USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

HEATED NITRIC ACID HOT BLOCK DIGESTION AND ICP/MS ANALYSIS FOR LEAD (Pb) ON TSP HIGH-VOLUME FILTERS

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TABLE OF CONTENTS

1 Scope and Applicability

Ambient air suspended particulate matter is collected for 24 hours on a TSP filter as described in Appendix B of Part 50, *Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method)*. The lead in the particulate matter is solubilized in a heated dilute nitric acid solution and quantitated using inductively coupled plasma – mass spectrometry (ICP-MS).

The method sensitivity is adequate for determining lead at concentrations equal to, or less than, 5% of the level of the lead NAAQS (0.15μg/m^3) for Pb-TSP. Results reported for monitoring or compliance purposes are calculated in μg/m^3at local temperature and pressure conditions.

2 Summary of Method

Particulate matter is collected on filters over a 24-hour period. Lead on a strip from the TSP filter is solubilized by immersion in a dilute nitric acid (approximately 3.5%) solution, covering the solution with a watch glass, and refluxing at 95 ºC for an hour in a hot block. After extraction, the solubilized lead is diluted to a specified volume with reagent water and mixed before analysis.

Sample solutions are introduced by pneumatic nebulization into a plasma, in which desolvation, atomization, and ionization occurs. 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. The ions transmitted through the quadrupole are detected by an electron multiplier or Faraday detector. Ion intensities at each mass are recorded and compared to those obtained from external calibration standards to generate concentration values for the samples. Results are corrected for instrument drift and matrix effects using internal standards. Additional corrections are applied as necessary to correct for isobaric and polyatomic elemental interferences.

3 Definitions

Calibration Blank (CB) - A volume of reagent grade water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument.

Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

Initial Calibration (ICAL) – a multi-point calibration analyzed daily.

Internal Standard - Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

Laboratory Duplicates (LD1 and LD2) - Two aliquots of the same sample taken in the laboratory and extracted and analyzed separately with identical procedures. Analysis of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

Laboratory Fortified Blank (LFB) - An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is extracted and analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements. The LFB is also referred to as a blank spike (BS) or Laboratory Control Sample (LCS).

Laboratory Fortified Sample Matrix (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is extracted and analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

Laboratory Reagent Blank (LRB) - An aliquot of blank matrix, a portion of unexposed filter in this procedure, that is treated exactly as a sample including exposure to all glassware, 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, reagents, or apparatus.

Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.

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.

Quality Control Sample (QCS) - A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards.

Quantitation Limit (QL) - The concentration at which confidence in the reported value requires no qualifying remarks. A standard is run at the QL to verify acceptable data quality.

Quantitation Limit Standard (QLS) - A standard used to check the accuracy of the analysis at the quantitation limit.

Stock Standard Solution - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Tuning Solution - A solution used to determine acceptable instrument performance prior to calibration and sample analyses.

4 Health & Safety Warnings

The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be available to all personnel involved in the chemical analysis. Specifically, concentrated nitric acid present various hazards and is moderately toxic and extremely irritating to skin and mucus membranes. Use this reagent in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

The acidification of samples containing reactive materials may result in the release of acid fumes or toxic gases. Acidification of samples should be done in a fume hood.

Analytical plasma sources emit radio frequency radiation in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. The inductively coupled plasma should only be viewed with proper eye protection from UV emissions.

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. Whenever feasible, the laboratory shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. Reduce the toxicity of waste by purchasing lower concentration stock standards and lower concentration reagents, to replace toxic chemicals whenever possible.

It is the responsibility of the user of this method to comply with relevant disposal and waste regulations. Laboratory waste generated by this procedure includes acidic aqueous waste with metals, spent vacuum pump oil, and solid waste (gloves, disposable labware, contaminated paper, etc.).

5 Interferences

Isobaric elemental interferences result when isotopes of different elements have the same nominal mass-to-charge ratio and cannot be resolved with the instrument's spectrometer. One way to solve this problem is to measure a different isotope for which there is no interference. Alternatively, one can monitor another isotope of the interfering element and subtract an appropriate amount from the element being analyzed, using known isotope ratio information. Corrections for most of the common elemental interferences are programmed into the software.

Abundance sensitivity interference refers to the degree of peak overlap that can occur between adjacent peaks. The interference can occur when the shoulder of a large peak significantly overlaps the peak of a neighboring minor peak, thereby contributing to its intensity. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

Isobaric polyatomic interferences result when ions containing more than one atom have the same nominal mass-to-charge ratio as an analyte of interest and cannot be resolved by the instrument's spectrometer. When possible, one should choose an interference-free isotope to measure. For lead, polyatomic interferences are not typically an issue.

Physical interferences result from the physical processes associated with the transport of sample to the plasma, sample behavior within the plasma, and transmission through the interface region between the plasma and the mass spectrometer. Viscosity and surface tension differences can affect results, as can deposits on the sample and skimmer cones caused by large quantities of dissolved solids in the samples. The interferences can be compensated for by the use of internal standards that approximate the analytical behavior of the elements being determined.

Memory interferences are related to sample transport and result when there is carryover from one sample to the next. Sample carryover can result from sample deposition on the sample and skimmer cones and from incomplete rinsing of the sample solution from the plasma torch and the spray chamber between samples. These memory effects are dependent upon both the analyte being measured and sample matrix and can be minimized through the use of suitable rinse times.

The rinse times necessary for a particular analyte should be estimated prior to analysis. This can be achieved by aspirating a standard containing the analyte at a concentration ten times the highest calibration standard for the normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce the analyte signal to less than ten times the method detection limit should be noted. The minimum rinse time between samples should be set to this time. Memory interferences may also be assessed within an analytical run by using three or more replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should check for the possibility of a memory effect. If the analyte concentration in the previous sample is

high enough to suspect analyte carryover, the sample should be re-analyzed after a long rinse period.

During sample preparation, contamination is of prime concern. The work area, including bench tops and fume hoods, should be kept scrupulously clean in order to eliminate environmental contamination. Samples, extracts, and reagents should be covered at all times to prevent airborne contamination.

6 Personnel Qualifications/Responsibilities

The analytical procedure in this method should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS), the interpretation of spectral and matrix interferences and procedures for their correction. A minimum of six months experience with commercial instrumentation is recommended. The sample preparation steps may be completed by an analyst unfamiliar with ICP-MS but who has training and experience in the extraction of samples for the determination of metals. A minimum of six months experience extracting samples (filters, water, soil, etc.) for trace level (µg/L in solution) lead is recommended.

7 Equipment and Supplies

The mention of trade names or commercial products in this method is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited the method represent those products and settings used during method development by the EPA Region 9 Laboratory. Glassware, reagents, supplies, equipment, and settings other than those listed in this method may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

7.1 Inductively coupled plasma mass spectrometer (ICP-MS)

- Instrument capable of scanning the mass range 5-250 amu with a minimum resolution capability of 1 amu peak width at 5% peak height. Instrument may be fitted with a conventional or extended dynamic range detection system.
- Radio-frequency generator compliant with FCC regulations.
- A variable-speed peristaltic pump is required for solution delivery to the nebulizer.
- A mass-flow controller on the nebulizer gas supply is required. A water-cooled spray chamber may be of benefit in reducing some types of interferences (e.g., from polyatomic oxide species).
- 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.

EPA Region 9 Laboratory uses a Perkin Elmer Elan DRC Plus Inductively Coupled Plasma Mass Spectrometer.

7.2 Environmental Express Hot Block Digestion System or equivalent capable of maintaining a temperature of 95°C.

7.3 Air displacement pipette(s) capable of delivering volumes ranging from 100-2500 µL with a tolerance of 2% and an assortment of high quality disposable pipet tips. Tips must be lead-free.

7.4 Glassware, Class A - volumetric flasks, pipettes, and graduated cylinders.

7.5 Polypropylene Digestion Vessels, Environmental Express P/N SC475 or equivalent (50-mL, graduated and certified to within 0.5% by volume), polypropylene screw caps, and polypropylene ribbed watch glasses to cover digestion vessels.

7.6 Paper cutter, pizza cutter, scissors, or other suitable cutting tool capable of making straight cuts to make accurately measured strips.

7.7 Plastic or Teflon wash bottles

7.8 Tweezers – plastic, Teflon or stainless steel

7.9 Filter - QMA, High Purity Quartz, Microfiber Filters, 8 x 10 in, Whatman or equivalent.

7.10 Disposable plastic syringes, 5-mL Luerlock, with 25 mm, 0.45 micron PTFE filters. Materials must be lead-free.

7.11 Reagents

Reagents may contain elemental impurities that might affect the integrity of analytical data. Owing to the high sensitivity of ICP-MS, high-purity reagents should be used whenever possible.

7.11.1 Nitric acid, concentrated (specific gravity 1.41).

7.11.2 Nitric acid, dilute (1+19, v/v) - Add 50 mL conc. nitric acid to 400 mL of reagent grade water and dilute to 1 L.

7.11.3 Argon gas supply - high purity grade (99.99%). When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional cylinders.

7.11.4 Reagent water

All references to reagent grade water in this method refer to ASTM Type I water (ASTM D1193). Suitable water may be prepared by passing distilled water through a mixed bed of anion and cation exchange resins.

7.11.5 Standard Solutions

The following instructions for solution preparation are provided as guidance for instrument operation and calibration. The analyst must refer to the instrument manufacturer's recommendations regarding instrument setup and calibration to assure that appropriate solutions and concentrations are employed. Solutions must be diluted in Class A volumetric glassware using air-displacement or Class A pipettes to measure standard solutions.

Standard Stock Solutions - Stock standards may be purchased from a reputable commercial source or prepared from ultra high-purity grade chemicals or metals (99.99-99.999% pure). Stock solutions should be stored in FEP bottles. Multi-element solutions containing lead are acceptable.

- Lead solution, stock 1 mL = 1000 µg Pb: Dry lead nitrate ($PbNO_3$) for one hour at 105°C; dissolve 0.1599 g $PbNO_3$ in 5 mL (1+1) nitric acid. Dilute to 100 mL with reagent grade water.

CAL Standards - Prepare initial calibration standards at a minimum of three levels. Use a stock standard solution as the source and dilute to the appropriate volume with 1% (v/v) nitric acid. CAL standards containing 10 µg/L, 20 µg/L, and 100 µg/L of Pb are generally acceptable. Prepare fresh every two weeks or as needed.

ICV / CCV - The ICV standard and CCV standard are identical and only differentiated by their place within the analytical sequence. A solution with 50 µg/L of lead is appropriate with the above CAL standard concentrations. Prepare the solution as needed from the same source as the CAL solutions in 1% (v/v) nitric acid. Prepare fresh every two weeks or as needed.

QLS - Prepare the QLS standard to contain 3.6 µg/L of lead. Prepare the solution from the same source as the CAL standards in 1% (v/v) nitric acid. Prepare fresh every two weeks or as needed.

CB - Dilute concentrated nitric acid with reagent water to obtain a 1% (v/v) nitric acid solution.

QCS - Prepare the QCS to contain 50 µg/L of lead. Prepare the solution from a source different from the CAL standards in 1% (v/v) nitric acid. Prepare fresh every two weeks or as needed.

Internal Standard Solution

- Obtain or prepare holmium and terbium as single-element stock standards.
- Prepare internal standard solution to contain 100 µg/L each of, holmium, and terbium in 1% (v/v) nitric acid. (Note: this solution may contain additional elements used as internal standards for other ICP-MS methods.)

Tuning Solution

- Obtain or prepare barium, beryllium, cerium, cobalt, indium, lead, magnesium, thorium, and uranium single-element stock standards.
- If necessary, prepare an intermediate standard to contain 1,000 µg/L of barium, beryllium, cerium, cobalt, indium, lead, magnesium, thorium, and uranium from the single-element stock standards.
- Prepare a working solution from the intermediate standard at 1.0 µg/L in 1% (v/v) nitric acid.

Rinse solution - Dilute concentrated nitric acid with reagent water to obtain a 2% (v/v) nitric acid solution.

8 Procedure

8.1 Sample Collection

Sampling procedures are detailed in Appendix B of Part 50, Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method). Sampling organizations may also send unexposed filters to the laboratory for analysis for quality control purposes (i.e. filter lot, trip, equipment blanks). Unexposed 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 that the sampling organization consult 40 CFR Appendix G to part 50, section 6.1 for guidance.

8.2 Sample Handling and Preservation

A representative strip from a TSP filter (high-volume filter, 8 by 10 inch, glass fiber or quartz) is required. Filters should be received in the laboratory in separate holders under chain-of-custody. Cold storage is not required for filters to be analyzed for lead; however, if filters were stored cold, they must be allowed to reach room temperature prior to analysis.

Store filters in the original holder and extracts in the extraction vessel (with the filter strip in the solution) under ambient conditions.

8.3 Sample Preparation

The hot block should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately, but no higher than, 90-95 ºC in a extraction vessel covered with a ribbed watch glass. Preheat the hot block for 30 minutes.

8.3.1 Filter Handling Procedure

Samples with physical deformities are not quantitatively analyzable. The analyst should visually check filters prior to proceeding with preparation for holes, tears, or non-uniform deposit which would prevent representative subsampling. Document any deformities and qualify the data appropriately.

Care must be taken to protect filters from contamination. Filters must be kept covered prior to sample preparation.

With the whole TSP filter still in its container, using clean tweezers carefully remove the filter from its holder and transfer to a clean paper cutter (or use a cutting tool and straightedge as described in Appendix G of Part 50). Cut a suitable strip (1 by 8 inches or ¾ by 8 inches). Make certain that no particulates fall off before or after cutting the strip. Using the tweezers, roll the filter strip and transfer to the corresponding labeled extraction vessel.

The cutting tools and tweezers must be cleaned after contact with each filter because particulates may transfer to the blades or surfaces that contact the exposed filter. Gently wipe the blades with a paper towel dampened with deionized water. If the paper towel is visibly dirty, wipe the blade with another dampened paper towel until no further particulates transfer to the paper towel. Allow the tools to air dry or blot dry with a lint-free tissue. Do not use wet or damp tools to cut or handle filters because the moisture will attract particulates from the filters.

8.3.2 QC Sample Preparation:

8.3.2.1 LRB - Transfer a strip of blank filter of the same dimensions as selected for exposed filters to a labeled 50-mL extraction vessel.

8.3.2.2 LFB - Transfer a strip of blank filter of the same dimensions as selected for exposed filters to a labeled 50-mL digestion vessel. Spike the filter with the lead stock standard solution (or a multi-element solution containing lead) or preferably, a solid certified reference material. Use an amount that will result in a concentration of 500 µg/L in the solution.

8.3.2.3 LD - Transfer an exposed filter strip of the designated QC sample of the same dimensions as selected for exposed filters to a 50-mL extraction vessel.

8.3.2.4 LFM - Transfer an exposed filter strip of the designated QC sample of the same dimensions as selected for exposed filters to a 50-mL extraction vessel. Using an air displacement pipette, spike the filter with the lead stock standard solution (or a multi-element solution containing lead). Use an amount that will result in a concentration of 500 µg/L in the solution.

8.4 Extraction Procedure

Transfer a 20-mL aliquot of dilute nitric acid (1:19, v/v) to each extraction vessel, ensuring that the filter strip is covered with acid. Place the vessel on the hot block. Cover with a ribbed watch glass.

Heat at 95 ºC for 60 to 70 minutes. Do not let the sample evaporate to dryness.

Remove the vessels from the hot block and allow to cool. In the graduated extraction vessel, bring the extract to a final volume of 50 mL by diluting to the 50-mL mark on the vessel with reagent grade water. Cap the vessel and shake vigorously for 5 seconds. Set aside the extract (with the filter strip in the extraction vessel) for at least 30 minutes to allow the nitric acid trapped in the filter to diffuse into the extract.

Shake the extract vigorously for 5 seconds (with the filter strip in the extraction vessel) and let settle for at least an hour. The sample is now ready for analysis.

8.5 Instrument or Method Calibration and Standardization

The analyst is advised to follow the recommended operating conditions provided by the instrument manufacturer. The following guidance is intended to be general; instrument specifics or technological developments may dictate modified procedures or criteria. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements and to maintain quality control data verifying instrument performance and analytical results.

8.5.1 Precalibration routine

The following precalibration routine must be completed prior to calibrating the instrument until such time it can be documented with periodic performance data that the instrument meets the criteria listed below without daily tuning.

Initiate operating configuration of instrument and data system. Allow a period of not less than 30 minutes for the instrument to warm up. During this process align the torch and conduct mass calibration and resolution checks using the tuning solution. Resolution at isotopes 206, 207, and 208 is critical for quantitation of lead. 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 analytes of less than 5%.

8.5.2 Internal Standardization

Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. For lead analysis, a minimum of one internal standard must be used, and an alternate is recommended. Procedures described in this method detail the use of two internal standards; terbium and holmium. Internal standards must be present in all samples, standards and blanks at identical levels. This may be achieved by directly adding an aliquot of the internal standards to the CAL standard, blank or sample solution or alternatively by mixing with the solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil. The concentration of the internal standard should be sufficiently high that good precision is obtained in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Depending on the sensitivity of the instrument, a concentration range of 10-100 µg/L of each internal standard is recommended. Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

8.5.3 Calibration

Prior to initial calibration, set up instrument software routines for quantitative analysis. The instrument must be calibrated using one of the internal standards. At a minimum, masses 206, 207 and 208 must be monitored for lead and the sum of the isotopes used for quantitation. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

8.5.3.1 Perform a multi-point calibration (ICAL) daily. Analyze a minimum of three CAL standards and a CB. A linear or linear-through-zero calibration equation is required and the correlation coefficient (r^2) for the curve must be 0.995 or greater. Forcing the curve through zero will result in more consistent recovery of the QLS but is not required if adequate recovery is obtained using a linear curve.

8.5.3.2 An ICV is analyzed immediately following initial calibration and the CCV at a frequency of one per 10 analytical samples and at the end of the analytical run. The recovery of the analyte in the ICV and CCV is calculated as follows:

$$\%R = \frac{M}{T} \times 100$$

Where
%R = percent recovery
M = measured concentration at the instrument, µg/L
T = true concentration of the analyte in the ICV/CCV, µg/L

The ICV and CCV recoveries must fall within 95 to 105 percent. If the %R for lead in the ICV falls outside of the QC criteria, the instrument must be re-calibrated. Samples cannot be analyzed until an acceptable ICV is analyzed. If the %R for lead in the CCV falls outside of the QC criteria, the instrument must be re-calibrated. Once an acceptable calibration is obtained, the samples preceding the out-of-control CCV must be re-analyzed.

8.5.3.3 The stability of the baseline must be monitored by analyzing a CB immediately after every ICV/CCV standard. If the value of the CB result is less than ½ the QL, the result is acceptable. If the value of the CB result equals or exceeds one-half the QL, the analysis may not continue. The cause of the high CB result must be determined and the problem corrected. The instrument must be re-calibrated and all samples not bracketed by acceptable CB results must be re-analyzed.

8.5.3.4 Analyze a QCS daily to verify the calibration standards and acceptable instrument performance. If the measured concentration is not within ± 10% of the true value, the method performance is unacceptable. The source of the problem must be identified and corrected before proceeding with analyses.

The recovery of the analyte in the QCS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where
%R = percent recovery
M = measured concentration at the instrument, µg/L
T = true concentration in the QCS, µg/L

8.5.3.5 To verify the ability to detect target analytes near the QL, a QLS must be analyzed at the beginning of the analytical run and after each 40 analytical samples. The recovery of lead in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where
%R = percent recovery
M = measured concentration at the instrument, µg/L
T = true concentration in the QLS, µg/L

If the QLS recovery does not meet the recovery criteria of 60 to 140 percent, determine the cause, take corrective action, and re-analyze the QLS.

8.5.3.6 The system must be flushed with the rinse solution between blanks, standards and samples. Allow sufficient time to remove traces of the previous sample. The required time is instrument dependent and must be determined by aspirating a high level standard and observing the instrument response return to background when the rinse solution is introduced. Solutions to be measured should be aspirated for 30 seconds prior to the acquisition of data to allow equilibrium to be established.

8.6 Typical Analytical Sequence

The following table shows a typical analytical sequence. Samples are indicated as S1, S2, S3…S20. All sample extracts are analyzed at a 10 times dilution with 1% v/v nitric acid. The analyst must make appropriate additional dilutions using 1% v/v nitric acid as the diluent on the basis of screening data, sample history, or other information. All results must be less than the highest calibration standard or further dilution is required. Extracts that contain particulates should be allowed to settle for a longer period of time. If particulates do not settle after 24 hours, filter an aliquot of the extract using a disposable plastic syringe equipped with a 0.45 micron PFTE filter prior to analysis to prevent damage to the instrument. Filtration must be reported to the client with the analytical result.

Seq.	Description	Seq.	Description	Seq.	Description
1	CB	15	S2	29	S14
2	Cal Std 1	16	S3	30	CCV
3	Cal Std 2	17	S4	31	CB
4	Cal Std 3	18	CCV	32	S15
5	Cal Std 4	19	CB	33	S16
6	ICV	20	S5	34	S17
7	CB	21	S6	35	S18
8	QCS	22	S7	36	S19
9	QLS	23	S8	37	S20
10	LRB	24	S9	38	CCV
11	LFB	25	S10	39	CB
12	S1	26	S11	40	
13	S1-LD	27	S12	41	
14	S1-LFM	28	S13	42	

8.7 Analyte Identification and Quantitation

Lead is quantitated from the sum of three isotopes, masses 206, 207, and 208. A linear or linear-forced-through zero calibration must be constructed. Only results between the

QLS concentration and the highest calibration standard may be reported without qualification (i.e. results between 3.6 and 100 µg/L, adjusted for sample preparation and dilutions).

9 Data and Records Management

After set-up and calibration, most ICP-MS instrument data systems report results for the analyzed solution in units of µg/L. The instrument calculations include elemental correction calculations, internal standard calculations, and calibration factors.

Report results for all filters delivered to the laboratory along with the associated batch quality control (LRB, LFB, LD, and LFM). Reporting units will vary depending upon the sampling organizations requirements but will usually be µg Pb/filter or µg Pb/m^3 (when the sampling organization provides total volume, in m^3). Sample results that exceed the calibration range must be reanalyzed at a higher dilution. Results below the QL should be reported as "not detected" or "ND" at the QL expressed as µg Pb/filter or µg Pb/m^3. Results should not be corrected for the concentration of lead in the LRB or the field, trip, or filter lot blanks provided by sampling organizations.

To report results in µg/filter using the following equation and report three significant figures:

$$C_{filt} = M \times \frac{V_{sol}}{strip} \times D \times 9\ strips\ per\ filter\ [or\ 12\ strips\ per\ filter]$$

Where:

C_{filt}	=	concentration, in µg/filter
M	=	measured concentration at the instrument, in µg/L
V_{sol}	=	volume of sample solution after sample extraction, in L
D	=	dilution factor, performed after sample extraction

To report results as µg/m^3, use the following equation and provide results to three decimal places for ACS reporting as required in 40 CFR Part 50 Appendix R:

$$C_{vol} = \frac{C_{filt}}{V_{air}}$$

Where

C_{vol}	=	Concentration, µg Pb/m^3
V_{Air}	=	volume of air sampled, in m^3

The number of strips/filter is based on the exposed area of the 8" x 10" filter and assumes a ½" unexposed border. This leaves 7" x 9" as the exposed area of the filter or 63 square inches. One strip is 1" x 8" but the exposed area is 1" x 7"or 7 square inches which

represents one ninth of the exposed area. A similar calculation for ¾" x 8" strips yields 12 strips per filter.

10 Quality Control and Quality Assurance

Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and calibration solutions as a continuing check on performance. Table 10.1 summarizes the routine requirements for ongoing quality control. The laboratory is required to maintain performance records that define the quality of the data thus generated.

10.1 Initial Demonstration of Performance (mandatory)

The initial demonstration of performance is used to characterize instrument performance (determination of linear calibration ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to analyses conducted by this method.

10.1.1 Linear Calibration Ranges

Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established for lead by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. The upper LDR limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed. The LDRs should be verified whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

10.1.2 Quality control sample (QCS)

When beginning the use of this method, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. To verify the calibration standards the determined mean concentration from a minimum of three analyses of the QCS; the result must be within ±10% of the stated QCS value. If the calibration standards and/or acceptable instrument performance cannot be verified, the source of the problem must be identified and corrected before either proceeding on with the initial determination of method detection limits or continuing with on-going analyses.

10.1.3 Method detection limits (MDL) should be established using at least seven (7) filter strips from an unexposed TSP filter fortified at a concentration of two to five times the estimated quantitation limit. The size of the filter strip must be the same as the laboratory selects in Section 8.3.1 to process filters from sampling organizations. Process the fortified filter strips through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Compute the MDL as follows:

$$MDL = t_{(n-1,1-\alpha=0.99)}(S)$$

where:

MDL	=	method detection limit
n	=	number of replicates analyzed
$t_{(n-1,1-\alpha=.99)}$	=	students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.
S	=	standard deviation of the replicate analyses

Refer to 40 CFR Part 136, Appendix B for complete requirements for MDLs. MDLs must be determined prior to the analysis of any field samples by the laboratory and annually thereafter, when a new operator begins work, or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

10.2 Assessing Laboratory Performance (mandatory)

10.2.1 Laboratory reagent blank (LRB) - The laboratory must analyze at least one LRB with each batch of 20 or fewer filters. LRB data are used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing. LRB values $\geq$ ½ the QL indicate potential laboratory or reagent contamination but may also be the result of background levels of lead in the filter extracted as the LRB and therefore unrelated to the exposed filters in the batch. When LRB values constitute 10% or more of the analyte level determined for a sample or are $\geq$ ½ the QL whichever is greater, re-extraction may be required for TSP filters; consult the laboratory supervisor for direction. The result (in µg/filter) for the LRB must be reported to the sampling organization.

10.2.2 Laboratory fortified blank (LFB) - The laboratory must analyze at least one LFB with each batch of 20 or fewer filter strips. Calculate accuracy as percent recovery using the following equation:

$$\%R = \frac{M}{T} \times D \times 100$$

Where

%R	=	percent recovery
M	=	measured concentration at the instrument, µg/L
T	=	true concentration in the LFB, µg/L
D	=	dilution factor, performed after sample extraction

If the recovery falls outside the required control limits of 80-120%, the method is judged out of control, and the source of the problem must be identified and resolved before continuing analyses. The result (in percent recovery) for the LFB must be reported to the sampling organization.

10.2.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 80-120%. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the mean percent recovery (x) and the standard deviation (S) of the mean percent recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x - 3S

The optional control limits must be equal to or better than the required control limits of 80-120%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

10.2.4 Instrument performance - For all determinations the laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration run the CB and CCV immediately following each calibration routine, after every ten analyses and at the end of the sample run. The results of the analyses of the standards will indicate whether the calibration remains valid. The lead recovery within the standard solutions must be within ±5% of calibration. If the calibration cannot be verified within the specified limits, the instrument must be recalibrated. If the sample matrix is responsible for the calibration drift, it is recommended that the previous 10 samples are reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

10.3 Assessing Analyte Recovery and Data Quality

Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate strips from a filter for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, laboratory or program, the following laboratory fortified matrix (LFM) procedure is required.

10.3.1 The laboratory must add a known amount of analyte to a minimum of 5% of the routine samples. In each case the LFM strip must be a duplicate of the strip used for lead analysis and the spike added prior to sample preparation steps. The added analyte concentration must be the same as that used in the LFB.

Calculate the percent recovery for lead, corrected for background concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range of 70-130%. Recovery calculations are not required if the concentration of the analyte added is less than 30% of the sample background concentration. Percent recovery may be calculated using the following equation:

$$\%R = \frac{C_{LFM} - C_{samp}}{s} \times 100$$

Where

$\%R$	=	percent recovery
C_{LFM}	=	measured concentration in the LFM, in µg/filter.
C_{samp}	=	measured concentration in the routine sample, in µg/filter
s	=	spiked concentration added to the LFM, in µg/filter

If recovery falls outside the designated range and laboratory performance is shown to be in control, the recovery problem encountered with the fortified filter is judged to be matrix related, not system related. The data user must be informed that the result for that analyte in the unfortified sample is suspect due to either the heterogeneous nature of the sample or an uncorrected matrix effect.

10.3.2 Laboratory duplicate

One laboratory duplicate must be analyzed for every 20 or fewer field samples in a batch. Treat the laboratory duplicate as a routine sample. In each case the strip must be a duplicate of the strip used for lead analysis and taken through the preparation steps separately.

To assess precision, the relative percent difference (RPD) of the LD1 and LD2 is compared to the acceptance criterion of ≤20 percent. Calculate the RPD between the routine sample (LD1) and the laboratory duplicate (LD2) using the following equation:

$$RPD = \frac{\left|C_{LD} - C_{filt}\right|}{\left(C_{LD} + C_{filt}\right)/2} X\ 100$$

Where

RPD	=	relative percent difference
C_{LD}	=	measured concentration in LD, in µg/filter
C_{filt}	=	measured concentration in sample filter, in µg/filter

Apply precision criteria for samples with analyte levels ≥ QL. If control limits are exceeded, re-analyze the sample and duplicate once. If the control limits are exceeded again, flag the associated sample result indicating that the particulate matter may not be homogenous across the TSP filter.

10.4 Internal Standard Response

Monitor the signal intensity for the internal standard masses throughout the analytical run. This information is useful in detecting instrument drift, sensitivity shift; dissolved solids content, and inherent internal standard (i.e., a natural constituent in a sample). The absolute intensity of the internal standard must not deviate more than 60 - 125% from its original intensity in the calibration blank. If deviations greater than these are observed, flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of two, add the internal standards and reanalyze. If after flushing the response of the internal standards in the calibration blank is out of limits, terminate the analysis and determine the cause of the drift. Possible causes of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

Table 10.1 Quality Control Measures and Acceptance Criteria

Parameter	Frequency	Criteria
Correlation Coefficient	Each ICAL	≥ 0.995
ICV	After ICAL	95 - 105%
CCV	Every 10 Samples	95 - 105%
CB	After each ICV/CCV	< ½ QL
QCS	After ICAL	90 - 110%
QLS	After ICAL & after every 40 analytical samples	60 - 140%
LRB	Each Batch	< ½ QL
LFB	Each Batch	80 - 120%
MD, Precision	Every 20 samples	≤ 20 RPD
LFM, Accuracy	Every 20 samples	70 - 130%
Internal Standard	Every analysis	60 - 125% of initial CB

11 References

40 CFR Part 136, Appendix B. *Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11*.

40 CFR Part 50, Appendix B. *Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method)*

40 CFR Part 50, Appendix G. *Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air*.

U.S. Environmental Protection Agency Method 200.8, *Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, EMMC Version, May 1994.*

U.S. Environmental Protection Agency SW846 Method 6020A, *Inductively Coupled Plasma-Mass Spectrometry, Revision 1, February 2007.*