample vials are disposed of in the laboratory waste bin.

## **17.0 MAINTENANCE**

Instrument maintenance should be performed in accordance with the instrument manufacturer's recommendations.

## **18.0 SHORTHAND PROCEDURE**

The flow chart shown in Figure 21-1 shows the procedural steps and sequence for analysis of inorganic samples.

## **19.0 DOCUMENTATION AND DOCUMENT CONTROL**

- 19.1 All information concerning sample preparation, standard preparation, instrument conditions, etc., must be documented in the appropriate binders (i.e., Extraction Log, Daily Performance Reports, Standards Log etc.) and/or electronically in either the LIMS or the local instrument computer.
- 19.2 All calculations and the type of method for determining concentration must be recorded in the analyst's notebook. Any unusual problems or conditions must also be noted.
- 19.3 Record all maintenance performed on the instrument in the maintenance logbook for this particular instrument.
- 19.4 Record all sample analyses, including quality control samples, performed by the instrument in the ICP-MS run logbook for this particular instrument.
- 19.5 All analysis-related logbooks should be reviewed periodically by the analysis task lead or secondary reviewer.
- 19.6 It is imperative the project documentation be updated and backed up electronically following each analysis. Analysts will copy raw instrument and QC files to a designated corporate network shared drive at the completion of each analysis sequence or batch.
- 19.7 Reporting
  - 19.7.1 The filter results must be reported in  $\mu\text{g/mL}$  as analyzed. Any additional dilutions done must be accounted for in the instrument software. The internal standard recoveries must be included in the result calculation. Final results should be reported in  $\mu\text{g/m}^3$  to three significant figures as shown in Section 12.1. If required by the sampling organization, results can also be reported in  $\text{ng/m}^3$  by dividing the  $\mu\text{g/m}^3$  results by 1000.
  - 19.7.2 Sample results should not be corrected based on lead results from the laboratory blanks, field, trip, or filter lot blanks provided by sampling

agency. Samples are flagged if the LRB is detected as described in Section 13.2.4.

19.7.3 As stated in Section 11.2.6, samples with Pb concentrations greater than 90% of the current LDR must be diluted and re-analyzed. The diluted value will be reported to the sampling agency.

19.7.4 Data should meet all specifications as presented in Table 21-2. If data does not meet specifications, corrective reporting actions listed must be followed (flag or invalidate data).

## 20.0 REFERENCES

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## 21.0 TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

**Table 21-1. Estimated Method Detection Limits (MDLs) for Pb in TSP Hi-Vol Filters**

<b>Element</b>	<b>MDL (<math>\mu\text{g/L}</math>)</b>	<b>MDL (<math>\mu\text{g/filter}</math>)</b>	<b>MDL (<math>\mu\text{g/m}^3</math> assuming 2000 <math>\text{m}^3</math>)</b>
Lead	0.473	0.213	0.000106

**Table 21-2. Summary of Quality Control Procedures for Metals Analysis**

Parameter	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Standards (IC)	Daily, at least 5 calibration points	Correlation coefficient $\geq 0.998$ & RSD $\leq 10$ . IC standards with concentrations below an analyte's MDL may have a %RSD $> 10$ but $< 20$	1) Repeat analysis of calibration standards 2) Reprepare calibration standards and reanalyze
Initial Calibration Verification (ICV)	Immediately after calibration	Recovery 90-110%	1) Repeat analysis of ICV 2) Recalibrate and reanalyze
Initial Calibration Blank (ICB)	Immediately after ICV	Absolute value must be $\sim$ MDL	1) Locate and resolve contamination problems before continuing 2) Reanalyze or recalibrate or flag failing elements
High Standard Verification (HSV)	After ICB and before the ICS	Recovery 95-105%	1) Repeat analysis of HSV 2) Reprepare HSV
Low Level Calibration Verification (LCV)	After the first and last CCV	Recover 70-130%	1) Repeat analysis of LCV 2) Correct any issues 3) Recalibrate and reanalyze the analysis
Continuing Calibration Verification (CCV)	Analyze before samples, after every 10 samples, and at the end of the run	Recovery 90-110%	1) Repeat analysis of CCV 2) Reprepare CCV 3) Recalibrate and reanalyze samples since last acceptable CCV
Continuing Calibration Blanks (CCB)	Analyzed after each CCV	Absolute value must be $\sim$ MDL, if not, see ICB criteria	1) Reanalyze CCB 2) Reanalyze samples since last acceptable CCB
Laboratory Reagent Blank (LRB)	1 per 20 samples, a minimum of 1 per batch	Absolute value must be $\sim$ MDL	1) Reanalyze 2) If $> 5x$ the MDL then sample results for Pb must be blank subtracted
Method Blank (MB/BLK2)	1 per 20 samples, a minimum of 1 per batch	Absolute value must be $\sim$ MDL, however the MB is used only for the purposes of MDL generation	The QC is not required by the method and there is no corrective action
Laboratory Control Sample (LCS)	1 per 20 samples, a minimum of 1 per batch	Recovery 80-120%	1) Reanalyze 2) Reprepare sample batch
Duplicate (DUP)	1 per 20 samples, a minimum of 1 per batch	$\pm 20\%$ RPD for sample and duplicate values $\sim$ ten times the MDL	1) Repeat duplicate analysis 2) Check for matrix interference 3) Flag data
Matrix Spike (MS) and Matrix Spike Duplicate (MSD)	1 per 20 samples per sample Batch	Recovery 75-125%, except when the parent sample concentration is $>$ four times the spike concentration or a matrix interference is suspected	1) Reanalyze 2) Reprepare sample batch
Standard Reference Material (SRM)	1 per 20 samples, a minimum of 1 per batch	Recovery 80-120%	1) Reanalyze 2) Flag sample batch
Serial Dilution	1 per batch	Recovery 90-110% of undiluted sample if the analyte concentration is minimally a factor of 50 above the MDL in the original sample	1) Reprepare dilution 2) Flag data
Internal Standards (ISTD)	Every Calibration, QC and Field Sample	Recovery 60-125% of ISTD response in the calibration blank	1) Reprepare sample 2) If recovery $> 125\%$ , dilute sample and reanalyze 3) If drift suspected, stop analysis and determine cause. Recalibrate if necessary

**Table 21-3. Analytical Isotopes for Quantitation and Monitoring of Reported Elements**

Element	Quantitation Isotope	Monitored/Confirmation Isotope(s)
Bismuth (ISTD)	209	NA
Lead	206, 207, 208*	NA

NA = Not applicable/none.

\*See Section 4.3.6

**Figure 21-1. Flow Diagram for ICP-MS Preparation and Analysis for PM<sub>10</sub> or TSP Filters**

