

Analysis of Heavy Metals by ICP-MS

1. Scope:

This document provides a procedure for analyzing fertilizers, animal feed, hemp, soil, water and premixes for arsenic, cadmium, lead, mercury, and selenium by inductively coupled plasma attached to a mass spectrometer (ICP-MS).

2. Principle:

Samples are extracted in acid to decompose the matrix and release analytes of interest. Liquid samples are introduced into an argon plasma as aerosol droplets. The ICP torch and radio frequency coil generate the argon plasma, which serves as the ion source of the ICP-MS. Samples are extracted according to RA-SP-HM-EXT.

3. Safety:

The SDS for all chemicals shall be read before performing any part of this method. Gloves, safety glasses, and a lab coat shall be worn when handling hazardous materials and reagents.

Nitric and hydrochloric acids are very toxic and extremely corrosive and shall be used in a fume hood. The acidification of samples containing reactive materials may result in the release of toxic gases and can be exothermic. Sample acidification and digestion shall be performed carefully in a fume hood.

4. Definitions:

- CCV Continuing Calibration Verification. An intermediate range calibration standard run after samples to demonstrate instrument remains in calibration.
- ICV Initial Calibration Verification. An intermediate range second source standard prepared from standards obtained from a vendor that is different from the vendor the calibrations standards were obtained from.
- IS Internal Standard. The IS includes Ga, Ge, In, Ir, Li6, Rh, Sc, Tb, Tm, and Y and is mixed with the sample during sample introduction into the instrument to account for matrix variations.
- MB Method Blank. A solvent (reagent) blank that is subjected to the entire extraction process to demonstrate all aspects of the extraction are free from interferences.
- QC Quality Control. A NIST, Magruder, or AAFCO sample that is extracted with each set to demonstrate recovery.
- RB Reagent Blank. Used to demonstrate reagents are free from interferences and to determine background levels from the instrument.

5. Interferences:

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

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

Transport interferences are specific physical interferences associated with the sample nebulization and transport process through the instrument. These usually result from sample matrix components that influence the aerosol formation or cause a change in the surface tension or viscosity. Some matrices can cause signal suppression or enhancement.

6. Equipment, Supplies, and Reagents:

5.1 Equipment

- 5.1.1 ICP-MS which consists of an inductively coupled plasma source, ion optics, a quadrupole spectrometer, an autosampler, a recirculatory (chiller) and a computer that controls the instrument, data acquisition, and data handling.
- 5.1.2 ICP-MS operating conditions for standard and kinetic energy discrimination (KED) modes.

Parameter	Operating Condition	Parameter	Operating Condition
Plasma Power	1.6 KW	Detector Mode	Pulse Counting
Coolant Flow Rate	13.5 L/m	Data Acquisition	Peak Hopping
Auxiliary Flow Rate	1.2 L/m	Mass Range	1-240 amu
Nebulizer Flow Rate	1.02 L/m	Dwell Time	50-200 ms
Solution Uptake Rate	0.6 mL/min	Nebulizer	Meinhard Concentric
Spray Chamber	Cyclonic		

5.2 Supplies

- 5.2.1 Argon Gas
- 5.2.2 Helium Gas

- 5.2.3 Pipettes - 100µL to 10mL
- 5.2.4 Polypropylene funnels
- 5.2.5 Whatman 541 filter paper
- 5.2.6 Polypropylene sample vessels (100mL)*
- 5.2.7 Polypropylene sample vials (50mL and 15mL)*
- 5.2.8 Disposable watch glass
- 5.2.9 Filter Mate, PTFE certified filter and plunger*

*Lot numbers for these items shall be tracked on the preparation sheets

5.3 Standards (equivalents are acceptable):

- 5.3.1 Stock standards:
 - 10 µg/mL Hg standard (Perkin Elmer Cat# PLHG2-1AY)
 - 100 µg/mL multi-element calibration standard 2 that contains As, Cd, Pb, and Se (Perkin Elmer Cat# N9301721)
 - 20 µg/mL secondary source standard (SPEX CertiPrep Cat# CL-CAL-1)
 - 100 ppb secondary source Hg standard (Inorganic Ventures Cat# IV-STOCK-72-125ML)
- 5.3.2 Internal standard – 1,000 ppm (Perkin Elmer Environmental Internal Standard Mix Cat# N9307808 and N9307738)
- 5.3.3 Tuning solution - 1 µg/mL that contains Be, Ce, Fe, In, Li, Mg, Pb, and U (Perkin Elmer NexION Setup Solution Cat# N8145051)
- 5.3.4 Gold standard – 100 µg/mL (SPEX CertiPrep Cat# CLAU1-1Y) – Used for Hg analysis only.

5.4 Reagents (equivalents are acceptable):

- 5.4.1 Hydrochloric acid, ultrapure trace metal grade CAS # 7647-01-0 (Fisher # A508-P500)
- 5.4.2 Nitric acid, ultrapure trace metal grade (65%) CAS # 7697-37-2 (Fisher # A509-P212)
- 5.4.3 LCMS grade water CAS # 7732-18-5 (Fisher # W6-4)
- 5.4.4 2% nitric acid v/v instrument rinse solution prepared by mixing 80 mL concentrated HNO₃ with LCMS water to a final volume of 4L. This solution is also used as the RB and the diluent for working standards. When analyzing for Hg, 16mL of gold standard is added to this solution (final Au concentration is 400 ppb).

6 Standard/QC Preparation:

- 6.1 Stock standards are purchased as custom multi-element mixes from an ISO 17034 or ISO 17025 guide 34 accredited vendor, accompanied by a certificate of analysis. Standards are stored at room temperature.
- 6.2 Calibration standards are dilutions of stock standards and other calibration standards. Dilutions are made with the 2% nitric acid solution (see section 5.4.4). Calibration standards may be prepared at other concentrations if needed. See attached ICP-MS standard and mercury standard preparation sheets (standards for Hg analysis are prepared separately from other elements).
- 6.3 The ICV solution is prepared by diluting 0.5mL of the 20 µg/mL stock solution into 10mL of diluent prepared in 5.4.4. This intermediate solution is further diluted by adding 0.25mL in 50mL of diluent prepared in 5.4.4.
- 6.4 The CCV is a mid-level standard used for the calibration curve and is run after every 12 samples (12 samples at most but may be run after fewer samples).
- 6.5 The IS is prepared by diluting 0.1mL of internal standard stock solution into 100mL of diluent prepared in 5.4.4.
- 6.6 A QC, RB, and MB are prepared with every set. The nitric acid solution prepared in 5.4.4 is used for the RB. The MB is 1g of H₂O that is subjected to the entire extraction process. See RA-SP-HM-EXT for details on how to prepare these items.

7. Instrument Preparation and Calibration:

- 7.1 At instrument start up, verify the outlet gas pressure for air is 60 psi and 80-100 psi for argon.
- 7.2 Verify the chiller is holding the temperature at 18°C and ~60 psi of pressure.
- 7.3 Empty the instrument waste container if needed.
- 7.4 Inspect torch, injector, skimmer and samples cones, and nebulizer for clogs and cleanliness. If any show signs of build-up or staining, remove and follow the cleaning procedure outlined in section 11.1.
- 7.5 Verify the solution flows freely through the nebulizer and the sample capillary is clean and in good condition.
- 7.6 Inspect pump rollers to ensure they are clean and move freely.

- 7.7 Inspect the sample pump tubing and sample capillary tubing to ensure it is clean, is in good condition, and is correctly installed around the pump head. The sample (yellow/orange) and IS tubing (yellow/green) should last for 10-16 hours of analysis time. The waste tubing (grey/grey) needs to be changed when notable flat spots appear or there is a reduction in rinse flow.
- 7.8 Verify the spray chamber drain is properly set up on the peristaltic pump so the waste is pumped out of the spray chamber.
- 7.9 Rinse the sample introduction system for at least 10 minutes with 2% nitric acid solution.
- 7.10 Turn on the instrument and allow the instrument to become thermally stable for at least 30 minutes before tuning. Verify the instrument is set up according to manufacturer's operating instructions.
- 7.11 Tune the instrument prior to calibration with tuning solution to verify the resolution and mass calibration are within required specifications and have reached thermal stability. Resolution at low mass is indicated by magnesium and resolution at high isotopes is indicated by lead.
- 7.12 The instrument is calibrated each day of operation using the MB and at least 5 calibration standards used to establish analytical curves.
- 7.13 Sample Analysis
 - 7.13.1 The instrument is flushed with rinse solution between samples and standards during the analytical run.
 - 7.13.2 At the end of the analysis flush system with instrument rinse solution followed by deionized water.
 - 7.13.3 The analytical sequence should follow this format to meet all quality control criteria:
 - RB
 - Calibration Standards
 - ICV
 - RB
 - MB
 - QC
 - Up to 10 samples
 - CCV
 - RB
 - Can repeat up to 10 samples followed by a CCV and RB as many times as necessary as long as instrument remains in calibration.

8. QA/QC:

- 8.1 The correlation coefficient of the curve is based on a linear regression algorithm based on the intensity counts of both the target elements and the internal standards and must be $r^2 \geq 0.990$. If the calibration fails, repeat the calibration and any sample analysis. If it fails a second time, investigate, prepare the standards again and recalibrate.
- 8.2 The ICV recovery shall be 90-110%. It can be reanalyzed twice but must be successful twice in succession. If it fails, recalibrate and repeat the analysis. If it fails, investigate and prepare a fresh ICV standard, recalibrate, and repeat the analysis.
- 8.3 The QC recovery shall be within 3 standard deviations of the certified value for AAFCO and Magruder samples. For spiked matrix, recovery shall be within 20%. If the QC fails it is re-injected. If it is still outside the acceptable range, the set is re-extracted.
- 8.4 QC recoveries shall be control charted and monitored for trends.
- 8.5 Any analytes detected in the RB or MB shall be below the reporting limit. If not, there is a contamination problem that must be resolved before continuing.
- 8.6 The CCV recovery shall be 85-115%. If it fails, the analysis can be repeated. If it fails again, the instrument must be recalibrated, and samples re-analyzed.
- 8.7 The intensities of all internal standards are monitored in every sample and shall be 70-130%. If the intensities are outside this range, dilute and reanalyze the sample.
- 8.8 If the concentration of any element in the sample exceeds the highest standard, dilute the sample and reanalyze.
- 8.9 Samples are analyzed 3 times in succession by the instrument. The %RSD of the 3 analyses shall be $\leq 10\%$
- 8.10 The reporting limits are:

As	1 PPM
Cd	1 PPM
Hg	Refer to validation
Pb	3 PPM
Se	Refer to validation

9. Uncertainty:

The main sources of uncertainty are sample homogeneity, a physical interference such as matrix, viscosity, and/or surface tension, and issues with the sample introduction system

(sample probe, tubes, spray chamber, torch, and injector). Other, minor sources of uncertainty stem from sample preparation (weighing, acid digestion, filtration, dilution, and final volume), reagent (hydrochloric and nitric acids), and chemical/spectral interferences.

10. Calculations:

Sample Concentration (final concentration) is calculated as follows:

$$\text{Sample Conc.} = \frac{C \times V \times D}{W}$$

Where C = Concentration from instrument read out
D = Dilution factor (if applicable)
V = Final volume (mL) after sample digested and brought to volume
W = Initial weight of sample (grams)

ICV Percent recoveries are calculated as follows:

$$\text{ICV} = \frac{\text{ICV recovery ppb} \times 100}{\text{ICV theoretical ppb}}$$

CCV Percent recoveries are calculated as follows:

$$\text{CCV} = \frac{\text{CCV recovery ppb} \times 100}{\text{CCV theoretical ppb}}$$

11. Instrument Maintenance:

- 11.1 Soak the torch and injector in 5% HNO₃ for at least 4 hours or overnight to remove deposits. Rinse with deionized water and dry thoroughly using clean air or nitrogen. Never touch the torch (quartz) with bare hands.
- 11.2 Soak the nebulizer in 5% HNO₃ or *aqua regia* for at least 4 hours. If deposits persist, increase the acid concentration up to 20%. Rinse with deionized water and dry thoroughly using clean air or nitrogen. Do not clean the nebulizer using sonication or a wire as they may damage it.

12. Preventive Maintenance:

- 12.1 On a weekly basis (when system is in use), inspect the torch, glassware, and injector. The glassware should be clean and dry with no traces of deposits or signs of melting.

- 12.2 Clean the torch and injector annually (see section 11.1)
- 12.3 Clean the nebulizer every 6 months (see section 11.2).
- 12.4 Replace cones annually.

13. References:

- 13.1 United States Environment Protection Agency. Inductively Coupled Plasma-Atomic Emission Spectroscopy - Method 6010C, SW846. Test Methods for Evaluating Solid Waste.
<https://www.epa.gov/sites/production/files/2015-07/documents/epa-6010c.pdf>
- 13.2 AOAC Official Method 2017.02 Arsenic, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Selenium, and Zinc in Fertilizers.
- 13.3 ICP-MS Operator Manual

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