GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

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: 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 Lower limits of quantitation 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 lower limits of quantitation obtainable by the furnace technique. The 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.

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. 9.10).

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 Prior to employing this method, analysts are advised to consult each type of procedure (e.g., sample preparation methods) that may be employed in the overall analysis for additional information on quality control procedures, development of QA acceptance criteria, calculations, and general guidance. Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.6 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel, including analysts who are knowledgeable in the chemical and physical interferences described in this method. Each analyst must demonstrate the ability to generate acceptable results with 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 quantitation 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 volatilize. 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, Chapter Three, and the manufacturer's instructions for a definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to Method 7000 for a discussion of interferences.

4.2 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.

4.3 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.

4.4 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.

4.5 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.

4.6 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 (see 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.

4.7 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.

4.8 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.

4.9 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 needed, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

4.10 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.

4.11 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.

4.12 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. Refer to Chapter Two for additional guidance.

4.13 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.

4.14 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 needed 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.

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

4.15.1 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.

4.15.2 Arsenic

4.15.2.1 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.

4.15.2.2 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.

4.15.3 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.

4.15.4 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.

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

4.15.6 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.

4.15.7 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.

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

4.15.9 Molybdenum -- Molybdenum is prone to carbide formation; use a pyrolytically coated graphite tube.

4.15.10 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.

4.15.11 Selenium

4.15.11.1 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.

4.15.11.2 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.

4.15.11.3 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.

4.15.12 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.

4.15.13 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).

4.15.14 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

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents.

5.3 Hydrofluoric acid is a very toxic acid and penetrates the skin and tissues deeply if not treated immediately. Injury occurs in two stages; first, by hydration that induces tissue necrosis and then by penetration of fluoride ions deep into the tissue and by reaction with calcium. Boric acid and other complexing reagents and appropriate treatment agents should be administered immediately. Consult appropriate safety literature and have the appropriate treatment materials readily available prior to working with this acid. See Method 3052 for specific suggestions for handling hydrofluoric acid from a safety and an instrument standpoint.

5.4 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

5.5 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

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 needed. 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 needed 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 Reagent grade or trace metals grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents 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 lowest limit of quantitation.

7.2 Reagent water -- All references to water in the method refer to reagent water, unless otherwise specified. Reagent water must be free of interferences.

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 lowest limit of quantitation, 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 lowest limit of quantitation, 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 Secs. 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 of 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 of beryllium sulfate, $BeSO_4$, in reagent water containing 2 mL of nitric acid (conc.) and dilute to 1 L with reagent water.

7.6.5 Cadmium -- Dissolve 1.000 g of 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 of iron wire in 10 mL of 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 of redistilled HNO_3, and dilute to 1 L with reagent water.

7.6.11 Manganese -- Dissolve 1.000 g of manganese metal in 10 mL of 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 of nickel metal or 4.953 g of nickel nitrate, $Ni(NO_3)_2•6H_2O$ in 10 mL of 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 small volume of reagent is described. Larger volumes may be prepared if needed.

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 of thallium nitrate, $TlNO_3$, in reagent water, acidify with 10 mL of 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 of 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 25 g 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.

7.8 Blanks

Two types of blanks are required for the analysis of samples prepared by any method other than Method 3040. The calibration blank is used in establishing the analytical curve and the method blank is used to identify possible contamination resulting from either the reagents (acids) or the equipment used during sample processing including filtration.

7.8.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial (ICB) and continuing calibration blank (CCB) determinations.

7.8.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis (refer to Sec. 9.5).

7.9 The initial calibration verification (ICV) standard is prepared by the analyst (or a purchased second source reference material) by combining compatible elements from a standard source different from that of the calibration standard, and at concentration near the midpoint of the calibration curve (see Sec. 10.2.1 for use). This standard may also be purchased.

7.10 The continuing calibration verification (CCV) standard should be prepared in the same acid matrix using the same standards used for calibration, at a concentration near the mid-point of the calibration curve (see Sec. 10.2.2 for use).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

See the introductory material in Chapter Three, "Inorganic Analytes."

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to a 3000 series method (Method 3015, 3020, 3031, 3050, 3051, or 3052) for appropriate QC procedures to ensure the proper operation of the various sample preparation techniques.

9.3 Instrument detection limits (IDLs) are a useful tool to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limit of

quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Sec. 10.2.3.

IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least every three months or at a project-specific designated frequency and kept with the instrument log book.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation (a 3000 series method) and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.5 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, prefiltering, 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 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank should be reprepared and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other DQOs, then the sample data may be used despite the contamination of the method blank. Refer to Chapter One for the proper protocol when analyzing blanks.

9.6 Laboratory control sample (LCS)

For each batch of samples processed, at least one LCS 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, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory derived limit developed through the use of historical analyses. In the absence of project-specific or historical data generated criteria, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data should be no wider that ±

20%. If the laboratory control sample is not acceptable, then the laboratory control sample should be re-run once and, if still unacceptable, all samples after the last acceptable laboratory control sample should be reprepared and reanalyzed.

Concurrent analyses of reference materials (SRMs) containing known amounts of analytes in the media of interest are recommended and may be used as an LCS. For solid SRMs, 80 - 120% accuracy may not be achievable and the manufacturer's established acceptance criterion should be used for soil SRMs.

9.7 Matrix spike, unspiked duplicate, or matrix spike duplicate (MS/Dup or MS/MSD)

Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

For each batch of samples processed, at least one MS/Dup or MS/MSD sample set should 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/Dup or MS/MSD is used to document the bias and precision of a method in a given sample matrix.

Refer to Chapter One for the definitions of bias and precision, and for the proper data reduction protocols. MS/MSD samples should be spiked at the same level, and with the same spiking material, as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory-derived limit developed through the use of historical analyses per matrix type analyzed. In the absence of project-specific or historical data generated criteria, these limits should be set at ± 25% of the spiked value for accuracy and 20 relative percent difference (RPD) for precision. Acceptance limits derived from historical data should be no wider that ± 25% for accuracy and 20% for precision. Refer to Chapter One for additional guidance. If the bias and precision indicators are outside the laboratory control limits, if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 20%, then the interference test discussed in Sec. 9.8 should be conducted.

9.7.1 The relative percent difference between spiked matrix duplicate or unspiked duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{\left(\frac{|D_1 + D_2|}{2}\right)} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (spiked or unspiked duplicate).

9.7.2 The spiked sample or spiked duplicate sample recovery should be within ± 25% of the actual value, or within the documented historical acceptance limits for each matrix.

9.8 If less than acceptable accuracy and precision data are generated, the following additional quality control tests are recommended prior to reporting concentration data for the elements in this method. At a minimum these tests, outlined in Secs. 9.8.1 and 9.8.2, should be performed with each batch of samples prepared/analyzed with corresponding unacceptable data quality results. These tests will then serve to ensure that neither positive nor negative interferences are affecting the measurement of any of the elements or distorting the accuracy of the reported values. If matrix effects are confirmed, the laboratory should consult with the data user when feasible for possible corrective actions which may include the use of alternative or modified test procedures or possibly the method of standard additions so that the analysis is not impacted by the same interference.

9.8.1 Post digestion spike addition

The same sample from which the MS/MSD aliquots were prepared (asuming the MS/MSD recoveries are unacceptable) should also be spiked with a post digestion spike. Otherwise another sample from the same preparation should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. If this spike fails, then the dilution test (Sec. 9.8.2) should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

9.8.2 Dilution test

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, then a chemical or physical interference effect should be suspected. For both a failed post digestion spike or an unacceptable dilution test agreement result, the method of standard additions should be used as the primary means to quantitate all samples in the associated preparation batch.

9.9 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard additions (MSA) is recommended (see Sec. 9.10 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. Sec. 9.8 provides tests to determine the potential for an interference and evaluates the need for using the MSA.

9.10 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.

9.10.1 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.

9.10.2 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.

9.10.3 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.

9.11 Ultra-trace analysis requires the use of clean chemistry preparation and analysis techniques. Several suggestions for minimizing analytical blank contamination are provided in Chapter Three.

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 calibration 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 lowest limit of quantitation 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 lowest limit of quantitation 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.

10.2.3 The lower limits of quantitation should be established for all analytes for each type of matrix analyzed and for each preparation method used and for each instrument. These limits are considered the lowest reliable laboratory reporting concentrations and should be established from the lower limit of quantitation check sample

and then confirmed using either the lowest calibration point or from a low-level calibration check standard.

10.2.3.1 Lower limit of quantitation check sample

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. Ideally, this check sample and the low-level calibration verification standard will be prepared at the same concentrations with the only difference being the LLQC sample is carried through the entire preparation and analytical procedure. Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within ± 30% of their true value. This check should be used to both establish and confirm the lowest quantitation limit.

10.2.3.2 The lower limits of quantitation determination using reagent water represents a best case situation and does not represent possible matrix effects of real-world samples. For the application of lower limits of quantitation on a project-specific basis with established data quality objectives, low-level matrix-specific spike studies may provide data users with a more reliable indication of the actual method sensitivity and minimum detection capabilities.

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 lower limit of quantitation. The laboratory can use a reporting limit that is below the lower limit of quantitation 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 the lower limits of quantitation. 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 below.

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. 9.8.

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.

12.2 Results need to be reported in units commensurate with their intended use and all dilutions need to be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 For relevant performance data, see the methods of Ref. 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's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

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 Sec. 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. W. G. Rohrbough, 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 following pages contain the tables and figure referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

EXAMPLE FURNACE ATOMIC ABSORPTION
LOWER LIMITS OF QUANTITATION FOR ANALYTES IN REAGENT WATER

Metal	Furnace Procedure [a, b] Lower Limit of Quantitation (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: Ref. 1.

TABLE 2

INSTRUMENT PARAMETERS

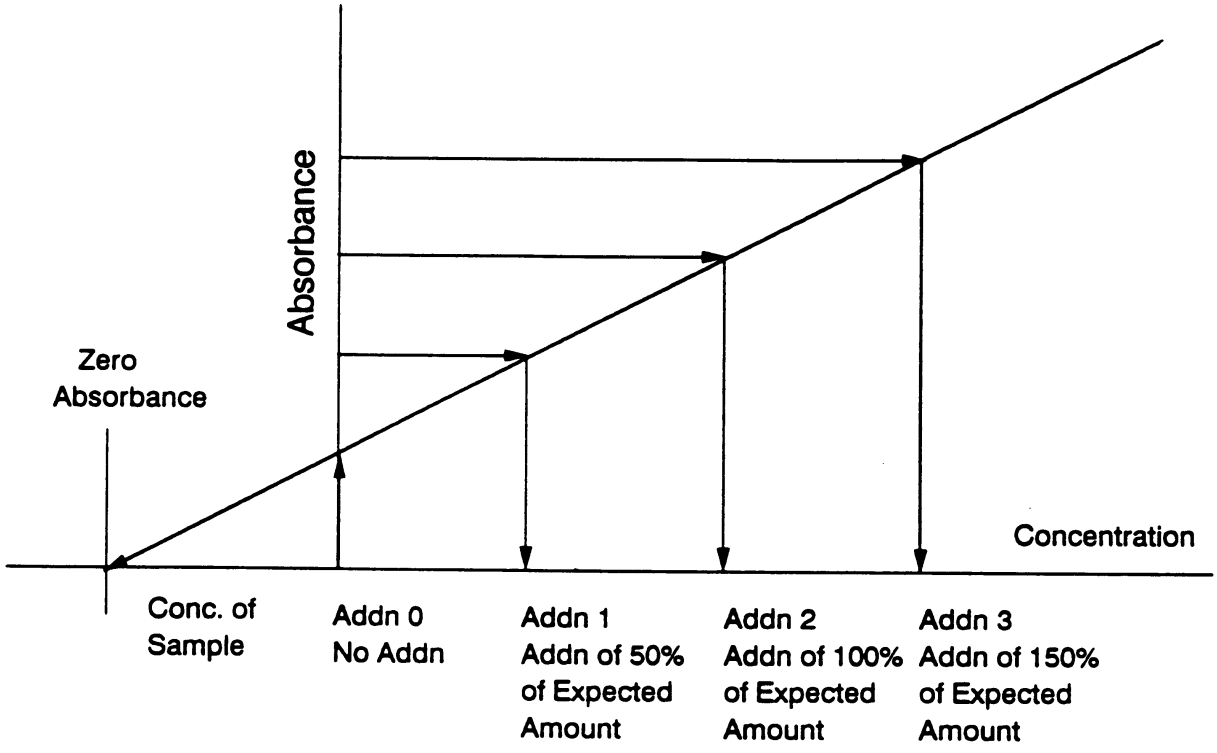
ELEMENT	WAVELENGTH (nm)	PURGE GAS[1]	COMMENTS
Sb	217.6, 231.1	argon or nitrogen	
As	193.7	argon	
Ba	553.6	argon	nitrogen should not be used
Be	234.9	argon	
Cd	228.8	argon	
Cr	357.9	argon	nitrogen should not be used
Co	240.7	argon	
Cu	324.7	argon or nitrogen	
Fe	248.3, 248.8, 271.8, 302.1, 252.7	argon 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	

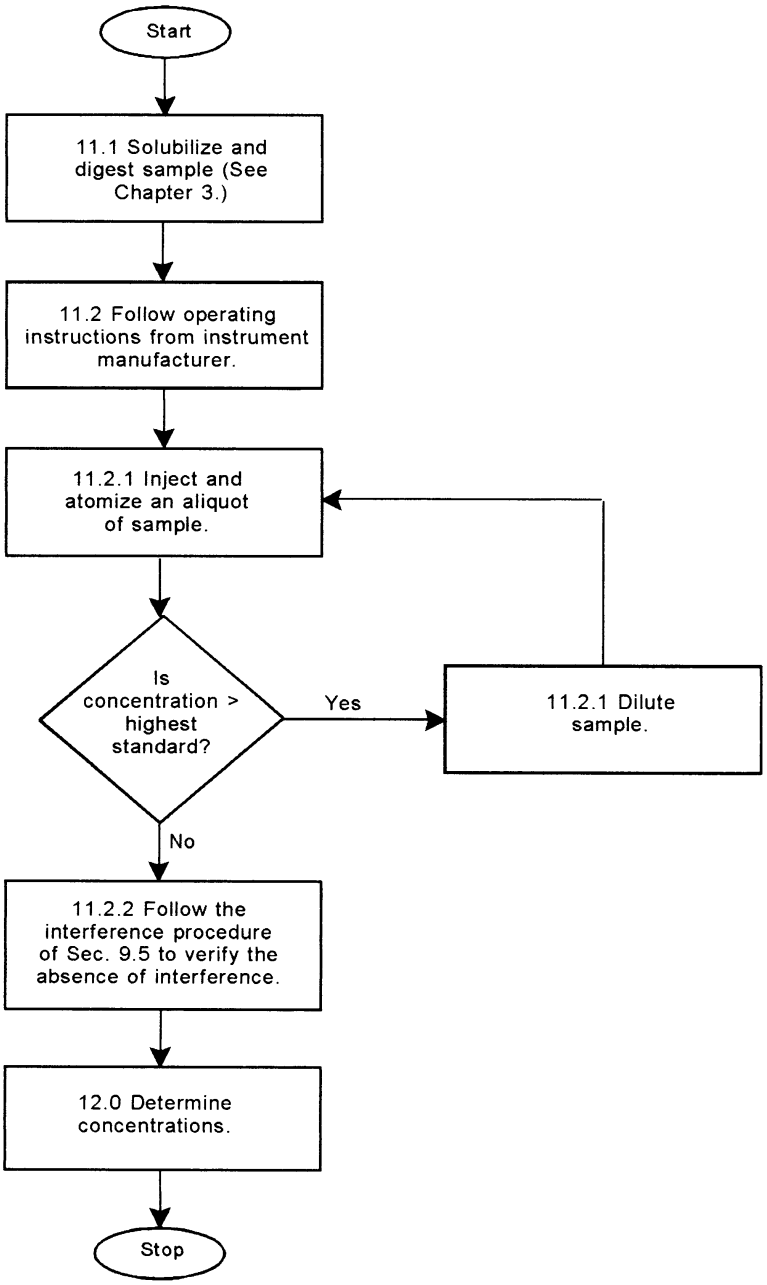
Note: If more than one wavelength is listed, the primary line is underlined.
[1]The argon/H_2 purge gas is also applicable.

Source: Ref. 1

FIGURE 1

STANDARD ADDITION PLOT




Start
11.1 Solubilize and digest sample (See Chapter 3.)
11.2 Follow operating instructions from instrument manufacturer.
11.2.1 Inject and atomize an aliquot of sample.
Is concentration > highest standard?
Yes
11.2.1 Dilute sample.
No
11.2.2 Follow the interference procedure of Sec. 9.5 to verify the absence of interference.
12.0 Determine concentrations.
Stop