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Standard Operating Procedure for the Determination of Metals In Ambient Particulate Matter Analyzed By Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)

Work Assignment 5-03

Prepared for:
Office of Air Quality Planning and Standards
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DISCLAIMER

Through its Office of Air Quality Planning and Standards, the U.S. Environmental Protection Agency funded and managed the research described in this procedure under EPA contract No. 68-D-00-264 to Eastern Research Group, Inc. Mention of trade names or commercial products in this procedure does not constitute endorsement or recommendation for their use. This procedure has not been subjected to the EPA's review and is not an EPA approved document.

1.0 IDENTIFICATION AND PURPOSE

This standard operating procedure (SOP) provides the sample preparation procedures for Teflon, PM10, or TSP filters and analysis for metals by Inductively Coupled Plasma - Mass Spectrometer (ICP-MS).

2.0 MATRIX OR MATRICES

This procedure applies to the preparation and analysis of metals on Teflon, PM10, or TSP filters obtained by low-volume sampling.

3.0 METHOD DETECTION LIMIT

3.1 Method Detection Limits (MDL)

3.1.1 The method detection limit (MDL) for each isotope is calculated according to 40 CFR, Vol. 49, No. 209, Appendix B to Part 136. At least 7 replicates are prepared and analyzed for this study. An example of MDL attainable by this method is shown in Table 24.1.

3.1.2 The y-intercept for each linear calibration must be set to zero.

3.1.3 Use the same internal standards and instrument settings (sweeps and dwell) for MDL and field sample analysis.

3.1.4 The MDL determination should be reported in ng/mL and ng/m^3 (assuming 20 m^3 for Teflon filters and 1700 m^3 for PM10 or TSP filters).

3.1.5 The MDLs should be repeated once per year.

3.2 Instrument Detection Limits (IDL)

The IDL is used to compare instrument performance over time or to verify performance to manufacturer's specifications. Although the IDL is not used in data QC evaluations, the IDL can be useful in comparing instrument performance over time.

3.2.1 To determine an IDL, use settings for sweeps and dwell time that yield the most outstanding results.

3.2.2 Run at least 7 replicates of a blank solution and a concentration 3.5 times the MDL. Use the standard deviation value appropriate for the degrees of freedom in the Federal Register's equation listed in Section 3.1.1.

4.0 SCOPE AND APPLICATION

This procedure describes the acid extraction and trace elemental analysis of ambient air samples using an inductively coupled plasma-mass spectrometer (ICP-MS). The

extraction procedures are suitable for low-volume ambient air samples collected on exposed Teflon, and high-volume ambient air sampling collected on PM10 or TSP filters.

5.0 METHOD SUMMARY

This SOP covers the preparation and analysis of metals on Teflon, PM10, or TSP filters exposed to ambient air and submitted to the laboratory. The filters are extracted in 4% nitric acid via sonication for 3 hours. The extract is analyzed by ICP-MS. The ICP-MS analysis is completed using the manufacturer software following conditions established during calibration and quality control checks of instrument performance.

6.0 DEFINITIONS

CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification
DI water	Deionized water
DQO	Data Quality Objective
HSV	High Standard Verification
IC	Initial Calibration
ICB	Initial Calibration Blank
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICS	Interference Check Standard
ICV	Initial Calibration Verification
LCS	Laboratory Calibration Spikes
MB	Method Blank
MDL	Method Detection Limit
mL	milliliter(s)
mm	millimeter(s)
MS	Matrix Spike
ng/m^3	nanogram(s) per cubic meter
NIST	National Institute of Standards and Technology
QCS	Quality Control Sample
RSD	Relative Standard Deviation
RPD	Relative Percent Deviation
SD	Standard Deviation
:g/mL	microgram(s) per milliliter(s)

7.0 INTERFERENCES

The background level of metals 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.

7.1 Laboratory Interferences

7.1.1 Wear talc-free gloves when handling unexposed or exposed filters.

7.1.2 Clean all equipment used in the sample preparation and analysis following standard dishwashing procedures followed by acid washing filters in 10 or 50% HNO_3 acid.

7.1.3 Use Type I deionized (DI) water, with a resistivity of greater than 17.3 megaohms or greater, for sample extraction and standard preparation. Record the water resistivity prior to use.

7.2 Chemical Interferences

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

7.2.1 Nitric acid must be less than 2% for ICP-MS analysis to minimize the damage to the interface and to minimize isobaric molecular interferences.

7.2.2 If higher acid extraction concentrations are required, dilute to 2%.

7.2.3 The final dilutions of sample extracts must equal the acid content of the calibration standards in order to compensate for potential interferences.

7.2.4 The concentrations of dissolved solids in analysis solutions should be less than 2% to protect the sample interface on the instrument. Higher concentrations may plug the sample cone orifice.

7.2.5 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 (NaHCO3) sample matrix is known to cause this problem.

7.3 Instrument Interferences

7.3.1 Isobaric molecular and doubly charged ion interferences are caused by more than one atom (example, the contribution of ArCl on the 75As signal) or more than one charge (example, MoO+ ions on Cd isotopes).

7.3.2 Spectral interferences result from the presence of other isotopes or ions that have the same atomic weight or mass number as the analyte.

7.3.3 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.

7.3.4 Matrix interferences are caused by elemental properties of the samples in solution. For matrices of known composition, match the composition of the standards to that of the samples. For matrices of unknown composition, use an internal standard that has been matched to the analyte(s) so that the two elements are similarly affected by matrix changes.

7.3.5 Memory interferences can occur when there are large concentration differences between samples or standards that are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, 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.

8.0 SAFETY

8.1 Personal protection should be used for all work used in the inorganic laboratory, (e.g., gloves, safety glasses, laboratory coats, etc.).

8.2 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.

8.3 Make sure that sample vials are kept in racks to prevent spills.

8.4 All personnel should be trained in the exaction and analysis of acid samples for inorganic analysis.

8.5 Strong acids must not be stored with organic solvents or samples.

8.6 Follow applicable laboratory safety procedures and Health and Safety Manuals.

9.0 EQUIPMENT

Inductively Coupled Plasma-Mass Spectrometer - consists of an inductively coupled plasma source, ion optics, a quadrupole spectrometer, a computer that controls the instrument, data acquisition, and data handling, a printer, an autosampler and a recirculator. The quadrupole mass spectrometer has a mass range of 2 to 270 atomic mass units (amu).

9.1 Typical Operating Conditions

Plasma forward power	1.6 kW
Coolant flow rate	13.5 Lpm
Auxiliary flow rate	0.6 Lpm
Nebulizer flow rate	0.78 Lpm
Solution uptake rate	0.6 mL/min
Spray chamber temperature	15 /C

Detector mode	Pulse counting
Replicate integrations	3
Mass range	8 - 240 amu
Dwell time	320 microsecond
Number of MCA channels	2048
Number of scan sweeps	85
Total acquisition time	3 min/sample

10.0 MATERIALS

10.1 Polypropylene sample vials with screw caps.

10.2 Sonication bath with the heating capability to 69 degrees Celsius (°C).

10.3 Micro-pipettes with disposable tips, 100 microliter (:L) to 10 milliliter (mL).

10.4 Repeating pipeter, 20 mL.

10.5 Volumetric flasks, 50 mL.

10.6 Polypropylene funnels and Whatman 541 filter paper, or Environmental Express "FilterMate".

10.7 Miscellaneous: talc-free gloves; disposable laboratory wipes; self adhesive labels.

11.0 CHEMICALS, REAGENTS, AND STANDARDS

11.1 Nitric Acid, ultrapure and concentrated.

11.1.1 To prepare the 0.5% Nitric Acid Solution, dilute 0.5 mL of nitric acid in 100 mL of DI water.

11.2 De-ionized water, filtered with a resistivity of greater than 17.3 megaohms.

11.3 Argon gas, high purity.

11.4 Calibration Standards: National Institute of Standards and Technology (NIST) traceable material, 10 :g/mL stock in one percent nitric acid.

11.5 Secondary Source Control Standard: secondary source of the intermediate range calibration standard is run as a check of the precision of the instrument and calibration.

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

12.1 <u>Preparation and Handling of Filters</u>

Whenever the filter is handled, clean Teflon® coated or plastic tweezers are used with disposable PVC gloves.

12.2 Preservation and Storage of Filters

Samples can be stored for up to 180 days in ambient conditions.
A unique identification number is placed on the outside of the envelope.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Tuning Solution

The tuning solution contains elements representing all of the mass regions of interest, thereby verifying that the resolution and mass calibration of the instrument are within the required specifications. The solution is also used to verify that the instrument has reached thermal stability. The tuning solution should include 10 ng/mL of Be, Mg, Co, In, and Pb. If needed other elements can be added, such as Cu, Rh, Cd, Ba, Ce, U.

13.2 Calibration

13.2.1 Allow a period of not less than 30 minutes for instrument warm up. During this process, conduct mass calibration and resolution checks using the tuning solution. 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 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.

13.2.2 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%.

13.2.3 Prior to initial calibration, set up proper instrument software routines for quantitative analysis. The instrument must be calibrated, using a minimum of 4 calibration points, for the analytes to be determined using the calibration blank and calibration standards prepared at one or more calibration levels. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

13.2.4 The rinse blank should flush the system between solution changes for blanks, standards, and samples. Allow sufficient rinse time to remove traces of the previous sample or a minimum of 1 min. Solutions should aspirate for at least 30 seconds prior to the acquisition of data to establish equilibrium.

13.2.5 All quality control requirements presented in Table 24-2 must be met.

13.3 Internal Standardization

Selecting the proper internal standard, at ideal concentrations, can eliminate the need for correction equations.

13.3.1 Internal standards for this method are Sc, ^{89}Y, ^{115}In, Tb, and ^{209}Bi for analytes beginning with Mass 6 and ending with Mass 238. If needed other elements can be added, such as ^{6}Li, and ^{69}Ga.

13.3.2 Concentrations of the internal standards for this method should be 10 nanogram per milliliter (ng/mL).

13.3.3 The concentration of the internal standard must be added equally to the reagent blank, calibration standards, and samples.

13.3.4 Internal standardization must be used in all analyses to correct for instrument drift and physical interferences.

13.4 Instrument Performance

13.4.1 After establishing calibration, verify all analytes by analyzing the Initial Calibration Verification Sample (ICV), which should be obtained from a second source outside the laboratory. If measurements exceed ± 10% of the established ICV value, terminate the analysis, identify and correct the problem, and re-analyze the ICV before continuing analysis.

13.4.2 To verify that the instrument is properly calibrated on a continuing basis, run the calibration blank and calibration standards as surrogate samples after every 10 analyses. The results of the analyses of the standards will indicate whether the calibration remains valid. If the indicated concentration of any analyte deviates from the true concentration by more than 10%, re-analyze the standard. If the analyte is again outside the 10% limit, the instrument must be re-calibrated and the previous ten samples re-analyzed. The instrument responses from the calibration check may be used for re-calibration purposes. If the sample matrix is responsible for the calibration drift, the previous 10 samples should be re-analyzed in groups of five between calibration checks to prevent a similar drift induced error from reoccurring.

14.0 PROCEDURE

14.1 Filter Extraction

Sonication Preparation - applicable to Teflon, TSP, and PM10 filters.

14.1.1 If preparing a TSP or PM10 filter, cut a 1 x 8 " strip from the exposed filter.

14.1.2 Place filter strip or Teflon filter in an extraction tube as far down as possible.

14.1.3 Pour 20 mL of the 4% nitric acid into the extraction tube with the filter.

14.1.4 To recover mercury for ICP-MS analysis, spike 1 ppm of gold into extraction tube. Cap the tube.

14.1.5 Sonicate for 3 hours using a heated (69 /C) sonication bath.

14.1.6 Check the filter occasionally during sonication. If it floats out of the acid, use a clean pyrex or quartz glass rod to adjust the filter to the bottom of the tube.

14.1.7 After sonication, allow the sample to cool to room temperature.

14.1.8 Set up a filter funnel, Whatman 541 filter paper (or equivalent), and 50 mL volumetric for each sample or use a FilterMate devise.

14.1.9 Filter sample and dilute to 50 mL with clean DI water.

14.1.10 Transfer the sample extract to a polypropylene bottle or leave in FilterMate. The sample extract is ready to be analyzed.

Hot Acid Digestion - applicable to TSP and PM10 filters.

14.1.1 If preparing a TSP or PM10 filter, cut a 1 x 8 " strip from the exposed filter.

14.1.2 Place filter strip or Teflon filter in 250mL quartz beaker.

14.1.3 Pour 30 mL of the 10% nitric acid onto the filter.

14.1.4 To recover mercury for ICP-MS analysis, spike 1 ppm of gold into extraction tube. Cap the tube.

14.1.5 Reflux gently for 30 minutes at 95 /C.

14.1.6 After refluxing, add 10 mL of clean DI water and allow the extract to cool for 30 minutes.

14.1.7 Filter the extract using Whatman 541 filter paper (or equivalent), syringe filter, or "FilterMate".

14.1.8 Dilute to 20 mL with clean DI water.

14.1.9 Transfer the extract to a polypropylene bottle. The sample extract is ready to be analyzed.

14.2 Filter Analysis

14.2.1 To tune the ICP-MS, a tuning solution is analyzed prior to analyzing samples with at least five replicates with a RSD of ± 5%.

14.2.2 After the initial calibration is completed, a calibration check is required at the beginning and end of each analysis period and at intervals of ten samples to verify the calibration. The RPD must be within ± 10%. The calibration check does not meet this criteria, the check, and any bracketed samples, should be re-analyzed. If the calibration check does not meet criteria a second time, the instrument should be re-calibrated.

14.2.3 Analyze a continuing calibration blank after the continuing calibration check. The blank must not contain any target metal above the MDLs.

14.2.4 Samples with analyte concentrations above the calibration range must be diluted and re-analyzed.

15.0 CALCULATIONS

15.1 Analyte Concentration

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

C = [(**:**g metal/L) x (Digestion volume (i.e., 0.050 L) L/filter)/V_{std}

Where:

C = concentration, **:**g metal/m^3

:g metal/L = metal concentration determined from Section 14.2.

Filter extract volume (L/filter) = total sample extraction volume from extraction procedure (i.e., 0.05 L).

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

15.2 Relative Percent Difference (RPD)

The RPD is calculated as follows:

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

Where:

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

15.3 Percent Recovery

Percent Recovery is calculated as follows:

Percent Recovery = (Analytical result/Theoretical result) x 100

15.4 If an element has more than 1 monitored isotope, 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 that the primary recommended isotopes; therefore, differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

15.5 Correct data values for instrument drift or sample matrix induced interferences by applying internal standardization correction factors. Corrections for characterized spectral interferences should also be applied to the data.

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16.0 QUALITY CONTROL

Method Quality Objectives (MQO) and data assessment criteria, are determined from the results of the quality control samples. The MQO criteria is presented in Table 24-2.

16.1 Sample Collection Quality Control

16.1.1 Filters which are dropped or become contaminated with any foreign matter (i.e., dirt, finger marks, ink, liquids, etc.) are invalid.

16.1.2 Filters with tears or pinholes, which occurred before or during sampling, are invalid.

16.1.3 A power failure during a sample analysis invalidates the sample collected during that run.

16.2 Initial Calibration

Analyze at least four calibration levels with an correlation factor (R) greater than or equal to 0.995. If calibration fails this criteria, repeat the analysis. If criteria is still not met, reprepare the standards and perform the calibration again.

16.3 Initial Calibration Verification

Analyze the initial calibration verification (ICV) immediately after the initial calibration. If the recovery criteria, 90-110%, is not met, repeat the analysis.

16.4 Initial Calibration Blank

Analyze the initial calibration blank (ICB) immediately after the ICV and prior to analysis of the high standard verification. The analytes must be at levels below the MDL. If not, locate and resolve the contamination problem before continuing. Any sample result for analytes less than 5 times the amount of the blank must be flagged or analysis must be repeated.

16.5 Interference Check Standard

Analyze the interference check standard (ICS) immediately after the analysis of the HSV, and prior to the analysis of the samples. The ICS must be analyzed every 8 hours of continuous operation and again at the end of the analysis batch. If the recovery criteria, 80-120%, is not met, repeat the analysis. If the recovery criteria is not met again, re-prepare the ICS and analyze. Samples containing levels of the interferences above the levels in the ICS should be considered for dilution.

16.7 Continuing Calibration Verification (CCV)

Analyze a mid-range calibration standard after every 10 sample analyses to verify the initial calibration. If the recovery criteria, 90-110%, is not met, repeat the analysis. If the recovery criteria is not met again, the instrument must be re-calibrated and samples must be re-analyzed.

16.8 Continuing Calibration Blanks

Analyze a continuing calibration blank (CCB) immediately following each CCV. The analytes must be at levels below the MDL. If not, locate and resolve the contamination problem before continuing. Any sample result for analytes less than 5 times the amount of the blank must be flagged or analysis must be repeated.

16.9 Method Spikes and Method Spike Duplicates

Analyze one method spike and one method spike duplicate per batch of samples to determine that the matrix effects from the filters at a frequency of one per batch of samples prepped. The method spikes and method spike duplicates should be within ±20% RPD of the target values. If the spikes are outside of these limits, check the calibration and extraction procedures.

16.10 Method Blanks

Analyze a method blank (MB) for every 20 sample analyses. The MB contains all the reagents in the sample preparation procedure and must be prepared and analyzed as a sample to determine the background levels from the instrument. The analytes must be at levels below the MDL. Any sample result for analytes less than 5 times the amount of the blank must be flagged or analysis must be repeated.

16.11 Matrix Spikes

Analyze one matrix spike (MS) per batch of samples at a minimum, or 1 per 20 samples, to determine the matrix effects from the filter. If the recovery criteria, 75-125%, is not met, re-prepare the batch.

16.12 Laboratory Control Spike (LCS)

A laboratory control spike must be prepared from a secondary source of calibration standards and analyzed with each sample batch. If the recovery criteria, 80-120% (exception of Ag and Sb), is not met, re-prepare the sample batch.

16.13 Internal Standards

The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to register between 60 to 125% of the intensity of that internal standard in the initial calibration standard, the following procedure is implemented:

16.13.1 If the intensities are too high, the sample must be diluted and reanalyzed with the addition of appropriate amounts of internal standards.

16.13.2 Repeat dilution until the internal standard intensities fall within the prescribed window.

16.13.3 Check that the intensity levels of the internal standards for the calibration blank and interference check standard agree within 20% of the intensity level of the internal standard of the original calibration solution. If they do not agree, stop the analysis, find and correct the problem, re-calibrate if needed and re-analyze the affected samples.

16.14 Serial Dilution

The ICP serial dilution analysis must be performed on one sample per batch. After a fivefold serial dilution, the analyte concentration must be within 90 and 110% of the undiluted sample results. If it does not agree within these limitations, re-prepare and analyze the dilution. If it fails a second time, an interference effect must be suspected and the data must be flagged.

16.15 Rinse Blank

Flush the system between standards and samples with 2% nitric acid in DI water.

17.0 PREVENTION

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

18.0 CORRECTIVE ACTION

Corrective action for any analyses data quality issues should be developed by each laboratory. Table 24.2 gives the data quality guidelines and the associated recommended corrective actions.

19.0 WASTE MANAGEMENT

The ICP-MS analyst is responsible for ensuring the safe storage and disposal of all chemical standards and reagents associated with this method.

19.1 Ordering Chemicals

19.1.1 Storage of excess chemicals takes up valuable lab space. Prior to ordering chemicals, assess needs carefully. Order only amounts that will be utilized within the following year.

19.1.2 Purchase smaller volumes whenever possible to minimize disposal costs of unused portions.

19.2 Disposing of Chemicals

19.2.1 The ICP-MS analyst is responsible for notifying the hazardous waste coordinator of disposal needs.

19.2.2 The ICP-MS analyst is responsible for keeping chemicals and reagents separate and in their original containers.

20.0 MAINTENANCE

A service contract would provide for preventive maintenance on a semiannual basis and for repair services for the instrumentation as required. All maintenance activities should be documented in instrument maintenance logs. Experienced analysts can perform routine maintenance.

20.1 The following maintenance procedures need to be addressed daily.

20.1.1 Check sample waste container level.

20.1.2 Inspect argon tank supply and its pressure to the instrument.

20.1.3 Inspect chiller connections for possible leaks.

20.1.4 Inspect torch and aerosol injector tubes.

20.1.5 Inspect nebulizer for clogs.

20.1.6 Inspect sample capillary tubing to be sure it is clean and in good condition.

20.1.7 Check peristaltic pump tubing before operation.

20.1.8 At the end of the day, flush system for 5 minutes with the plasma on with a maximum of 2% nitric acid, followed by deionized water.

20.2 The following maintenance procedures need to be addressed quarterly.

20.2.1 Clean touch components and replace any worn O-rings on the torch assembly.

20.2.2 Inspect and clean the RF coil.

20.2.3 Clean nebulizer spray pattern. Clean and replace tip as necessary.

20.2.4 Check nebulizer components and replace worn O-ring on the transducer face.

20.2.5 Clean drain fitting for leaks.

20.2.6 Check that pump rollers are clean and remove and clean pump head as necessary.

21.0 SHORTHAND PROCEDURE

The flow chart shown in Figure 24-1 shows the procedural steps for analysis of filter samples for metals.

22.0 DOCUMENTATION AND DOCUMENT CONTROL

22.1 All information concerning sample preparation, standard preparation, instrument conditions, etc., must be written in the analyst's notebook.

22.2 The instrument calibration values, i.e., DI water conductance readings must be written in the project notebook. A list of the analyses must be recorded in addition to the following information: system number, date of analysis.

22.3 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.

22.4 Record all maintenance performed on the instrument in the maintenance logbook for this particular instrument.

22.5 Record all analyses including quality control samples, performed by the instrument in the logbook for this particular instrument.

22.6 Reviewer must sign laboratory notebook weekly.

23.0 REFERENCES

ICP-MS Operator Manual.

EPA Compendium Method IO-3.5A for the Determination of Metals in Ambient Particulate Matter using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS).

Standard Operating Procedure (S.O.P.) For The Trace Elemental Analysis of Low-Volume Samples Using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) (SOP MLD 061), California Air Resources Board, May 2002.

Standard Operating Procedure (S.O.P.) For Metals Analysis by Atomic Absorption Spectrophotometry (SOP MLD 005), California Air Resources Board, October 2003

24.0 TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

Table 24-1. MDLs for Metals

Compound	(ng/filter)	Assuming a 1600 m^3 volume (ng/m^3)
Antimony	15.7	0.785
Arsenic	3.11	0.155
Beryllium	2.01	0.101
Cadmium	2.24	0.112
Chromium (total)	18.7	0.934
Cobalt	7.42	0.371
Lead	9.16	0.458
Manganese	2.56	0.128
Mercury	7.07	0.354
Nickel	20.7	1.03
Selenium	3.49	0.174

Figure 24-1. Flow Diagram for ICPMS Preparation and Analysis for PM10 or TSP Filters

Parameter	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (IC)	Daily, at least 4 calibration points	Correlation coefficient ≥0.995	1) Repeat analysis of calibration standards. 2) Re-prepare calibration standards and reanalyze.
Initial Calibration Blank (ICB)	Immediately after ICV	Analytes below MDL	1) Locate and resolve contamination problems before continuing. 2) Reanalyze
High Standard Verification (HSV)	Following the ICB	Recovery 95-105%	1) Repeat analysis of HSV. 2) Re-prepare HSV.
Initial Calibration Verification (ICV)	Immediately after calibration	Recovery 90-110%	1) Repeat analysis of calibration check standard. 2) Repeat analysis of calibration standards. 3) Re-prepare calibration standards and reanalyze.
Interference Check Standard (ICS)	Following the HSV, every 8 hours and at the end of each run	Recovery 80-120%	1) Repeat analysis of ICS. 2) Re-prepare ICS.
Continuing Calibration Verification (CCV)	Analyze before the 1st sample, after every 10 samples, and at the end of the run	Recovery 90-110%	1) Repeat analysis of continuing calibration verification sample. 2) Re-prepare continuing calibration. 3) Reanalyze samples since last acceptable continuing calibration verification.
Continuing Calibration Blanks (CCB)	Analyzed after each CCV	Must be below MDL	1) Locate and resolve contamination problems before continuing. 2) Reanalyze samples since last acceptable continuing calibration verification.
Method Blanks (MB)	1 per 20 samples, a minimum of 1 per batch	Analytes below MDL	1) Reanalyze. 2) Re-prepare blank and reanalyze. 3) Repeat analyses of all samples since last clean blank.
Method Spike/Method Spike Duplicate	1 per 20 samples, a minimum of 1 per batch	Recovery 80-120%	1) Re-prepare sample batch. 2) Reanalyze.
Laboratory Control Sample (LCS)	1 per 20 samples, a minimum of 1 per batch	Recovery 80-120%, with the exception of Ag and Sb	1) Re-prepare sample batch. 2) Reanalyze.
Matrix Spike (MS)	1 per 20 samples per sample batch	Recovery 75-125%, with the exception of Ag and Sb	1) Re-prepare sample batch. 2) Reanalyze.
Duplicate Samples	1 per batch	RPD < 20%	1) Repeat analysis. 2) Re-prepare.
Serial Dilution	1 per batch	Recovery 90-110% of undiluted sample	1) Re-prepare dilution 2) Flag data.

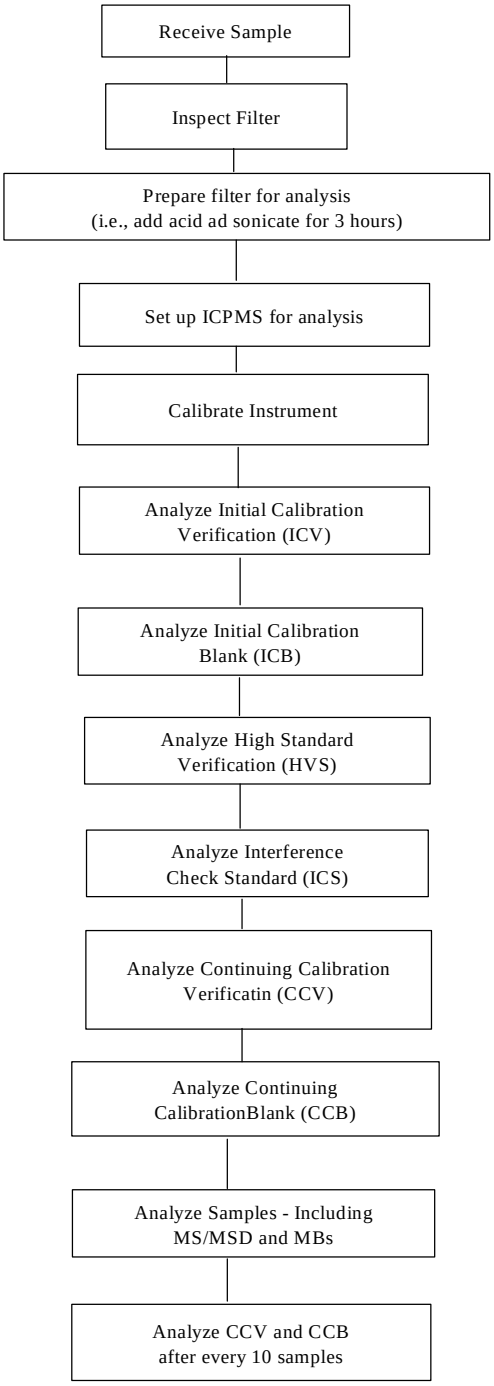

Figure 24-1. Summary of Quality Control Procedures for Metals Analysis