



# STANDARD OPERATING PROCEDURES

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## DETERMINATION OF METALS BY GRAPHITE FURNACE ATOMIC ABSORPTION (GFAA) (EPA/SW-846 Methods 3015/7000A/7421/7740/7841/7060A)

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#### 1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) is based on Environmental Protection Agency (EPA) Methods SW-846/3015, 7000A, 7421, 7740, 7841 and 7060A and those requirements set forth in the latest approved version of the National Environmental Laboratory Accreditation Committee (NELAC) Quality Systems section. This method is applicable for the GFAA analysis of arsenic (As), lead (Pb), selenium (Se) and thallium (Tl) in waters.

Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrophotometers. The data shown in Table 1, Appendix A provide some indication of calibration ranges and detection limits obtainable by furnace techniques. For certain samples, lower concentrations may also be determined. The detection limits in Table 1, Appendix A are typically those achieved using the instrumentation at the Response Engineering and Analytical Contract (REAC) facility. When using furnace techniques, chemical reactions may occur at elevated temperatures, which may result in either suppression or enhancement of the element being analyzed. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (Section 4.0) and, if detected, treat them accordingly, using successive dilution and/or matrix modification (Section 9.0).

This method may not be changed without the expressed approval of the Inorganic Group Leader, the Analytical Section Leader and the Quality Assurance Officer (QAO). Only those versions issued through the REAC document control system may be used. Modifications made to the procedure due to interferences in the samples or for any other reason must be documented in the case narrative and on a nonconformance memo.

#### 2.0 METHOD SUMMARY

A representative 45-milliliter (mL) aqueous sample is digested in 5 mL of concentrated nitric acid (HNO<sub>3</sub>) in a Teflon® digestion vessel using microwave heating. After the digestion process, the sample is cooled, and then filtered or allowed to settle in a clean sample bottle prior to analysis.

When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is injected into the graphite tube in the furnace, evaporated to dryness, charred, and atomized. A greater percentage of available analyte atoms is vaporized and dissociated for absorption in the tube rather than the flame; therefore, smaller sample volumes may be used and detection of lower concentrations is possible. The principle is essentially the same as with direct aspiration atomic absorption, except that a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element 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 metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected sample to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

#### 3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Sample holding times, suggested collection amounts, preservative, and type of containers are as follows:



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Measurement	Collection Amount Required	Containers	Type of Preservative	Holding Time
<u>Metals</u>				
Total Available	1000 mL	P, G	HNO <sub>3</sub> to pH < 2	6 months
Dissolved	1000 mL	P, G	Filter on site HNO <sub>3</sub> to pH < 2	6 months

P - plastic, G - glass, mL - milliliters

#### 4.0 INTERFERENCES AND POTENTIAL PROBLEMS

During the microwave process, many samples that contain organics will result in higher vessel pressures that have the potential to cause venting of the digestion vessels. This can result in loss of analytes and/or sample. A smaller volume of sample diluted to 45 mL may be used but the dilution must be taken into account during the final calculation of analyte concentration.

Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects that must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, the serial dilution test (Section 9.8) may be used. Samples that indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.
2. Modify the sample matrix either to remove interferences or to stabilize the analyte.

Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

Continuum background correction cannot correct for all types of background interference. When the background interference cannot be corrected, chemically remove the analyte or use an alternate background correction technique (e.g., Zeeman background correction).

Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. This will minimize broad-band absorption.



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Anion interference studies in the graphite furnace indicate that, under conditions other than isothermal, the nitrate anion is preferred. Therefore, nitric acid should be used for any digestion or solubilization step. If another acid in addition to  $\text{HNO}_3$  is required, a minimum amount should be used. This applies particularly to hydrochloric and to a lesser extent to sulfuric and phosphoric acids.

Carbide formation resulting from the chemical environment of the furnace has been observed. When carbides form, the metal is released very slowly from the metal carbide as atomization continues. Additional atomization time may be required before the signal returns to baseline levels. Carbide formation is greatly reduced and the sensitivity increased with the use of pyrolytically coated graphite.

Spectral interference can occur when an absorbing wavelength of another element present in the sample falls within the width of the absorption line of the element of interest. Results will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp or an impurity in the lamp cathode falls within the bandpass of the slit setting for the element of interest, provided the other element is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. Pyrolytic graphite tubes can be contaminated by the production process and handling. Five to 10 high-temperature burns may be required to clean the tubes before use.

#### 5.0 EQUIPMENT/APPARATUS

- Atomic Absorption Spectrophotometer, single- or dual-channel, single-or double-beam instrument having a grating monochromator, photomultiplier detector, Zeeman background correction, adjustable slits, a wavelength range of 190 to 800 nanometers (nm), and provisions for simultaneous background correction and interfacing with a suitable recording device and autosampler.
- Hollow Cathode Lamps or Ultra AA Superlamps, single-element lamps are preferred but multielement lamps may be used. Electrodeless discharge lamps may also be used and provide better sensitivity for some elements.
- Graphite Furnace, capable of reaching the specified temperatures
- Data Acquisition System, Strip-Chart Recorder, Integrator, or Printer, capable of providing a permanent record. Any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, peak shape, etc., will be easily recognized.
- Microwave Digestion System, with temperature control and rotating turntable, well ventilated with corrosion-resistant cavity
- Microwave digestion vessels, Teflon, capable of holding ~75 milliliters (mL), designed for temperatures up to  $260^\circ\text{C}$  with self-regulating pressure control
- Glass dispensers, 2-liter (L), 1-L, 1-gallon, checked quarterly for accuracy



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- Graduated Cylinder, Class A, 50 mL
- Volumetric flasks, Class A, assorted volumes
- Electronic Variable Volume Autopipettors, BIOHIT 500-5000 microliters ( $\mu\text{L}$ ) and BIOHIT 100-1000  $\mu\text{L}$  or equivalent
- Balance, top-loading, capable of reading to 0.01 grams (g), for weighing digestion vessels before and after digestion
- Pyrolytically Coated Graphite Tubes, commercially available, with platforms, as required
- Henke SASS plastic syringes or equivalent
- Corning SCFA 0.45 microns ( $\mu\text{m}$ ) filters or equivalent

#### 6.0 REAGENTS

- Deionized (DI) water, Type I Water (American Society for Testing and Materials [ASTM] D1193), for the preparation of all reagents and calibration standards and as dilution water
- Nitric acid, concentrated, trace metal grade
- Nitric Acid, 10 percent (%) volume to volume (v/v), for the preparation of working standards, also to be used for the Initial Calibration Blank/Continuing Calibration Blank (ICB/CCB)
- Gases, commercially available argon or nitrogen
- Stock Calibration Standards, 1000 milligrams per liter (mg/L), commercially available, accompanied by a certificate of analysis

NOTE: Stock standard solutions may also be prepared from high purity metals, oxides, or nonhygroscopic reagent-grade salts using DI water and redistilled  $\text{HNO}_3$  (see individual methods for specific instructions). Sulfuric, hydrochloric or phosphoric acids should be avoided as they produce an adverse effect on many elements.

- Intermediate Calibration Standard, 10 mg/L - Dilute 1 mL of the stock calibration standard to 100 mL in a Class A volumetric flask with 10% nitric acid.
- Intermediate Calibration Standard, 1.0 mg/L - Dilute 10 mL of the 10 mg/L intermediate calibration standard to 100 mL in a Class A volumetric flask with 10% nitric acid
- Working Calibration Standard, 25 micrograms per liter ( $\mu\text{g/L}$ ) - Dilute 2.5 mL of the 1.0 mg/L intermediate calibration standard to 100 mL in a Class A volumetric flask with 10% nitric acid.
- Stock Initial Calibration Verification/Continuing Calibration Verification Standard (ICV/CCV), 1000



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mg/L, commercially available, accompanied by a certificate of analysis, source independent of calibration

- Intermediate ICV/CCV Standard, 10 mg/L - Dilute 1 mL of the stock ICV/CCV standard to 100 mL in a Class A volumetric flask with 10% nitric acid.
- Intermediate ICV/CCV Standard, 1.0 mg/L - Dilute 10 mL of the 10 mg/L intermediate ICV/CCV standard to 100 mL in a Class A volumetric flask with 10% nitric acid.
- Working ICV/CCV Standard, 15 µg/L - Dilute 1.5 mL of the 1.0 mg/L intermediate ICV/CCV standard to 100 mL in a Class A volumetric flask with 10% nitric acid.
- Laboratory Control Sample (LCS), 15 µg/L ICV/CCV standard, prepared and digested with each batch of samples
- Stock Spiking Solution, 1000 mg/L, commercially available, accompanied by a certificate of analysis, for As, Pb, Se and Tl.
- Intermediate Spiking Solution, 5.0 mg/L - Dilute 0.5 mL of the 1000 mg/L stock spiking solution to 100 mL in a Class A volumetric flask using 10% nitric acid.
- Modifiers, commercially available or prepared as follows:

Nickel Nitrate Solution (1%): Dissolve 1.0 g of ACS grade  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or equivalent in Type I water and dilute to 100 mL.

Phosphoric Acid Solution (1%): Add 1.0 mL concentrated  $\text{H}_3\text{PO}_4$  in Type I water and dilute to 100 mL.

Sulfuric Acid Solution (1%): Add 1.0 mL concentrated  $\text{H}_2\text{SO}_4$  in Type I water and dilute to 100 mL.

Palladium Chloride/Citric Acid Solution: Add 2.0 mL of 5%  $\text{PdCl}_2$  solution, 2.0 g citric acid (or equivalent) and dilute to 100 mL with Type I water.

**NOTE:** Premixed certified standards will be stored according to the manufacturer's documented storage requirements. These standards may be kept in storage up to the manufacturer's stated expiration date. Once dilutions are made, the standards will be stored for a period not to exceed six months or the manufacturer's expiration date, whichever is less.

**NOTE:** All calibration standards and spiking solutions will be prepared and documented in accordance with REAC SOP #1012, *Preparation of Standard Solutions and Reagents*.

**NOTE:** Stock concentrations may vary depending on the vendor; thus, the concentration of intermediate standards may also vary. Preparation instructions may differ based on the volumes prepared and the concentrations of standards available. The final working standard concentrations will remain as stated in the above section.



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#### 7.0 PROCEDURES

##### 7.1 Glassware Preparation

All glassware or Teflon® containers should be cleaned using the following sequence: detergent, tap water, 1:1 nitric acid, tap water and Type I water. If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure. Sample bottles are rinsed prior to use with 1:1 nitric acid followed by Type I DI water.

##### 7.2 Water Sample Digestion

1. Weigh the empty digestion vessel, valve and cap to 0.01 g . Record the weight on the sample digestion log.
2. Check the pH of the aqueous sample to ensure that the pH is <2. Record the pH on the sample digestion log. Adjust the sample pH to <2 with additional HNO<sub>3</sub> if the pH is not <2. Do not add more than 1% of the total volume of sample. Note the volume of HNO<sub>3</sub> added on the sample digestion log. A nonconformance memo must be written if the pH is greater than or equal to 2.0 prior to adjustment.
3. Measure 45 mL of a well mixed sample in a Class A graduated cylinder. Transfer the sample to a digestion vessel and mark the digestion vessel with the sample number.
4. Measure 45 mL of DI water in a Class A graduated cylinder and transfer to a digestion vessel. Mark the digestion vessel as the method blank. One method blank must be prepared for each analytical batch not to exceed 20 samples.
5. Measure 45 mL of the 15 ug/L LCS in a Class A graduated cylinder and transfer to a digestion vessel. Mark the digestion vessel as the LCS. One LCS must be prepared for each analytical batch not to exceed 20 samples.
6. Measure two separate well-mixed 45-mL portions of the sample chosen for the MS/MSD in a Class A graduated cylinder. Transfer these portions of samples to separate digestion vessels, add 0.5 mL of the 5 mg/L intermediate spiking solution to each and mark the digestion vessels as the MS and MSD. At least one MS/MSD must be digested with every 10 samples or per project.
7. Add 5 mL of concentrated HNO<sub>3</sub> to each vessel. Check to make sure that the pressure relief disks are in the caps and hand tighten the caps on the vessels. Weigh each digestion vessel and record the weight on the sample digestion log.
8. Evenly distribute the vessels in the carousel according to the manufacturer's instructions. When fewer than the recommended number of vessels are digested, be sure to include additional vessels with the same volume of DI water and concentrated HNO<sub>3</sub> as the samples.





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9. Program the microwave digestion unit according to the manufacturer's recommended specifications to bring the samples to  $160 \pm 4$  degrees Centigrade ( $^{\circ}\text{C}$ ) in 10 minutes and will rise slowly to between 165 and  $170^{\circ}\text{C}$  in the second 10 minutes. Power settings may be adjusted as long as they result in the same time and temperature conditions.
10. At the end of the digestion, allow the digestion vessels to cool for a short period of time in the microwave and then on the bench or in a water bath. Once the vessels are cool, weigh and record the weight of each digestion vessel assembly. If the weight has decreased more than 10%, discard the sample.
11. Uncap and vent each vessel in a fume hood and transfer the sample to an acid-cleaned sample bottle. If the digested sample contains particulates, filter prior to GFAA analysis using the plastic syringes and the  $0.45 \mu\text{m}$  filters, or equivalent.
12. Correct the concentration values from analysis by a dilution factor of 1.11 (45 mL sample + 5 mL of acid/45 mL of original sample)

#### 7.3 Operating Conditions

Furnace devices (flameless atomization) are most useful for extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the instrument manufacturer. Typical GFAA operating conditions are listed in Table 2, Appendix A.

#### 7.4 Calibration

For best results, calibration standards should be prepared fresh each time a batch of samples is analyzed. Standards may also be used until their expiration date (maximum 6 months) provided there is no loss in sensitivity. Using the GFAA program, aliquot 0 microliters ( $\mu\text{L}$ ), 2  $\mu\text{L}$ , 4  $\mu\text{L}$ , 8  $\mu\text{L}$ , 16  $\mu\text{L}$  and 20  $\mu\text{L}$  to obtain working standards of 0  $\mu\text{g/L}$ , 2.5  $\mu\text{g/L}$ , 5  $\mu\text{g/L}$ , 10  $\mu\text{g/L}$ , 20  $\mu\text{g/L}$  and 25  $\mu\text{g/L}$ .

Beginning with the blank and working toward the highest standard, analyze the calibration standards. Inject the calibration standards two times to secure an average reading for each calibration standard. The average of each standard's response is used to generate the calibration curve using linear regression. The percent relative standard deviation (%RSD) should be  $<20\%$  excluding the zero point.

#### 7.5 Analytical Sequence

Using the following sequence, analyze each sample, quality control (QC) sample and QC standard (e.g. ICV) using two replicate measurements for each sample to secure an average reading for each standard or sample:

1. Immediately following calibration, analyze the 15  $\mu\text{g/L}$  ICV standard. The percent recovery



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must be within  $\pm 10\%$ .

2. Immediately following the ICV, analyze the ICB. The concentration must be less than ( $<$ ) the reporting limit (RL). The RL is set at the lowest standard from the calibration curve (i.e.,  $2.5 \mu\text{g/L}$ ).
3. Immediately following the ICB, analyze the method blank, LCS and up to eight additional digested samples for a total of 10 samples.
4. Analyze the CCV after every 20 sample injections or approximately every 10 samples, and at the end of the analytical sequence.
5. Analyze the CCB immediately following the CCV and at the end of the analytical sequence.
6. If the concentration found is greater than the highest standard, dilute the sample in the same acid matrix and reanalyze. Refer to Section 9.9.
7. To verify the absence of interference, follow the serial dilution analysis procedure in Section 9.8. The sample chosen for the MS/MSD is typically run for the serial dilution analysis; however, another sample may be chosen if the concentration in the undiluted sample is not at least 25 times the instrument detection limit (IDL).

#### 8.0 CALCULATIONS

##### 8.1 Sample Concentration

For determination of metal concentration in liquid samples by furnace, read the metal concentration in  $\mu\text{g/L}$  from the calibration curve or directly from the read-out system of the instrument.

If sample dilution was performed:

$$\mu\text{g/L metal in sample} = A \frac{C + B}{C}$$

where:

A =  $\mu\text{g/L}$  of metal in diluted aliquot from calibration curve  
B = Acid blank matrix used for dilution, mL  
C = Sample aliquot, mL

##### 8.2 Laboratory Control Sample

Percent recovery (%R) must be within 75-125% and calculated as:



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$$\%R = \frac{(LCS - B)}{SA} \times 100$$

where:

LCS = LCS result,  $\mu\text{g/L}$   
B = Method blank result,  $\mu\text{g/L}$   
SA = Spike added,  $\mu\text{g/L}$

#### 8.3 Matrix Spike/Matrix Spike Duplicate Sample

Spike sample percent recovery (%R) must be within 75-125% and calculated as:

$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

where:

SSR = Spiked sample result  
SR = Sample result  
SA = Spike added

The Relative Percent Difference (RPD) of matrix spike and matrix spike duplicate samples should be within  $\pm 20\%$  and calculated as:

$$RPD = \frac{(S - D)}{(S + D)/2} \times 100$$

where:

S = %R for matrix spike sample  
D = %R for matrix spike duplicate sample

#### 9.0 QUALITY CONTROL

All quality control data should be maintained and available for easy reference or inspection.

##### 9.1 Calibration Curve

A minimum correlation coefficient ( $r$ ) of 0.995 must be achieved for the calibration to be valid. If  $r$  is  $< 0.995$ , a new calibration curve must be run.

##### 9.2 Initial Calibration Verification



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The calibration curve must be verified by the analysis of an ICV standard (at or near mid-range) from an independent source. The ICV result must be within 10% of the true value for the calibration to be considered valid. If the ICV is outside QC limits, the instrument must be re-calibrated.

#### 9.3 Continuing Calibration Verification

The working standard curve must be verified by analyzing the CCV standard (at or near the mid-range) after every 20 sample injections or approximately every 10 samples. CCV results must be within  $\pm 20\%$  of the true value, or the previous ten samples must be reanalyzed.

#### 9.4 Initial/Continuing Calibration Blanks

The ICB/CCB results must be less than the reporting limit (RL) for the sequence to continue.

#### 9.5 Method Blank

A method blank using the same volume of DI water must be prepared for each analytical batch of samples not to exceed 20 samples. The method blank result must be less than the RL. A method blank containing an analyte concentration  $>RL$  may be used in instances when the sample concentrations are at least 10 times the method blank concentration.

#### 9.6 Laboratory Control Sample

The LCS must be obtained from an independent source, and must be prepared with each analytical batch of samples using the same preparation method as that employed for the samples with the frequency of one in 20 samples. The LCS sample may be either a certified reference material or DI water matrix spiked with the target analytes from an independent source at or near mid-range of the calibration. LCS results for each analyte must be within the specifications supplied by the vendor or within 75 - 125% of the true value and are calculated as in Section 8.2.

#### 9.7 Matrix Spike/Matrix Spike Duplicate

At least one MS and one MSD sample must be digested with every 10 samples, or with each project type to verify the accuracy of the method. The spike level after autosampler dilution should be within the calibration range. In the event there is not sufficient sample available in the batch to run a MS/MSD, a LCS/laboratory control sample duplicate (LCSD) must be run. Recoveries are calculated as in Section 8.3.

The Relative Percent Difference (RPD) of MS/MSD samples must be within  $\pm 20\%$  and calculated as in Section 8.3.

#### 9.8 Serial Dilution

A sample (typically the sample chosen for the MS/MSD) from each project in an analytical batch is analyzed at a 5x dilution in conjunction with the samples. The concentration in the undiluted sample must be greater than or equal to 25x the IDL to obtain a meaningful comparison. The results of the



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serial dilution are multiplied by the dilution factor and compared to the original determination (undiluted sample). Agreement within  $\pm 10\%$  between the concentrations for the undiluted sample and the diluted sample indicates the absence of matrix interferences for undiluted samples meeting the 25x IDL criteria.

Samples may also be successively diluted and analyzed to eliminate interferences. These samples will be identified as dilution samples and not as serial dilutions.

#### 9.9 Dilution Analysis

If the concentration of any analyte in any sample exceeds the calibration range, the sample must be diluted and reanalyzed. Results are reported from the lowest dilution free of any interference. If the GFAA instrument provides automatic sample dilution, manual dilution is not required for samples within the auto dilution range. Samples with concentrations too high for auto dilution must be manually diluted.

If the MS/MSD recoveries indicate potential matrix effects, select one typical sample for each analytical batch to determine if interferences are present. The concentration of the analyte should be at least 25x the IDL. Dilute the sample (minimum of 2x, maximum 5x) and reanalyze. Based on the analyst's professional judgement, report results from the diluted sample if matrix interferences are observed.

#### 9.10 Initial Demonstration of Capability

Initial proficiency in GFAA analysis must be demonstrated by each analyst initially and each time significant changes are made in the procedure or for instrumentation. Each analyst will generate precision and accuracy data using a reference standard other than the source used for calibration. Four replicates of a well-mixed reference standard is analyzed using the procedures outlined in this SOP. Calculate the average mean in  $\mu\text{g/L}$  and the standard deviation (s) in  $\mu\text{g/L}$ . The QAO will tabulate the results from all of the analysts per matrix per parameter, and calculate control limits.

#### 9.11 Method Detection Limit Studies

Method detection limit (MDL) studies will be run on an annual basis for each GFAA instrument for the water matrix to verify the minimum concentration that can be measured and reported with 99% confidence. A minimum of seven replicates will be used for the study (EPA 1984).

#### 9.12 System Troubleshooting

If the instrument will not start, check to make sure the water chiller/circulator is on, argon gas supply is on and set to the correct pressure, and the graphite tube is in good condition. The GFAA software will provide some indication of instrument trouble. If repeated attempts fail, contact the manufacturer for service.

For any QC problems during analysis, the operator should check the furnace head alignment, lamp alignment, graphite tube condition, sample injection needle, etc. and reanalyze samples.



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#### 9.13 Nonconformance Memo

A nonconformance memo will be generated any time an employee notices a deficiency suspected of being a nonconformance. This nonconformance memo will be forwarded to the Quality Assurance Officer for verification of corrective action.

#### 10.0 DATA VALIDATION

Data will be assessed by the Data Validation and Report Writing Group using the most current version of REAC SOP #1017, *Data Validation Procedure for Routine Inorganic Analysis*. However, data is considered satisfactory for submission purposes when all of the requirements listed in the method are met.

#### 11.0 HEALTH AND SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for following the chemical hygiene plan and laboratory safety program regarding the safe handling of the chemicals specified in this method.

When working with potentially hazardous materials, refer to EPA, Occupational Safety and Health Administration (OSHA) and corporate health and safety practices. More specifically, refer to REAC SOP #3013, REAC Laboratory Safety Program.

#### 12.0 REFERENCES

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1986. *Test Methods for Evaluating Solid Waste*, SW-846, 3rd ed. Methods 7421, 7740, 7481.

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1992. *Test Methods for Evaluating Solid Waste*, SW-846, 3<sup>rd</sup> ed., Method 7000A.

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1994. *Test Methods for Evaluating Solid Waste*, SW-846, 3<sup>rd</sup> ed., Method 7060A.

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. 1994. *Test Methods for Evaluating Solid Waste*, SW-846, 3<sup>rd</sup> ed., Method 3015.

Varian Analytical Instruments. *SpectrAA 220Z Operation Manual*.

Varian Analytical Instruments. *SpectrAA 880Z Operation Manual*.

National Environmental Laboratory Accreditation Committee (NELAC), *Quality Systems*, current approved version.

U.S. Environmental Protection Agency. 1984. Federal Register, 40 Code of Federal Regulations (CFR) Part 136, Appendix B, *Definition and Procedure of the Determination of the Method Detection Limit - Revision 1.11*,



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October 26, 1984.

13.0 APPENDICES

A - Tables



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APPENDIX A  
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TABLE 1. Typical GFAA Calibration Ranges and Detection Limits

ANALYTE	CALIBRATION RANGE <sup>(1)</sup> µg/L	Water <sup>(2)</sup> µg/L
		Arsenic (p)
Lead (p)	2.5 - 25	2.5
Selenium (p)	2.5 - 25	2.5
Thallium (p)	2.5 - 25	2.5

<sup>(1)</sup> Typical calibration range, which can be extended to higher or lower concentration depending on sensitivity of the analyte and linearity of the calibration.

<sup>(2)</sup> Based on sample preparation Method #3015 and Varian AA instruments.

p - Indicates the use of pyrolytic graphite with the furnace procedure.



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TABLE 2. Typical GFAA Operating Conditions

Varian SpectrAA Parameters	Element			
	Arsenic	Lead	Selenium	Thallium
Drying Stage Temp., °C	80 - 600	80 - 300	60 - 300	100 - 400
Ashing Temp., °C	1400 - 1500	700 - 800	1100 - 1200	1000 - 1200
Atomization Temp., °C	2600 - 2700	2300 - 2400	2500 - 2600	2400 - 2500
Purge Gas	Argon	Argon	Argon	Argon
Wavelength, nm	193.7 alternate: 197.2	283.3 alternate: 217.0, 261.4	196.0 alternate: 204.0	276.8 alternate: 258.0
Zeeman Background Correction	On	On	On	On
Type of Injection	Hot	Hot	Hot	Hot
Modifier Used	Nickel Nitrate, 1 %	Phosphoric Acid, 1 %	Nickel Nitrate, 1 %	Palladium Chloride / Citric Acid or 1% H <sub>2</sub> SO <sub>4</sub> (alternate)
Tube Used	PCPGT	PCPGT	PCPGT	PCPGT (with platform) <sup>1</sup>
Lamp Current, mA	10 - 15*	5 - 12*	10 - 15*	10 - 15*

PCPGT - Pyrolytically-Coated Partitioned Graphite Tube

\* Lamp current may vary based on manufacturer or vendor, or type of lamp.

<sup>1</sup> No platform is required if 1% H<sub>2</sub>SO<sub>4</sub> is used