METHOD 7010

GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

1.0 SCOPE AND APPLICATION

1.1 Metals in solution may be readily determined by graphite furnace atomic absorption spectrophotometry (GFAA). The method is simple, quick, and applicable to a large number of metals in environmental samples including, but not limited to, ground water, domestic and industrial wastes, extracts, soils, sludges, sediments, and similar wastes. With the exception of the analyses for dissolved constituents, all samples require digestion prior to analysis. Analysis for dissolved elements does not require digestion if the sample has been filtered and then acidified.

NOTE: The analyst should be aware that organo-metallic species may not be detected if the sample is not digested.

This method is applicable to the following elements:

Element		CASRN[a]
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

[a]Chemical Abstract Service Registry Number

1.2 Method 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 provide some indication of the detection limits obtainable by the furnace technique. The detection limits given in Table 1 are somewhat dependent on equipment (such as the type of spectrophotometer and furnace accessory, the energy source, the degree of electrical expansion of the output signal), and are greatly dependent on sample matrix. Method detection limits (MDLs) must be established, empirically, for each matrix type analyzed (refer to Chapter One for guidance) and are required for each preparatory/determinative method combination used.

1.3 Users of this method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis. When using furnace techniques, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element (see Sec. 4.0). To ensure valid data with furnace techniques, the analyst must examine each sample for interference effects (see Sec. 9.0) and, if detected, treat them accordingly, using either successive dilution, matrix modification, or the method of standard additions (see Sec. 9.7).

1.4 Other elements and matrices may be analyzed by this method as long as the method performance is demonstrated for these additional elements of interest, in the additional matrices of interest, at the concentration levels of interest in the same manner as the listed elements and matrices (see Sec. 9.0).

1.5 Use of this method is restricted to analysts who are knowledgeable in the chemical and physical interferences as described in this method.

2.0 SUMMARY OF THE METHOD

2.1 Although methods have been reported for the analysis of solids by atomic absorption spectrophotometry, the technique generally is limited to metals in solution or solubilized through some form of sample processing. Refer to Chapter Three for a description of appropriate digestion methods.

2.2 Preliminary treatment of wastes, both solid and aqueous, is always necessary because of the complexity and variability of sample matrix. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Chapter Three.

2.3 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms is vaporized and dissociated for absorption in the tube rather than the flame, the use of smaller sample volumes or detection of lower concentrations of elements 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 specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

3.0 DEFINITIONS

Refer to Chapter One and Chapter Three for a listing of applicable definitions.

4.0 INTERFERENCES

4.1 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 which must be determined and taken into consideration in the analysis of each different matrix encountered. See Sec. 9.6 for additional guidance.

4.2 Background correction is important when using flameless atomization, especially below 350 nm. Certain samples, when atomized, may absorb or scatter light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high. Zeeman background correction is effective in overcoming composition or structured background interferences. It is particularly useful when analyzing for As in the presence of Al and when analyzing for Se in the presence of Fe.

4.3 Memory effects occur when the analyte is not totally volatilized during atomization. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. This situation is detected through blank burns. The tube should be cleaned by operating the furnace at full power for the required time period, as needed, at regular intervals during the series of determinations.

4.4 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 and light scattering.

4.5 Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, refer to Chapter Two. A single background correction device to be used with this method is not specified; however, it must provide an analytical condition that is not subject to the occurring interelement spectral interferences of palladium on copper, iron on selenium and aluminum on arsenic.

4.6 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.

4.7 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. In this way, broad-band absorption will be minimized.

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

4.9 Carbide formation resulting from the chemical environment of the furnace has been observed. Molybdenum may be cited as an example. When carbides form, the metal is released very slowly from the resulting metal carbide as atomization continues. Molybdenum may require

30 seconds or more atomization time before the signal returns to baseline levels. Carbide formation is greatly reduced and the sensitivity increased with the use of pyrolytically coated graphite. Elements that readily form carbides are noted with the symbol (p) in Table 1.

4.10 Spectral interference can occur when an absorbing wavelength of an element present in the sample, but not being determined, falls within the width of the absorption line of the element of interest. The results of the determination 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 from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

4.11 It is recommended that all graphite furnace analyses be carried out using an appropriate matrix modifier. The choice of matrix modifier is dependent on analytes, conditions, and instrumentation and should be chosen by the analyst as the situation dictates. Follow the instrument manufacturers instructions for the preferred matrix modifier. If necessary, refer to Chapter Two for additional guidance.

4.12 It is recommended that a stabilized temperature platform be used to maximize an isothermal environment within the furnace cell to help reduce interferences. Refer to Chapter Two for additional guidance.

4.13 Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in Sec. 6.6. Pipet tips are a frequent source of contamination. The analyst should be aware of the potential for the yellow tips to contain cadmium. If suspected, they should be acid soaked with 1:5 nitric acid and rinsed thoroughly with tap and reagent water. The use of a better grade of pipet tip can greatly reduce this problem. Special attention should be given to assessing the contamination in method blanks during the analysis. Pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use. In addition, auto sampler tips may also be a potential source of contamination. Flushing the tip with a dilute solution of nitric acid between samples can help prevent cross-contamination.

4.14 Specific interference problems related to individual analytes are located in this section.

4.14.1 Antimony: High lead concentration may cause a measurable spectral interference on the 217.6 nm line. Choosing the secondary wavelength or using background correction may correct the problem.

4.14.2 Arsenic:

4.14.2.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample preparation Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A matrix modifier such as nickel nitrate or palladium nitrate should be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

4.14.2.2 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid erroneously high results. Aluminum is a severe positive interferant in the analysis of arsenic, especially using D_2 arc background correction. Although Zeeman background correction is very useful in this situation, use of any appropriate background correction technique is acceptable.

4.14.3 Barium: Barium can form barium carbide in the furnace, resulting in less sensitivity and potential memory effects. Because of chemical interaction, nitrogen should not be used as a purge gas and halide acids should not be used.

4.14.4 Beryllium: Concentrations of aluminum greater than 500 ppm may suppress beryllium absorbance. The addition of 0.1% fluoride has been found effective in eliminating this interference. High concentrations of magnesium and silicon cause similar problems and require the use of the method of standard additions.

4.14.5 Cadmium: Cadmium analyses can suffer from severe non-specific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction is required to avoid erroneously high results. Excess chloride may cause premature volatilization of cadmium; an ammonium phosphate matrix modifier may minimize this loss.

4.14.6 Chromium: Low concentrations of calcium and/or phosphate may cause interferences; at concentrations above 200 mg/L, calcium's effect is constant and eliminates the effect of phosphate. Therefore, add calcium nitrate (calcium nitrate solution: dissolve 11.8 g of calcium nitrate in 1 L reagent water) to ensure a constant effect. Nitrogen should not be used as the purge gas because of a possible CN band interference.

4.14.7 Cobalt: Since excess chloride may interfere, it is necessary to verify by standard additions that the interference is absent unless it can be shown that standard additions are not necessary.

4.14.8 Lead: If poor recoveries are obtained, a matrix modifier may be necessary. Add 10 uL of phosphoric acid to 1 mL of prepared sample.

4.14.9 Molybdenum: Molybdenum is prone to carbide formation; use a pyrolytically coated graphite tube.

4.14.10 Nickel: Severe memory effects for nickel may occur in graphite furnace tubes used for other GFAA analyses, due to the use of a nickel nitrate matrix modifier in those methods. Use of graphite furnace tubes and contact rings for nickel analysis that are separate from those used for arsenic and selenium analyses is strongly recommended.

4.14.11 Selenium:

4.14.11.1 Elemental selenium and many of its compounds are volatile; therefore, samples may be subject to losses of selenium during sample preparation. Likewise, caution must be employed during the selection of temperature and times for

the dry and char (ash) cycles. A matrix modifier such as nickel nitrate or palladium nitrate should be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

4.14.11.2 In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction must be employed to avoid erroneously high results. High iron levels can give overcorrection with deuterium background. Although Zeeman background correction is very useful in this situation, use of any appropriate background correction technique is acceptable.

4.14.11.3 Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). The addition of nickel nitrate such that the final concentration is 1% nickel will lessen this interference.

4.14.12 Silver: Silver chloride is insoluble, therefore HCl should be avoided unless the silver is already in solution as a chloride complex. In addition, it is recommended that the stock standard concentrations be kept below 2 ppm and the chloride content increased to prevent precipitation. If precipitation is occurring, a 5%:2% HCl:HNO_3 stock solution may prevent precipitation. Daily standard preparation may also be needed to prevent precipitation of silver. Analysts should be aware that this technique may not be the best choice for this analyte and that alternative techniques should be considered.

4.14.13 Thallium: HCl or excessive chloride will cause volatilization of thallium at low temperatures. Verification that losses are not occurring must be made for each matrix type (as detailed in 9.6.1).

4.14.14 Vanadium: Vanadium is refractory and prone to form carbides. Consequently, memory effects are common, and care should be taken to clean the furnace before and after analysis.

5.0 SAFETY

Refer to Chapter Three for a discussion on safety related references and issues.

6.0 EQUIPMENT AND SUPPLIES

6.1 Atomic absorption spectrophotometer - Single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a graphical display. The instrument must be equipped with an adequate correction device capable of removing undesirable nonspecific absorbance over the spectral region of interest and provide an analytical condition not subject to the occurrence of interelement spectral overlap interferences.

6.2 Hollow cathode lamps - Single-element lamps are preferred but multielement lamps may be used. Electrodeless discharge lamps may also be used when available. Other types of lamps meeting the performance criteria of this method may be used.

6.3 Graphite furnace - Any furnace device capable of reaching the specified temperatures is satisfactory. For all instrument parameters (i.e., drying, ashing, atomizing, times and temperatures) follow the specific instrument manufacturers instructions for each element.

6.4 Data systems recorder - A recorder is recommended for furnace work so that there will be a permanent record and that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, peak shape, etc., can be easily recognized.

6.5 Pipets - Microliter, with disposable tips. Sizes can range from 5 to 100 µL as required. Pipet tips should be checked as a possible source of contamination when contamination is suspected or when a new source or batch of pipet tips is received by the laboratory. The accuracy of variable pipets must be verified daily. Class A pipets can be used for the measurement of volumes equal to or larger than 1 mL.

6.6 Glassware - All glassware, polypropylene, or fluorocarbon (PFA or TFE) containers, including sample bottles, flasks and pipets, should be washed in the following sequence: 1:1 hydrochloric acid, tap water, 1:1 nitric acid, tap water, detergent, tap water, and reagent water. Chromic acid should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme. If it can be documented through an active analytical quality control program using spiked samples and method blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure. Leaching of polypropylene for longer periods at lower acid concentrations is necessary to prevent degradation of the polymer. Alternative cleaning procedures must also be documented. Cleaning for ultra-trace analysis should be reviewed in Chapter Three.

6.7 Volumetric flasks of suitable precision and accuracy.

7.0 REAGENTS AND STANDARDS

7.1 Reagents: Analytical reagent grade or trace metals grade chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents should be analyzed to demonstrate that the reagents do not contain target analytes at or above the MDL .

7.2 Reagent water: All references to water in this method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

7.3 Nitric acid , HNO_3: Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the method blank does not contain target analytes at or above the MDL, then the acid may be used.

7.4 Hydrochloric acid (1:1), HCl: Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the method blank does not contain target analytes at or above the MDL, then the acid may be used.

7.5 Purge Gas: A mixture of H_2 (5%) and argon (95%). The argon gas supply must be high-purity grade, 99.99% or better. If performance can be documented, alternative gases may be used.

7.6 Stock standard metal solutions: Stock standard solutions are prepared from analytical reagent grade high purity metals, oxides, or nonhygroscopic salts using reagent water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000 mg of the metal per liter. Commercially available standard solutions may also be used. When using pure metals (especially wire) for standards preparation, cleaning procedures, as detailed in Chapter Three, should be used to ensure that the solutions are not compromised. Examples of appropriate standard preparations can be found in Sections 7.6.1 through 7.6.18.

7.6.1 Antimony: Carefully weigh 2.743 g of antimony potassium tartrate, $K(SbO)C_4H_4O_6 \bullet 1/2H_2O$, and dissolve in reagent water. Dilute to 1 L with reagent water;

7.6.2 Arsenic: Dissolve 1.320 g of arsenic trioxide, As_2O_3, or equivalent in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL conc. HNO_3 and dilute to 1 L with reagent water.

7.6.3 Barium: Dissolve 1.779 g barium chloride, $BaCl_2 \bullet 2H_2O$, in reagent water and dilute to 1 L with reagent water.

7.6.4 Beryllium: Dissolve 11.659 g beryllium sulfate, $BeSO_4$, in reagent water containing 2 mL nitric acid (conc.) and dilute to 1 L with reagent water.

7.6.5 Cadmium: Dissolve 1.000 g cadmium metal in 20 mL of 1:1 HNO_3 and dilute to 1 L with reagent water.

7.6.6 Chromium: Dissolve 1.923 g of chromium trioxide, CrO_3, in reagent water, acidify with redistilled HNO_3, and dilute to 1 L with reagent water.

7.6.7 Cobalt: Dissolve 1.000 g of cobalt metal in 20 mL of 1:1 HNO_3 and dilute to 1 L with reagent water. Chloride or nitrate salts of cobalt(II) may be used. Although numerous hydrated forms exist, they are not recommended, unless the exact composition of the compound is known.

7.6.8 Copper: Dissolve 1.000 g of electrolytic copper in 5 mL of redistilled HNO_3 and dilute to 1 L with reagent water.

7.6.9 Iron: Dissolve 1.000 g iron wire in 10 mL redistilled HNO_3 and reagent water and dilute to 1 L with reagent water. Note that iron passivates in conc. HNO_3, and therefore some water should be present.

7.6.10 Lead: Dissolve 1.599 g of lead nitrate, $Pb(NO_3)_2$, in reagent water, acidify with 10 mL redistilled HNO_3, and dilute to 1 L with reagent water.

7.6.11 Manganese: Dissolve 1.000 g manganese metal in 10 mL redistilled HNO_3 and dilute to 1 L with reagent water.

7.6.12 Molybdenum: Dissolve 1.840 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}•4H_2O$, and dilute to 1 L with reagent water.

7.6.13 Nickel: Dissolve 1.000 g nickel metal or 4.953 g nickel nitrate, $Ni(NO_3)_2•6H_2O$ in 10 mL HNO_3 and dilute to 1 L with reagent water.

7.6.14 Selenium: Dissolve 0.345 g of selenious acid (actual assay 94.6% H_2SeO_3) or equivalent and dilute to 200 mL with reagent water.

NOTE: Due to the high toxicity of selenium, preparation of a smaller volume of reagent has been described. Larger volumes may be prepared if required.

7.6.15 Silver: Dissolve 1.575 g of anhydrous silver nitrate, $AgNO_3$, in reagent water. Add 10 mL of HNO_3 (conc.) and dilute to 1 L with reagent water. Because this standard is light sensitive, store in a amber glass bottle in a refrigerator.

7.6.16 Thallium: Dissolve 1.303 g thallium nitrate, $TlNO_3$, in reagent water, acidify with 10 mL conc. HNO_3, and dilute to 1 L with reagent water.

7.6.17 Vanadium: Dissolve 1.785 g of vanadium pentoxide, V_2O_5 , in 10 mL of conc. HNO_3 and dilute to 1 L with reagent water.

7.6.18 Zinc: Dissolve 1.000 g zinc metal in 10 mL of conc. HNO_3 and dilute to 1 L with reagent water.

7.7 Common matrix modifiers: The use of a palladium modifier is strongly recommended for the determination of all analytes. This will correct for general chemical interferences as well as allow for higher char and atomization temperatures without allowing the premature liberation of analyte. Other matrix modifiers may also be used as recommended by the instrument manufacturer or when an interference is evident.

7.7.1 Palladium solution (Pd/Mg): Dissolve 300 mg of palladium powder in concentrated HNO_3 (1 mL of HNO_3 , adding 0.1 mL of conc. HCl, if necessary). Dissolve 200 mg of $Mg(NO_3)_2$ in reagent water. Pour the two solutions together and dilute to 100 mL with reagent water.

7.7.2 Nickel nitrate solution (5%): Dissolve 25g of $Ni(NO_3)_2•6H_2O$ in reagent water and dilute to 100 mL.

7.7.3 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate solution to 100 mL with reagent water.

7.7.4 Ammonium phosphate solution (40%): Dissolve 40 g of ammonium phosphate, $(NH_4)_2HPO_4$, in reagent water and dilute to 100 mL.

7.7.5 Palladium chloride: Weigh 0.25 g of $PdCl_2$ to the nearest 0.0001 g and dissolve in 10 mL of 1:1 HNO_3. Dilute to 1 L with reagent water

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See Chapter Three.

9.0 QUALITY CONTROL

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

9.2 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process as described in Chapter One. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate steps of the analytical process. These steps may include but are not limited to digestion, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs then the method blank would be considered acceptable. In the absence of project-specific DQOs, if the blank is less than the MDL or less than 10% of the lowest sample concentration for each analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once and if still unacceptable, then all contaminated samples after the last acceptable method blank must be reprepped and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

9.3 For each batch of samples processed, at least one laboratory control sample must be carried throughout the entire sample preparation and analytical process as described in Chapter One. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value. After the determination of historical data, ±20% must still be the limit of maximum deviation to express acceptability. If the laboratory control sample cannot be considered acceptable, the laboratory control sample should be re-run once and if still unacceptable then all samples after the last acceptable laboratory control sample must be reprepped and reanalyzed. Refer to Chapter One for more information.

9.4 Matrix Spike/Matrix Spike Duplicates (MS/MSDs): At the laboratory's discretion, a separate spike sample and a separate duplicate sample may be analyzed in lieu of the MS/MSD. For each batch of samples processed, at least one MS/MSD sample must be carried throughout the entire sample preparation and analytical process as described in Chapter One. MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/MSD is used to document the bias and precision of a method in a given sample matrix. Refer to the definitions of bias and precision, in Chapter One, for the proper data reduction protocols. MS/MSD samples should be spiked at the same level as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value for precision and $\leq$ 20 relative percent difference (RPD). After the determination of historical data, 20% must still be the limit of maximum deviation for both percent recovery and relative percent difference to express acceptability. Refer to Chapter One for guidance. If the bias and precision indicators are outside the laboratory control limits or if the percent recovery is less than 80% or greater than 120% or if the relative percent difference is greater than 20%, the interference test as discussed in Sec. 9.5.2 and 9.7 should be conducted.

9.5 Interference tests

9.5.1 Recovery test (post-digestion spike) - The recovery test must be done on every sample. To conduct this test withdraw an aliquot of the test sample and add a known amount of analyte to bring the concentration of the analyte to 2 to 5 times the original concentration. If spiking at 2-5 times would exceed the linear range of the instrument, a lesser spike may be used. If all of the samples in the batch have analyte concentrations below the detection limit, spike the selected sample at the project-specific action level or when lacking project-specific action levels, between the low and midlevel standards. Analyze the spiked sample and calculate the spike recovery. If the recovery is <85% or >115%, MSA should be used for the sample.

9.5.2 Dilution test - The dilution test is to be conducted when interferences are suspected (Sec. 9.5.1) and the sample concentration is high enough to allow for proper interpretation of the results. To conduct this test, determine the apparent concentration in the undiluted sample. Dilute the sample by a minimum of five fold (1+4) and reanalyze. Agreement within an RPD of 10 between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences, and such samples may be analyzed without using the method of standard additions. If agreement between the dilutions is greater than 10%, the MSA should be used for all samples in the batch.

9.6 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) is recommended (see Section 9.7 below). Other options including, the use of different matrix modifiers, different furnace conditions, different preparatory methods or different analytical methods may also be attempted to properly characterize a sample. Section 9.5 provides tests to determine the potential for an interference and evaluates the need for using the MSA.

9.7 Method of standard additions - The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique attempts to compensate for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The method of standard additions may be appropriate for analysis of extracts, on analyses submitted as part of a delisting petition, whenever a new sample matrix is being analyzed and on every batch that fails the recovery test.

9.7.1 The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_S of a standard analyte solution of concentration C_S. To the second aliquot (labeled B) is added the same volume V_S of reagent water. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average,

avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

9.7.2 Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the indigenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1. A linear regression program may be used to obtain the intercept concentration.

9.7.3 For the results of this MSA technique to be valid, the following limitations must be taken into consideration:

1. The apparent concentrations from the calibration curve must be linear (0.995 or greater) over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve.

2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

3. The determination must be free of spectral interference and corrected for nonspecific background interference.

9.8 All quality control measures described in Chapter One should be followed.

9.9 Independent source laboratory control sample or standard reference materials (SRMs) should be used to help assess the quality of the analytical scheme.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration standards - All analyses require that a calibration curve be prepared to cover the appropriate concentration range. Usually, this means the preparation of a blank and standards which produce an absorbance of 0.0 to 0.7. Calibration standards can prepared by diluting the stock metal solutions in the same acids and acid concentrtions as the samples.

10.1.1 Calibration standards can be prepared fresh each time a batch of samples is analyzed. If the ICV solution is prepared daily and the ICV is analyzed within the acceptance criteria, calibration standards do not need to be prepared daily and may be prepared and stored for as long as the calibration standard viability can be verified through the use of the ICV. If the ICV is outside of the acceptance criteria, the calibration standards must be prepared fresh and the instrument recalibrated. Prepare a blank and at least three

calibration standards in graduated amounts in the appropriate range of the linear part of the curve.

10.1.2 The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing.

10.1.3 Beginning with the blank and working toward the highest standard, inject the solutions and record the readings. Calibration curves are always required.

10.2 A calibration curve must be prepared each day with a minimum of a calibration blank and three standards. The curve must be linear and have a correlation coefficient of at least 0.995.

10.2.1 After initial calibration, the calibration curve must be verified by use of an initial calibration blank (ICB) and an initial calibration verification (ICV) standard. The ICV standard must be made from an independent (second source) material at or near mid-range. The acceptance criteria for the ICV standard must be ±10% of its true value and the ICB must not contain target analytes at or above the MDL for the curve to be considered valid. If the calibration curve cannot be verified within the specified limits, the cause must be determined and the instrument recalibrated before samples are analyzed. The analysis data for the ICV must be kept on file with the sample analysis data.

10.2.2 The calibration curve must also be verified at the end of each analysis batch and/or after every 10 samples by use of a continuing calibration blank (CCB) and a continuing calibration verification (CCV) standard. The CCV standard should be made from the same material as the initial calibration standards at or near midrange. The acceptance criteria for the CCV standard must be ±10% of its true value and the CCB must not contain target analytes at or above the MDL for the curve to be considered valid. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable CCV/CCB must be reanalyzed. The analysis data for the CCV/CCB must be kept on file with the sample analysis data.

10.3 It is recommended that each standard should be analyzed (injected) twice and an average value determined. Replicate standard values should be within ±10% RPD.

10.4 Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Tube life depends on sample matrix and atomization temperature. A conservative estimate would be that a tube will last at least 50 firings. A pyrolytic coating will extend that estimated life by a factor of three.

10.5 If conducting trace analysis, it is recommended that the lowest calibration standard be set at the laboratory's quantitation level. The laboratory can use a reporting limit that is below the quantitation level but all values reported below the low standard should be reported as estimated values.

11.0 PROCEDURE

11.1 Preliminary treatment of waste water, ground water, extracts, and industrial waste is always necessary because of the complexity and variability of sample matrices. Solids, slurries, and

suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Chapter Three. Samples which are to be analyzed only for dissolved constituents need not be digested if they have been filtered and acidified.

11.2 Furnace devices (flameless atomization) are a most useful means of 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 manufacturer of a particular instrument. A generalized set of instructions follows:

11.2.1 Inject an aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

11.2.2 To verify the absence of interference, follow the interference procedure given in Sec. 9.5.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 For determination of metal concentration by GFAA: Read the metal value from the calibration curve or directly from the read-out system of the instrument.

12.1.1 If dilution of sample was required:

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

where:

A = µg/L of metal in diluted aliquot from calibration curve.
B = Starting sample volume , mL.
C = Final volume of sample, mL.

12.1.2 For solid samples, report all concentrations in consistent units based on wet weight. Ensure that if the dry weight was used for the analysis, percent solids should be reported to the client. Hence:

$$\text{mg metal/kg sample} = \frac{A \times V}{W}$$

where:

A = mg/L of metal in processed sample from calibration curve.
V = Final volume of the processed sample, L.
W = Weight of sample, Kg.

12.1.3 Different injection volumes must not be used for samples and standards. Instead, the sample should be diluted and the same size injection volume be used for both samples and standards.

13.0 METHOD PERFORMANCE

13.1 See the individual methods from reference 1.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 and 2, Figure 1, and a flow diagram of the method procedures.

TABLE 1

FURNACE ATOMIC ABSORPTION DETECTION LIMITS FOR ANALYTES IN REAGENT WATER

Metal	Furnace Procedure[a,b] Detection Limit (µg/L)
Antimony	3
Arsenic	1
Barium(p)	2
Beryllium	0.2
Cadmium	0.1
Chromium	1
Cobalt	1
Copper	1
Iron	1
Lead	1
Manganese	0.2
Molybdenum(p)	1
Nickel	1
Selenium	2
Silver	0.2
Thallium	1
Vanadium(p)	4
Zinc	0.05

NOTE: The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

[a]For furnace sensitivity values, consult instrument operating manual.

[b]The listed furnace values are those expected when using a 20-µL injection and normal gas flow, except in the cases of arsenic and selenium, where gas interrupt is used.

Source: Reference 1.

TABLE 2

INSTRUMENT PARAMETERS

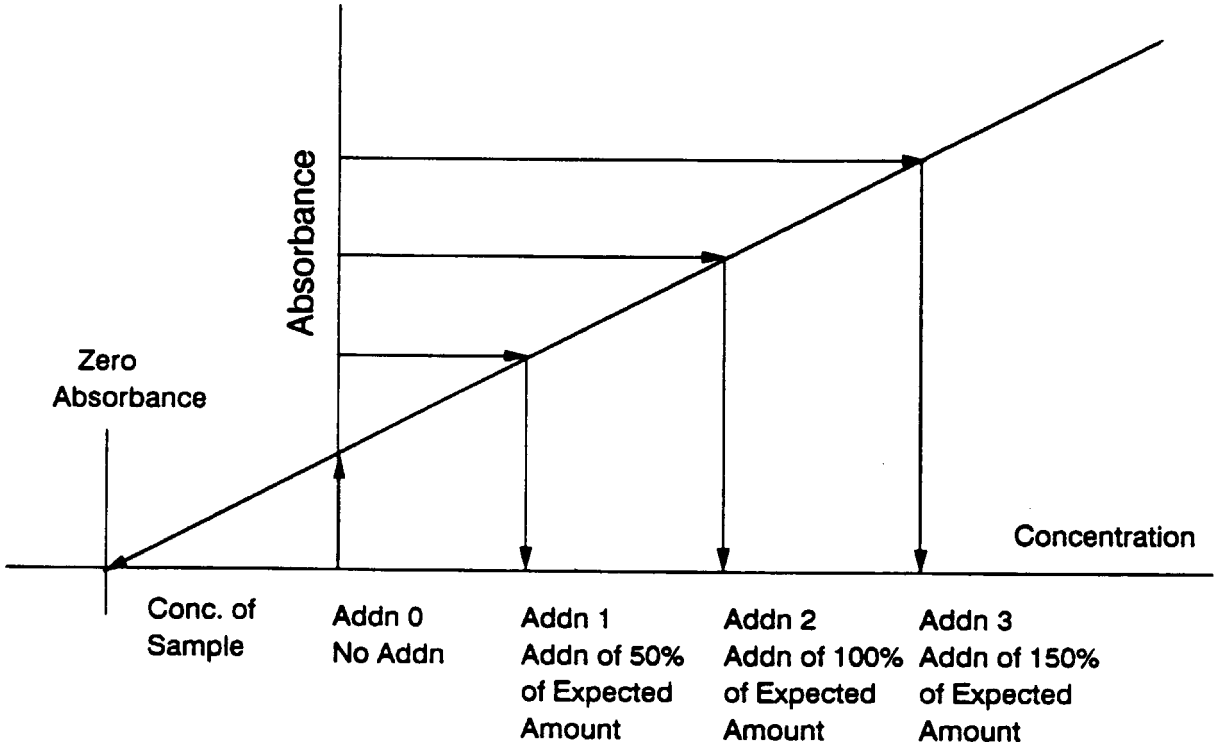
ELEMENT	WAVELENGTH (nm)	PURGE GAS[1]	COMMENTS
Sb	217.6, 231.1	argon or nitrogen	
As	193.7	argon	
Ba	553.6	argon	nitrogen should not be used
Be	234.9	argon	
Cd	228.8	argon	
Cr	357.9	argon	nitrogen should not be used
Co	240.7	argon	
Cu	324.7	argon or nitrogen	
Fe	248.3, 248.8, 271.8, 302.1, 252.7	argon or nitrogen	
Pb	283.3, 217.0	argon	
Mn	279.5, 403.1	argon or nitrogen	
Mo	313.3	argon	nitrogen should not be used
Ni	232.0, 352.4	argon or nitrogen	
Se	196.0	argon	
Ag	328.1	argon	
Tl	276.8	argon or nitrogen	
V	318.4	argon	nitrogen should not be used
Zn	213.9	argon or nitrogen	

Note: If more than one wavelength is listed, the primary line is underlined.
[1]The argon/H_2 purge gas is also applicable.

Source: Reference 1

FIGURE 1

STANDARD ADDITION PLOT



GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY