

REVISIONS

METHOD 7000A

ATOMIC ABSORPTION METHODS

1.0 SCOPE AND APPLICATION

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters and domestic and industrial wastes. While drinking water free of particulate matter may be analyzed directly, ground water, other aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis for both total and acid leachable metals. Analysis for dissolved elements does not require digestion if the sample has been filtered and acidified.

1.2 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 direct aspiration and by furnace techniques. For clean aqueous samples, the detection limits shown in the table by direct aspiration may be extended downward with scale expansion and upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. For certain samples, lower concentrations may also be determined using the furnace techniques. 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. Detection limits should be established, empirically, for each matrix type analyzed. When using furnace techniques, however, 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. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see Step 3.2.1) and, if detected, treat them accordingly, using either successive dilution, matrix modification, or method of standard additions (see Step 8.7).

1.3 Where direct-aspiration atomic absorption techniques do not provide adequate sensitivity, reference is made to specialized procedures (in addition to the furnace procedure) such as the gaseous-hydride method for arsenic and selenium and the cold-vapor technique for mercury.

2.0 SUMMARY OF METHOD

2.1 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy, the technique generally is limited to metals in solution or solubilized through some form of sample processing.

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metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Step 3.2 (Sample Preparation Methods).

2.3 In direct-aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp or an electrodeless discharge lamp is directed through the flame into a monochromator, and onto a detector that measures the amount of absorbed light. Absorption depends upon the presence of free unexcited ground-state atoms in the flame. Because the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.4 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 INTERFERENCES

3.1 Direct aspiration

3.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome phosphate interference in magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

3.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. Although complexing agents are employed primarily to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

3.1.3 The presence of high dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scattering. If background correction is not available, a nonabsorbing wavelength should be checked. Preferably, samples containing high solids should be extracted.

3.1.4 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess (1,000 mg/L) of an easily ionized element such as K, Na, Li or Cs.

3.1.5 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.

3.1.6 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.1.7 All metals are not equally stable in the digestate, especially if it contains only nitric acid, not nitric acid and hydrochloric acid. The digestate should be analyzed as soon as possible, with preference given to Sn, Sb, Mo, Ba, and Ag.

3.2 Furnace procedure

3.2.1 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. To help verify the absence of matrix or chemical interference, the serial dilution technique (see Step 8.6) may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.
2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see Step 8.7.2).

3.2.2 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.

3.2.3 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, e.g., Zeeman background correction.

3.2.4 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.

3.2.5 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.

3.2.6 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. If 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.

3.2.7 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.

- 3.2.8 For comments on spectral interference, see Step 3.1.5.

3.2.9 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 Step 4.8. Pipet tips are a frequent source of contamination. 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 reagent blanks in both analysis and in the correction of analytical results. Lastly, 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.

4.0 APPARATUS AND MATERIALS

4.1 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.

4.2 Burner - The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

4.3 Hollow cathode lamps - Single-element lamps are preferred but multielement lamps may be used. Electrodeless discharge lamps may also be used when available.

4.4 Graphite furnace - Any furnace device capable of reaching the specified temperatures is satisfactory.

4.5 Graphical display and 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.

4.6 Pipets - Microliter, with disposable tips. Sizes can range from 5 to 100 μ L as required. Pipet tips should be checked as a possible source of contamination prior to their use. The accuracy of automatic pipets must be verified daily.

4.7 Pressure-reducing valves - The supplies of fuel and oxidant should be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

4.8 Glassware - All glassware, polypropylene, or Teflon containers, including sample bottles, flasks and pipets, should be washed in the following sequence: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, 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 reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

5.0 REAGENTS

5.1 Reagent grade chemicals shall 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 provide proof that all constituents are below the MDLs.

5.2 Reagent water. All references to water in this method refer to reagent water unless otherwise specified. Reagent grade water will be of at least 16 Mega Ohm quality.

5.3 Nitric acid (concentrated), 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.

5.4 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.

5.5 Fuel and oxidant - High purity acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or a cylinder of compressed air and should be clean and dry. Nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

5.6 Stock standard metal solutions - Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic salts using 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. Where the sample viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used (see Step 8.7).

5.7 Calibration standards - For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorbance of 0.0 to 0.7. Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time a batch of samples is analyzed. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve. 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. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal. Calibration curves are always required.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Metallic Analytes.

7.0 PROCEDURE

7.1 Preliminary treatment of waste water, ground water, EP 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, Step 3.2, Sample Preparation Methods. Samples which are to be analyzed for dissolved constituents need not be digested if they have been filtered and acidified.

7.2 Direct aspiration (flame) procedure

7.2.1 Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for a particular instrument. In general, after choosing the proper lamp for the analysis, allow the lamp to warm up for a minimum of 15 minutes, unless operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant. Adjust the burner and nebulizer flow rate for maximum percent absorption and stability. Balance the photometer. Run a series of standards of the element under analysis. Construct a calibration curve by plotting the concentrations of the standards against absorbances. Set the curve corrector of a direct reading instrument to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples is run.

7.3 Furnace procedure

7.3.1 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.

7.3.2 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.

7.3.3 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.

7.3.4 Inject a measured microliter 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.

7.3.5 To verify the absence of interference, follow the serial dilution procedure given in Step 8.6.

7.3.6 A check standard should be run after approximately every 10 sample injections. 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.

7.4 Calculation

7.4.1 For determination of metal concentration by direct aspiration and furnace: Read the metal value in ug/L from the calibration curve or directly from the read-out system of the instrument.

7.4.2 If dilution of sample was required:

$$\text{ug/L metal in sample} = A \left(\frac{C + B}{C} \right)$$

where:

- A = ug/L of metal in diluted aliquot from calibration curve.
- B = Acid blank matrix used for dilution, mL.
- C = Sample aliquot, mL.

7.4.3 For solid samples, report all concentrations as ug/kg based on wet weight. Hence:

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

where:

- A = ug/L of metal in processed sample from calibration curve.
- V = Final volume of the processed sample, mL.
- W = Weight of sample, grams.

7.4.4 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. If dilution of the sample was required:

$$\text{ug/L of metal in sample} = Z \left(\frac{C + B}{C} \right)$$

where:

- Z = ug/L of metal read from calibration curve or read-out system.
- B = Acid blank matrix used for dilution mL.
- C = Sample aliquot, mL.

8.0 QUALITY CONTROL

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

8.2 A calibration curve must be prepared each day with a minimum of a calibration blank and three standards. After calibration, the calibration curve must be verified by use of at least a calibration blank and a calibration check standard (made from a reference material or other independent standard material) at or near the mid-range. The calibration reference standard must be measured within 10 % of it's true value for the curve to be considered valid.

8.3 If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a mid-range standard or reference standard after every 10 samples. This sample value must be within 20% of the true value, or the previous ten samples need to be reanalyzed.

8.4 At least one matrix spike and one matrix spike duplicate sample shall be included in each analytical batch. A laboratory control sample shall also be processed with each sample batch. Refer to Chapter One for more information.

8.5 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 8.7 below). Section 8.6 provides tests to evaluate the need for using the MSA.

8.6 Interference tests

8.6.1 Dilution test - For each analytical batch select one typical sample for serial dilution to determine whether interferences are present. The concentration of the analyte should be at least 25 times the estimated detection limit. Determine the apparent concentration in the undiluted sample. Dilute the sample by a minimum of five fold (1+4) and reanalyze. If all of the samples in the batch are below 10 times the detection limits, perform the spike recovery analysis described below. Agreement within 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.

8.6.2 Recovery test - If results from the dilution test do not agree, a matrix interference may be suspected and a spiked sample should be analyzed to help confirm the finding from the dilution test. Withdraw another 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 all of the samples in the batch have analyte concentrations below the detection limit, spike the

selected sample at 20 times the detection limit. Analyze the spiked sample and calculate the spike recovery. If the recovery is less than 85% or greater than 115%, the method of standard additions shall be used for all samples in the batch.

8.7 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 compensates 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 shall be used for analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

8.7.1 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 the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

$$C_x = \frac{S_B^V C_s}{(S_A - S_B) V_x}$$

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.

8.7.2 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 than the expected absorbance from the endogenous 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.

8.7.3 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 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. If the slope is significantly different (greater than 20%), caution should be exercised.

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.

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

9.0 METHOD PERFORMANCE

9.1 See individual methods.

10.0 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.

TABLE 1.
ATOMIC ABSORPTION CONCENTRATION RANGES

Metal	Direct Aspiration		Furnace Procedure ^{a,c} Detection Limit (ug/L)
	Detection Limit (mg/L)	Sensitivity (mg/L)	
Aluminum	0.1	1	--
Antimony	0.2	0.5	3
Arsenic ^b	0.002	--	1
Barium	0.1	0.4	--
Beryllium	0.005	0.025	0.2
Cadmium	0.005	0.025	0.1
Calcium	0.01	0.08	--
Chromium	0.05	0.25	1
Cobalt	0.05	0.2	1
Copper	0.02	0.1	1
Iron	0.03	0.12	1
Lead	0.1	0.5	1
Lithium	0.002	0.04	--
Magnesium	0.001	0.007	--
Manganese	0.01	0.05	0.2
Mercury ^d	0.0002	--	--
Molybdenum(p)	0.1	0.4	1
Nickel	0.04	0.15	--
Osmium	0.03	1	--
Potassium	0.01	0.04	--
Selenium ^b	0.002	--	2
Silver	0.01	0.06	0.2
Sodium	0.002	0.015	--
Strontium	0.03	0.15	--
Thallium	0.1	0.5	1
Tin	0.8	4	--
Vanadium(p)	0.2	0.8	4
Zinc	0.005	0.02	0.5

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

^aFor furnace sensitivity values, consult instrument operating manual.

^bGaseous hydride method.

^cThe listed furnace values are those expected when using a 20-uL injection and normal gas flow, except in the cases of arsenic and selenium, where gas interrupt is used.

^dCold vapor technique.