National Human Exposure Assessment Survey (NHEXAS)

Maryland Study

Quality Systems and Implementation Plan for Human Exposure Assessment

Emory University
Atlanta, GA 30322

Cooperative Agreement CR 822038

Standard Operating Procedure   **NHX/SOP-L08**

Title: Analysis of Metals by ICP-MS

Source: Harvard University/Johns Hopkins University

U.S. Environmental Protection Agency
Office of Research and Development
Human Exposure & Atmospheric Sciences Division
Human Exposure Research Branch

1.   Title of Standard Operating Procedure

      Harvard University/Johns Hopkins University Standard Operating Procedures:
      **L08   Analysis of Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS),
      Rev. 1.0**

2.   Overview and Purpose

      This standard operating procedure (SOP) describes the analysis of metals by inductively coupled
      plasma-mass spectrometry (ICP-MS) in environmental samples, namely air filters, soil, dermal
      wipes, and dust by vacuum. The analysis will be carried out in the Trace Metals Laboratory at
      Emory University. These samples will be digested and extracted at Emory according to the
      procedure outlined in SOP L06 "Extraction of Metals from Sampling Media."

3.   Discussion

      The extracted samples will be analyzed primarily by Graphite Furnace Atomic Absorption
      Spectrometry (GF-AAS), as described in HSPH SOP L07 "Analysis of Metals by Graphite
      Furnace Atomic Absorption Spectrometry (GF-AAS)," but ICP-MS will be used for confirmatory
      analysis. These techniques are the only options because they are well-tested, have the required
      sensitivity for examining the toxic metals of interest in NHEXAS, and are available at the Trace
      Metals Laboratory at Emory. The choice of analytical method will depend on whether more than
      one metal will be analyzed, and on which method provides more favorable limit of detection,
      sensitivity, and accuracy. Given that arsenic (As) cannot be analyzed by ICP-MS (due to
      interferences by species forming with the carrier gas, argon), As must be analyzed by AAS.

      This procedure details the preparation, operation, calibration, and maintenance of the ICP-MS
      instrument for the analysis of metals. Reference to the appropriate manuals is made in the various
      sections below.

4.   Personnel Responsibilities

      4.1   Sample Collection

             The collection of samples will be the responsibility of the Field Technician and Field
             Coordination Center staff.

      4.2   Sample Shipment

             Laboratory personnel will be responsible for receiving and documenting the arrival of
             samples to the laboratory on the chain-of-custody form.

      4.3   Sample Extraction

             The digestion and extraction of samples is the responsibility of laboratory personnel, as
             described in HSPH SOP L06 "Extraction of Metals from Sampling Media." Laboratory
             personnel will be responsible for following all safety regulations at all times.

      4.4   Analysis

Analytical laboratory personnel at HSPH will be responsible for all aspects of the analysis of extraction and digestion products of the air filter, soil, dust, and dermal wipe samples. Laboratory personnel are required to adhere to strict quality assurance and quality control procedures, as well as to all safety regulations at all times.

5.   Required Equipment and Reagents

   5.1   Equipment

   Perkin Elmer Sciex ELAN 5000 Inductively Coupled Plasma-Mass Spectrometer
   exhaust vent for ICP-MS
   personal computer to operate instrument with the XENIX Operating System, the ELAN
        5000 Instrument software, and printer
   refrigerated recirculating water cooler

   5.2   Reagents

   liquid argon tank
   high-purity water (Milli-Q or equivalent)
   concentrated nitric acid, trace metal grade
   standard reference material, NIST 1643c (Trace Elements in Water)
   standard stock solutions of the elements of interest using certified primary standards

6.   Instrument Maintenance

   6.1   General

   Certain of the components of the ICP-MS instrument must be checked prior to operation of the instrument. The following sections identify the maintenance steps required, and their recommended frequency. The detailed procedures are in Chapter 3 of the Perkin Elmer *Reference Manual;* the relevant pages are mentioned in the appropriate sections below.

   The Trace Metals Laboratory has a routine maintenance service contract with Perkin Elmer to check optical, mechanical, electronic, and pneumatic systems.

   6.2   Daily

   Sample Waste Container Level: Check the level of the waste solution in the container, and dispose of properly.

   Quartz Torch: Visually check the torch condition and measure for proper alignment (*Reference Manual*, p. 3-7 and p. 3-16).

   Spray Chamber and Nebulizer: check for cleanliness, physical damage, and leaks (*Reference Manual*, p. 3-8 to 3-10).
   Rotary Vane (roughing) Pump Oil: Visually check the condition and level of the oil.

   6.3   Weekly

Rotary Vane (roughing) Pump Oil: Drain the mist eliminator (*Reference Manual*, p. 3-57 to 3-59).

Peristaltic Pump: Visually inspect for acceptable roller pressure, condition of the sample introduction tubing, correct pump rotation, and condition of the drain tubing (*Reference Manual*, p. 3-10 to 3-12).

Sampler and Skimmer Cones: Visually check the condition of each cone for cleanliness and proper orifice size, weekly or as necessary (*Reference Manual*, p. 3-47 to 3-51).

Sensitivity: Check weekly or as necessary (*Reference Manual*, p. 3-13 to 3-14).

6.4   Monthly

Filters: Check and clean to ensure that the fans provide the proper operating temperature (*Reference Manual*, p. 3-52 to 3-53).

Water Filter: Check to make sure that the proper water circulation occurs throughout the instrument (*Reference Manual*, p. 3-54 to 3-56).

Power and Gas Flows: Check that these are properly set (*Reference Manual,* p. 3-16 to 3-18).

6.5   Every Three Months

Rotary Vane (roughing) Pump Oil: Change the pump oil (*Reference Manual*, p. 3-57 to 3-59).

6.6   As Necessary

Pre-optimization Test: Check the resolution, mass calibration, and ion optics settings (*Reference Manual*, p. 3-18 to 3-38).

CEM and Deflector Voltage: Check and adjust each to the proper voltage (*Reference Manual*, p. 3-39 to 3-46).

6.7   Annually

Change the oil every 9,000 hours or once a year (*Reference Manual*, p.3-61 to 3-62).

7.   Procedure

   7.1   Instrument Start-Up

      Ø   Check the waste container.

      Ø   Check the liquid argon level in the tank.

      Ø   Connect the tubing to the peristaltic pump. Make sure that the tubing lies within the upper and lower channels on the clips.

      Ø   Place the sample tube(s) into a solution of high-purity water.

      Ø   Turn on the pump.

      Ø   Note the base vacuum pressure in the User Logbook.

      Ø   Make sure that the plasma chamber is closed and locked.

      Ø   Press the "Power ON/OFF" button to ignite the plasma. The power button will flash and then remain on when the plasma ignites. The plasma chamber will become open to the vacuum. You will be able to observe the valve lifting open. Also, the four gas switches located next to the channel selector will light up. The radio frequency power indicator, located next to the power button, will go from a 0000 reading to a 1000 reading.

      Ø   Check the small orange framed window to observe the plasma. It should have a dull blue core and bright blue edges.

      Ø   Turn on the computer and screen.

      Ø   Wait about two hours for the instrument to warm up.

   7.2   Instrument Optimization

Setting	Recommended Value
Sample Flow Rate	1.5 mL/min
Plasma Argon Flow Rate	15.0 L/min
Nebulizer Flow Rate	1.100 L/min
Auxiliary Flow Rate	0.8 L/min
Plasma Power	1000 watts forward
Lens Settings	Lens P = 42 Lens B = 50 Lens E1 = 25 Lens S2 = 42

7.3   Calibration

The instrument must be calibrated with appropriate standards at the appropriate concentration ranges, using an external standards calibration. A minimum of four standards in addition to the calibration blank is required.

7.4   Sample Analysis

7.4.1   Instrument Set-Up

In preparation for sample analysis, set up a "Data-Set File" within the instrument's operational software program. This file identifies the sample's sequence number and the sample identification code. Name the file (by sample batch identification code) in which the generated data will be stored.

7.4.2   Sample Run

Begin the analysis by identifying the Data-Set File to be analyzed.

7.4.3   Data Output

Immediately following the analysis of a sample, a print-out of the concentrations of the various elements analyzed is generated. The print-out includes the mean, standard deviation, and relative standard deviation percent (RSD%) of the replicate concentrations. The data are stored under the filename chosen in section 7.4.1.

7.5   Analytical Report

After analyzing each batch of samples, the Laboratory Technician will prepare an Analytical Report. Submit it to the Laboratory Supervisor and retain a hard copy as well as magnetic media. The report will contain the following information:

Ø Laboratory Technician's name, date of analysis, sample batch ID code, and instrument used
Ø statement that the samples were logged in properly and validated, and that the ID numbers of samples analyzed are in the table with the results
Ø elements for which the samples were analyzed
Ø procedure used (reference relevant SOPs)
Ø any deviations from standard procedure, and how they might have affected the results
Ø final results (in tabular form) arranged by ID number of sample

8.   Quality Assurance Procedures

8.1   Calibration Blank

A system blank is first obtained with the sampling pump off. Subsequently, a calibration blank is run. It consists of the appropriate acid diluted in high-purity (typically 5% HNO_3). The blank is analyzed at the beginning of the calibration process, and prior to the analysis of

the first sample to ensure that it has a low concentration.

8.2   Calibration

Due to possible variations in the instrument from day to day, a new calibration curve is produced each day. The calibration curve must consist of a minimum of four standards; a 0 µg/L standard must be included, and one blank. To be acceptable, the correlation coefficient, R^2, must be ³ 0.999.

8.3   Standard Reference Material

To verify that the instrument is calibrated properly, immediately after calibration an aqueous SRM is analyzed (Trace Elements in Water SRM 1643c, from NIST, the National Institute of Standards and Technology). Analysis of samples proceeds only if the SRM's concentration is within the given concentration range. If not, recalibration will be necessary. To ensure that the instrument continues to operate properly throughout the analysis, the aqueous SRM is analyzed every 10 samples, and also after the last sample.

8.4   Replicate Analysis

The mass spectrometer spends a certain amount of time at each mass spectral peak (dwell time), before moving to the next mass peak. Multiple sweeps are used so that each mass peak is measured several times to increase confidence in the measurement. Only one reading is required for each repeat measurement (replicate) (*Users Manual,* p. 3-17). The instrument will be set with an optimal dwell time of 500 ms, each reading will consist of five sweeps, and three replicate measurements will be made. This will apply for all standards and samples. The relative standard deviation percent (RSD%), which is defined as follows, is calculated for each set of replicates:

$$RSD\% = [SD/mean] ´ 100 \quad \text{(where SD is the standard deviation)}$$

RSD% will be examined for each set of replicates. Those with RSD% ³ 5% are unacceptable. Such samples will be re-analyzed until the RSD% is acceptable; usually one re-analysis is sufficient.   RSD% is a function of the absolute element concentration: samples with low concentrations will have more error associated with them. Thus, poorer precision is expected for samples with very low element concentrations. Hence, the ³ 5% rejection criterion will not apply to blanks.

8.5   Tolerance Limits and Detection Limits

The tolerance limits for the method will be determined as 3´ the standard deviation of 15 or more repeated analyses of a standard reference material (see Section 8.3 above).

The detection limits for ICP-MS are as follows (in µg/L): cadmium 0.003, chromium 0.02, and lead 0.001 (Perkin Elmer, September 1991). The exact detection limits for our instrument will be determined, though they are expected to be similar to the above-mentioned levels.

8.6   Records

A record of all maintenance performed will be kept in a Maintenance Logbook.

An instrument logbook will be maintained in the following format.

Date	Analyst	Matrix	Element Analyzed	Blank Absorbance	Lamp Energy	Calibration Curve Obtained	Comment Code

All documentation, including raw data, sample identification, and sample preparation will be kept in the study records.

All raw analysis and all raw data results will be kept in print-out form as well as on disk.

9.   Safety

Analysts are instructed to follow all safety regulations at all times.

The *Reference Manual* (Chapter 1) details various safety measures with regard to the following parameters: hazards, ultraviolet radiation, high voltages, radio frequency radiation, toxicity, high temperature, handling of gases, drain vessels, exhaust venting requirements, chemical reagents inside the instrument, waste disposal, and sample handling.

10. References

Harvard University/Johns Hopkins University Standard Operating Procedures:
L06 Extraction of Metals from Sampling Media
L07 Analysis of Metals by Graphite Furnace Atomic Absorption Spectrometry (GF-AAS)

Perkin Elmer. *ELAN 5000 Inductively Coupled Plasma-Mass Spectrometer: Reference Manual,* May 1992.

Perkin Elmer. *ELAN 5000 Inductively Coupled Plasma-Mass Spectrometer: Users Manual.*

Perkin Elmer. *The Guide to Techniques and Applications of Atomic Spectroscopy: AA, GFAA, ICP, ICP-MS,* September 1991.

U.S. EPA. "Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry", *Methods for the Determination of Metals in Environmental Samples.* Office of Research and Development, EPA/600/4-91/010. June 1991.