

# 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-L07**

**Title:** Analysis of Metals by GF-AAS

**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

**Notice:** The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), partially funded and collaborated in the research described here. This protocol is part of the Quality Systems Implementation Plan (QSIP) that was reviewed by the EPA and approved for use in this demonstration/scoping study. Mention of trade names or commercial products does not constitute endorsement or recommendation by EPA for use.

1 Title of Standard Operating Procedure

Harvard University/Johns Hopkins University Standard Operating Procedures:  
**L07 Analysis of Metals by Graphite Furnace-Atomic Absorption Spectrometry  
(GF-AAS), Rev. 1.0**

2 Overview and Purpose

This standard operating procedure (SOP) describes the preparation, operation, calibration, and maintenance of the graphite furnace-atomic absorption spectrometry (GF-AAS) instrument for the analysis of metals in environmental samples: namely air filters, dermal wipes, soil, and dust by vacuum. The analysis will be carried out in the Trace Metals Laboratory at the Harvard School of Public Health (HSPH). These samples will be digested and extracted at HSPH according to the procedure outlined in HSPH SOP L06 "Extraction of Metals from Sampling Media."

3 Discussion

Extracted samples may be analyzed by GF-AAS or by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), as described in HSPH SOP L08 "Analysis of Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)." 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 HSPH. For the NHEXAS samples, GF-AAS is the first choice and ICP-MS the backup method.

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. Direct analysis, with the use of a matrix modifier, e.g., palladium (Xiao-Quan et al.) to eliminate interferences, will be the method of choice. For substantiation as needed, it may be analyzed by gaseous hydride generation (arsine), for example using sodium tetrahydroborate.

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, documenting, and verifying the arrival of every sample to the laboratory, using chain-of-custody forms and database software.

4.3 Sample Extraction

The digestion and extraction of samples are 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 Model 4100 ZL Atomic Absorption Spectrometer  
Perkin Elmer Zeeman-THGA Furnace System  
Perkin Elmer Model AS-70 Autosampler  
graphite tubes with L'vov platforms  
hollow cathode lamps for the elements of interest (As, Cd, Cr, Pb)  
dedicated personal computer to operate instrument, with Perkin Elmer operational software  
and database software for sample tracking and records  
2-mL polystyrene or polyethylene sample cups and caps  
glassware for preparation of standards and spikes  
autopipettes for transferring liquids  
swabs for cleaning furnace

### 5.2 Reagents

argon gas, ultra-high-purity  
ultra-high-purity water, >18 MΩ, e.g., Milli-Q or Nanopure  
concentrated nitric acid, trace metal grade  
standard reference material, NIST 1643c (Trace Elements in Water)  
standard stock solutions for the elements of interest using certified primary standards

## 6 Instrument Maintenance

### 6.1 General

Certain components of the AAS instrument must be checked prior to operation. The following is a summary of the maintenance and checks, with detailed procedures given in Chapter 4 of the *Model 4100ZL Atomic Absorption Spectrometer: Instrument Manual* (the relevant sections of the manual are referred to below).

The Trace Metals Laboratory will have a routine maintenance service contract with Perkin Elmer to check optical, mechanical, electronic, and pneumatic systems annually following the expiration of the warranty (December 1995).

Follow all general laboratory safety guidelines, as well as specific procedures for working with the AAS.

For safety reasons, and to avoid contaminating new samples, ensure that the spectrometer, and the work area in general, are kept absolutely clean. Wipe up any spillages immediately before they cause further contamination. This is especially important when working with toxic

substances, and when measuring trace amounts of any elements. The GF-AAS instrument is located on a separate bench from the sample preparation area and the laboratory hood.

## 6.2 Weekly

Furnace: Check the condition of the contact cylinders, and replace them when necessary (*Instrument Manual*, Section 4.3.2).

## 6.3 Monthly

Spectrometer: Check the air filter on the first working day of each month. If it is dirty, change it (*Instrument Manual*, Section 4.6.3).

Furnace: Check the absorbance of the furnace windows (*Instrument Manual*, Section 4.3.4). The inherent absorbance of the window is between 0.07 and 0.1 (max.) absorbance unit. The absorbance must be measured (1) with the furnace removed from the atomizing compartment, then (2) with the furnace replaced in the atomizing compartment.

If the net absorbance is more than 0.1, remove the windows and check them visually. Clean with lens paper as needed.

If the windows are not clean after this procedure, run the condition program twice, then run the furnace twice without any acid or blank.

# 7 Procedure

## 7.1 Instrument Preparation

(to be done every day, or at the beginning of each shift if there is more than one shift in a day)

### 7.1.1 Turn on Purge Gas

Open the valve of the tank of high purity argon.  
Check the gauge to be sure that the pressure is 52 psi.

### 7.1.2 Start Computer

Run internal diagnostics. Open the windows that will be needed. No more than five windows may be open at a time. Windows most used include Align Lamps, Display Data, Display Calibration, Display Peaks, Furnace Control, and AS-70 Control.

### 7.1.3 Check Autosampler and Cooling System

Check the autosampler waste bottle before each startup and occasionally during the run. Never allow it to overflow, or allow the liquid to reach the end of the drain tube. If it contains hazardous, toxic, or flammable substances, dispose of the waste properly, according to safety regulations.

Check the autosampler tubing and connections (*Instrument Manual*, Section 4.5.1).

Cooling System: Check the water level in the closed circle water cooling system, and fill it when necessary (*Instrument Manual*, Section 4.7.1).

Keep the rinsing liquid bottle filled with ultra-high-purity water. Check it before and occasionally during each usage.

### 7.1.4 Align the Lamps

Align the lamp and optimize the lamp energy (*User's Manual*, p. 2-9 to 2-11).

### 7.1.5 Furnace and Graphite Tube

The purpose of this step is to remove adsorbed gases and surface contamination from the graphite to ensure reproducible performance.

Open the Furnace Control window on the computer. Check the integrity of the graphite tube; there should be no pitting or buildup (*Instrument Manual*, Section 4.3.1).

If the graphite tube is pitted or contaminated, install a new tube and condition it (*User's Manual*, p. 2-12 to p.2-15).

Before each use, blow out any particles from the narrow sections of the graphite contact cylinders. Use a jet of clean air or inert gas, such as a commercial air blower containing compressed air (*Instrument Manual*, Section 4.3.2). Use swabs and ultra-high-purity water to remove particles from surfaces.

Perform a dry run on the graphite furnace and tube to ensure its integrity and determine that the absorbance is  $< 0.005$ . If it is higher, check the fume extraction unit components (*Instrument Manual*, Section 4.4). Look at the furnace windows to be sure they are clean.

**Caution:** Never directly view the graphite furnace when it is heated to incandescence without wearing UV-absorbing eye protection. It may emit potentially hazardous UV radiation.

Exhaust hood: Check its operation. Make sure that the damper is open.

#### 7.1.4 Align the Autosampler Arm

The sampling arm must be aligned to ensure that the tip of the sampling capillary enters the sample injection hole of the graphite tube without striking the edges of the hole, or any inside surface of the graphite tube, and that it does not strike the bottom of the sample cup when it dips into the solution.

Check this alignment before the start of every analysis run, and also every time the furnace is opened and the graphite tube or contact cylinders are changed (*User's Manual*, p. 2-16 to 2-25).

To check that the tip enters the graphite tube properly: Choose "Sampler Standby" on the computer. Move the shutter to block the light. Adjust the mirror at the right of the graphite tube so that you see a circle of light. When the tip enters the tube you should see it in the circle.

### 7.2 Instrument Start-Up

For each element, check the "Element Parameter" window on the computer. Use the manufacturer's recommended default settings for parameters such as slit width, wavelength, integration time, peak height/area, etc. Optimize the settings for each specific analysis. Set the number of replicates to 3.

### 7.3 Calibration

In the "Element Parameter" window on the computer, choose the "Calibration" window. Check or set the calibration concentrations for the appropriate standards. Five standards in addition to the calibration blank are required.

### 7.4 Sample Analysis

#### 7.4.1 Sample Dilution

Based on prior knowledge of the expected concentration level of the element of interest in the sample matrix being analyzed, carry out serial dilution(s) as appropriate such that the concentration falls within the calibration range (using 2% HNO<sub>3</sub> as the diluent). A volume of 1 to 2 mL as the final volume will be sufficient. Use labeled sample cups for the dilution(s).

#### 7.4.2 Instrument Set-Up

In preparation for sample analysis, set up an "ID/Weight File" within the instrument's operational software program. This file identifies the sample location on the Autosampler's sample tray with a sample identification code.

Name the file (by sample batch identification code) in which the generated data will be stored. Batch ID codes include the date and a letter to indicate the sequence of the batch, e.g. 951025-A. This is a separate system from sample ID numbers, which indicate the matrix, Cycle, etc.

#### 7.4.3 Sample Run

Once the ID/Weight file has been generated, named, and saved, the analysis is ready to begin. Begin the analysis by identifying the ID/Weight file to be analyzed.

#### 7.4.4 Data Output

Immediately following the analysis of a sample, a printout of the sample absorption and calculated concentration is generated. After the sample replicates have been analyzed, the printout includes the mean, standard deviation, and relative standard deviation percent (RSD%) of the replicate concentrations. The data are also stored under the filename chosen in section 7.4.2.

Check the logbook for any sample that must be re-run with a different dilution. Find the sample ID number on the list and write a note on the printout.

### 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:

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

## 8 Quality Assurance Procedures

### 8.1 Calibration Blank

The calibration blank consists of the appropriate acid diluted in high-purity water (typically 2% HNO<sub>3</sub>). 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.

If the concentration is high, the operator will prepare and run another blank. If it is still high, the operator will check the water purity and instrumental parameters such as graphite tubes and contact rings.

### 8.2 Calibration

Due to possible variations in the instrument from day to day, a new calibration curve is produced at least once each day. The calibration curve must consist of five standards and one blank. To be acceptable, the correlation coefficient,  $R^2$ , must be  $\geq 0.995$ .

Each standard should be checked in random order during the course of each run (in addition to SRM) so that each has a frequency of ~10%.

### 8.3 Standard Reference Material (SRM)

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 after every 10 samples, and also after the last sample.

### 8.4 Replicate Analysis

All standards will be analyzed in triplicate, and all samples in replicate. Triplicates and replicates will be consecutive "sips" from the same sample solution. The relative standard deviation percent (RSD%), which is defined as follows, is calculated for each set of replicates:

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

RSD% will be examined for each set of replicates. Those with  $\text{RSD\%} \geq 15\%$  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 readings at the low end of the calibration curve range where there is more error associated with the measurements. Thus, poorer precision is expected for samples with very low element concentrations. Hence, the  $\geq 15\%$  rejection criterion will not apply to blanks.



## 8.5 Tolerance Limits and Detection Limits

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

According to the U.S. EPA (1983), the detection limits for the GF-AAS method are as follows: arsenic (gaseous hydride method) 1 µg/L, cadmium 0.1 µg/L, chromium 1 µg/L, and lead 1 µg/L. The exact detection limits for our instrument will be determined, and 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 log will be maintained as a computer database, as follows:

Date	Analyst	Matrix: A = air D = dust G = gauze S = soil O = other	# Firings (run/total)	Lamp Energy	Length of Run (hrs: min)	Absorbance				Com- ment Code
						40 ppb Pb	40 ppb As	10 ppb Cd	30 ppb Cr	

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

All raw analyses and all raw data results will be kept in printout form as well as on disk.

## 1 Safety

Analysts are cautioned not to look directly into the hollow cathode lamps or the graphite furnace for any continued period of time, particularly during the atomization step.

The *Instrument Manual* details various safety measures with regard to the following parameters: magnetic field, electricity, UV radiation, exhaust venting, high temperatures, compressed gases, and general chemical safety considerations.

## 2 References

Harvard University/Johns Hopkins University Standard Operating Procedures:

L03 Operation of an Ultra-High Purity Water System

L06 Extraction of Metals from Sampling Media

L08 Analysis of Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Perkin Elmer. *AS-90 Autosampler for Atomic Spectroscopy: Operator's Manual*.

Perkin Elmer. *Model 4100ZL Atomic Absorption Spectrometer: Instrument Manual*, Release 2.1, Sept. 1992.

Perkin Elmer. *Model 4100ZL Atomic Absorption Spectrometer: User's Manual*.

Perkin Elmer. *The THGA Graphite Furnace: Techniques and Recommended Conditions*.

U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. Environmental Monitoring and Support Laboratory, EPA-600/4-79-020. March 1983.

U.S. EPA. "Method 200.9: Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry," *Methods for the Determination of Metals in Environmental Samples*. Office of Research and Development, EPA/600/4-91/010. June 1991.

Xiao-Quan, Shan, Ni Zhe-Ming, and Zhang Li. "Determination of Arsenic in Soil, Coal Fly Ash and Biological Samples by Electrothermal Atomic Absorption Spectrometry with Matrix Modification." *Analytica Chimica Acta*, 151:179-185 (1983).