

California Environmental Protection Agency



SOP MLD 061

**STANDARD OPERATING PROCEDURE (SOP) FOR
THE TRACE METAL ANALYSIS OF
AMBIENT AIR PARTICULATE SAMPLES USING
INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (ICP-MS)**

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Monitoring and Laboratory Division (MLD)**

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APPENDIX A TABLE 1

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1.0 SCOPE

This document details a dilute-mixed-acid refluxing technique to remove particulates from low-volume air sampling filters. This document also specifies the quality control measures required to validate trace metal analysis using an ICP-MS equipped with an ultrasonic nebulizer (USN) and a desolvator.

- 1.1 The reflux procedure herein is specific for low-volume ambient air samples collected on exposed Teflon filters sized 37- and 47-millimeters in diameter.
 - 1.1.1 Teflon filters appear to have inconsistent elemental contamination of analytes commonly reported for air samples collected on Teflon filters. See Appendix A of this document.
 - 1.1.2 Predominate contaminants include, but may not be limited to, Magnesium, Aluminum, Silicon, Phosphorus, and Potassium.
 - 1.1.3 Minor contaminants may include Sulfur, Scandium*, Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc, Gallium*, Germanium*, Arsenic, Selenium, Yttrium*, Zirconium, Cadmium, Tin, Antimony, Mercury, and Lead. Elements denoted with an asterisk (*) are typical internal standards (Section 10.4). Contamination levels of these elements do not necessarily disqualify their use as internal standards.
- 1.2 This method is not analyte specific. The analyst is responsible for demonstrating the accuracy and precision of the method for the analytes of interest prior to reporting any data.
- 1.3 Although not specified herein, this reflux method is also suitable for segments of high-volume ambient air samples collected on quartz or glass micro-fiber filter segments, provided the extracts are vacuum-filtered of all debris greater than 0.45-microns before analysis by ICP-MS.
- 1.4 Specifics on the optimization and operation of the ICP-MS are not included in this SOP. A detailed explanation of the extensive parameters necessary for proper instrument operation are best described in the vendor's instrument manual and maintenance video. ^[1, 2]

- 1.5 Northern Laboratory Branch (NLB) uses the acronym ICP-MS as designated by the instrument manufacturer(s) and patent holder(s) of this technology. The United States Environmental Protection Agency (U.S. EPA) alternately uses the acronyms ICP-MS and ICP/MS. Literature searches should include both acronyms.
- 1.6 The analyst using this method should be knowledgeable in the recognition and correction of spectral, chemical and physical interferences in ICP-MS.

2.0 SUMMARY OF METHOD

An exposed ambient air particulate filter is refluxed in a dilute-mixed-acid solution. The resulting solution is cooled to room temperature, brought up to final volume, and subsequently analyzed for elemental content using an ICP-MS.

- 2.1 Teflon filters used for low-volume air sampling appear to have inherent elemental contamination of common analytes of interest. See Appendix A.
- 2.2 Depending on the elements of interest, a viable alternative to the reflux extraction technique might be a milder extraction using weak acid and a heated sonication bath.
- 2.3 For special projects, the analyst should request that sampling air volumes be high enough to accommodate the analysis volumes needed for using the USN.
- 2.4 This method uses the USN serially configured with a desolvator unit. A pneumatic nebulizer is an acceptable alternative.

3.0 DEFINITIONS

3.1 ICP-MS:

An analytical instrument that uses radio-frequency inductively coupled plasma (ICP) configured in series with a mass spectrometer (MS). The ICP aerosolizes a liquid sample into a state of ionization. The MS separates the resulting ions by their mass-to-charge ratios, and subsequently quantifies the number of ions detected using an electron multiplier detector. Mass-to-charge ratio overlaps, interferences, and background ions are assessed and valid correction equations applied when necessary.

3.2 USN / Desolvator:

A two-fold device that: 1) uses transducer-based sonication to convert liquid samples into aerosols prior to being introduced into the plasma for ionization;

and, 2) heats, then cools the nebulized sample to remove much of the primary solvent, which for this method is water. The desolvator lessens the interference effects of compounds created from hydroxides, oxides, and dioxides.

3.3 Concentration units:

Microgram-per-milliliter ($\mu\text{g}/\text{ml}$) equals part-per-million (ppm).

Nanogram-per-milliliter (ng/ml) equals part-per-billion (ppb).

Picogram-per-milliliter (pg/ml) equals part-per-trillion (ppt).

4.0 SAFETY

4.1 A power failure is one of the most common causes of hydrogen gas buildup in the ICP-MS interface. Hydrogen gas flow does not immediately terminate and hydrogen gas may slowly accumulate within the ICP-MS and/or the exhaust duct after a power failure.

4.1.1 Make sure the exhaust duct is always operating and returns to normal function after a power glitch or failure.

4.1.2 Eliminate from the laboratory as many ignition sources as possible, such as open flames, devices that can spark, and sources of static electricity.

4.2 The ICP-MS system can affect the function of a pacemaker and other implanted medical devices.

4.3 Direct viewing of the plasma is hazardous to your eyes because of strong ultraviolet rays. To view the plasma when adjusting, wear ultraviolet protective glasses or view through the plasma view window on the ICP-MS.

4.4 The ICP-MS contains numerous components and assemblies that contain beryllium and beryllium oxide.

4.4.1 Make aware all persons who handle, use, or dispose of these parts and assemblies of the dangers and necessary precautions. Never throw out these parts with general or domestic waste. Disposal must meet state, local and federal disposal guidelines for hazardous waste.

4.5 The analyst must review all instrument and compressed gas safety precautions before beginning operation of the USN, desolvator, and ICP-MS systems.

4.6 Use general good laboratory practices and all safety requirements (no sandals, no eating, no raucous behavior, etc.) set forth by laboratory protocol.

5.0 LABORATORY INTERFERENCES

- 5.1 Clean all equipment used in the sample preparation and analysis in a manner consistent with good laboratory practices for metals analysis.
- 5.2 Avoid contamination of samples by keeping sample preparation areas organized.
- 5.3 Wear clean talc-free gloves when handling unexposed or exposed filters.
- 5.4 For all sample extraction and standard preparation, use de-ionized water (DI) that meets American Society for Testing and Materials (ASTM), Type I.
 - 5.4.1 DI resistivity value must be greater than 17.8-megaohms.
 - 5.4.2 Record the DI resistivity value prior to use.
 - 5.4.3 As a good practice, back rinse the end of the DI delivery tube before filling containment vessels.

6.0 CHEMICAL INTERFERENCES

- 6.1 Pay close attention to the nature of solutions introduced to the ICP-MS.
 - 6.1.1 Keep total acid at less than 2% (volume/volume) to minimize the damage to the interface and to minimize isobaric molecular interferences.
 - 6.1.2 The concentration of dissolved solids in analysis solutions should be less than 2% because of the sample interface on the instrument. Higher concentrations may plug the sample cone orifice.
 - 6.1.3 Precautions must be taken to protect the channel electron multiplier from detector fatigue caused by exposure to high chemical concentrations (high ion currents). This fatigue can last from several seconds to many 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 1% sodium bicarbonate (NaHCO_3) sample matrix is known to cause this problem.
- 6.2 The final dilutions of sample extracts must match the acid content of the calibration standards. Use the reagent blank to make dilutions.

7.0 INSTRUMENT INTERFERENCES

7.1 Four things will help minimize ICP-MS interferences: 1) maintain low oxide and doubly charged ratios, 2) match as near as possible the matrices of the standards and samples, 3) select appropriate internal standards at appropriate concentrations, and 4) avoid interference-prone isotopes.

7.1.1 Include Cerium in the internal standard mixture. Monitor the ratios of $^{156}\text{CeO} / ^{140}\text{Ce}$ and $^{70}\text{Ce}^{+2} / ^{140}\text{Ce}$ during tuning, calibration, and sample analysis. Keep the oxide ratio less than 0.1%, and the doubly charged ratio less than 0.9% at all times.

7.2 Most ICP-MS software now comes embedded with the interference correction equations recommended in U.S. EPA Methods 200.8 and 6020. These equations may over-correct the data.

8.0 APPARATUS AND MATERIALS

8.1 ICP-MS (Section 3.1 and Figure 18.1)

8.2 USN serially configured with a desolvator (Section 3.2 and Figure 18.2)

8.3 Peristaltic pumping system with acid-tolerant tubing

8.4 Boiling flasks, flat-bottom

8.5 Air-cooled reflux condensers (Snyder columns work well; watch glass-covered beakers result in loss of sample volume, a loss which may not be solely water)

8.6 Heating mantles, electric

8.7 Supply of unexposed, unhandled Teflon filters to use as method blanks

8.8 Sample vials, metal-free polypropylene, equipped with screw-top caps

8.9 Micro-pipettes with metal-free disposable tips, 100-microliter (100- μl) to 10-milliliter (10-ml) capacity

8.10 Glass storage: volumetric flasks, class-A; two-liter amber bottle with adjustable dispenser

8.11 Miscellaneous: protective-wear, talc-free gloves, disposable laboratory wipes/towels, self-adhesive labels, waterproof ink pen, timer, laboratory film

9.0 REAGENTS

- 9.1 Nitric acid (HNO₃), concentrated, ultra-grade or high-purity grade
- 9.2 Hydrochloric acid (HCl), concentrated, "spectrometric grade"
- 9.3 DI, ASTM Type I, filtered, resistivity greater than 17.8-megaohms
- 9.4 High purity gases (99.9% pure): argon, helium, and hydrogen
 - 9.4.1 Liquid argon tanks allow for longer runs than gas cylinders
 - 9.4.2 Use hydrogen cylinders. Hydrogen generators deliver inherent water content to the system, which in turn adds to analysis interference
- 9.5 ICP-MS Grade Reference Standards, National Institute of Standards and Technology (NIST) traceable material, in 2% nitric acid; dilute to make necessary analysis solutions
- 9.6 Secondary source of Reference Standards, NIST traceable material, in 2% nitric acid; dilute to make necessary analysis solutions

10.0 ANALYSIS SOLUTIONS

10.1 Calibration Standards

- 10.1.1 Calibration standards must be of NIST-traceable quality. Diluted concentrations of the calibration standards should be within the linear range of the ICP-MS for each element.
- 10.1.2 To avoid precipitation problems and short storage-life, be sure that the elements used in the calibration standard dilutions are compatible. Use a chemical reference to verify compatibility.
- 10.1.3 Monitor calibration standards closely for stability. Verify stability using a quality control standard.

10.2 Quality Control Standard

The quality control standard is the initial calibration verification solution. It must be NIST-traceable and must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range. An independent standard is defined as a standard composed of analytes from a source different from those used in the standards for instrument calibration.

10.3 Detector Response Standard

Use a relatively high concentration solution of all analytes to determine the response overlay of the pulse and analog portions of the electron multiplier. Update the algorithms daily. Include the elements used as Internal Standards (Section 10.4) in this solution.

10.4 Internal Standards

10.4.1 Internal standards should be NIST-traceable and should be no more than 70 atomic mass units (amu) removed from the analyte of interest.

10.4.2 Select concentrations based on interference correction needs. Select a high enough concentration to make normal shifts in the sample matrices inconsequential.

10.4.3 Unnecessarily high internal standard concentrations will contribute to detector fatigue (Section 6.1.3).

10.4.4 Before preparing the mixed internal standard, analyze each stock solution separately to determine possible spectral interferences or the presence of impurities. Mixed internal standards must be prepared as needed with the realization that concentrations can change on aging.

10.4.5 Internal standards may be added in-line at the time of analysis using a channel of the peristaltic pump and an appropriate mixing manifold, or added manually to the calibration standards and samples.

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

10.5 Tuning Solution

The tuning solution should contain 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.

10.6 Optimization Solution

Use the Calibration Standards (Section 10.1) and Tuning Solution (Section 10.5) when performing the optimization procedures for the USN and ICP-MS.

10.7 Interference Check Solution (ICS)

The ICS is intended to evaluate corrections for known interferences on analytes. Prepare an ICS with known concentrations of interfering elements to demonstrate the magnitude of the interferences and provide an adequate test of any corrections.

11.0 SAMPLE PREPARATION

- 11.1 In this document, the term “sample” includes duplicates, spikes, and blanks.
- 11.2 Sample preparation is a manual task, without the benefits of computer tagging. Use diligence to ensure that each sample is uniquely identified at the onset, and that the sample identification is properly carried throughout the analysis process.
- 11.3 Prepare sample labels using a waterproof pen. On each label, write at a minimum the sample identification number and the date of the extraction.
- 11.4 Method blanks using unexposed filters kept in the laboratory should be labeled to distinguish them from other types of blanks, e.g. Trip Blanks, brought in from the field.
- 11.5 Never begin a reflux without noting the sample identity in the REFLUX LOG. Also, note any unusual sample conditions.
- 11.6 Never place a sample into an undesignated boiling flask.
- 11.7 Never pour a refluxed solution into an unlabelled vial.

12.0 FILTER SAMPLE EXTRACTION VIA REFLUX

- 12.1 Prepare the mixed-acid reflux solution of 3.2% nitric acid (32-ml per 1-L) and 1.2% (12-ml per 1-L) hydrochloric acid.
 - 12.1.1 Wash and condition-rinse a two-liter amber glass bottle fitted with an adjustable dispensing unit. Fill this bottle with the mixed-acid reflux solution.
 - 12.1.2 Adjust the dispenser unit to deliver a 15-ml aliquot of the mixed acid; if spikes (Section 14.10) fail, verify the dispensed volume by weight (consider the dilute acid solution to be the same density as DI).
 - 12.1.3 Depending on the analytes of interest, adjust the reflux volumes (and the subsequent diluent volumes) so that the final acid concentration for

each sample is consistent with the calibration standards. For example, if the reflux volume is reduced from 15-ml to 10-ml, then the diluent volume should also be reduced, in this case from 30-ml to 20-ml.

- 12.2 For each sample, enter the sample identity directly to the REFLUX LOG and an identical sample identity to the final storage vial. Any additional information or comments about the condition of the filter prior to reflux should be noted on the REFLUX LOG.
- 12.3 Repeat the following steps (12.3.1 – 12.3.13) for each sample listed on the REFLUX LOG:
 - 12.3.1 Place each Teflon filter into a clean, acid-rinsed, dry boiling flask, making sure that the filter lays exposed-side down.
 - 12.3.2 Dispense an aliquot of the mixed-acid reagent (Section 12.1.2) into the boiling flask containing the filter sample. Swirl gently, keeping the exposed side face-down in the acid solution.
 - 12.3.3 Attach a Snyder column.
 - 12.3.3.1 Using a beaker and watch glass assembly, heated on a hot plate, can work as a reflux vessel, but is cumbersome and results in a volume loss, which may not be solely water.
 - 12.3.4 Place the boiling flask and Snyder column as a single unit onto heating mantle. Adjust temperature to achieve a slow-rolling condensation on the sides the flask. Reflux begins when individual condensation droplets begin to connect. Write the REFLUX START TIME on the REFLUX LOG.
 - 12.3.5 Every 30 minutes, gently swirl the sample solution, and verify that the filter remains facedown in the solution. The rolling of the condensation should be very slow and continuous, and overall indicative of a very gentle reflux. DO NOT OVERHEAT.
 - 12.3.5.1 The condensation should never extend beyond the top of the lowest segment on the condenser. (See Figure 12.3.5.1)

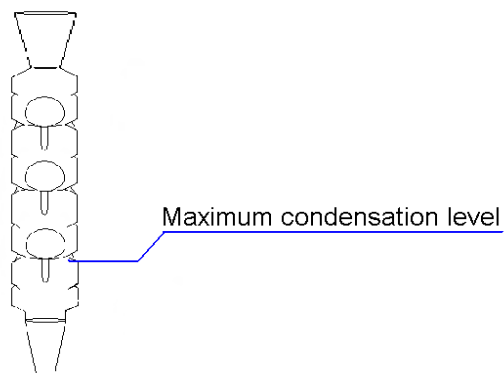


Figure 12.3.5.1 Maximum condensation level using a Snyder column.

- 12.3.6 If the reflux is done correctly, there should be no notable loss of sample volume.
- 12.3.6.1 To verify this, reflux reagent spikes to test the heat setting on each mantel to determine the temperature setting that allows reflux to occur without notable volume loss. The recovery of this heated spike should be within +/-20% of the expected value.
- 12.3.6.2 Do not use an unexposed filter in the test spikes used to test the heat settings. The unexposed filters have variable contamination that may make the reflux seem invalid.
- 12.3.7 Following two hours of a gentle reflux, turn off the heating mantle. Record the REFLUX STOP TIME onto the REFLUX LOG.
- 12.3.8 After five minutes of cooling, carefully remove, as a single unit, the boiling flask and condenser from the heating mantle. Place in the hood directly in front of the mantle.
- 12.3.9 Place a lightly adhered piece of laboratory film over the top of the Snyder column. Write the mantel number on the film. When the unit reaches room temperature (in about 20 minutes), adhere the laboratory film firmly to the top of the condenser.
- 12.3.10 Let the unit stand at room temperature overnight.

- 12.3.11 For each sample, pre-dispense a 30-ml aliquot of DI to use as a rinse for the lower segment of the condenser and the boiling flask.
- 12.3.11.1 This pre-allotted rinse amount is also the diluent for the final sample volume. The rinse amount should be taken from (and then added back to) the final volume for a specific sample.
 - 12.3.11.2 Deliver the pre-allotted rinse amount to the final container before you start rinsing.
 - 12.3.11.3 It is a good idea to pre-mark the meniscus for every lot number of graduated vials as a secondary check of this procedure.
- 12.3.12 For each sample, use a separate pipette tip to rinse the lower segment of the condenser, the sample filter, and the emptied boiling flask.
- 12.3.12.1 Add small rinse amounts to the lower condenser segment to flush the reflux condensation into the boiling flask. A steady, gentle rotation of the rinse solution inside the lower condenser segment will collect the condensation.
 - 12.3.12.2 Rest the slightly tilted condenser so that the rinse clean-out falls freely from the lower condenser segment into the boiling flask. Rinse the contents of the boiling flask into the final container.
 - 12.3.12.3 Do not increase (or decrease) the rinse amount allotted to each individual sample.
 - 12.3.12.4 Rinse the filter, but do not add filter to the final sample container.
- 12.3.13 Once the sample is brought to the final volume of 45-ml, it is ready for analysis by ICP-MS. Add the Internal Standards (Section 10.4) to each sample manually or in-line before the sample reaches the USN.

13.0 ANALYSIS

The setup, tuning, and optimization procedures for the USN, desolvator, and ICP-MS are too extensive to detail in this document. Follow the manufacturers' instructions for all operational procedures needed to generate valid results. ^[1, 2]

14.0 PERFORMANCE CRITERIA / QUALITY CONTROL (QC)

All QC data should be maintained in an organized manner and be available for easy reference or inspection.

14.1 Limit of Detection (LOD)

LOD is a calculated value that represents the minimum reportable concentration of an analyte with 99% confidence. Calculate the LOD for each isotope according to the MLD061 reference method, EPA600/R-94-111 Method 200.8, as follows:

$$\text{LOD} = (t)_{(n-1=0.99)} \times \text{SD} = 3.14 \times \text{SD}$$

where, SD = standard deviation of n repetitions of the lowest standard expressed in instrument units of nanogram per milliliter (ng/ml), and the $(t)_{(n-1=0.99)}$ is the Student's t value for a 99% confidence level and a SD estimate with a degree of freedom equal to n-1. For seven replicates, the t value equals 3.14.

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

- 14.1.1 For the method LOD, use the exact internal standards and the exact instrument settings (sweeps and dwell) used to analyze the ambient samples.
- 14.1.2 Never report sample data at a concentration that is lower than the known inherent background of the sampling media.
- 14.1.3 Adjust the LOD(s) to reflect the uncertainty caused by the known background level(s) of the sample collection media. Do not subtract inconsistent background levels from the reported data.
- 14.1.4 To determine the inherent background of a sample media, analyze seven filter blanks. Apply the SD into the LOD equation (Section 14.1) as an indication of the expected inherent contamination. Set the LOD(s) accordingly, i.e., above the contamination level(s).
- 14.1.5 Repeat the LOD determination a minimum of five times, each time on a different day. Use this added information, specifically the fluctuation of results, to assist in setting the final LOD value reported for each analyte.
- 14.1.6 For sample types analyzed on a limited or one-time basis, it may not be possible to establish a method LOD over several days. At a minimum, run seven replicates of the lowest standard, and use the cumulative standard deviations of the actual samples analyzed as guides to setting an LOD for the special study method.

- 14.1.7 Based on the analytical tendencies of actual ambient samples, the published method LOD, set in aerometric units of nanogram-per-cubic-meter (ng/m^3), must be set after the analyst evaluates the calculated values in nanogram-per-milliliter (ng/ml).
- 14.1.8 Judgment as to the conversion of the calculated LOD (ng/ml) into the published LOD (ng/m^3) may be necessary, especially if the air volumes are vastly different within a sample set or project.
- 14.2 Verifying the Method LOD
- 14.2.1 Verify the published method LOD(s) no less than once per year.
- 14.2.2 Verification of the method LOD should yield a value less than the reported LOD value.
- 14.2.3 If the verified value is higher than the reported value, investigate the cause. It may be necessary to evaluate sample data obtained after the last valid LOD verification.
- 14.3 Control Standard (NIST-traceable, refer to Section 10.2)
- The control standard is prepared using a stock source secondary to the stock source used to prepare the calibration standards.
- 14.3.1 Without a history of ICP-MS analysis, the control limits for a quantitative method have been initially set at $\pm 10\%$ of the target value for each analyte.
- 14.3.2 Document each control value as a percent ratio of the actual value over the target value.
- 14.4 Standard Checks (NIST-traceable)
- At pre-set intervals during a batch analysis, verify the calibration using a mid-range standard or the control standard. All reportable results must be analyzed or reprocessed with a valid calibration.
- 14.4.1 Results must be within $\pm 10\%$ of the target value for each analyte to verify that the calibration in use is valid.
- 14.4.2 If a standard check exceeds the limit, the analysis must be stopped and the instrument must be recalibrated or have the existing calibration re-sloped by re-analysis of one or more of the standards.

14.4.3 Document each standard check value as a percent ratio of the actual value over the target value.

14.4.4 Reprocessed data must include reprocessing of all QC samples associated with the reprocessed sample results.

14.5 Duplicates

If enough sample solution is available, analyze every tenth sample in duplicate as a record of the method precision.

Calculate the relative percent difference (RPD) between duplicate determinations as follows:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2/2)} \times 100$$

where D_1 and D_2 equal the concentrations determined for the first and second aliquots, respectively.

14.5.1 For analyte values greater than the limit of Quantitation (LOQ), defined as five times the LOD, the RPD should be less than 30%. If exceeded, investigate the reason and correct the cause when possible. If deemed correctable, then re-analyze any samples analyzed during the out-of-limit conditions.

14.6 Internal Standards

Monitor the intensities of all internal standards for every analysis.

14.6.1 When the intensity of any internal standard fails to register between 60 to 200% of the initial calibration standard, then complete the procedures in 14.6.2 and 14.6.3.

14.6.2 Dilute the sample five-fold and re-analyze with the addition of appropriate amounts of internal standards. Repeat dilution until the internal standard intensities fall within the prescribed window.

14.6.3 Verify that the intensity levels of the internal standards for the calibration blank and interference check standard agree within +/- 20 percent 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, recalibrate, verify the new calibration, and reanalyze the affected samples.

14.7 Interferences

- 14.7.1 When correction equations are used, all QC criteria must also be met.
- 14.7.2 Monitor a molecular species, such as ^{156}CeO , to indicate the overall presence of specific types of interference, which, in this case, are oxides.
- 14.7.3 For every analysis, monitor species that will demonstrate directly or indirectly that the results remain unaffected by molecular ions of hydrogen, oxygen, chlorine, nitrogen, carbon and sulfur.
- 14.7.4 Add single-element assayed analytes to test sample aliquots to observe any impact on the analyte signals.
- 14.7.5 Use only the observed responses for each sample in generating the corrections. For example, if the mathematical correction requires the subtraction of an abundance ratio of Cd isotopes, those specific Cd isotopes must be determined individually for each sample.

14.8 Dilution Test

A dilution of 1-ml sample to 4-ml reagent blank should agree within +/-10% of the undiluted concentration, provided the analyte concentration falls within the linear range of the instrument and is at least 20 times above the LOD. Non-agreement suggests an interference effect. If possible, when analyzing the dilution, include another isotope of the same element and/or use likely corrections. Before comparing results, reprocess the undiluted result (including the calibration and all QC) with any correction(s) inserted for the dilution test.

14.9 Blanks

There are three types of blanks required for the analysis: the calibration blank, the extraction (method) blank, the rinse blank.

14.9.1 Calibration Blank

The calibration blank is used in establishing the calibration curve before analysis of samples. It should be a solution of 1.1% nitric acid and 0.4% hydrochloric acid, and include the exact internal standard(s) (Section 10.4) that will be a part of the standard calibration and sample analysis. If additional components (such as trace hydrofluoric acid) are needed for stability of some analytes, then the additional components must be included in the calibration blank, standards, and samples.

14.9.2 Extraction (Method) Blank

The extraction blank, which is carried through the complete sample preparation and analysis process (Sections 12 and 13), contains an unexposed Teflon filter and the same volumes of reagents as the sample solutions. Results for the extraction (method) blanks must be less than two times the LOD for each analyte reported. If these blanks should ever exceed two times the LOD, investigate the sample preparation, specifically the cleanliness of the glassware, pipettes and every other incidental apparatus needed for this method. Be aware that the elemental contamination on the unexposed filters varies.

14.9.3 Rinse Blank

The rinse blank is used to flush the system between all samples and standards. The rinse blank should consist of no more than 2% nitric acid for the rinse cycle between samples. Increase to no more than 5% acid for short-term cleaning purposes.

14.10 Spikes (Post-Digestion)

Post-digestion spikes should be prepared from ambient samples using NIST-traceable standards, and should be prepared at concentrations within the linear range for every element of interest.

Add post-digestion spikes to an aliquot of a prepared sample or its dilution. Spikes are fundamental in assuring the reliability of the method parameters and, subsequently, the data generated. The spike recovery should be within 80 to 120% of the expected value, based on the original concentration of each element of interest in the unspiked sample.

Calculate the percent recovery (%R) as follows:

$$\% R = \frac{(Actual)}{(Expected)} \times 100$$

where the *Actual* value equals the determined concentration (ng/ml) of the spiked aliquot, and the *Expected* value equals the expected concentration (ng/ml) of the spiked aliquot.

14.10.1 Every batch of 40 or less samples must include a high and low post-digestion spike.

14.10.1.1 A high spike should be at a concentration greater than 10 times the LOD for each reported analyte.

- 14.10.1.2 A low spike should be at a concentration greater than twice the Limit of Quantitation (LOQ). The LOQ is five times the LOD.
- 14.10.1.3 For method development, run test spikes of varying concentrations, from low to high, using the ambient sample matrix.
- 14.10.2 For special project method testing, or where there is limited ambient sample available, sacrifice an ambient sample for testing and subsequent spiking (method confirmation) to provide a record of the reliability of the analysis method.
- 14.10.3 If the spike recovery exceeds the specified limits, consider that the spiked sample may become out of the linear range after spiking. If the spike is out and the concentration remains in the linear range, this may indicate an under or over correction of an interference.

15.0 INSTRUMENTATION MAINTENANCE

The ICP-MS analyst is responsible for inspecting the functionality of all instrumentation required for this method. Consult the instrument manual to determine the inspection and maintenance requirements. ^[1, 2]

16.0 ICP-MS CHEMICAL STORAGE AND HAZARDOUS WASTE

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

16.1 Ordering and Storage of Chemicals

16.1.1 ICP-MS requires dozens of chemicals, which invites safety and storage problems. Purchase small volumes whenever possible to minimize storage and disposal costs of unused portions. Order only chemical amounts needed within the following year.

16.2 Disposal of Chemicals, General Solutions

16.2.1 Notify the Division's Hazardous Waste Coordinator of the ICP-MS disposal needs annually.

16.2.2 For disposal of the ICP-MS chemicals, the Hazardous Waste Coordinator should have the waste removal vendor do an inventoried lab-pack in favor of a drum.

16.2.2.1 Drums of mixed chemicals are more difficult to profile and create more problems to dispose of than do lab-packs.

16.3 Disposal of Chemicals, Dilute Solutions

16.3.1 The autosampler rinse solution, which is less than 1% acidified DI water, can be disposed of in the laboratory sink when followed by a minute of flushing with tap water.

16.3.2 Standard dilutions in the parts-per-billion range or less, which is the typical operating range of the ICP-MS, can be disposed of in the laboratory sink, followed by a minute of flushing with tap water.

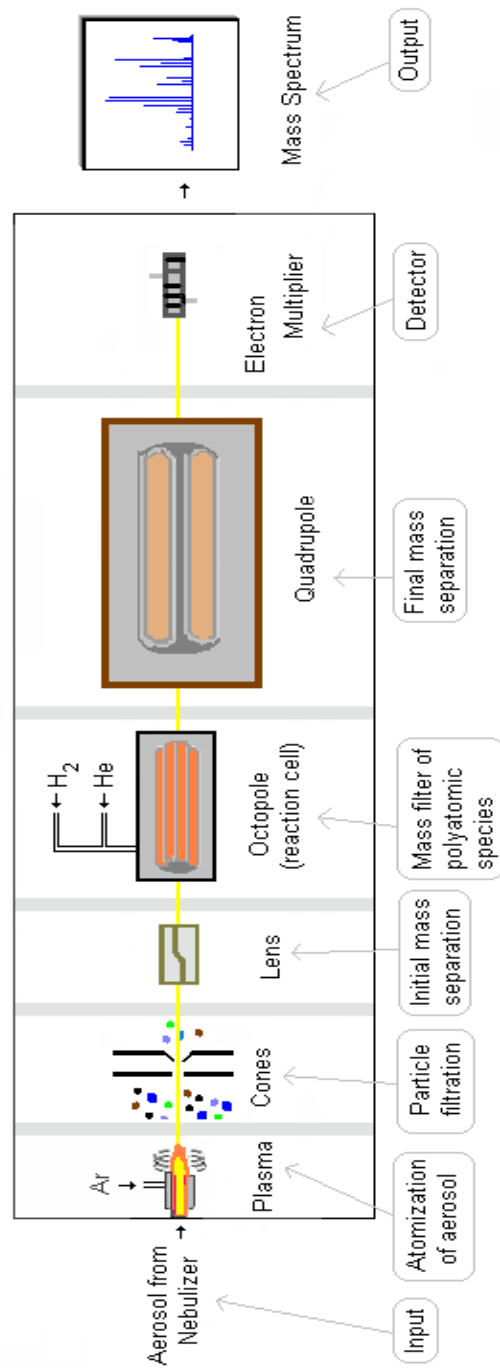
16.3.2.1 The exception is mercury (Hg) dilutions, which must be collected by the analyst, and disposed of by the waste vendor.

17.0 REVISION HISTORY OF METHOD 061

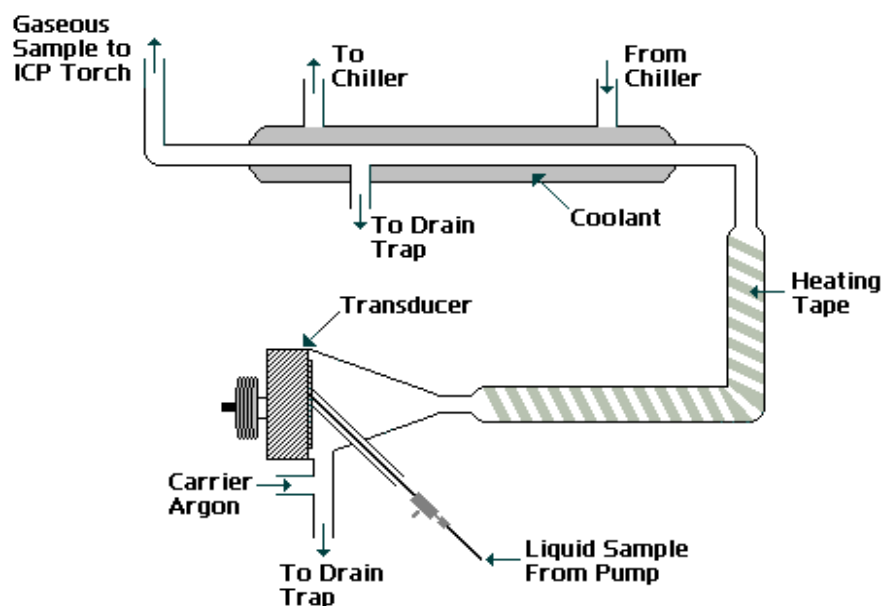
REVISION	EFFECTIVE DATE	PRIMARY CHANGE(S) FROM PREVIOUS REVISION
MLD061, Draft	08/01/2000	Startup of NLB trace metal analysis of low-volume ambient filter samples using ICP-MS; developed from U.S. EPA Methods 200.8 and 6020 (9/94) ^[3,4]
MLD061, Revision 0.0	01/01/2002	Extraction procedure changed to eliminate use of ethanol, a contributor to numerous carbon-bonded interferences. Changed optimization and tuning procedures, and changed solutions to accommodate instrument malfunctions and failures.
MLD061, Revision 1.0	01/01/2007	Extraction procedure changed to reflux technique; extraction solvent changed to include hydrochloric acid; malfunctioning Perkin Elmer 6100 instrument replaced with Agilent 7500ce.

18.0 INSTRUMENT SCHEMATICS

18.1 Inductively Coupled Plasma - Mass Spectrometer



18.2 Ultrasonic Nebulizer / Desolvator



19.0 REFERENCES

1. Agilent 7500 ICP-MS ChemStation (G1834B) Operator's Manual, Part Number G3270-90112, Yokogawa Analytical Systems, Tokyo, Japan.
2. Agilent 7500 Series ICP-MS Maintenance Video (DVD), English/Japanese Version, September 2005 Rev. A, Part Number G3270-65100, Agilent Technologies, Tokyo, Japan.
3. U.S. EPA 600/R-94-111 Method 200.8, Trace Elements in Water and Wastes – ICP/MS, May 1994.
4. U.S. EPA SW-846 Ch 3.3 Method 6020, Metals by Inductively Coupled Plasma/Mass Spectrometry, August 1994.

MLD061, Revision 1: APPENDIX A ELEMENTAL CONTAMINATION OF TEFLON FILTERS

Gelman Sciences' 37-mm "Teflo" Teflon filters, used by ARB for Total Metals low-volume air sampling, appear to have inconsistent elemental contamination. This contamination could contribute to inaccuracy in reported air sample concentrations. Limits of Detection (LOD) for this method have been set based on the observed contamination levels of the unexposed filters.

Predominate contaminants on the unexposed filters include, but may not be limited to, Magnesium, Aluminum, Silicon, Phosphorus, and Potassium. Minor contaminants include, but may not be limited to, Sulfur, Scandium*, Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc, Gallium*, Germanium*, Yttrium*, Zirconium, Tin, Antimony, and Lead. Elements denoted with an asterisk (*) are typical internal standards (Section 10.4) for this method. Contamination levels of these elements do not necessarily disqualify their use as internal standards.

Elemental Content of Unexposed 37-Millimeter Teflon Filters Currently Used

Seven unexposed Teflon filters, randomly selected from factory-sealed packages, were refluxed using the procedures of this method. See "Extract-1" results in Table 1.

These same seven filters were then quadruple-rinsed by DI, quadruple-rinsed by a 2% mixture of nitric and hydrochloric acids, and re-quadruple-rinsed by DI. After drying overnight, delimited top and bottom by multiple layers of ISO Cleanroom Class 7 wipers, these filters underwent reflux and analysis a second time. See "Extract-2" results in Table 1.

Spike Recoveries Using "Previously-Refluxed" Filters

After repeating the rinsing and drying process of the filters analyzed for the Table 1 results, the seven "previously-refluxed" (cleaned) filters were spiked using a third source of NIST-traceable material, meaning a source different than that used for the calibration standards or control, and refluxed using the procedures outlined in this method. Spike recovery results ranged between 91 to 120% for all analytes of interest.

Elemental Contamination Check of MLD061, Revision 1

To verify the elemental cleanliness of the glassware, sample vials, pipettes, ultra-grade reagents, gloves, laboratory towels, and every other incidental equipment or apparatus used for this method, excluding the Teflon filters, seven "no-filter" spiked solutions were prepared, using the third source NIST-traceable material, and refluxed using the procedures outlined in this method. Spike recovery results ranged between 93 to 111% for all analytes of interest.

CONCLUSIONS

Running the filters through two reflux extractions appears to have minimally “cleaned” some of the elemental contamination, based on the spike results. However, since the level of contamination could not be uniformly “cleaned” off the filters, in as much as the collected air particulates appear to be removable by reflux extraction, the inconsistent Teflon filter contamination appears to be an imbedded artifact that is non-uniformly extractable, suggesting it may originate from the filter manufacturing process.

Detection limits for this method have been set based on the observed contamination levels of the unexposed filters analyzed directly from the manufacturer’s packaging (Extract-1 values in Table 1). The two exceptions are for Vanadium and Sulfur, which each showed extremely high results on Filter 5, relative to the other six 37-mm blanks. On a previously conducted test of unexposed 47-mm filters, the average contamination found for Vanadium and Sulfur was 3.32 ppb and 0.15 ppb, respectively. The Filter 5 results seem to be an irregularity on just one filter. Consequently, the Filter 5 results for these two elements were not included in setting the method detection limits.

TABLE 1: Elemental Content of Unexposed 37-millimeter Teflon Filters Currently Used

	Filter 1 ppb		Filter 2 ppb		Filter 3 ppb		Filter 4 ppb		Filter 5 ppb		Filter 6 ppb		Filter 7 ppb		Mean ppb		SD ppb		Minimum LOD Allowed based on 3.14 x SD ppb	Method LOD ppb
	Extract1	Extract 2	Extract1	Extract 2	Extract1	Extract 2	Extract1	Extract 2	Extract1	Extract 2	Extract1	Extract 2	Extract1	Extract 2	Extract1	Extract 2	Extract1	Extract 2		
S	4.36	5.00	3.11	3.28	3.17	5.55	3.94	3.67	48.29	2.84	4.19	2.42	4.93	3.18	10.28	3.71	16.77	1.15	52.7 *	20 *
Ti	0.15	0.12	0.14	0.10	0.07	0.14	0.12	0.13	2.18	0.08	0.20	0.16	0.13	0.10	0.43	0.12	0.77	0.03	2.43	3
V	0.02	0.03	0.00	0.00	0.00	0.00	0.09	0.00	5.79	0.00	0.00	0.00	0.04	0.01	0.85	0.01	2.18	0.01	6.84 *	0.5 *
Cr	1.28	0.08	1.12	0.19	0.92	0.06	1.71	0.06	1.01	0.23	1.12	0.10	1.29	0.07	1.21	0.11	0.26	0.07	0.81	1
Mn	0.08	0.05	0.06	0.04	0.04	0.05	0.13	0.03	0.02	0.03	0.08	0.04	0.09	0.09	0.07	0.05	0.04	0.02	0.11	0.5
Fe	5.26	1.67	6.78	1.50	2.14	0.02	2.45	1.16	1.55	1.35	5.18	1.46	5.43	15.29	4.11	3.21	2.02	5.36	6.3	10
Ni	0.73	0.19	0.11	0.21	0.07	0.00	0.16	0.05	0.06	0.12	2.13	0.07	0.72	0.21	0.57	0.12	0.75	0.08	2.35	3
Co	0.03	0.02	0.00	0.00	0.01	0.00	0.19	0.00	0.00	0.00	0.01	0.00	0.03	0.00	0.04	0.00	0.07	0.01	0.21	0.5
Cu	0.43	0.15	0.19	0.27	0.18	0.00	0.50	0.10	0.23	0.15	0.37	0.18	0.40	0.24	0.33	0.16	0.13	0.09	0.40	0.5
Zn	1.65	1.49	1.26	1.02	1.02	1.77	1.09	1.33	0.68	0.95	1.36	0.83	1.06	0.91	1.16	1.19	0.30	0.35	0.95	1
As	0.02	0.03	0.00	0.00	0.00	0.00	0.08	0.03	0.00	0.00	0.00	0.00	0.01	0.00	0.02	0.01	0.03	0.01	0.09	0.5
Se	0.02	-0.05	-0.06	-0.06	-0.05	-0.02	0.07	-0.08	-0.06	-0.07	-0.03	-0.08	0.05	-0.09	-0.01	-0.06	0.05	0.02	0.17	0.5
Sr	0.09	0.09	0.05	0.09	0.05	0.23	0.13	0.07	0.04	0.06	0.08	0.06	0.08	0.08	0.07	0.10	0.03	0.06	0.10	0.5
Zr	0.10	0.07	0.12	0.06	0.06	0.09	0.24	0.20	0.15	0.15	0.19	0.14	0.15	0.12	0.14	0.12	0.06	0.05	0.19	0.5
Mo	0.03	0.05	0.08	0.04	0.05	0.16	0.35	0.08	0.00	0.01	0.04	0.01	0.05	0.01	0.09	0.05	0.12	0.05	0.37	0.5
Rh	0.02	0.01	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.02	0.00	0.05	0.5
Pd	0.08	0.00	0.00	0.00	-0.01	0.00	0.07	-0.02	-0.01	-0.02	0.01	-0.02	0.07	-0.03	0.03	-0.01	0.04	0.01	0.13	0.5
Cd	0.03	-0.01	0.02	0.03	0.01	0.00	0.01	0.00	0.00	-0.01	0.01	0.00	0.02	0.00	0.01	0.00	0.01	0.01	0.03	0.5
Sn	0.11	0.05	0.03	0.02	0.01	0.04	0.02	0.04	0.01	0.03	0.08	0.14	0.17	0.12	0.06	0.06	0.06	0.05	0.19	0.5
Sb	0.15	0.04	0.44	0.07	0.00	0.16	0.01	0.22	0.07	0.09	0.69	0.58	0.13	0.43	0.21	0.23	0.26	0.20	0.81	1
Pt	0.06	0.03	0.03	0.05	0.03	0.08	0.04	0.02	0.02	0.02	0.07	0.02	0.09	0.06	0.05	0.04	0.03	0.02	0.08	0.5
Pb	0.14	0.09	0.09	0.04	0.04	0.04	0.32	0.07	0.03	0.04	0.13	0.04	0.17	0.07	0.13	0.06	0.10	0.02	0.31	0.5

Extract1: Unexposed Teflon filter, randomly selected from factory-sealed package, analyzed using the procedures of this method

Extract2: Same filter used for Extract1, refluxed and analyzed a second time using the procedures of this method

Minimum allowable Limits of Detection (LOD) for method based on mean results of Extracts 1&2 inserted into the LOD equation given in Section 14.1 of MLD061, Revision 1.

* The V and S results for Filter 5 were discounted in setting the Method LOD. The exceptionally high V and S results for Filter 5 seem to be an irregularity on just one filter.

Standard deviation (SD) calculated per EXCEL.



Air Resources Board




Matthew Rodriguez
Secretary for
Environmental Protection

Mary D. Nichols, Chairman
1001 I Street • P.O. Box 2815
Sacramento, California 95812 • www.arb.ca.gov

Edmund G. Brown Jr.
Governor

TO: Brenda Saldana, Manager
Inorganics Laboratory Section

FROM: Patrick Rainey, Manager 
Quality Management Section

DATE: August 7, 2015

SUBJECT: STANDARD OPERATING PROCEDURE FOR THE TRACE
METAL ANALYSIS OF AMBIENT AIR PARTICULATE
SAMPLES USING INDUCTIVELY COUPLED PLASMA –
MASS SPECTROMETRY

Thank you for your submission of the addendum (see attached) to the Standard Operating Procedure (SOP) for Trace Metal Analysis of Ambient Air Particulate Samples Using Inductively Coupled Plasma – Mass Spectrometry. The Quality Management Section has reviewed the addendum along with the SOP and determined that it covers all of the required elements. The addendum is approved.

Please direct comments or questions to Darsi Goto at (916) 324-9656 or by email at darsi.goto@arb.ca.gov.

Attachment

cc: Mike Miguel, Chief
Quality Management Branch

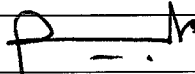
Darsi Goto
Quality Management Section

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our website: <http://www.arb.ca.gov>.

California Environmental Protection Agency

QUALITY MANAGEMENT DOCUMENT ADDENDUM

Section 1. ARB Document	
<input type="checkbox"/> Quality Management Plan (QMP)	
<input type="checkbox"/> Quality Assurance Project Plan (QAPP)	
<input checked="" type="checkbox"/> Standard Operating Procedure (SOP)	

Section 2. Information		
Submitter Name:	Prasanna Jayalath	BA 8-7-15
Submitter Signature/Date:		August 6, 2015

Section 3. Document Title <small>(specify exact title, revision #, and date of ARB Document(s) that your District proposes to modify)</small>	Date
SOP MLD 061 Revision Number 1.0	January 1, 2007

Section 4. Revision(s)
(specify exact section(s), page number(s) and language in existing ARB document that will be modified and then specify modification (including any spreadsheets or forms).)

Summary

The toxic metal program in ILS has been upgraded recently with state of the art instrumentation. The addendum to MLD SOP 061 Revision Number 1.0 includes changes made to sample extraction method, sample introduction and the modes of analysis.

The ultrasonic nebulizer (USN)/Desolvator (section 3.2) has been replaced by Perkin Elmer cyclonic spray chamber for the sample introduction. Therefore, references to the "ultrasonic nebulizer (USN)/Desolvator" in MLD SOP 061 Revision Number 1.0 have been eliminated in this addendum.

In order to minimize the unavoidable Isobaric molecular interferences, Kinetic Energy Discrimination (KED) mode is now used in addition to the standard mode for toxic metal analysis.

Section 1.0 (page 5)

ARB modification to Section 1.0 (page 5), **Delete Section 1.0** and replace with "This document describes a methodology used by Monitoring and Laboratory Division (MDL) Inorganics Laboratory Section (ILS) staff to analyze trace metals in ambient air particulate samples by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)."

Section 2.0 (page 6)

ARB modification to Section- **Delete Section 2.0** and replace with "An exposed ambient air particulate filter is refluxed in a dilute-mixed-acid solution. This extract is diluted and introduced into the ICP through a nebulizer and spray chamber by flowing argon stream. By coupling radio-frequency power into flowing argon, plasma is created. As the sample passes through the plasma, the thermal energy decomposes and atomizes the sample and then ionizes the atoms. These ions are introduced into a collision/reaction cell (CRC) that uses KED technology to reduce isobaric polyatomic interferences before the ions are introduced into a quadrupole mass spectrometer. The ions are sorted according to their mass-to-charge ratio and measured with a detector."

Section 2.4 (page 6)

ARB modification to Section- **Delete section 2.4**

Section 3.2 (page 6)

ARB modification to Section- **Delete section 3.2** and replace with

3.2 Autoblock III Workstation

The Autoblock III workstation is a state of the art semi-automatic sample digestion system. It digests up to 54 samples simultaneously, adding up to six different reagents while controlling sample temperatures in a self-contained-HEPA filtered environment. The Autoblock III uses low cost disposable digestion vessels that speed and simplify the digestion procedures and eliminates the use of glassware and time consuming intensive glassware cleaning.

Section 4.5 (page 7), states that "The analyst must review all instrument and compressed gas safety precautions before beginning operation of the USN, desolvator, and ICP-MS systems."

ARB modification to Section- **Delete Section 4.5** and replace with

4.5 "The analyst must review all instrument and compressed gas safety precautions before beginning operation of the Autoblock III workstation and the NexION 300X ICP-MS systems."

4.5.1 The Nexlon 300X ICP-MS is fully interlocked to protect the user from hazards such as high voltage, radio frequency generators and intense ultra-violet light, but formal training is required to operate this instrument.

4.5.2 No special training is required to operate Autoblock III workstation. Follow the operation manual of the instrument carefully.

Section 8.2 (page 9)

ARB modification to Section- Delete section 8.2 and replace with

8.2 Autoblock III workstation (Section 3.2)

Section 8.3 (page 9)

ARB modification to Section- Delete section 8.3

Section 8.4 (page 9)

ARB modification to Section- Delete section 8.4

Section 8.5 (page 9)

ARB modification to Section- Delete section 8.5

Section 8.6 (page 9)

ARB modification to Section- Delete "Heating mantles, electric" and replace with "Extraction vessels (50 mL)"

Section 8.10 (page 9)

ARB modification to Section- Delete section 8.10

Section 11.6 (page 12), states that "Never place a sample into an undesignated boiling flask"

ARB modification to Section- Delete "boiling flask" and replace with "Extraction vessel (50 mL)."

Section 12.0 (page 12) manual sample extraction procedure has been discontinued and Autoblock III semi-automatic workstation is in place.

ARB modification to Section- Delete section 12.0 and replace with

12.0 Automated Sample Extraction

This section describes the sample preparation steps when performing automated extraction using the Autoblock III workstation.

12.1 Prepare the mixed-acid extraction solution of 3.3% nitric acid (v/v; 33 mL per 1-L) and 1.2% (v/v; 12 mL per 1-L) hydrochloric acid.

12.2 Turn on the Autoblock and load "MLD 061" reflux method file (let heat block to warm for 30 minutes prior to beginning the actual reflux).

12.2.1 Fill the solvent bottles as necessary. Port 1: DI water; port 2: mixed acid extraction solution; ports 3-5: DI water.

12.2.2 Prime the pump, lines will automatically prep and purge. Verify that all delivery lines are free of air bubbles before initiating the RUN mode.

12.3 Place each Teflon filter into a sample vessel (50 mL PTFE tube), make sure that the filter is sitting on the bottom of the vessel.

12.4 Arrange samples according to the REFLUX LOG and load racks onto the lift arms in the down position.

12.5 Press the RUN METHODS button to begin (instrument will add 30 mL of mix acid extraction solution to each vessel and start reflux for 2 hours).

12.5.1 Place a thermometer and sample probe into a DI water vessel to monitor sample temperature (sample probe temperature is 15-20°C less than the graphite block temperature).

Table 1. Teflon filter reflux program "MLD 061" for Autoblock III workstation.

Step	Description	Time (minutes)
Heat	Graphite block warm up 95° C	30
Inject	Inject 30 mL to selected columns	
Pause	Ensure volume level is correct and then gently cover the sample vial with a reflux cap	
Wait	Reflux (2h) at 95° C	120
Cool	Cool for 30 mins	30

- 12.5.2 PAUSE: Ensure volume level is correct then gently cover the sample vial with a reflux cap.
- 12.5.3 WAIT: Reflux sample in gently closed vessel at 95°C for 2 hours.
- 12.5.4 COOL: The racks will be raised out of the graphite block and cool for 30 minutes.
- 12.5.5 After 30 minutes of cooling, carefully remove the racks and keep them in the hood at room temperature overnight.
- 12.5.6 Carefully remove the sample filter with acid cleaned plastic tweezers (PTFE) and rinse with minimum amount of DI water (~ 0.5 mL). Collect rinse into the corresponding vessel and discard the filter.

12.6 Withdraw 3.33 mL of a sample and dilute to 10.0 mL with DI water.

Section 13 (page 15), states that “The setup, tuning, and optimization procedures for the USN, desolvator, and ICP-MS are too extensive to detail in this document. Follow the manufacturers’ instructions¹ for all operational procedures needed to generate valid results.”

ARB modification to Section- Delete section 13 and replace with “The setup, tuning, and optimization procedures for ICP-MS are too extensive to detail in this document. Follow the manufacturers’ instructions¹ for all operational procedures needed to generate valid results.”

Section 18.2 (page 24)

ARB modification to Section- Delete Section 18.2

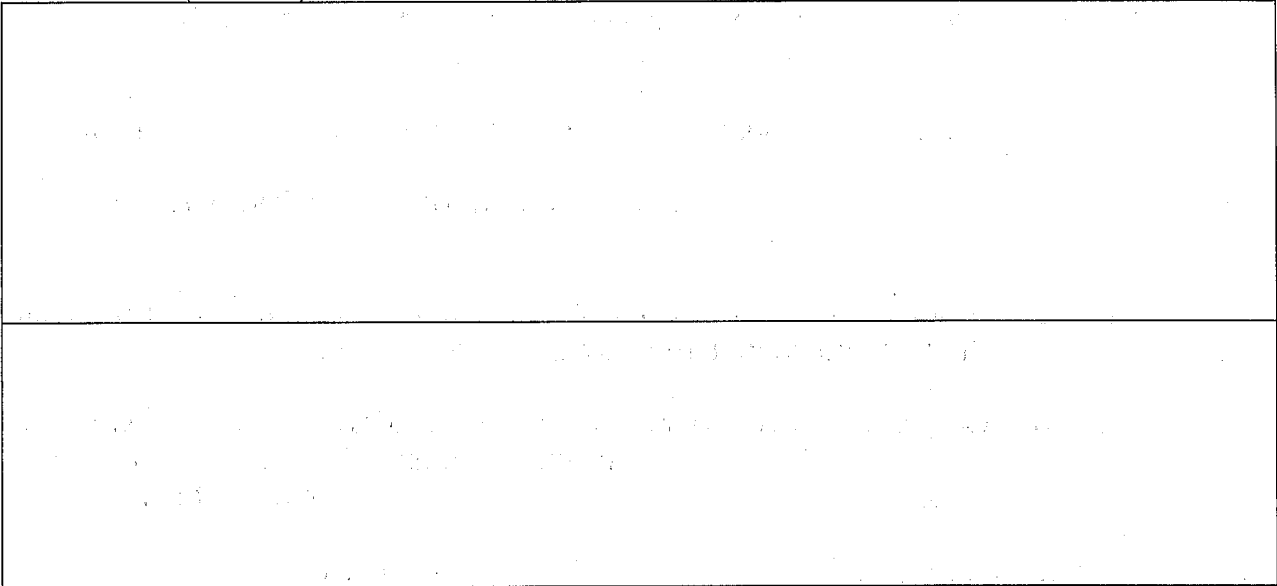
Section 19.0 (page 24)

ARB modification to Section- Delete References 1 and 2 and replace with

1. Software Reference Guide: NexION® Software Version 1.5 for ICP-MS Instrument Control.

APPENDIX A (page 25)

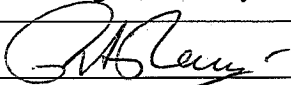
ARB modification to Section- Delete APPENDIX A



Section 5. Justification for Deviation(s)
(provide explanation of why modification(s) to existing ARB document is necessary)

The toxic metal program in ILS has been upgraded recently with state of the art instrumentation. The new **NexION 300X ICP-MS** with the Universal Cell Technology (UCT) allows the analyst to use most appropriate collision/reaction cell mode to minimize plasma based and matrix based polyatomic molecular interferences effectively. The ultrasonic nebulizer/Desolvator has been replaced by Perkin Elmer's, standard nebulizer with cyclonic spray chamber. The Kinetic Energy Discrimination mode (KED Mode) method was developed to produce quality and reliable toxic metal data. The **Autoblock III** semi-automatic sample extraction workstation has a high throughput capability, and it also expedites the reporting of ambient toxic metal data by eliminating cumbersome, time consuming, and intensive glassware cleaning.

Section 6. Attachment(s) <input type="checkbox"/>	# of Pages
<i>(specify attachment titles and number of pages, include modified spreadsheets or forms)</i> None	N/A

Section 7. ARB Approval		
Name/Phone Number:	Patrick Rainey	916 327-4756
Title:	Manager, Quality Management Section	
Signature/Date:		8/6/2015
Addendum Number	A03 MLD 061	

Completed form must be scanned/emailed or mailed to:

Mr. Patrick Rainey
 1927 13th Street, P.O. Box 2815
 Sacramento, California 95811
prainey@arb.ca.gov



Air Resources Board




Matthew Rodriguez
Secretary for
Environmental Protection

Mary D. Nichols, Chair
1001 I Street • P.O. Box 2815
Sacramento, California 95812 • www.arb.ca.gov

Edmund G. Brown Jr.
Governor

TO: Brenda Saldana, Manager
Inorganics Laboratory Section

FROM: Patrick Rainey, Manager 
Quality Management Section

DATE: April 27, 2016

SUBJECT: ADDENDUM FOR STANDARD OPERATING PROCEDURE FOR THE
TRACE METALS ANALYSIS OF AMBIENT AIR PARTICULATE
SAMPLES USING INDUCTIVELY COUPLED PLASMA-MASS
SPECTROMETRY.

Thank you for your submission of the addendum (A12MLD061-see attached) for the Standard Operating Procedure (SOP) for Trace Metals Analysis of Ambient Air Particulate Samples Using Inductively Coupled Plasma-Mass Spectrometry (SOP MLD 061). The Quality Management Branch has reviewed the addendum along with the SOP and Addendum A03MLD061 and determined that it covers all of the required elements. The addendum is approved. Please include a copy of the addendum(s) along with the SOP for use when performing the procedure.

Please direct comments or questions to Darsi Goto at (916) 324-9656 or by email at darsi.goto@arb.ca.gov.

Attachment

cc: Mike Miguel, Chief
Quality Management Branch

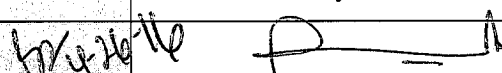
Darsi Goto
Quality Management Section

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our website: <http://www.arb.ca.gov>.

California Environmental Protection Agency

QUALITY MANAGEMENT DOCUMENT ADDENDUM

Section 1. ARB Document	
<input type="checkbox"/> Quality Management Plan (QMP)	
<input type="checkbox"/> Quality Assurance Project Plan (QAPP)	
<input checked="" type="checkbox"/> Standard Operating Procedure (SOP)	

Section 2. Information	
Submitter Name:	Prasanna Jayalath
Submitter Signature/Date:	 April 26, 2016

Section 3. Document Title	Date
<i>(specify exact title, revision #, and date of ARB Document(s) that your District proposes to modify)</i>	
SOP MLD 061 Revision Number 1.0	January 1, 2007

Section 4. Revision(s)
<i>(specify exact section(s), page number(s) and language in existing ARB document that will be modified and then specify modification (including any spreadsheets or forms))</i>

Summary

This addendum to MLD SOP 061 Revision Number 1.0 includes changes made to the sample extraction method, the types of blanks, and blank subtraction criteria.

This addendum is to be used in conjunction with Addendum A03MLD061 and SOP MLD 061 Revision Number 1.0.

Section 7.1.1 (page 9)

ARB modification to Section- Delete section 7.1.1

Section 10.0 (page 10)

ARB modification to Section- Add section 10.8

10.8 ICP-MS Rinse Solution

Pump rinse solution into the sample introduction system to prevent carry-over of the analyte of interest from one sample measurement to the next. The rinse solution should consist of no more than 2% nitric acid for the rinse cycle between samples. Increase to no more than 5% acid for short-term cleaning purposes.

Section 12.1 (page 12)

ARB modification to Section- Delete section 12.1 and replace with

12.1 Prepare the mixed-acid extraction solution of 6% nitric acid (v/v; 60 mL per 1-L) and 4% (v/v; 40 mL per 1-L) hydrochloric acid.

Section 14.9 (page 19)

ARB modification to Section- Delete section 14.9 and replace with

14.9 Blanks

There are three types of blanks required for the analysis: the calibration blank, the method blank, and the filter blank.

14.9.1 Calibration Blank

The calibration blank is used in establishing the calibration curve before analysis of samples. It should be a solution of 2% nitric acid and 1.3% hydrochloric acid, and include the exact internal standard(s) (Section 10.4) that will be a part of the standard calibration and sample analysis. If additional components (such as trace hydrofluoric acid) are needed for stability of some analytes, then the additional components must be included in the calibration blank, standards, and samples.

14.9.2 Method Blank

The method blank provides a documented history of the contamination levels expected from the complete sample preparation and analysis process (Sections 12 and 13), and must use the same volumes of reagents as the sample solutions. No blank subtraction is performed.

14.9.2.1 Method blank results are acceptable if the concentration of each analyte of interest is less than the reporting limit or if the sample results are at least ten times higher than the method blank results for each analyte.

14.9.2.2 If the method blank does not meet the acceptance criteria, a fresh aliquot of the same method blank must be prepared and analyzed to confirm unacceptable results. If the reanalysis of the method blank is acceptable, proceed with the analysis. If the acceptance criteria stated in 14.9.2.1 are still not met, all affected analytes must be invalidated. The source of contamination should be investigated, identified, and corrected.

14.9.3 Filter Blank

Filter blanks are routinely used to determine filter contamination. The filter blank contains an unexposed Teflon filter and the same volume of reagents as the sample solutions and follows all steps in sample preparation and analysis. No blank subtraction is performed.

14.9.3.1 Filter blank results are acceptable if the concentration of each analyte of interest is less than the reporting limit or if the sample results are at least ten times higher than the filter blank results for each analyte.

14.9.3.2 If the filter blank does not meet the acceptance criteria, a fresh aliquot of the same filter blank must be prepared and analyzed to confirm unacceptable results. If the reanalysis of the filter blank is acceptable, proceed with the analysis. If the acceptance criteria stated in 14.9.3.1 are still not met, all affected analytes must be invalidated. The source of contamination should be investigated, identified, and corrected.

Section 5. Justification for Deviation(s)

(provide explanation of why modification(s) to existing ARB document is necessary)

The sample extraction procedure has been changed to ensure satisfactory dissolution of analytes of interest. The sample analysis procedure has been changed to better align with National Air Toxics Trend Stations (NATTS) analytical procedure.

Section 6. Attachment(s)

(specify attachment titles and number of pages, include modified spreadsheets or forms)

of Pages

Total Metals Current Analyte List

1

Section 7. ARB Approval

Name/Phone Number:

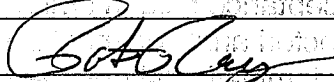
Patrick Rainey

916 327-4756

Title:

Manager, Quality Management Section

Signature/Date:



4/27/16

Addendum Number

AIR MLD 061

Completed form must be scanned/mailed or mailed to:

Mr. Patrick Rainey
 1927 13th Street, P.O. Box 2815
 Sacramento, California 95811
prainey@arb.ca.gov

MLD 061 method is applicable to the following elements

Analyte	Chemical Abstract Services Registry Number (CAS)
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-98-7
Nickel (Ni)	7440-02-0
Selenium (Se)	7782-49-2
Strontium (Sr)	7440-24-6
Tin (Sn)	7440-31-5
Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6
Zirconium (Zr)	7440-67-7
