

IML 2009

Procedure for the Determination of Lead in Ambient Air TSP by Hot Plate Acid Extraction and ICP-MS Analysis By Inter-Mountain Labs (IML)

1.0 Scope and Application.

1.1 There are many parts to analyzing lead (Pb) in ambient air. The following are all needed to measure Pb in ambient air: the collection of Total Suspended Particulates (TSP) onto filters, the sampling of the TSP filters into strips of known proportion, the digestion of the TSP filter strip samples into a known volume of solution, and the determination of the concentration of Pb in the solution. This procedure covers the sampling of the TSP filters into strips of known proportion, the digestion of the TSP filter strip samples into a known volume of solution and the determination of the concentration of Pb in solutions of digested filter strips.

2.0 Summary of Method.

2.1 The TSP filters are sampled and are extracted on a hot plate in acid then brought up to a volume of 100mL as described in Appendix A of this document. The EPA reference method for extraction is defined in 40 CFR Appendix G to part 50.

2.2 Sample material in solution is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer at masses 206 amu, 207 amu, and 208 amu for Pb. The ICP-MS instrument must have a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are registered by a continuous dynode electron multiplier or Faraday detector and the ion information is processed by a data handling system. This method was designed from EPA Methods IO-3.5 and 6020A.

3.0 Definitions.

3.1 Calibration Blank: A volume of reagent water acidified with the same acid matrix as in the calibration standards.

3.2 Calibration Standard: A solution prepared from the dilution of stock standard solutions. The calibration solutions are used to calibrate the instrument response with respect to analyte concentrations.

3.3 Continuing Calibration Blanks (CCB): The CCB is a solution that is matrix-matched to the calibration solutions and does not contain the analyte of

interest.

- 3.4 Continuing Calibration Verification (CCV): The CCV standard is prepared from the calibration standard stocks near the midpoint of the calibration curve and is used to verify the calibration.
- 3.5 Duplicates: A duplicate is a replicate of an actual sample to provide precision information about the analysis.
- 3.6 High Standard Verification (HSV): The HSV is a calibration standard in the high-end of the calibration curve and is used to verify the calibration.
- 3.7 Initial Calibration Blank (ICB): The ICB is a solution that is matrix-matched to the calibration solutions and does not contain the analyte of interest.
- 3.8 Initial Calibration Verification (ICV): The ICV is a calibration standard near the midpoint of the calibration curve and is used to verify the calibration.
- 3.9 Instrument Detection Limit (IDL): The concentration equivalent of the analyte signal, which is equal to three times the standard deviation of the blank signal at the selected analytical mass(es).
- 3.10 Interference Check Solution (ICS): The ICS is a calibration standard that is fortified with high levels of known interferents and is used to verify ability to ensure against interference effects.
- 3.11 Internal Standard: Pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same solution. The internal standard must be an analyte that is not a sample component.
- 3.12 Laboratory Control Spike (LCS): A sample blank that has been fortified with the analyte of interest or a sample which has a known value for the analyte of interest and has been processed through the entire analytical method. For this procedure, a blank filter that is spiked with a known concentration of lead and subjected to extraction and analysis in the same manner as samples.
- 3.13 Lower Limit of Quantitation (LLOQ): The LLOQ is prepared from the calibration standard stocks at the value of the reporting limit and is used to verify the reporting limit.
- 3.14 Matrix Spike (MS): The MS is a sample replicate of an actual sample that has been laboratory-fortified with analyte to provide information about the effect of the sample matrix on the analysis.

- 3.15 Method Blank: A blank filter 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 method blank is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.
- 3.16 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. MDLs are intended as a guide to instrumental limits typical of a system optimized for multi-element determinations and employing commercial instrumentation and pneumatic nebulization sample introduction. However, actual MDLs and linear working ranges will be dependent on the sample matrix, instrumentation, and selected operating conditions.
- 3.17 Nebulizer: A device creating a fine spray of sample solution to be carried into the plasma for measurement. Its performance is critical for good analysis.
- 3.18 Stock Standards Solution: A concentrated solution containing one or more analytes prepared in the laboratory using assayed reference compounds or purchased from a reputable commercial source.
- 3.19 Quality Control Sample (QCS): A solution containing known concentrations of method analytes, which is prepared by matching the calibration standards matrix containing a known amount of target analyte in the range of the calibration standards. The QCS is obtained from a source external to the laboratory calibration standards and is used to verify the accuracy of the calibration standards.
- 3.20 Tuning Solution: A solution used to determine acceptable instrument performance prior to calibration and sample analysis.

4.0 Interferences, Considerations.

- 4.1 Isobaric elemental interferences- These are caused by isotopes of different elements that form singly- or doubly-charged ions of the same nominal mass-to-charge ratio and that cannot be resolved by the mass spectrometer. Lead (Pb) has three isotopes (206 amu, 207 amu, and 208amu) that are free of isobaric elemental interference. All three of these isotopes should be used to increase sensitivity of the method.
- 4.2 Abundance sensitivity- This is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance

sensitivity is affected by ion energy and quadrupole operation pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

- 4.3 Isobaric polyatomic ion interferences- These are caused by ions consisting of more than one atom that have the same nominal mass-to-charge ratio as the isotope of interest, and that cannot be resolved by the mass spectrometer. These ions are commonly formed in the plasma or interface system from support gases or sample components. Pb is not known to have common isobaric polyatomic ion interference, hence no equations for the correction of data are recommended for the analysis of Pb. Polyatomic ion interferences are highly dependent on sample matrix and chosen instrument conditions.
 - 4.4 Physical interferences- These interferences are associated with the physical process that govern the transportation of sample into the plasma, sample conversion process in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the sampler and/or skimmer cones, reducing the effective diameter of the orifices and therefore ion transmission. Internal standards may be effectively used to compensate for many physical interference effects. Internal standards ideally should have similar analytical behavior to the elements being determined.
 - 4.5 Memory interferences- These interferences result when isotopes of elements in the previous sample contribute to the signals measured in a new sample. Memory effects can be a result of sample deposits on sampler and skimmer cones, plasma torch, and spray chamber. These interferences can be minimized by flushing with a rinse blank between samples.
- 5.0 Sample Collection, Preservation, Sub-Sampling, Preparation, and Handling.
- 5.1 Samples should be collected on filters per EPA Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method), 40 CFR Appendix B to part 50 or other appropriate method.

- 5.2 Filters should be transported to the laboratory using guidance recommended in EPA Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method), 40 CFR Appendix B to part 50 and Quality Assurance Handbook for Air Pollution Measurement System, Volume 1 Principles, EPA – 600/9-76-005 or as otherwise recommended by the regulating body.
 - 5.3 Filters should be sub-sampled and digested with acid into a solution of known volumes as described in appendix A of this document.
 - 5.4 Solutions should be kept in clean sealed containers at room temperature. The solutions can be analyzed acceptably for up to six months from date of filter digestion and solution preparation.
 - 5.5 Blank filters can have positive values for lead (Pb). Each manufacturer lot of filters may need to be investigated to ensure that filters will meet the data quality objectives of a given project. It is recommended to consult 40 CFR Appendix G to part 50, section 6.1 for guidance.
- 6.0 Safety.
- 6.1 This method utilizes acids and standards that are potentially hazardous if not handled appropriately. Refer to MSDS sheets for handling instruction and personal protective equipment requirements.
 - 6.2 Samples are many times collected from areas suspected to contain hazardous or toxic materials. Treat all samples as potentially toxic and handle with appropriate gloves, clothing, ventilation, and eye protection.
 - 6.3 ICP-MS instruments operate at high currents of electricity and high-intensity radio frequencies. Care should be taken to avoid placement of liquids upon instrument. All instrument manufacturer safety guards and equipment must be installed and working properly.
- 7.0 Apparatus and Materials.
- 7.1 Inductively Coupled Plasma/Mass Spectrometer (ICP/MS) Instrument. An ICP-MS instrument capable of scanning the masses 5-250 amu with a minimum resolution capability of 1 amu peak width at 5% peak height is required for this procedure. The instrument may be fitted with a conventional or extended dynamic range detection system. The ICP-MS should have a mass flow controller on the nebulizer gas supply. If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise,

changes in instrument response or damage to the multiplier may result. Samples having high concentrations of elements beyond the linear range of the instrument and with isotopes falling within scanning windows should be diluted prior to analysis. Because of the diversity of instrument hardware, no detailed instrument operating conditions are provided. The analyst is advised to follow the recommended operating conditions provided by the manufacturer. The analyst must verify that the instrument configuration and operating conditions satisfy the analytical requirements and maintain quality control data, verifying instrument performance and analytical results. IML uses the ICP-MS system from Varian, Model 820-MS.

- 7.2 Argon Gas: Argon of sufficient quality to achieve MDL requirements. (Follow instrument manufacturer's recommended grade in order to meet customer method detection limit requirements.)
- 7.3 Auto-Sampler: An appropriate auto-sampler working in conjunction with the ICP-MS equipped with a variable-speed peristaltic pump as manufacturer requires for solution delivery to the nebulizer.
- 7.4 Chiller: Kodiak-Series Chiller or equivalent plasma cone and coil chiller as required by the ICP-MS instrument manufacturer.
- 7.5 Computer: Dell PentiumD with monitor and printer or equivalent processor as required for processing the ICP-MS data as required by the ICP-MS instrument manufacturer.
- 7.6 Labware: When measuring trace level elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching and (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, Teflon®, etc.), including the sample container, should be cleaned prior to use. Labware may be soaked overnight and thoroughly washed with laboratory-grade detergent and water, rinsed with de-ionized water, and soaked for 4 hours in a mixture of 20%V/V concentrated HNO₃/reagent water as appropriate for the material, followed by multiple rinsing with de-ionized water and stored clean.
- 7.7 Glassware Assorted: 100 mL class A volumetric flasks, graduated cylinders, 150-200 mL beakers, funnels and calibrated pipettes.

- 7.8 Plastic Ware Assorted: Plastic Solo[™] cups, mechanical pipette tips, containers with lids, and test tubes fitted for the auto-sampler. IML uses two sizes of plastic Solo[™] cups; 1oz - part no. p100 and 4oz - part no. p400. IML uses two different pipette tips from Eppendorf 5mL - part no. 022492080 and 1 mL – part no. 022495055. IML uses Stockwell Scientific plastic test tubes – part no. 85942.
- 7.9 Mechanical Pipettes Assorted: Convenient and variable deliveries to dilute solutions as required. Pipettes in the range of 1mL - 10mL should be accurate to 1% and verified weekly.
- 8.0 Reagents.
- 8.1 Stock Element Standards: Single or Multi-Element Standards purchased from vendors that supply certificates of traceability to national standards and measurement uncertainty. Standards are given expiration dates by the manufacturers for each standard.
- 8.2 Concentrated Nitric Acid: HNO₃, trace metals grade. Follow manufacturer's recommendations for long-term storage.
- 8.3 Reagent Water: IML DI water or equivalent to ASTM type I water. Assign a one-year expiration date to this solution for long-term storage of this solution.
- 8.4 Diluent: 2% V/V concentrated nitric acid solution made with trace metals grade HNO₃ and diluted to 2% with reagent water. Assign a one-year expiration date to this solution for long-term storage of this solution. The following quality controls can be prepared from these basic instructions: ICB and CCB.
- 8.5 Calibration Standards: Standards for Pb are prepared from a stock Pb standard solution and diluted with diluent, 2% HNO₃, to the manufacturer's recommended concentration range. IML uses the range of standards 1 µg/L to 200 µg/L of Pb in a 2% HNO₃ solution. Standards are given expiration dates conforming to the manufacturer's expiration dates for each given standard. The following quality controls can be prepared from these basic instructions: ICV, QCS, HSV, LLOQ, and CCV.
- 8.6 Tuning Solution: Tuning solution is prepared from Stock Element Standards. The Stock Element Standards are diluted to produce a tuning solution recommended by the ICP-MS manufacturer. IML tuning solution consists of 5 µg/L for each the following elements: Ba, Be, Ce, Co, In, Mg, Pb, Th, and Tl in a 2% HNO₃ solution. Tuning solutions are given

expiration dates conforming to the manufacturer's expiration dates for each given standard.

8.7 Internal Standards Solution: The internal standards solution is prepared from Stock Element Standards to produce an internal standard. The Stock Element Standards are diluted with diluent to produce an internal standard solution that is appropriate for the matrix and the specific ICP-MS instrument. Internal standards should not be found in measurable concentrations in the matrix to be analyzed. IML internal standards solution consists of 100 µg/L for each the following elements: Ge, ⁶Li, Re, Rh, Sc, In, Th, and Y in a 2% HNO₃ solution. IML uses the internal standard Re for calculating lead in solution. Standards are given expiration dates conforming to the manufacturer's expiration dates for each given standard.

8.8 Interference Check Solution: The Interference Check Solution is prepared from Stock Element Standards. The Stock Element Standards are diluted with diluent to produce an interference check solution that contains the target analyte, Pb, with a mixture of other elements that are expected to be in the samples and any potential interfering elements. IML interference check solution contains: 20 µg/L of Pb; 500 µg/mL of Cl; 100 µg/mL of C; 50 µg/mL each of Al, Ca, Fe, K, Mg, Na, P, and S; 1 µg/mL each of Mo and Ti. Standards are given expiration dates conforming to the manufacturer's expiration dates for each given standard. The quality controls sample of ICS can be prepared from these basic instructions.

9.0 Calibration and Standardization.

9.1 Calibration standards must consist of at minimum 3 standards and a blank covering the range appropriate for the ICP-MS. IML uses the range of standards 1 µg/L to 200 µg/L of Pb in a 2% HNO₃ solution.

9.2 The instrument must be calibrated for each run.

9.3 Calibration data is accepted based upon a minimum correlation coefficient of 0.995 for the standard curve based on a linear fit and a maximum read-back error of ±30% for the lowest standards and ±10% for all other standards.

10.0 Quality Control.

10.1 Original records, whether paper records or electronic records, must be protected and preserved. Examples include: electronic run files; bench sheets, instrument log, digestion logs, and standard dilution logs.

- 10.2 Initial Calibration Verification (ICV): The ICV is analyzed following initial calibration to verify the initial calibration. The concentration should be within 90% to 110% of the actual concentration.
- 10.3 Initial Calibration Blank (ICB): The ICB is analyzed following initial calibration to verify the status of the calibration. The ICBs are compared to the method detection limits. The absolute value of the instrument response must be less than the reporting limits. If not, analysis must be repeated.
- 10.4 High Standard Verification (HSV): The HSV is analyzed following initial calibration to verify the status of the calibration. The HSV measured concentration should be within 95% to 105% of the actual concentration.
- 10.5 Interference Check Solution (ICS): The ICS is analyzed at the beginning and end of the run and for every 8 hours of continuous operation. The results for the analytes should be within 80% to 120% of the actual concentration.
- 10.6 Continuing Calibration Verification (CCV): CCV standards are prepared from the calibration standard stocks and near the midpoint of the calibration curve. The CCV standards are analyzed every 10 samples, and at the end of the run. The CCV measured concentration should be within 90% to 110% of the actual concentration.
- 10.7 Continuing Calibration Blanks (CCB): The CCB standards are analyzed every 10 samples, and at the end of the run. The results of the CCB are evaluated with the same requirements as the ICB.
- 10.8 Method Blank: A method blank is used to determine if concentrations reflect background levels from sample digestion. If the instrument measured response is greater than the reporting limits, then the sample analysis for the affected analyte(s) must be repeated.
- 10.9 Laboratory Control Spike (LCS): The LCS is the same as a laboratory-fortified blank. A LCS is prepared and analyzed with each sample batch (or 1 per 20 samples). The results for the analytes should be within 80% to 120% of the actual concentration. If the results are not within the criteria, then the analysis must be repeated.
- 10.10 Matrix Spike (MS): The MS sample is prepared and analyzed with each sample batch (or 1 per 20 samples). These samples are used to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion, (i.e., prior to the addition of other reagents). The percent recovery for the

analyte as part of the MS should be between 75% and 125% for all analytes.

- 10.11 Duplicates: Duplicate samples are prepared and analyzed with each sample batch. These samples are used to estimate method precision, expressed as relative percent difference (RPD). The RPD between duplicate sample final concentrations should be less than $\pm 20\%$.
 - 10.12 Serial Dilution: A serial dilution analysis can be performed to check dilution accuracy. It is recommended to perform this once each day. After a five fold serial dilution, the analyte concentration should be within 90% and 110% of the undiluted sample results.
 - 10.13 Internal Standard: The absolute response of the internal standard must not deviate more than 60%-125% of the original response of the calibration blank. The internal standard should be monitored routinely. The choice of internal standard is based on proximity to the mass of interest, the expectation of the internal standard to have a negligible concentration in the samples of interest, and its stability. IML uses the internal standard Re for calculating lead in solution. Another potential internal standard is Iridium (Ir).
 - 10.14 MDLs: These shall be performed every 6 months or whenever a significant change in background or instrument response is expected (e.g., detector change). Seven blank filter aliquots are laboratory fortified and processed through the full method, using guidance consistent with 40 CFR Appendix B to part 136.
 - 10.15 Quality Control Sample (QCS): The QCS is required to be analyzed for every set of prepared calibration standards. The QCS checks the accuracy of the calibration standards against a second source. The QCS concentration should be within 90% to 110% of the actual concentration.
 - 10.16 Lower Limit of Quantitation (LLOQ): A LLOQ can be performed to verify the reporting limit. The LLOQ should be run each day with a recovery of greater than $\pm 50\%$ of the assigned value.
- 11.0 Procedure.
- 11.1 Follow maintenance procedures as recommended by the instrument manufacturer. IML uses the following guide: Peristaltic Pump tubing and 2% HNO₃ rinse water are changed every other day. Pump oil is changed monthly on pump #1 and every six months on pump #2. Water and air filters are cleaned every 6 months or more frequently if needed. Chiller water level must be monitored periodically and changed every 6 months.

The ICP-MS sampler and skimmer cones, extraction lens, lens stack, and end plate are cleaned or replaced as needed. Perform cleaning or changing of the nebulizer, spray chamber, auto-sampler tubing, torch, and instrument tubing as needed.

- 11.2 Follow manufacturer's initiation procedures of the ICP-MS. IML uses the following initiation: Initiation of the ICP-MS begins with checking for adequate Argon gas, engaging peristaltic pump tubing, emptying waste and filling 2% HNO₃ water reservoir. Turn on the computer monitor. In the computer software enter "ICPMS EXPERT", "Instrument Set-Up", and click on the "Plasma" icon. In the "Plasma Align" tab start a time scan using 5ppb tuning solution. Allow the instrument to warm-up for at least 30 minutes.
- 11.3 After warm-up conduct mass calibration and resolution checks using the tuning solution. Resolution at low mass is indicated by magnesium isotopes 24, 25, 26. Resolution at high mass is indicated by lead isotopes 206, 207, 208. For good performance, adjust spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass. Instrument stability must be demonstrated by running the tuning solution a minimum of five times with resulting relative standard deviations of absolute signals for all tuning solution analytes of less than 5%.
- 11.4 Prior to initial calibration, set up proper instrument software routines for quantitative analysis. The instrument must be calibrated for the analytes to be determined using a calibration blank and, at minimum, three calibration standards. All readings shall contain a minimum of three replicate integrations for data acquisition. Use the average of the integrations for instrument calibration and sample data acquisition. Rinse with diluent in between samples and standards.
- 11.5 Set up the auto sampler and sample sequence tables as required by the manufacturer. Set up the auto sampler sequence to read samples as follows (Any sequence that meets the quality control requirements is allowable. An example is shown for clarification purposes):

Blank
Calibration Standard (lowest to highest)
ICB
ICV
QCS
HSV
ICS
LLOQ

10 Samples*
CCB
CCV
10 Samples*
CCB
CCV
10 Samples*
CCB
CCV
10 Samples*
.....etc
ICS
CCB
CCV

*Samples include: Samples, Method Blanks, Laboratory Control Samples, Duplicate Samples, Matrix Spike Samples, and Serial Dilution Samples

IML uses the following instructions to complete the sequence commands: Enter sample run data by clicking on "File", "New From Template", and choose appropriate file set up. Enter file name and "ok", set up worksheet by choosing "2. Sequence", and enter number of samples to be run, then "ok".

- 11.6 Prepare samples for analysis as per manufacturer's recommendations. IML dilutes all sample digestates by 11, (1+10), with diluent in order to accomplish: manufacturer's recommendations on total dissolved solids content, matching acid concentrations, reduction of particulate matter in the solution to be analyzed, and to reduce cone cleaning maintenance. Account for the dilution factor within your quality system or as the software allows. IML uses the following instructions to complete the sequence commands: Enter sample labels and dilutions. Go to "3. Worksheet".
- 11.7 Place all samples and standards in the auto-sampler racks. Initiate the sequence by following instrument manufacturer instructions for start-up. IML uses the following instructions to complete the sequence commands: Click "Run".
- 11.8 Review data for compliance with quality control criteria requirements. If data set meets requirements then report results. If data set does not meet quality control criteria, assess problem and reanalyze samples.
- 11.9 Follow ICP-MS instrument manufacturer's instructions for shutdown. IML uses the following instructions: Flush with Blank Solution for 30 seconds on "fast pump" then click on the "Plasma" icon. Release the peristaltic

pump tubing.

12.0 Calculation.

12.1 ICP-MS data is generated in $\mu\text{g/L}$.

12.2 Dilution factors, which may be multiplied by the instrument software, must be reviewed to take instrument detection limits into account.

12.3 To convert from $\mu\text{g/L}$ in solution to $\mu\text{g/m}^3$ in air

$$X = (C \cdot V \cdot F) / A$$

Where:

X = concentration of Pb in $\mu\text{g/m}^3$ in air sampled.

C = concentration of the Pb in solution of digested filters in $\mu\text{g/L}$.

V = volume of sample in liters, (0.1L for the reference Pb digestion).

F = the inverse of the fraction of the sub-sampled strip, (IML's is 12).

A = volume of air determined that was sampled in m^3 .

12.4 To calculate calibration and quality control values in sections 9 and 10 of this procedure see EPA's SW-846 guidance in method 6020A.

13.0 Reporting Limits, Method Detection Limits, and Reporting Guidance.

13.1 See EPA guidance for detection limit requirements 40 CFR Appendix B to part 136.

13.2 The reporting limit is typically defined as 2-5 times the MDL.

13.3 Report values that fall between the highest calibration standard and the lowest calibration standard. If the LLOQ is used, the LLOQ value can be used as the low-end reporting limit instead of the lowest calibration standard.

13.4 If a quality control sample is out of acceptance, take corrective actions and repeat analysis. Flag all quality control failures which cannot be resolved by repeating the analysis, such as a matrix spike recovery.

14.0 References.

14.1 Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma-Mass Spectrometry. Compendium Method IO-3.5, June 1999.

- 14.2 EPA Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method), 40 CFR Appendix B to part 50.
- 14.3 EPA Reference Method For the Determination of Lead in Suspended Particulate Matter Collected From Ambient Air, 40 CFR Appendix G to part 50.
- 14.4 EPA SW-846 Method 6020A Revision 1, Inductively Coupled Plasma-Mass Spectrometry, February 2007.
- 14.5 EPA Method 200.8 TITLE: Determination Of Trace Elements In Waters And Wastes By Inductively Coupled Plasma - Mass Spectrometry, (Supplement I, Rev. 5.4, May 1994).
- 14.6 ISO/IEC 17025: General requirements for the competence of testing and calibration laboratories, 2005.
- 14.7 Standard Methods for the Examination of Water and Wastewater, 21st Edition, APHA 2005.
- 14.8 ASTM Method D 5673 – 05, Standard Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry, 2005.
- 14.9 Quality Assurance Handbook for Air Pollution Measurement System, Volume 1 Principles, EPA – 600/9-76-05.
- 14.10 Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11, 40 CFR Appendix B to part 136.

Appendix A

Standard Operating Procedures for Air Filter Reference Method Digestion

1.0 Scope and Application.

This digestion procedure is used for the preparation of air filter samples, for analysis by Inductively Coupled Plasma (ICP) spectroscopy, FAA, ICP-MS, and GFAA for metals. The procedure is used to determine the total amount of the metal in the sample. This method is based on the EPA Reference Method For the Determination of Lead in Suspended Particulate Matter Collected From Ambient Air, 40 CFR Appendix G to part 50. See the aforementioned method for any clarifications or interpretations.

2.0 Summary of Method.

A mixture of trace metals grade nitric acid, DI water, and the filter to be analyzed are refluxed in a covered beaker on a hotplate. If the sample contains suspended solids, it must be allowed to settle after digestion or centrifuged if needed.

3.0 Definitions.

NA

4.0 Interferences, Considerations.

Interferences are discussed in the referring analytical method.

5.0 Sample Collection, Preservation and Handling.

Refer to SOP for filter collection. Ambient large fiber filters should be received folded in half lengthwise with the particulate material inward and enclosed in protective envelopes. Store these filters within a protective envelope between 15°– 30°C until analysis. Handle filters using latex gloves while cutting and transferring to a beaker. Samples may be analyzed within six months from extraction into solution.

6.0 Safety.

6.1 Concentrated nitric acid should be handled inside an approved fume hood.

6.2 Protective clothing, gloves, and safety glasses should be worn.

7.0 Apparatus and Materials.

100 – 200 mL glass beakers, many
Watch glasses

100 mL volumetric flasks
Fume hood
Protective clothing
Gloves
Safety glasses
Hot Plate
Die (Cutter)
Template (Board) and Hammer
Balance, top loader

8.0 Reagents and Consumable Materials.

- 8.1** De-ionized reagent water (DI water): Monitor water for impurities.
- 8.2** Concentrated nitric acid, trace metal grade (HNO_3): Analyze acid to determine level of impurities.
- 8.3** Extraction Solution (3M HNO_3). Prepare by adding 384 mL of concentrated trace metals grade HNO_3 to DI water and bringing to a volume of 2 L.

9.0 Calibrations and Standardization.

NA

10.0 Quality Control.

- 10.1** Digestion information is recorded in the filter digestion logbook or electronic record.
- 10.2** For each analytical batch of 20 samples or fewer processed, preparation blanks (DI water and reagents) should be carried throughout the entire sample preparation and analytical process. For each analytical batch of 20 samples or fewer processed, filter blanks (unexposed filter and reagents) should be carried throughout the entire sample preparation and analytical process. A duplicate sample should be processed with each analytical batch of 20 samples or fewer.
- 10.3** Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each analytical batch of samples and whenever a new sample matrix is being analyzed.
- 10.4** For each batch of 20 samples or fewer processed, a lab control sample (LCS) which is a blank filter spiked with the same concentration of metals

as the matrix spike, should be carried throughout the entire sample preparation and analytical process.

11.0 Procedure.

- 11.1** Prior to use, clean all laboratory equipment that will come into contact with the filter samples to prevent contamination. Labware may be soaked overnight and thoroughly washed with laboratory-grade detergent and water, rinsed with DI water, and soaked for 4 hours in a mixture of 20%V/V concentrated HNO₃/reagent water followed by multiple rinsing with DI water and stored clean.
- 11.2** Using gloves, wipe template base and cutting blade with a clean, dry Kimwipe to prevent sample cross-contamination.
- 11.3** Unfold the 8" x 10" filter to be sectioned and carefully place sampled side up on the base template. Use a die cutting blade and hammer to cut a ¾" x 8" strip.
- 11.4** Label the beakers with the filter number. Carefully cut with ceramic scissors or otherwise non-contaminating implements and place (without disturbing sampled area of filter) the filter pieces down into the lower portion of the beaker to ensure acid volume will cover entire filter. In the event that a smaller filter is used, use the entire filter in the digestion process.
- 11.5** For spiked samples and LCSs add 5 mL of 20ppm spiking solution to appropriate vessels.
- 11.6** Using a preset calibrated automatic dispensing pipette (repeating Eppendorf), add 15 mL of extracting acid solution to all beakers. Note: The acid should cover the strip completely.
- 11.7** Place beakers on the hotplate, contained in a fume hood, and boil gently while covered with a watch glass for 30 minutes. Do not allow sample to dry. Remove beaker from hotplate and allow the sample to cool.
- 11.8** Rinse the beaker walls and watch glass with DI water. Decant the water from the filter into a labeled 100 mL volumetric flask.
- 11.9** Add approximately 40 mL of DI water to remaining filter material in the beaker and allow it to stand for at least 30 minutes. This critical step must not be deleted; it allows the acid to diffuse from the filter into the rinse. Transfer the extraction fluid in the beaker to the labeled 100 mL volumetric flask. Rinse the beaker and any remaining solid material with DI water

twice and add the rinses to the final container. Before bringing to final volume, cap the 100 mL volumetric flask and shake vigorously. Set aside and let settle for approximately 5 minutes. Fill to the mark and mix well.

11.10 The final extraction volume is 100 mL based upon the above procedure. The sample should be allowed to settle one hour before analysis, or centrifuge as needed.

12.0 References.

40CFR Chapter I Part 50 Appendix G--Environmental Protection Agency --National Primary and Secondary Ambient Air Quality Standards, -- Reference Method for the Determination of Lead in Suspended Particulate Matter Collected From Ambient Air.