CALIFORNIA AIR RESOURCES BOARD

Standard Operating Procedure for The Trace Metals Analysis of Ambient Air Particulate Samples using Inductively Coupled Plasma - Mass Spectrometry

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Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
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Standard Operating Procedure for The Trace Metals Analysis of Ambient Air Particulate Samples using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

1. Scope

This document describes a methodology used by the Monitoring and Laboratory Division (MLD) Inorganics Laboratory Section (ILS) staff to analyze trace metals in ambient air particulate samples by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

2. Summary of Method

An ICP-MS (Perkin-Elmer, Waltham, MA) coupled with an automated sample delivery system (ESI, Omaha, NE) is used for this method. An exposed ambient air particulate filter is refluxed in a dilute-mixed-acid solution to extract total metals in ambient air. The resulting solution is cooled to room temperature, brought up to final volume, and subsequently analyzed for elemental content using the ICP-MS instrument.

2.1. This method provides direction for the Kinetic Energy Discrimination (KED) mode operation for minimizing the molecular (polyatomic) interferences (Section 6.3). In the KED mode, molecular interferences are removed by collision with an inert gas (He) together with kinetic energy discrimination.

2.2. Teflon filters (2.0 µm, 37 mm) used for low-volume air sampling appear to have inherent elemental contamination of common analytes of interest.

3. Acronyms and Definitions

3.1. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS):

Inductively coupled plasma mass spectrometry is a multi-element analytical technique capable of trace level elemental analysis. Liquid samples are introduced into the ICP through a nebulizer carried by a flowing argon stream. By coupling radio-frequency power into flowing argon, plasma is created in which the predominant species are positive argon ions and electrons and has a temperature of 6000-8000K. The

sample passes through a region of the plasma, and the thermal energy atomizes the sample and then ionizes the atoms. The ions pass through the ion lens-focusing region, the universal cell, and then to the mass spectrometer, which acts as a mass filter to sort ions by a mass-to-charge ratio (m/z). Finally, ions are counted in rapid sequence at the detector, allowing individual isotopes of an element to be determined.

3.2. The 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.

3.3. ESI PrepFAST Autosampler

The PrepFAST autosampler is integrated with PerkinElmer ICP-MS instrument. The PrepFAST system automatically handles tedious manual sample preparation steps. The FAST portion of the delivery system uses a 6-port switching valve containing a Teflon sample loop. Automated dilution is utilized for both standard calibration and the sample dilution.

3.4. Acronyms

Acronym or Term	Definition
ºC	Degrees Celsius
K	Kelvin
mL	Milliliter
ng/m^3	Nanogram per cubic meter
amu	Atomic mass unit
ARB	California Air Resources Board
ASTM	American society for testing and materials
CFR	Code of federal regulations
COC	Chain of custody
CPS	Counts per second
DRC	Dynamic reaction cell
ESI	Elemental Scientific Inc.
HEPA	High-efficiency particulate arrestance
ICP-MS	Inductively coupled plasma-mass spectrometry

IDOC	Initial demonstration of capability
ILS	Inorganic laboratory section
KED	Kinetic energy discrimination
LCL	Lower control limit
LCS	Laboratory control standard
LIMS	Laboratory Information Management System
LSS	Laboratory Support Section
LWL	Lower warning limit
MDL	Method detection limit
MLD	Monitoring and laboratory division
NIST	National Institute of Science and Technology
NLB	Northern Laboratory Branch
ppb	Parts per billion
PTFE	Polytetrafluoroethylene
QC	Quality control
QCM	Quality control manual
QMB	Quality Management Branch
QMS	Quality Management Section
RL	Reporting limit
RPD	Relative percent difference
SOP	Standard operating procedure
UCL	Upper control limit
UWL	Upper warning limit

4. Personnel Qualifications and Training

The analyst should have experience using the ICP-MS instrumentation and interpreting and correcting spectral and matrix interferences. A minimum of six months of experience with commercial ICP-MS instrumentation is recommended.

Personnel should provide an initial demonstration of capability (IDOC) prior to performing this method on real-world samples (i.e. water). Personnel must be trained to understand the program's requirements per any applicable State and Federal regulations and guidance, NLB Laboratory QC Manual (Section 5.0), and this SOP. Personnel will also be shown how to operate the equipment needed to perform the method, the quality assurance components, and LIMS functionality pertaining to the program.

Documentation of training will be included in the program's laboratory notebook. Each training date must be initialed by the trainer (i.e. lead analyst) and the laboratory management.

5. Safety

All personnel must follow the general health and safety requirements found in the NLB Chemical Hygiene Plan.

5.1. General Safety

5.1.1. Wear gloves, lab coats, safety glasses while handling reagents and preparing samples.

Exercise special care when handling and dispensing concentrated nitric or hydrochloric acid. Use additional personal protective equipment, which protects the face, neck, and front of the body. Always add acid to the water to prevent violent reactions. ***If concentrated acids are exposed to any part of the body, quickly wash the affected area with copious quantities of water for at least 15 minutes.***

5.1.2. There are many potential hazards on an operating ICP-MS instrument including ultraviolet radiation, high voltages, radio-frequency radiation, and high temperatures. This information is detailed in the ICP-MS safety manual. The manual is located in Room 101 Cabinet 1.

5.1.3. The ICP-MS system can affect the function of a pacemaker and other implanted medical devices. Do not operate the instrument if you have a pacemaker or any other implanted medical devices.

5.1.4. The analyst must review and understand all instruments and compressed gas safety precautions before beginning operation of the AutoBlock III workstation and or ICP-MS system.

5.2. The newest ICP-MS instruments are fully interlocked to protect the user from hazards such as high voltage, radio frequency generators and intense ultra-violet light. Do not attempt to disable these interlocks or operate the ICP-MS if any safety interlock is disabled or malfunctioning.

5.2.1. No special training is required to operate AutoBlock III workstation. Follow the operation manual of the instrument carefully. The manual is located in Room 101 Cabinet 1.

5.3. Waste Disposal

All waste must be disposed of in accordance with Federal, State, and local regulations.

5.3.1. Waste to be picked by MLD/NLB hazardous waste program: contact the hazardous waste coordinator in the Laboratory Support Section (LSS) in NLB.

5.3.2. ICP-MS waste can be accumulated in the lab for 120 days without any treatment.

5.3.2.1. Hazardous waste containers must be labeled and stored properly. The following must be on the label:

5.3.2.1.1. Words “Hazardous Waste”

5.3.2.1.2. The composition of the waste

5.3.2.1.3. Accumulation start date

5.3.2.1.4. The physical state of the waste (solid or liquid)

5.3.2.1.5. Hazardous properties of the waste (corrosive, toxic)

5.3.2.1.6. Location

5.3.2.1.7. Name of the person generating the waste

5.3.2.2. Keep documentation and records of the contents of the ICP-MS waste in Inorganic Waste Drum log (Room 119) and the ICP-MS log book.

6. Interferences

This section provides information on laboratory contaminations, isobaric interferences, and molecular interferences that can affect ICP-MS results.

6.1. Laboratory Contaminations

6.1.1. Clean all equipment used in the sample preparation and analysis in a manner consistent with good laboratory practices for the trace metals analysis.

6.1.2. Avoid contamination of samples by keeping sample preparation areas organized.

6.1.3. Wear clean talc-free gloves when handling all (unexposed or exposed) filters.

6.1.4. For all sample extraction and standard preparation, use Nano-pure water that meets the American Society for Testing and Materials (ASTM), Type 1. The Nano-pure water resistivity value must be greater than 17.8 (MΩ). Record the water resistivity on the daily Nano-pure water resistivity sheet prior to use. The daily Nano-pure water resistivity sheet must be kept next to the Nano-pure water system.

6.1.5. Pay close attention to the nature of solutions introduced to the ICP-MS. Do not introduce high concentrated acid (not more than 8% nitric acid and 2% hydrochloric acid), which can result in matrix/transport effects, which may compromise accuracy in ICP-MS determination.

6.1.6. 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.

6.2. Isobaric Interferences

6.2.1. Isobaric interferences occur when isotopes of different elements form ions with the same nominal mass-to-charge ratio (m/z). This problem can usually be overcome by carefully selecting an alternative isotope. Most commonly used corrections for isobaric interferences are already present as default interference equations in the ICP-MS software.

6.2.2. In addition to elements in the sample, elements in the solvent (often a mineral acid e.g. HCl and HNO_3) and impurities of plasma gas such as neon (Ne), krypton (Kr), and xenon (Xe) can interfere. The interference by Kr on ^{78}Se can be avoided by using high purity (>99.999%) and Kr free argon.

6.3. Molecular Interferences

6.3.1. Molecular interferences are caused by molecular species formed in the plasma with a plasma gas (Ar) or matrix components (N, Cl, S, C, and O). Common molecular interferences are $^{40}Ar^{35}Cl$ on ^{75}As, $^{35}Cl^{16}O$ and $^{37}Cl^{14}N$ on ^{51}V, $^{40}Ar^{12}C$ on ^{52}C and $^{40}Ar^{16}O$ on ^{56}Fe. These molecular interferences are minimized by the use of the collision mode using KED with helium (He) as a collision gas or the reaction mode (Dynamic Reaction Cell-DRC) with ammonia (NH_3) or oxygen (O_2) as a reaction gas.

6.3.2. The removal of isobaric molecular interferences by KED mode works both by causing the interfering polyatomic interfering ions to dissociate

and by reducing the kinetic energy of the polyatomic interfering ions. Polyatomic ions have a larger collisional cross-section than the elemental ions and therefore collide with the helium atoms in the collision cell more frequently than the elemental ions. The interfering molecular ions lose kinetic energy due to the multi-collisions with the helium atoms. The interfering molecular ions with lower kinetic energy are rejected or discriminated by the potential energy barrier at the exit of the cell so that the higher-energy elemental ions are transmitted to the mass quadrupole mass analyzer.

6.3.3. In reaction mode (DRC mode), a highly reactive gas such as ammonia, oxygen, or methane is bled into the cell, which is a catalyst for the ion-molecule chemistry to take place. The gaseous molecules react with interfering ions through a number of different reaction mechanisms, converting them into a new species with a different mass/charge from the analyte or into a harmless neutral species.

7. Equipment and Supplies

7.1. Equipment

7.1.1. Inductively coupled plasma mass spectrometer (ICP-MS) with universal cell technology (Perkin Elmer Shelton, CT, www.perkinelmer.com).

7.1.2. Auto-sampler (ESI, Omaha, NE) automated sample delivery system.

7.1.3. Recirculating chiller (Polyscience; Perkin Elmer Shelton CT, www.perkinelmer.com).

7.1.4. Peristaltic pumping system with acid-tolerant tubing.

7.1.4.1. Green/Orange – Tygon® tubing 0.38 mm id (for sample introduction)

7.1.4.2. Green/Orange – MPP PVC tubing 0.38 mm id (for sample introduction with SC-FAST Autosampler)

7.1.4.3. Black/Black MPP PVC tubing 0.76 mm id (for sample introduction with ESI PrepFAST and ESI SC-FAST autosampler)

7.1.4.4. Gray/Gray - Santoprene® 1.3 mm id (for drain only)

7.1.5. Adjustable micro-pipettes with metal-free disposable tips, 1.0-microliter (1.0-µl) to 10.0-milliliter (10.0-mL) capacity.

7.1.6. AutoBlock III with 50 mL tubes (Environmental Express Inc., Mt. Pleasant SC).

7.1.7. Vortex Mixer (VWR).

7.2. Supplies:

7.2.1. Metal-free polypropylene sample vials from VWR or equivalent (15 mL).

7.2.2. ICP-MS Cones (nickel sample and skimmer cones, aluminum hyper-skimmer cone).

7.2.3. Concentrated nitric acid, Fisher Optima grade or equivalent.

7.2.4. Concentrated hydrochloric acid, Fisher Optima grade or equivalent.

7.2.5. Miscellaneous: protective-wear, talc-free gloves, disposable laboratory wipes/towels, self-adhesive labels, waterproof ink pen, timer, laboratory film (Parafilm).

7.2.6. High purity gases (99.999%)

7.2.6.1. Argon gas high purity grade (99.999%) krypton free

7.2.6.2. Helium ultrahigh purity grade (99.999%)

7.2.6.3. Oxygen research-grade (99.9995%)

7.2.7. ICP-MS Grade Reference Standards, National Institute of Standards and Technology (NIST) traceable material, in dilute acid solution; dilute to make necessary analysis solutions.

7.2.8. A secondary source of Reference Standards (for Laboratory quality control solutions), NIST traceable material, in dilute nitric acid; dilute to make necessary analysis solutions.

7.2.9. Nano-pure water, ASTM Type I, filtered, resistivity greater than 17.8 (MΩ) or equivalent.

8. Preparation of Chemical Reagents and Standards

Reagent or trace metal grade chemicals must be used at all times. Acids used in the preparation and for the sample analysis must be of high purity. Purchase small volumes whenever possible to minimize storage and disposal costs of unused portions. Order only chemical amounts needed within the following year. See Appendix A for the preparation of the chemical reagents and standards.

8.1. Calibration Standards

8.1.1. 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.

8.1.2. Prepare fresh calibration standards using NIST-traceable multi-element stock calibration standard before the analysis. Suggested concentrations are given in Appendix A, Table 1).

8.2. Quality Control Standards

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 of the calibration. An independent standard is defined as a standard composed of analytes from a source different from those used in the standards for instrument calibration.

8.3. Dual Detector Calibration Standard

Use a relatively high concentration solution (200 ppb) of all analytes to determine the response overlay of the pulse and analog portions of the electron multiplier. This solution must also include the elements used as Internal Standards (Section 8.4).

8.4. Internal Standards

Internal standards are routinely used with ICP-MS to minimize the impact of signal instability and to improve precision and accuracy. The ideal internal standard for any given analyte is one whose intensity changes are directly proportional to that of the analyte, i.e., the analyte-to-internal standard intensity ratio remains constant for all changes in the sample composition and instrument performance.

8.4.1. Internal standards should be NIST-traceable and should not be a sample component.

8.4.2. An element should be selected that matches the mass range, ionization potentials, and other chemical and physical properties of the elements being analyzed.

8.4.3. Internal standards may be added in-line at the time of analysis using a channel of the peristaltic pump (section 9.3 and 9.4) and an appropriate mixing manifold.

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

8.5. Tuning Solution

The tuning solution should contain elements representing all of the mass regions (low, mid, and high) of interest, thereby verifying that the resolution and mass calibration of the instrument is within the required specifications. The solution is also used to verify that the instrument has reached thermal stability. Multi-element tuning solution contains one ppb solution of lithium, cobalt, indium, cerium, and thallium in 1% HNO_3 acid.

8.6. Optimization Solution

Use the Calibration Standards (Section 8.1) and Tuning Solution (Section 8.5) when performing the optimization procedures for ICP-MS.

8.7. ICP-MS Rinse Solution

Pump rinse solution (2% Nitric acid) into the sample introduction system between samples to prevent carry-over of the analytes of interest from one sample measurement to the next.

9. Sample Preparation

In this document, the term “sample” includes duplicates, spikes, and blanks.

9.1. 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.

9.1.1. Print or write sample labels: each label should have a sample identification number and the date of the extraction (sample ID, site name, sampling month and year, and extraction date.

9.1.2. Conduct the sample extraction using the Automated Sample Extraction techniques as described in section 9.2.

9.2. Automated Sample Extraction

This section describes the sample preparation steps when performing automated extraction using the AutoBlock III workstation (see **Figure 9-1**). The AutoBlock operational manual is located in Room 101 Cabinet 1.

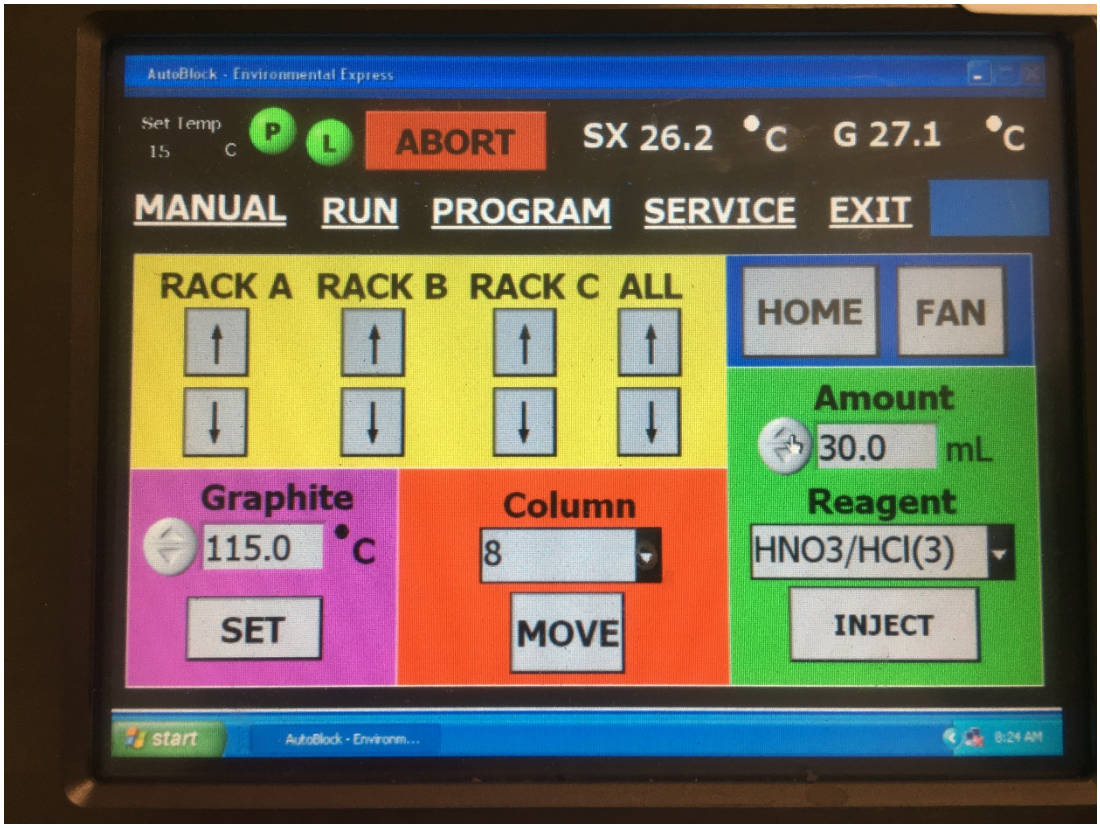

Figure 9-1 Autoblock III Screen

9.2.1. Prepare the mixed-acid extraction solution of 6% nitric acid (v/v; 60 mL per 1-L) and 4% hydrochloric acid (v/v; 40 mL per 1L) in a volumetric flask using Nano-pure water. For 50 samples, make 2-L of extraction solution.

9.2.2. Turn on the AutoBlock and load the “MLD 061” reflux method file using the program or select manual mode. In this mode, digestion functions

(heating, cooling, injecting reagents, etc.) are performed individually by the analyst. (let heat block to warm for 30 minutes prior to beginning the actual reflux).

9.2.2.1. Fill the solvent bottles (1L) as necessary. Port 1 and 2: Nano-pure water; port 3: mixed acid extraction solution (9.2.1); ports 4 and 5: Nano-pure water.

9.2.2.2. Prime the pump. Inject reagent line with 20 mL of Nano-pure water select port 1 (Nano-pure water 2 x 10 mL). Inspect tubing for any air bubbles. Verify that all delivery lines are free of air bubbles before initiating the RUN mode. Repeat for each port (Ports 2-5) as necessary.

9.2.2.3. Calibrate the pump (Note: Check all lines for air bubbles and clogs before calibrating). Follow the steps to calibrate sample injection tubing and the Calibrate Pump function under the SERVICE tab. Use Nano-pure water (Port 2) for the pump calibration. Refer AutoBlock operational manual for detailed instructions for the pump calibration. The accuracy of the pump calibration must be within ±2%.

9.2.2.4. Prime the lines with 6 mL (3 x 2 mL) of extraction solution (Port 3) before running the extraction method.

9.2.3. Disassemble filter cassette and place each Teflon filter in a labeled sample vessel (50 mL PTFE tube) using a Teflon tweezer. Make sure that the filter is sitting on the bottom of the vessel. This is done by gently gripping the polymethyl pentene (PMP) support ring with a gloved finger and bending the filter so that it fits in the tube.

9.2.4. Arrange sample vessels in the AutoBlock sample racks and load racks onto the lift arms in the UP position. Make sure all rows have sample vessels and placeholders (empty vessels) for the proper airflow.

9.2.5. Run “MLD061” method or add extraction solution using the manual method. If using the manual mode, select 30.0 mL of mix acid extraction solution (Port 3) and press the INJECT button to add the solution to the vessels in the selected column.

9.2.6. Set graphite block temperature at 115°C

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

9.2.6.2. Ensure volume level is correct then gently cover the sample vial with a cap (do not tight, turn the cap clockwise half a turn).

9.2.6.3. Reflux samples at 95°C for 2 h.

9.2.6.4. After 2 hours of refluxing, select ALL RACKS UP sample racks will be raised out of the graphite block and let the samples cool for 2 h.

9.2.7. After 30-60 minutes of cooling, carefully remove the racks and keep them in the hood at room temperature overnight.

9.2.8. Carefully remove the sample filter with acid cleaned PTFE tweezers and rinse the filter with a minimum amount of Nano-pure water (~1mL). Collect rinse into the corresponding vessel and discard the filter. Bring the final sample volume to 30 mL with Nano-pure water.

9.2.9. Cap the sample vessels firmly. Store samples at room temperature for immediate analysis or keep in the refrigerator at 4°C for prolonged storage (see section 13.3 for sample storage and holding time).

9.3. ESI SC-FAST Automated Sample Introduction System

This section describes the sample preparation steps for the analysis using the NexION 300X ICP-MS instrument integrated with SC-FAST autosampler. The sample is filled into a sample loop and then injected into a diluent liquid stream and transported to the nebulizer. The internal standard is continuously added inline.

9.3.1. Prepare 1000 mL of 50 ng/mL internal standard solution (Appendix A) and place the internal standard probe in the internal standard container.

9.3.2. **For All samples (Method Blank, Filter Blank, Samples, and Sample Duplicates) except Spikes**: To a labeled 15 mL metal-free sample vial, pipette 2.0 mL of a sample, dilute to 6.0 mL with Nano-pure water (1:3 dilution). Cap the vial tightly and then vortex for one minute using a vortex mixer.

9.3.3. **For Spike samples**: To a labeled 15 mL metal-free sample vial, pipette a second 2.0 mL aliquot of a randomly selected sample and

add 0.20 mL of spike solution (Appendix A). Dilute to 6.0 mL with Nano-pure water. Cap the vial tightly, and then vortex for one minute using a vortex mixer.

9.4. ESI PrepFAST Automated Sample Preparation System

This section describes the sample preparation steps for the analysis using the NexION 2000P ICP-MS instrument integrated with PrepFAST autosampler. The PrepFAST autosampler is a sample/standard auto dilution system. Extracted sample is injected into a diluent liquid stream and transported to the nebulizer. The sample and the internal standard are added inline.

9.4.1. Prepare 1000 mL of 50 ng/ml internal standard solution (Appendix A) and place the internal standard probe in the internal standard container.

9.4.2. All samples (Method Blank, Filter Blank, and Samples) except Sample duplicates and Spikes: Place 50 mL extracted sample directly in the autosampler.

9.4.3. **For Sample duplicates**: To a labeled 50 mL sample extraction vessel, pipette 15.0 mL aliquot of the selected sample and run as a duplicate.

9.4.4. **For Spike samples**: To a labeled 50 mL sample extraction vessel, pipette 10.0 mL aliquot of the selected sample and add 0.345 mL of spike solution (Appendix A). Cap the sample vessel tightly, and then vortex for one minute using a vortex mixer.

10. Instrument Setup and Tuning

Following is a detailed checklist of instrument starting and tuning. The analyst should be familiar with both the Maintenance Guide NexION 300 ICP-MS System and the Software Reference Guide-Syngistix software for ICP-MS Version 2.3 for ICP-MS instrument control before starting the NexION 300X and NexION 2000P ICP-MS instruments.

10.1. Pre-ignition Checklist and Instrument Setup

Do not operate the ICP-MS instrument unless you have formal training from the instrument manufacturer. Setup the instrument according to the manufacturer’s operating instructions.

10.1.1. Check the sample cones. The cones must be clean and free of any deposits. If necessary, clean dirty cones with 2% HNO_3 with Nano-pure water or replace dirty cones with clean, spare cones.

10.1.2. Check the Argon supply. The pressure gauge on the instrument should read 100 ± 5 psi.

10.1.3. Check to make sure that the collision gas (He) is turned on. The supply to the ICP-MS should be 30 ± 2 psi (operating).

10.1.4. Check the peristaltic pump tubing and adjust the tension of each tube.

10.1.5. Open Syngistix software on the desktop and open the **Control** icon in the Instrument group of the **Syngistix** tab. Select ICP-MS, and click the Plasma **Start/Stop** button (See **Figure 10-1**).

10.1.6. Place about 40 mL of rinse solution (section 8.7) in a 50 mL rinse solution vial.

10.1.7. For SC-FAST autosampler and the PrepFAST auto dilution system keep both rinse and internal standard probes in the rinse solution.

10.1.8. Allow the instrument to become thermally stable for at least 30 minutes before tuning.

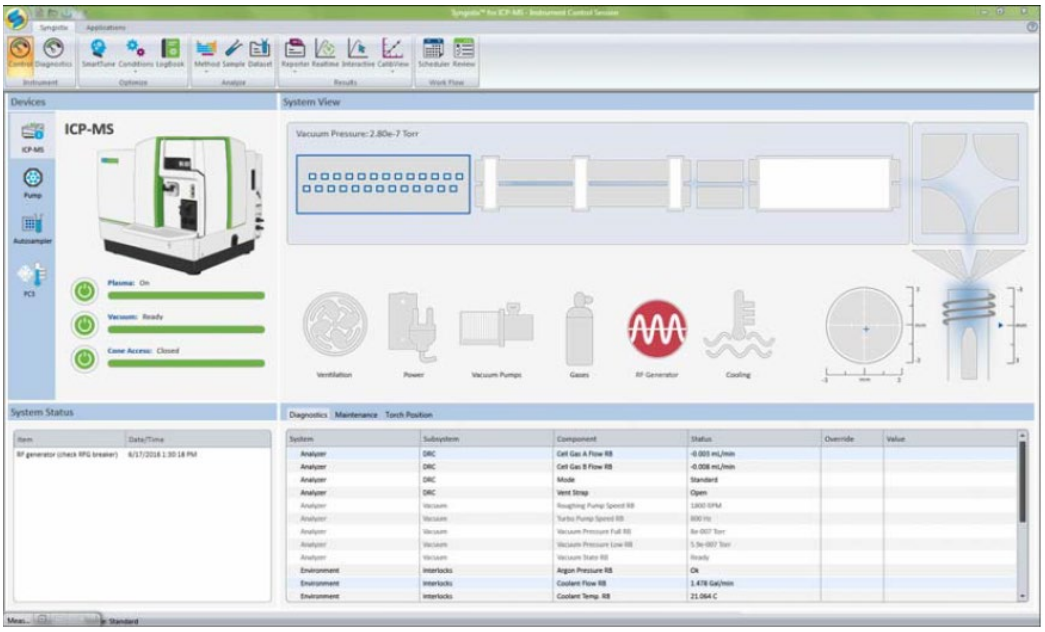

Figure 10-1 Control Screen

10.2. Instrument Tuning and Optimization

After 30 minutes warm-up, tune the instrument with the multi-element tuning solution (Section 8.5) containing elements representing all of the mass regions of interest. Perform and document a Lab Performance Check and any optimizations necessary. See below for the procedure.

10.2.1. Add approximately 40 mL of tuning solution to the 50 mL tuning vessel.

10.2.2. Insert both rinse and internal standard probes in the tuning solution.

10.2.3. Open SmartTune window and Select Smart tune Manual optimization.

10.2.4. Quick optimize Mass Calibration and Resolution, then the Lab Performance Check. If the instrument passes the optimization check, the instrument is tuned and ready to analyze. (Appendix B).

10.2.5. If the instrument does not pass the Lab Performance Check, re-examine the instrument set-up and sample introduction system. Perform instrument optimization checklist (Mass Calibration and Resolution, Lab Performance Check, Torch Alignment, Nebulizer Gas Flow (STD/KED), Auto Lens Optimization (KED mode), and Lab Performance Check).

10.2.6. If the instrument does not pass the optimization, perform a full optimization (see NexION training manual for instrument optimization).

11. Method Performance Criteria

An initial method detection limit (MDL) study must be performed on each instrument before samples can be analyzed. MDL determination is conducted when new methods are established, new standards are introduced, instruments are replaced, or other system changes occur. MDL studies are conducted annually per 40CFR part 136, Appendix B.

11.1. Method Detection Limits

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and statistically different from a blank. It is determined from analysis of a sample in a given matrix containing the analyte and sampling media.

Equation (1) $MDL = (t)_{(n-1=0.99)} \times SD = 3.143 \times SD$

where SD is the standard deviation of *n* repetitions of the lowest standard or the MDL spiked sample expressed in concentration 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 standard deviation estimate with a degree of freedom equal to n-1. For seven replicates, the *t* value equals 3.143. A summary of this procedure is as follows:

11.1.1. For the method MDL, use the exact internal standards and the exact instrument settings (sweeps and dwell) used to analyze the ambient samples. Follow all sample-preparing steps for the MDL determination.

11.1.2. In order to determine the MDL for a sample matrix, the analytes should be spiked into the matrix of interest (see sample preparation procedure, Section 9) at a level that is three to five times the estimated MDL. The estimated MDL is obtained by one or more of the following methods:

11.1.2.1. Previously acceptable MDL determination and related experience.

11.1.2.2. Concentration value that corresponds to an instrument signal-to-noise ratio ~ 3 to 5 fold.

11.1.2.3. Instrumental limitations.

11.1.3. Prepare a minimum of seven replicates (insert a Teflon filter to each 50mL extraction vial and spike the appropriate amount of MDL spike solution) and follow the entire sample preparation procedure.

11.1.4. Determine the MDL as per Equation (1) in section 11.1

11.1.5. For an MDL to be valid it must have a valid calibration, standard checks, control, method blank, filter blank, and meet the following acceptance criteria:

11.1.5.1. MDL < spike concentration < 10 x MDL

11.1.5.2. MDL spike recovery within 50%-150%

11.1.6. In order to approximate the real-world samples, prepare and analyze three separate batches on non-consecutive dates to incorporate variability.

11.1.7. Prepare and analyze a minimum of seven filter blanks to account for background attributable to the sample media.

11.2. Limit of Quantitation

The limit of quantitation (LOQ) minimum concentration or amount of an analyte that a method can measure with a specified degree of confidence. The LOQ is equal to five times the standard deviation of the replicate analyses from the MDL determination.

Equation (2) LOQ = 5 x SD

SD = Standard deviation

11.3. Reporting Limits

Adjust the reporting limits (RLs) based on the LOQ (Equation 2) 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.

11.3.1. Based on the analytical tendencies of actual ambient samples, the published method RL(s), 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).

11.3.2. The conversion of the calculated RL (ng/mL) into the published RL (ng/m^3) may be necessary, especially if the air volumes are vastly different within a sample set or project.

12. Quality Control

All quality control (QC) data should be maintained in an organized manner and be available for easy reference or inspection. **See Appendix A for the preparation of the QC reagents.**

QC	Acceptance Criteria	Failed Criteria Corrective Action
Initial Calibrations	The ICP-MS is calibrated each day of operation using a calibration blank and at least 3 standards. Calibration correlation coefficient must be ≥ 0.995	Recalibration is required. Prepare new calibration standards and re-run the analysis.
Check standards	Check standards must fall within ± 20% of the target concentration. Check standards must be analyzed before any samples,	If the check standard is outside of the criteria limit, the sample results

	again after each group of ten samples, and finally at the end of the analysis.	are invalid. Take action to bring the system back into control and repeat the analyses.
Quality Control Standards	Quality Control Standards are analyzed after the calibration is complete. The initial limits are ± 8% for the warning limits and ± 10% for control limits from the target value. Once a minimum of 20 control values is obtained, the limits for the tolerance of the control results should be set as follows: Upper Control Limit (UCL) = Mean + 3SD Upper Warning Limit (UWL) = Mean + 2SD Mean or Target Value Lower Warning Limit (LWL) = Mean – 2SD Lower Control Limit (LCL) = Mean – 3SD	If the QC results are outside the control limits stop the sample analysis. The source of the problem should be identified and corrected before sample analysis is continued.
Duplicates	Duplicates are run at a frequency of at least 10% and consist of a separate aliquot of the sample. For analyte values greater than five times RL, the relative percent difference (RPD) should be within ± 30%. Analyte values less than 5 X RL, the RPD criteria are not evaluated and marked as “NA”.	If the results are outside the acceptance limits, investigate the reason and correct the cause. All samples in that duplicate batch must be reanalyzed. If the reanalysis fails, invalidate the samples associated with that batch
Matrix Spikes	Matrix spike is analyzed every 20 samples. The spike recovery limit is ± 20% of the expected value.	If the spike recovery exceeds the acceptable limits, stop the analysis. Reanalyze the spiked sample. If the spike falls within the acceptable criteria, continue the analysis. If the spiked recovery exceeds the acceptable limits again, investigate the problem. After the problem is corrected, reanalyze the spike and continue sample analysis. Failed matrix spikes are flagged, and are

		discussed in the final data report case narrative.
Matrix Spike Duplicate	The matrix spike duplicate acceptable limit is ± 20% of the matrix spiked sample.	If the results are outside the acceptance limits, investigate the reason and correct the cause. Failed matrix spike duplicates are flagged, and are discussed in the final data report case narrative
Calibration Blank	Results for the calibration blanks must be less than the RL.	If the calibration blank exceeds acceptable limits, the blank can be re-analyzed. If the re-analysis is successful, analysis can continue. If the reanalysis is not successful investigate the problem. After the problem is corrected, recalibrate and reanalyze all samples.
Method Blank	The method blank results are accepted, 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.	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 are still not met, all affected analytes must be invalidated. The source of contamination should be investigated, identified, and corrected.

		Refer to the NLB QC manual for blank corrective action criteria.
Filter Blank	Minimum of three filter blanks should be extracted and analyzed per sample batch. The filter blank results are accepted, if the concentration of each analyte of interest is less than the reporting limit of two of the three filter blanks or if the sample results are at least ten times higher than the method blank results for each analyte.	If the filter 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 filter blank is acceptable, proceed with the analysis. If the acceptance criteria are still not met, all affected analytes must be invalidated. The source of contamination should be investigated, identified, and corrected. Refer to the NLB QC manual for blank corrective action criteria.
Internal Standard	The intensities of the internal standards in all QC and samples should be 60 – 200% of the original response in the calibration blank.	If the responses are not within limits, flush the system with the rinse solution and monitor the intensities of the internal standard. If the intensities are within limits reanalyze the batch. If the intensities in the calibration blank are not within limits, stop the analysis, find and correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

13. Sample Management

Sample and data management consists of samples logged into the Laboratory Information Management System (LIMS), documentation of unusual occurrences and their resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval, submittal of data to clients, and archival procedures for sample media and respective chains of custody. Program and maintenance notebooks and/or logbooks are to be kept with the instrumentation at all times.

13.1. Sample Management

Sample management is the ability to effectively and efficiently get sample media to and from the laboratory and field, while maintaining all regulatory and hold time requirements, in addition to maintaining sample integrity and providing sample security and tracking capabilities. Sample management include: sample receipt, a chain of custody, sample control, sample tracking, log-in, validation, storage, and archive.

13.2. Sample Receipt

13.2.1. Once the samples are logged by the LSS sample handling team, prepare a monthly extraction worklist from the LIMS Reports.

13.2.2. Inspect filter samples and sign the chain of custody log.

13.3. Sample Storage and Holding Time

13.3.1. The filter samples can be stored under ambient conditions for 180 days.

13.3.2. If samples are stored for longer than 180 days, store in a refrigerator (at 4ºC).

13.3.3. Extracted samples can be stored under ambient conditions for 180 days.

13.3.4. If samples are stored for longer than 180 days, store in a refrigerator (at 4ºC) for a maximum of six months.

13.3.5. After six months, dispose used extracted samples appropriately (section 5.3).

13.4. Data Management

Data management describes the basic flow of analytical data from generation, review (verification and validation), and reporting. Laboratory staff and management are all integral parts of data management. The laboratory utilizes a laboratory information management system (LIMS) database to carry out data management activities.

13.4.1. The analyst must transfer total metals data from the ICP-MS system to LIMS electronically as comma-separated values (CSV) format. The analyst should verify (QC results, blanks results, duplicate results, and spike results) data before transfer to LIMS.

13.4.2. Prepare a monthly total metals data package with all supporting documents.

14. Calculations

14.1. Method Detection Limit (MDL)

MDLs are calculated according to the following equation:

Equation (1) $MDL = (t)_{(n-1=0.99)} \times SD = 3.143 \times SD$

Where:

SD = Standard deviation

$t_{(n-1)=0.99)}$ = Student's *t* value for a 99% confidence level
For seven replicates degrees of freedom (n-1 = 6), *t* = 3.143)

14.2. Limit of Quantitation (LOQ)

LOQs are calculated according to the following equation:

Equation (2) $LOQ = 5 \times SD$

14.3. Duplicates

The relative percent difference (RPD) between sample duplicates is calculated according to the following equation:

Equation (3) $$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

Where:

D_1 = Sample result
D_2 = Sample duplicate result

14.4. Spike recoveries are calculated according to the following equation:

Equation (4)
$$\%R = \frac{C_s - C}{S} X\ 100$$

Where:

Cs = Spiked sample results
C = Sample results
S = Spike added

14.5. The concentration of total metals in ambient air is calculated according to the following equation:

Equation (5)
$$C_{air} = \frac{C_{ICP/MS}\ X\ V_{Exn}\ X\ 1000}{V_{air}}$$

Where:

C_{air} = Concentration of the element in ambient air (ng/m^3)
$C_{ICP/MS}$ = Concentration measured in the sample extract (ng/mL)
V_{Exn} = Extraction volume (30 mL)
V_{air} = Volume of air sampled (L)

15. Revision History of Method 061

Revision	Effective Date	Primary Changes 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)
MLD061, Revision 0.0	01/01/2002	Extraction procedure changed to eliminate the use of ethanol, a contributor to numerous carbon-bonded interferences. Changed optimization and tuning procedures, and change 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. Added Appendix A, Contamination on Teflon filters.
MLD061, Revision 1.0 Addendum # A03 MLD 061	8/06/2015	Agilent 7500ce ICP-MS instrument replaced with Perkin Elmer NexION 300X ICP-MS. Kinetic Energy Discrimination (KED) mode has been introduced to eliminate isobaric interferences.
MLD061, Revision 1.0 Addendum # A12 MLD 061	4/27/2016	Sample extraction solution changed (Nitric acid 6% and Hydrochloric acid 4%).
MLD061, Revision 2.0	11/18/2019	Purchased and installed new ICP-MS instrument; NexION 2000P with PrepFAST autosampler-2018. This revision includes changes made to the sample extraction procedure, sample introduction method, and the modes of analysis. Updated Appendix A; Preparation of Standards and Reagents, and added Appendix B; Suggested Lab Performance and Mass Calibration Criteria.

16. References

16.1. MLD061, SOP for the Trace Metals Analysis of Ambient Air Particulate Samples using Inductively Coupled Plasma - Mass Spectrometry, Revision 1.0, January 1, 2007.

16.2. California Air Resources Board MLD Northern Laboratory Branch: Final Chemical Hygiene Plan for Northern Laboratory Branch, 1927 13th Street, 1900 14th Street, June 2019.

16.3. California Air Resources Board MLD Northern Laboratory Branch: Laboratory Quality Control Manual, Revision 4.0, September 17, 2018. https://ww2.arb.ca.gov/sites/default/files/2018-10/nlbqcm.pdf

16.4. U.S. EPA Office of Water " Standard Operation procedure for Trace Element Analysis of Flue Gas Desulfurization Wastewaters Using ICP-MS Collision/Reaction Cell Procedure" March 2013.

16.5. U.S. EPA SW-846 Ch 3.3 Method 6020, Metals by Inductively Coupled Plasma/Mass Spectrometry, August 1994.

16.6. Software Reference Guide-Syngistix software Version 2.3 for ICP-MS instrument control, October 2017.

16.7. Maintenance Guide NexION 300 ICP-MS System.

16.8. Maintenance Guide NexION 2000P ICP-MS System.

16.9. Elemental Scientific SC-2DX Autosampler Manual.

16.10. AutoBlock III Operation Manual.

16.11. U.S. EPA 600/R-94-111 Method 200.8, Trace Elements in Water and Wastes – ICP/MS, May 1994.

16.12. U.S. EPA SW-846 Ch 3.3 Method 6020, Metals by Inductively Coupled Plasma/Mass Spectrometry, August 1994.

MLD061, Revision 2.0: APPENDIX A

Preparation of Standards and Reagents.

Stock standards are purchased as high purity grade solutions obtained from a reputable commercial source. Standard solutions must be NIST traceable. All standards and solutions ready to analyze on the ICP-MS must be prepared fresh daily. Properly label all standards and solutions (Name of the solution, Concentration, Date prepared, and Analyst Name or initials). If not dedicated to a particular standard or a reagent, acid wash volumetric flasks and reagent containers (polypropylene, polymethylpentene, or Teflon). For example, with 2% (v/v) HNO_3 and Nano-pure water (at least three times each) and verify cleanliness through analysis of rinsate.

1. Tuning Solution (1 ng/mL in 2% HNO_3)

   A tuning solution may be purchased as a multi-element (Ce, Co, In, Li, and Tl) solution. In a 1-L volumetric flask, pipette 20.0 mL of nitric acid into 300 mL of Nano-pure water. Add 100 µL of 10 mg/L of multi-element tuning solution and dilute to 1-L with Nano-pure water.

2. Quality Control Standards

   In a 200 mL volumetric flask, pipette 1.5 mL of 1.0 mg/L multi-element solution, 2.5 mL of 0.10 mg/L Be, and 5.5 mL of 20 mg/L Fe solution. Dilute to 200 mL with freshly prepared reagent blank.

3. Spike Solution

   In a 100 mL volumetric flask, pipette 10.0 mL of 1.0 mg/L multi-element solution, 5.0 mL of 0.10 mg/L Be, and 20.0 mL of 20 mg/L Fe solution. Dilute to 100 mL with freshly prepared reagent blank.

4. Dual Detector Calibration (2% HNO_3)

   In a 200 mL volumetric flask, pipette 4.0 mL of 10 mg/L multi-element solution, 10.0 mL of 0.1 mg/L Be, 2.0 mL of 20 mg/L Fe solution, and 0.40 mL of 100 mg/L internal standard solution. Dilute to 200 mL with Nano-pure water.

5. Internal Standard (50 ng/mL, in 1% HNO_3)

   An internal standard solution may be purchased as a multi-element (Li, Sc, Y, Ga, In, Ce, and Bi) solution. In a 1-L volumetric flask, pipette 10.0 mL of nitric acid into 300 mL of Nano-pure water. Add 0.50 mL of 100 mg/L of multi-element tuning solution and dilute to 1-L with Nano-pure water.

6. Reagent Blank (HNO_3 2% and HCl 1.33%)

   In a 1-L volumetric flask pipette 20.0 mL of nitric acid and 13.3 mL of hydrochloric acid into 300 mL Nano-pure water. Carefully fill the volumetric flask with Nano-pure water up to 1-L mark of the flask.

7. Calibration Blank

   To a 15 mL metal-free sample vial, pipette 10.0 mL of the freshly prepared reagent blank.

8. Calibration Standards

   Stock calibration standards are purchased as custom multi-element mixes or as single element solutions. The preparation of mid-level calibration standard is as follows:

   8.1. Mid-level Calibration Standard (STD 6, concentration 50 ng/mL)

   In a 200 mL volumetric flask, pipette 10.0 mL of 1.0 mg/L multi-element solution, 5.0 mL of 0.10 mg/L Be, and 25.0 mL of 20 mg/L Fe solution. Dilute to 200 mL with freshly prepared reagent blank.

   8.2. To a 15 mL metal-free sample vial, pipette 10.0 mL of freshly prepared STD 6.

   8.3. Use mid-level calibration standard (STD 6) to prepare other standards (Table 2). Suggested concentrations are given below (Table 1), but the laboratory may adjust concentrations as required. At a minimum, a 3-point curve must be used.

   8.4. Check Standard

   To a 15 mL metal-free sample vial, pipette 3.0 mL of freshly prepared STD 6 and add 7.0 mL of the reagent blank.

   The preparation of calibration standards and check standard from STD 6 are given in Table 2.

Table 1: Calibration Standards

Element		STD 1 (ng/mL)	STD 2 (ng/mL)	STD 3 (ng/mL)	STD 4 (ng/mL)	STD 5 (ng/mL)	STD 6 (ng/mL)
Antimony	Sb	0.5	1	2	10	20	50
Arsenic	As	0.5	1	2	10	20	50
Beryllium	Be	0.025	0.05	0.1	0.5	1	2.5
Cadmium	Cd	0.5	1	2	10	20	50
Chromium	Cr	0.5	1	2	10	20	50
Cobalt	Co	0.5	1	2	10	20	50
Copper	Cu	0.5	1	2	10	20	50
Iron	Fe	25	50	100	500	1000	2500
Lead	Pb	0.5	1	2	10	20	50
Manganese	Mn	0.5	1	2	10	20	50
Molybdenum	Mo	0.5	1	2	10	20	50
Nickel	Ni	0.5	1	2	10	20	50
Selenium	Se	0.5	1	2	10	20	50
Strontium	Sr	0.5	1	2	10	20	50
Tin	Sn	0.5	1	2	10	20	50
Titanium	Ti	0.5	1	2	10	20	50
Vanadium	V	0.5	1	2	10	20	50
Zinc	Zn	0.5	1	2	10	20	50
Zirconium	Zr	0.5	1	2	10	20	50

Table 2: Preparation of Calibration Standards and Check Standard

Calibration Standard	Amount of STD 6 (mL)	Amount of Reagent Blank (mL)
STD 1	0.10	9.90
STD 2	0.20	9.80
STD 3	0.40	9.60
STD 4	2.00	8.00
STD 5	4.00	6.00
STD 6	10.0	0.00
Check Standard	3.00	7.00

MLD061, Revision 2.0: APPENDIX B

Suggested Lab Performance and Mass Calibration Criteria

1. Mass Calibration

Table 3: Mass Calibration Criteria

Mass Calibration	0.05
Mass Resolution	0.03

2. Lab Performance Criteria

2.1. Optimization Settings:

Table 4: Lab Performance Criteria

Element	Criteria	Intensity (cps)
Tl (204.975)	>	30,000
Ce (139.905)	>	50,000
In (114.904)	>	80,000
Co (58.9932)	>	20,000
Li (7.016)	>	20,000
Background (220)	≤	2

2.2. Interferences:

Double charged ions (Ce^{++}/Ce) ≤ 3%

Oxides (CeO/Ce) ≤ 2.5%

2.3. Precision:
Precision should be < 3% but typically about 1% or less.