

National Human Exposure Assessment Survey (NHEXAS)

Arizona Study

Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona
Tucson, Arizona 85721

Cooperative Agreement CR 821560

Standard Operating Procedure

SOP-BCO-L-6.0

Title: Operation Calibration and Maintenance of the Perkin-Elmer
Zeeman/5000 System Atomic Absorption Spectrophotometer

Source: The University of Arizona

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.

**Operation, Calibration, and Maintenance of the
Perkin-Elmer Zeeman/5000 System
Atomic Absorption Spectrophotometer**

1.0 Purpose and Applicability

- 1.1 This standard operating procedure (SOP) outlines the start-up, calibration, operation, and maintenance procedures for the Perkin Elmer 5000 atomic absorption spectrophotometer (PE 5000 AA), and the Perkin Elmer 5000 Zeeman graphite furnace atomic absorption spectrophotometer (PE 5000Z GFAA).
- 1.2 These procedures are used for the determination of the trace target metals As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Se, V, and Zn in soil, house dust, filter, and surface and dermal wipe sample digestates, prepared as specified in SOP BCO-L-3.0, "Extraction of Metals from Soil, Dust, Air Filter, and Surface and Dermal Wipe Samples for AA (Graphite Furnace GFAA or Flame FAA) or ICP-AES Analysis."

2.0 Definitions

- 2.1 Method Blank - all reagents (and a blank filter or wipe, when appropriate) carried through the same digestion procedure as the samples.
- 2.2 Method Detection Limit (MDL) - that concentration of a given element which produces a signal three times the standard deviation of the method blank signal.
- 2.3 Method of Standard Additions (MSA) - a method for mathematically compensating for chemical interferences in a given sample.
- 2.4 Post-Digestion Spike (PDS) - a known amount of a given element spiked into an already digested sample solution. The volume of the spiking solution must not exceed 10% of the volume of the sample it is being added to.
- 2.5 Relative Percent Difference (RPD) - the absolute value of the difference of the concentration values of two replicate injections from one sample, as expressed as a percentage of their mean.
- 2.6 Zero Standard - a solution acidified similarly to the digested samples and other calibration solutions. This solution is not spiked with any analytes, nor digested.

- 2.7 Initial Calibration Verification (ICV): standard used to determine whether an instrument is calibrated to within a preset limit ($\pm 15\%$).
- 2.8 Continuous Calibration Verification (CCV): analytical standard run every 10 to 20 samples to verify that the instrument is calibrated to within a preset limit ($\pm 15\%$).

3.0 References

- 3.1 "Model 5000 Atomic Absorption Spectrophotometer," Perkin Elmer Operator's Manual, Rev. April 1979.
- 3.2 "Analytical Methods for Atomic Absorption Spectrophotometry," Perkin Elmer Publication, PE No. 0303-0152, January 1982.
- 3.3 "Zeeman 5000 System," Perkin Elmer Operator's Manual, September 1982.
- 3.4 "Analytical Methods for Furnace Atomic Absorption Spectroscopy," Perkin Elmer Publication, Rev. February 1980.
- 3.5 "Analytical Methods Using the HGA Graphite Furnace," Perkin Elmer Publication, March 1977.
- 3.6 "HGA 500 Graphite Furnace," Perkin Elmer Operator's Manual, March 1977.
- 3.7 "AS-40 Autosampler," Perkin Elmer Operator's Manual, 1978.
- 3.8 "Graphite Furnace AAS: A Source Book," Walter Slavin, PE No. 0993-8139, 1984.
- 3.9 "Series 7000 Professional Computer User's Manuals 1 and 2," for 7300 data station, Rev. October 1984.
- 3.10 "Atomic Absorption Spectroscopy," W. Slavin, Interscience Publishers, New York, NY, 1968.
- 3.11 "Standard Practice for Measurement of Metals in Workplace Atmosphere by Atomic Absorption Spectrophotometry," Standard D 4185, American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 11.03, 1990.
- 3.12 "Sample Analysis by Graphite Furnace Atomic Absorption (GFAA)," Section 4.5, Exhibit D, US EPA Contract Laboratory Program Statement of Work for Analysis of Ambient Air (AA), Rev. IAIR01.2, October 1993.

- 3.13 "Standard Specification for Reagent Water," Standard D 1193, American Society for Testing and Materials, Annual Book of ASTM Standards, Vol. 11.01, 11.03, 1991.

4.0 Discussion

- 4.1 For GFAA, a representative aliquot of a sample, together with an (optional) aliquot of element-specific matrix modifier, is placed in the furnace. Matrix modifier solutions are used to help control spectral and chemical interferences. A 5 μL aliquot is a typical sample injection volume that is injected automatically by the instrument. Injection of the modifier is performed after the sample injection, with $\% \text{ Modifier} = \text{mg} \times 100 / \mu\text{L}$. An analyst-specified, computer-controlled furnace program is run to dry, char, and atomize the sample. For FAA, samples are aspirated into the appropriate flame (nitrous oxide/acetylene or air/acetylene).
- 4.2 Radiation from a given excited atom is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor. The volatilized metal atoms to be measured are placed in the beam of radiation. A monochromator isolates the characteristic radiation from the hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL), and a photosensitive device measures the attenuated transmitted radiation.
- 4.3 Although analysis using GFAA can be more time-consuming than other techniques, GFAA offers lower method detection limits for many elements.
- 4.4 In FAA and GFAA, the occurrence of interferences is less common than in many other analytical techniques. Spectral interferences are extremely rare for both of these techniques. However, chemical interferences occur in FAA and GFAA when species present in the sample cause variations in the degree to which atoms are formed in the flame or furnace, or when different valence states of a single element have different absorption characteristics. Such interferences may be controlled by adjusting the sample matrix, or by the method of standard additions (MSA).
- 4.5 Background or nonspecific absorption can occur from particles produced in the flame or furnace, which can scatter light and produce an apparent absorption signal. Therefore, zero standards will be regularly analyzed and sample results will be corrected accordingly.

5.0 Responsibilities

- 5.1 The sampling and shipping will be performed by University of Arizona personnel, according to SOPs UA-F-8.0 and UA-F-9.0. The extractions and analyses will be performed within the Atmospheric Sciences and Applied Technology Department at Battelle.
- 5.2 Samples will be logged into Battelle upon receipt from Arizona by the Sample Custodian. The Sample Custodian will document the date the sample is retrieved by Battelle personnel for subsequent digestion.
- 5.3 Sample digestion will be carried out and recorded in the inorganic NHEXAS laboratory record book (LRB) by the inorganic sample preparation technician. The inorganic sample preparation technician is responsible for delivering sample and any related QA digestates to the analyst, together with a photocopy of the LRB page on which any sample weights or other pertinent information was recorded.
- 5.4 The analyst is responsible for calculating zero standard and method blank corrected target metals content for all samples, field blanks, and QA samples. Dust and soil metals concentrations will be reported as micrograms of metal per gram of dust/soil ($\mu\text{g/g}$). Wipe and filter metals concentrations will be reported as micrograms (μg) per sample.
- 5.5 The Project Laboratory Director is responsible for data review and submission of reviewed results to the Data Coordinator.
- 5.6 Should this SOP require revision, all changes must be reviewed and approved by the Project Laboratory Director prior to their adoption into practice.
- 5.7 After changes have been reviewed and admitted by the Project Laboratory Director, the SOP must be revised and reissued under the proper revision number.

6.0 Materials and Equipment

6.1 Materials

- 6.1.1 Perkin-Elmer/Zeeman Model 5000 Atomic Absorption Spectrophotometer.
- 6.1.2 Model HGA-500 graphite furnace control programmer.

- 6.1.3 Model AS-40 autosampler.
- 6.1.4 Model 7300 data station with HGA 3.0 software and printer.
- 6.1.5 Perkin-Elmer Pyrocoated graphite tubes and platforms.
- 6.1.6 Nitrous oxide/acetylene burner head.
- 6.1.7 Air/acetylene burner head.
- 6.1.8 High purity nitrogen, air, nitrous oxide, and acetylene gases.
- 6.1.9 Ten 100 mL Class A volumetric flasks, used to prepare calibration standards.
- 6.1.10 Eppendorf air displaced adjustable volume pipetters, 5-100 μ L, 100-1,000 μ L, 1,000-5,000 μ L, 5,000-10,000 μ L.
- 6.1.11 Target element EDLs or HCLs

6.2 Reagents

- 6.2.1 Concentrated nitric acid (HNO_3), trace metals analysis grade, or equivalent.
- 6.2.2 Concentrated hydrochloric acid (HCl), trace metals analysis grade or equivalent
- 6.2.3 Commercially-available single element stock solutions (1,000 and 10,000 $\mu\text{g/mL}$), traceable to NIST, J.T. Baker, or equivalent.
- 6.2.4 ASTM Type II water (ASTM D 1193).

7.0 Procedures

7.1 Safety

- 7.1.1 FAA units are potentially explosive if the nitrous oxide/acetylene flame is operated incorrectly. Personnel will not operate any FAA unit until the manufacturer's instruction manual has been read and understood. Additionally, all personnel must follow safety requirements pertaining to the handling, storage, and use of compressed gases.

- 7.1.2 Analysts are cautioned by the manufacturer of the EDL and HCL lamps to not look directly into them for an extended period of time.
- 7.1.3 Instrument exhaust gases contain the combustion products of the flame or furnace, and metal vapor from the sample, which are definite personnel hazards. Therefore instrument exhaust gases shall be mechanically vented from the laboratory.
- 7.1.4 Refer to the Operator's Manuals for more details.

7.2 Perkin Elmer 5000 AA Start-up Procedure

- 7.2.1 The spectrophotometer should already be on, and in stand-by mode. Switch from stand-by to run mode.
- 7.2.2 Table 1 lists the standard conditions for the FAA analysis of target elements. These settings may be optimized for each sample matrix.
- 7.2.3 Select the appropriate burner head and key in the appropriate gas flows. For an air-acetylene flame, set air flow at ~20 L/min, and acetylene flow at ~5 L/min. For a nitrous oxide-acetylene flame, set nitrous oxide flow at ~20 L/min, and acetylene flow at ~15 L/min.
- 7.2.4 If using an EDL, turn on the EDL power supply, and adjust power output to the specifications listed on the label of the lamp. Otherwise, key in the appropriate current setting for the HCL according to the specifications listed on the lamp's label.
- 7.2.5 Select and mount the appropriate burner head.
- 7.2.6 Press the SET-UP key. The main display will indicate a value of approximately 50 units. As the lamp warms up, the display value will change. When the value reaches 99 units, press the GAIN key to re-set the value to 50. This step may need to be performed several times before the alignment stabilizes. When the alignment is stable, press SET-UP to exit.
- 7.2.7 Switch on the automatic gas control system. Fuel and oxidant default values will appear. Enter the appropriate gas values for the selected element.
- 7.2.8 Close the door to the burner compartment and press the FLAME ON key. Aspirate a standard that gives an absorbance of approximately 0.2

absorbance units. Adjust the horizontal and rotational adjustment knobs until a maximum absorbance is obtained.

7.2.9 Aspirate a blank and press the AUTO ZERO key.

7.2.10 The instrument is ready for calibration.

7.3 Perkin Elmer 5000Z GFAAS Start-up Procedure.

7.3.1 Switch the spectrophotometer from stand-by mode to run mode

7.3.2 Table 2 lists the basic recommended settings for GFAA analysis of the target elements. These settings may be optimized for each sample matrix.

7.3.3 Refer to section 7.1 for lamp selection and handling.

7.3.4 Make sure there is Type II ASTM water in the autosampler's water supply bottle, and empty the waste bottle if necessary. Turn on the Perkin Elmer AS-40 autosampler.

7.3.5 Key in sample and modifier volumes.

7.3.6 The Perkin Elmer HGA 500 furnace controller should be on. Take the HGA 500 out of stand-by mode by pressing the standby button on its front panel.

7.3.7 Key the preliminary furnace program into the HGA 500, using the pretreatment and atomization temperatures listed in Table 2 as guides. Examples of, and guidelines for, furnace programs can be found in Refs. 3.5 and 3.8.

7.3.8 Turn on the water flow at a rate of roughly 3 L/min.

7.3.9 Turn on the purge gas, usually argon, at a pressure of roughly 40 psig. Flow rate is controlled via the HGA 500, and will vary from 0 to 300 mL/min. Substitute gases may be used, e.g., a mixture of 95% argon, 5% oxygen, according to the analytical demands of the sample matrix.

7.3.10 Install and condition the graphite tube according to the manufacturer's recommendations. (NOTE: To avoid eye damage, analyst should not look at the graphite furnace when it is operating at high temperatures, i.e., > 900°C).

7.3.11 Boot the HGA software on the Perkin Elmer 7300 data station.

7.4 Calibration of the PE 5000 AAS and PE 5000Z GFAAS

7.4.1 Prepare the appropriate number of calibration solutions for the PE 5000 flame and GFAAS analyses by diluting stock solutions to give the expected linear range of the samples. The concentrations of the standards should evenly span the concentration range of interest.

7.4.2 For flame calibration, enter the concentration of standard 1, then press S1.

7.4.2.1 Enter the concentration values for standards 2 and 3 in a similar manner.

7.4.2.2 Aspirate a blank solution and press AUTO ZERO.

7.4.2.3 Aspirate standard 1 and press S1. Standard 1 is complete when its associated light remains lit.

7.4.2.4 Aspirate standards 2 and 3 in a similar manner to complete the calibration.

7.4.3 For graphite furnace calibration, first place the calibration standards in order of increasing concentration in the AS-40 autosampler.

7.4.3.1 Each standard is robotically injected into the graphite furnace.

7.4.3.2 The identification of each sample is manually entered via the computer terminal.

7.4.3.3 Peak areas for each calibration standard and for the samples are printed out automatically.

7.4.4 Perform a linear regression on the data to relate the concentrations of the calibration standards to their respective peak areas. A linear regression calculation must yield a correlation coefficient greater than 0.995, otherwise the calibration must be repeated.

7.4.5 Once the calibration curve has been established, an initial calibration verification (ICV) solution must be analyzed. The ICV must be prepared from stock(s) other than those used to prepare the calibration solutions, and is usually prepared at a concentration roughly in the mid-range of the

calibration curve. The percent recovery of the ICV solution must be within 85 - 115% for the analyst to proceed with the quantification of samples.

7.5 Sample Analysis

- 7.5.1 For flame analysis, samples are analyzed by manually aspirating a given sample and pressing the READ key. Analysis values are displayed on the screen.
 - 7.5.1.1 Arrange samples in groups of five to ten. Samples can be analyzed chronologically or randomly. Each group is followed by a calibration standard and a blank.
 - 7.5.1.2 If a sample requires dilution, dilute the sample with deionized water fortified with the appropriate acid concentration. Record the sample dilution and analyze the sample.
 - 7.5.1.3 Manually record the concentration values in the analysis logbook. The analysis logbook contains: the sample identification, dilution if required, final concentration, analysis date, and the element analyzed. The analyst also documents instrument conditions such as the lamp used and its gain setting, the date, and the type of flame used.
- 7.5.2 For graphite furnace analysis, aliquot a portion of sample into a sample cup located in the autosampler. Identify each cup location and the corresponding sample in that location. Manually enter the sample identification code via the terminal.
 - 7.5.2.1 Arrange samples in groups of five to ten. Samples can be analyzed chronologically or randomly. Each group is followed by a calibration standard and a blank.
 - 7.5.2.2 If a sample requires dilution, dilute the sample with deionized water fortified with the appropriate acid concentration. Record the sample dilution and analyze the sample.
 - 7.5.2.3 Analysis values are displayed on the screen. Manually enter peak areas into a computer-based spreadsheet. The analysis logbook contains: the sample identification, dilution if required, final concentration, analysis date, and the element analyzed.

7.6 Maintenance

- 7.6.1 For FAA, the burners must be cleaned with a mild detergent and a soft cloth prior to each day's analyses. The nebulizer systems must be cleaned by aspirating deionized water for ~5 min at the end of the day's analyses.
- 7.6.2 For GFAA, most residual substances in the graphite tube, platform, and contact cylinders can be removed by burning out, or by carefully passing either a pipe cleaner or cotton swab through the tube.
- 7.6.3 The graphite tube and contact cylinders should be checked and cleaned periodically to make sure good contact is being made. If there is any sign of pitting or any sign of excessive wear or contamination, the tubes, platform, or cylinders should be cleaned or replaced.
- 7.6.4 The furnace quartz windows should be checked and cleaned periodically with a soft cloth and alcohol.
- 7.6.5 The AS-40 Autosampler requires little maintenance other than to keep it clean and free of dust. The waste bottle, wash reservoir, sampling capillary, pump, valves, and gasket kit should be checked regularly. If they have become damaged or show signs of deterioration, the parts should be replaced.
- 7.6.6 If non-routine maintenance or service is needed, the Project Laboratory Director or Perkin Elmer will be contacted for further instructions.

7.7 General Considerations

- 7.7.1 All samples must initially be run undiluted (i.e., final product of the sample preparation procedure). When an analyte concentration exceeds the calibrated linear range, reanalysis for that analyte(s) is required after the appropriate dilution. All sample dilutions shall be made with deionized water (ASTM Type II) appropriately acidified to maintain acid content and strength.
- 7.7.2 Laboratory glassware to be used in preparing metals solutions must be cleaned according to SOP BCO-L-10.0. Stock solutions to be used for preparing instrument or method calibration standards may be purchased from an outside vendor.
- 7.7.3 Pipette guns used to prepare calibration solutions must be calibrated according to SOP BCO-L-9.0.

7.8 Calculations

7.8.1 The initial calibration curve is expressed as:

$$y = mx + b$$

where y = peak area of the response; x = concentration of the target analyte in the calibration solution; m = slope of the linear regression; and b = intercept.

7.8.2 Once the regression is performed (through the use of a calculator or computer program), the concentration of the target analyte x is found from:

$$x = (y - b) / m$$

7.8.3 Bracketing is expressed similarly, with only a two-point calibration curve. However, the standard concentrations must bracket the unknown's concentration tightly. If the unknown has a concentration of x , then the upper standard concentration must be no greater than $2x$, and the lower standard concentration must be no less than $0.5x$.

7.8.4 For MSA, take three identical volumes from a sample. Spike the first portion with a volume of Zero Standard less than 2% of the volume of the sample. Designate this as the zero spike. Spike the second portion with the same volume of a solution containing a known amount of the target element. Designate this as the 50% spike. Spike the third portion with the same volume of a solution containing twice the known amount of the target element used for the second portion. Designate this as the 100% spike. All spike solutions must be acidified to the same acid content and concentration as the sample being analyzed. Measure the absorbances of the solutions (duplicate injections for the zero spike only). Consider the concentration of the zero spike to be zero, and perform a linear regression on the peak area of the response (y -axis) versus the metal concentrations of the spiked solutions (x -axis):

$$y = m'x + b'$$

where y = peak area of the response; x = metal concentrations of the spiked solutions; m' = slope of the linear regression; and b' = intercept.

The metal concentration in the sample C_{sam} is expressed as:

$$C_{sam} = |b'|$$

- 7.8.5 The RPD between duplicate injections from the same sample is expressed as:

$$RPD = (|C_1 - C_2|) / [(C_1 + C_2)/2]$$

where C_1 = concentration of target element in injection 1; C_2 = concentration of target element in injection 2.

- 7.8.6 Percent recovery in a PDS sample is expressed as:

$$\text{Recovery (\%)} = [(C_{spk+sam} - C_{sam})/C_{spk}] \times 100$$

where $C_{spk+sam}$ = concentration of target element in the spiked sample; C_{sam} = concentration of target element in the sample; C_{spk} = concentration of the target element spike.

- 7.8.7 Percent recovery of the ICV and/or CCV is expressed as:

$$\text{Recovery (\%)} = [(C_{meas} - C_{zs})/C_{known}] \times 100$$

where C_{meas} = concentration of the target analyte measured for ICV or CCV; C_{zs} = concentration of the target analyte in the zero standard; C_{known} = known concentration of the target analyte in the ICV or CCV.

- 7.8.8 MDL is expressed as:

$$MDL = 3 \times SD_{MB}$$

where SD_{MB} = standard deviation of the measured concentrations of the method blank for that analytical set.

- 7.8.9 Calculation of the metal concentration ($\mu\text{g/g}$) for soil and dust is expressed as:

$$C_{S/D} = [(C_{Metal} - C_{ZS}) - (C_{MB} - C_{ZS})] \times [V_1 / D] \times (V_2 / V_3)$$

where $C_{S/D}$ = concentration of metal ($\mu\text{g/g}$) in soil or dust; C_{metal} = concentration of metal ($\mu\text{g/mL}$), calculated using a calibration curve, bracketing, or MSA; C_{ZS} = concentration of the zero standard ($\mu\text{g/mL}$), calculated using a calibration curve; C_{MB} = concentration of the method

blank ($\mu\text{g/mL}$), calculated using a calibration curve, bracketing, or MSA; V_1 = volume (mL) of the digestate after the sample preparation procedure (100 mL), as described in SOP BCO-L-3.0; D = dry weight of soil; V_2 = (valid only if sample is diluted further), final volume of diluted digestate; V_3 = (valid only if sample is diluted further), volume of the aliquot taken from the digestate. (NOTE: the measurement units of V_2 and V_3 must be the same.)

7.8.10 Calculation of metal concentration (μg) for filter or wipe samples is expressed as:

$$C_{F/W} = [(C_{\text{Metal}} - C_{\text{ZS}}) - (C_{\text{MB}} - C_{\text{ZS}})] \times V_1 \times (V_2 / V_3)$$

where $C_{F/W}$ = concentration of metal (μg) in filter or wipe sample; C_{metal} = concentration of metal ($\mu\text{g/mL}$), calculated using a calibration curve, bracketing, or MSA; C_{ZS} = concentration of the zero standard ($\mu\text{g/mL}$), calculated using a calibration curve; C_{MB} = concentration of the method blank ($\mu\text{g/mL}$), calculated using a calibration curve, bracketing, or MSA; V_1 = volume (mL) of the digestate after the sample preparation procedure (100 mL), as described in SOP BCO-L-3.0; V_2 = (valid only if sample is diluted further), final volume of diluted digestate; V_3 = (valid only if sample is diluted further), volume of the aliquot taken from the digestate. (NOTE: the measurement units of V_2 and V_3 must be the same.)

7.9 Quality Control

7.9.1 Controls, Blanks, and Duplicates

- 7.9.1.1 The correlation coefficient for the initial calibration curve must be greater than 0.995 for the analyst to proceed with the quantification of samples.
- 7.9.1.2 The percent recovery of the ICV must be within 15% of the true value (85-115%) for the analyst to proceed with the quantification of samples.
- 7.9.1.3 If the analyst is using aqueous or matrix-matched standards to quantify samples, a continuing calibration verification solution (CCV) must be analyzed at a rate of no less than one every 15 samples. The percent recovery of the CCV must be within 15% of its true value (85 - 115%) for the analyst to continue quantifying samples. The CCV solution must also be at a

concentration level commensurate with the response levels evidenced by the samples being analyzed.

- 7.9.1.4 PDS samples will be analyzed at a rate of no less than one every fifteen samples to determine possible chemical interferences in the samples. PDS recoveries must be between 85 - 115% for the analyst to continue quantifying the samples without using MSA, or diluting the matrix in order to alleviate chemical interferences.
- 7.9.1.5 If the analyst is using MSA to quantify samples, the unspiked sample solution requires two replicate injections, which will be averaged, the two spiked sample solutions require only one apiece. The correlation coefficient for the linear regression of the added analyte versus measured absorbance must be >0.995 for the analyst to report results using MSA. If the correlation coefficient is <0.995 , the MSA must be repeated until a correlation coefficient of >0.995 is achieved.
- 7.9.1.6 All FAA and GFAA sample measurements require a minimum of two replicate injections. When the concentration of a sample is greater than five times the MDL, the RPD between duplicate injections of the same sample must be less than 50%; otherwise the injections must be repeated.
- 7.9.1.7 Zero standards and method blanks will be analyzed no less than three times each for each analytical run; and sample results will be corrected accordingly.
- 7.9.1.8 The MDL will be calculated from the method blank results obtained for that analytical run date, and reported for that day's analytical data set. Sample results below the MDL will be marked "<MDL".

7.9.2 Precision, Bias, and Detection Limits

- 7.9.2.1 Precision and bias are largely dependent upon the precision and bias of the digestion and the analytical procedure for each target compound, and the precision and bias of the sampling process.
- 7.9.2.2 When the errors involving the determination of digestion efficiency and analysis are combined, a relative precision of $\pm 30\%$ is indicated.

7.9.2.3 Estimated method detection limits for the target elements are presented in Tables 3 and 4.

8.0 Records

- 8.1 Computer data files containing the raw data, and any data workup will be archived on floppy disks.
- 8.2 Hard copies of raw data and any data workup will be kept in study folders marked with the name of the computer file containing the raw data and the analysis date.
- 8.3 Instrument operating conditions, such as the lamp used and its gain setting, the analysis date, the type of flame used, and the sample set identification code will be recorded in the analyst's laboratory record book.
- 8.4 Routine and/or non-routine maintenance will be recorded in the instrument maintenance log with the date, signature/initials of the person responsible.
- 8.5 Records of pipette gun calibration will be recorded in the pipette gun record book.
- 8.6 Electrical resistivity (megohms-cm, 25 °C) of all Type II water stations will be recorded with daily use in the deionized water stations log books.
- 8.7 Records of glassware acid bath maintenance will be recorded in the acid bath record book.

Table 1. Standard Conditions for Analysis of Target Elements Using FAA*.

Element	Wavelength (nm)	Slit (nm)	Flame Gases
As	193.7	0.7	Air-Acetylene
Ba	553.6	0.4	Nitrous oxide-Acetylene
Cd	228.8	0.7	Air-Acetylene
Cr	357.9	0.7	Air-Acetylene
Cu	324.8	0.7	Air-Acetylene
Mn	279.5	0.2	Air-Acetylene
Ni	232.0	0.2	Air-Acetylene
Pb	283.3	0.7	Air-Acetylene
Se	196.0	2.0	Air-Acetylene
V	318.4	0.7	Nitrous oxide-Acetylene
Zn	213.9	0.7	Air-Acetylene

* Ref. 3.2

Table 2. Recommended Settings for Analysis of Target Elements Using GFAA*.

Element	Wave-length (nm)	Slit	Modifier	Pretreatment (°C)	Atomization (°C)
As	193.7	0.7	0.02 mg Ni	1300	2300
Ba	553.6	0.4	--	1200	2550
Cd	228.8	0.7	0.2 mg PO ₄ + 0.05 mg Mg(NO ₃) ₂	900	1600
Cr	357.9	0.7	0.05 mg Mg(NO ₃) ₂	1650	2500
Cu	324.8	0.7	--	1000	2300
Mn	279.5	0.2	0.05 mg Mg(NO ₃) ₂	1400	2200
Ni	232.0	0.2	--	1400	2500
Pb	283.3	0.7	0.2 mg PO ₄ + 0.05 mg Mg(NO ₃) ₂	850	1800
Se	196.0	2.0	0.02 mg Ni + 0.05 mg Mg(NO ₃) ₂	900	2100
V	318.4	0.7	0.05 mg Mg(NO ₃) ₂	1100	2650
Zn	213.9	0.7	0.006 mg Mg(NO ₃) ₂	700	1800

* Ref. 3.4

Table 3. Estimated FAA Method Detection Limits.*

Element	Wavelength (nm)	Estimated Method Detection Limit (mg)
As	193.7	0.10
Ba	553.6	0.046
Cd	228.8	0.003
Cr	357.9	0.008
Cu	324.8	0.008
Mn	279.5	0.005
Ni	232.0	0.014
Pb	283.3	0.045
Se	196.0	0.059
V	318.4	0.19
Zn	213.9	0.005

* For soluble target elements in soil, dust, air filter, and surface and dermal wipe samples, extracted according to SOP BCO-L-3.0, "Extraction of Metals from Soil, Dust, Air Filter, and Surface and Dermal Wipe Samples for AA (Graphite Furnace or Flame) or ICP-AES."

Table 4. Estimated GFAA Method Detection Limits.*

Element	Wavelength (nm)	Estimated Method Detection Limit
		(µg/sample)
As	193.7	0.3
Ba	553.6	1.5
Cd	228.8	0.08
Cr	357.9	0.08
Cu	324.8	0.1
Mn	279.5	0.5
Ni	232.0	2.9
Pb	283.3	0.54
Se	196.0	0.57
V	318.4	9.0
Zn	213.9	0.08

* For soluble target elements in soil, dust, air filter, and surface and dermal wipe samples, extracted according to SOP BCO-L-3.0, "Extraction of Metals from Soil, Dust, Air Filter, and Surface and Dermal Wipe Samples for AA (Graphite Furnace or Flame) or ICP-AES."