Designation: ~~D3919 – 08~~ D3919 – 15

Standard Practice for
Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry[1]

This standard is issued under the fixed designation D3919; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. ~~Scope~~ Scope*

1.1 This practice covers the general considerations for the quantitative determination of trace elements in water and wastewater by graphite furnace atomic absorption spectrophotometry. Furnace atomizers are a most useful means of extending detection limits; however, the practice should only be used at concentration levels below the optimum range of direct flame aspiration atomic absorption spectrophotometry. Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of a particular instrument.

1.2 Wavelengths, estimated detection limits, and optimum concentration ranges are given in the individual methods. Ranges may be increased or decreased by varying the volume of sample injected or the instrumental settings or by the use of a secondary wavelength. Samples containing concentrations higher than those given in the optimum range may be diluted or analyzed by other techniques.

1.3 This technique is generally not applicable to brines and seawater. Special techniques such as separation of the trace elements from the salt, careful temperature control through ramping techniques, or matrix modification may be useful for these samples.

1.4 The analyst is encouraged to consult the literature as provided by the instrument manufacturer as well as various trade journals and scientific publications.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *graphite ~~furnace~~ furnace, n*—an electrothermal graphite device capable of reaching the specified temperatures required by the element being determined.

*A Summary of Changes section appears at the end of this standard.

3.2.2 *platform or similar ~~device—~~device, n—* a flat, grooved or ungrooved piece of pyrolytic graphite (which is inserted in the graphite ~~tube~~tube) on which the sample is placed (**1**).[3]

4. Summary of Practice

4.1 The element is determined by an atomic absorption spectrophotometer used in conjunction with a graphite furnace. The principle is essentially the same as with direct flame aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. The elemental 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. Radiation from a given excited element is passed through the vapor containing ground-state atoms of that element. The decrease in intensity of the transmitted radiation is a measure of the amount of the ground-state element in the vapor. A monochromator isolates the characteristic radiation from the hollow-cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

4.2 Dissolved elements are determined on a filtered sample with no pretreatment. See 9.5.

4.3 Total recoverable elements are determined following acid digestion and filtration. If suspended material is not present, this digestion and filtration may be omitted.

5. Significance and Use

5.1 Elemental constituents in potable water, receiving water, and wastewater need to be identified for support of effective pollution control programs. Currently, one of the most sensitive and practical means for measuring low concentrations of trace elements is by graphite furnace atomic absorption spectrophotometry. ICP-MS may also be appropriate but at a higher instrument cost. See Test Method D5673.

6. Interferences

6.1 Background absorption is caused by the formation of molecular species from the sample matrix that absorb or scatter the light emitted by the hollow cathode or electrodeless discharge line source. Without correction, this will cause the analytical results to be erroneously high. Three approaches exist for simultaneous background correction: continuum source, Zeeman, and Smith-Hieftje.

6.1.1 *Continuum Source*—The continuum source procedure involves the use of a deuterium arc source for the ultraviolet or a tungsten halide lamp for the visible region of the spectrum. Light from the primary spectral source and the appropriate continuum source are alternately passed through the graphite furnace. Narrow-band emission of the primary source is affected by the scatter and background absorption from the matrix as well as the absorption of light by analyte atoms. The broadband emission of the continuum source is affected only by the background absorption. The effect of the background is removed by taking a ratio of the energy of the two sources.

6.1.2 *Zeeman Correction*—The Zeeman correction system involves the use of an external magnetic field to split the atomic spectral line. When the magnetic field is off, both sample and background are measured. When the magnetic field is applied, the absorption line is shifted and only the background absorption is measured. Background correction is performed by electronically comparing the field-off and field-on measurements, yielding an analyte-only absorption response.

6.1.3 *Smith-Hieftje System*—This system involves cycling the atomic line source at high currents for brief intervals. These intervals cause nonexcited atoms of the source element to undergo the process of self-reversal by emitting light at wavelengths other than those of the analyte. This light is absorbed only by the background, so that interspersing periods of high and low source current permit correction of the background.

6.2 Some types of interference problems encountered in direct aspiration atomic absorption spectrophotometry can be observed with the furnace technique. Although quite rare, spectral interference may be encountered. When this occurs, the use of another wavelength is suggested. Additionally, the furnace technique is subject to chemical and matrix interference and the composition of the sample matrix can have a major effect on the analysis. Therefore, for each different matrix encountered, the possibility of these interferences should be considered.

6.3 Gases generated in the furnace during the atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either using background correction or choosing an alternative wavelength outside the absorption band should eliminate this interference. Nonspecific broadband absorption interference can also be compensated by background correction.

6.4 Memory effects occur if, during atomization, all the analyte is not volatilized and removed from the furnace. This condition is dependent on several factors, such as the volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. If this situation is detected through blank burns, the tube must be cleaned by operating the furnace at full power for the required time period at regular intervals in the analytical scheme.

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[3] The boldface numbers in parentheses refer to the list of references at the end of this standard.

6.5 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature. Also, some instruments utilize an ashing cycle in the presence of air. Take care, however, to prevent loss of analyte.

6.6 Samples containing large amounts of organic material should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way, broadband absorption will be minimized. The use of expendable-type laboratory ware should be considered to limit contamination.

6.7 Carbide formation, resulting from the chemical environment of the furnace, has been observed with certain elements that form carbides at high temperatures. Barium, molybdenum, nickel, titanium, and vanadium may be cited as examples. When this takes place, the element will be released very slowly from the carbide and longer atomization times may be required before the signal returns to baseline levels. This problem is greatly reduced and sensitivity increases with the use of pyrolytically coated graphite.

6.8 Ionization interferences have to date not been reported with furnace techniques.

6.9 Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. Keep the sample preparation work area scrupulously clean (see 9.1). Clean all glassware with dilute HNO_3 (1 + 1). Pipette tips have been known to be a source of contamination. If suspected, acid soak them with HNO_3 (1 + 1) and rinse thoroughly with water. The use of only high-quality pipette tips greatly reduces this problem. It is very important that special attention be given to reagent blanks in both the analysis and the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five, to possibly ten, high-temperature burns may be required to clean the tube before use.

6.10 Oxide formation is greatly reduced because atomization occurs in an inert atmosphere.

6.11 Several investigators who have studied interferences in the graphite furnace have concluded that nitrate is the preferred anion of the matrix. Therefore, nitric acid is preferable for any digestion or solubilization step. If the situation absolutely requires the use of another acid in addition to HNO_3, or in place of HNO_3 (for example, tin), use the minimum amount of acid. This applies particularly to hydrochloric and perchloric acids, but also to sulfuric and phosphoric acids to a lesser extent.

6.12 ~~Some types of interference problems encountered in direct aspiration atomic absorption spectrophotometry can be observed with the furnace technique. Although quite rare, spectral interference may be encountered. When this occurs, the use of another wavelength is suggested. Additionally, the furnace technique is subject to chemical and matrix interference and the composition of the sample matrix can have a major effect on the analysis. Therefore, for each different matrix encountered, the possibility of these interferences should be considered.~~ The tests as outlined in ~~6.2.1~~6.12.1 – ~~6.2.5~~6.12.5 are recommended prior to reporting analytical data. These tests will provide indication whether positive or negative interference effects are operative in any way on the analyte elements thereby distorting the accuracy of the reported values.

6.12.1 *Spiking Verification*—When the sample absorbance is 40 % or less of the absorbance of the highest standard on the standard curve, the amount of spike added to the sample should result in a net increase equal to 50 % of the highest standard concentration. The purpose of adding a large spike is to differentiate between matrix interferences and random errors. The recovery of the spike must be between 90 and 110 % for verification of the original determination. If the result of the original determination is above 40 % on the curve, two aliquots should be withdrawn and diluted at least 1 + 1. One of the aliquots should be spiked before dilution with an amount resulting in a net increase over the unspiked aliquot equivalent to 50 % of the highest standard concentration. The reported result should be based on the analysis of the diluted aliquot. For verification of this result, the spike recovery must be between 90 and 110 %. For spiking verification to be valid in either situation in the presence of nonspecific absorbance, simultaneous background correction must be used during analysis. If the result of the determination cannot be verified, the sample should be treated in one or more of the following ways:

6.12.2 *Serial Dilution*—Successively dilute and reanalyze the sample using spiking verifications to determine if the interference can be eliminated. This assumes that the analyte occurs at a sufficiently high concentration.

6.12.3 *Matrix Modification*—Matrix modifiers are frequently used to stabilize volatile or moderately volatile analyte metals such as lead, cadmium, chromium, and nickel. Metals such as these begin to volatilize at very low temperatures and require that the charring/ashing temperature be lowered. Lower charring/ashing temperatures reduce the chance of removing potential interferents from the matrix during the charring/ashing step. Adding certain chemical compounds or combinations of chemical compounds will reduce the volatility of selected metals by the formation of less volatile compounds during the charring/ashing process. The use of ammonium dihydrogen phosphate or phosphoric acid results in higher volatilization temperatures for many elements, thus permitting the use of higher charring/ashing temperatures to remove or reduce matrix interferences. Nickel nitrate has been shown to perform the same role for arsenic and selenium by forming high temperature arsenides and selenides. An alternate approach to the same problem is to reduce the temperature at which the matrix volatilizes, permitting it to be removed at a lower charring/ashing temperature. Sodium chloride in seawater can be volatilized by adding ammonium nitrate as a matrix modifier. The sodium nitrate and ammonium chloride formed are more volatile than the sodium chloride and can be volatilized at much lower charring/ashing temperatures. Other matrix modifiers include various organic acids such as citric and ascorbic acid. These acids are believed to reduce matrix interferences by preventing the formation of large salt crystals that can occlude the analyte. A table of additional matrix modifiers is given in Appendix X1. See also the literature (~~22-18~~–3).

6.12.4 *Platform Furnaces*—The pseudo-constant temperature furnace design suggested by L'Vov (1) has minimized matrix and gas phase interference problems. L'Vov placed a graphite platform inside the graphite tube furnace to approximate a constant temperature design. Since the platform is heated by radiation, it lags behind the tube walls in temperature, and delays the atomization of the analyte until the tube atmosphere is at a higher, more constant temperature. This results in reduced vapor-phase condensation and reduces the effect of the sample matrix on the analyte signal. The integrated absorbance signal is proportional to the number of atoms in the sample, independent of the rate at which atomization occurs. This type of furnace is commercially available or the modification can be made by the user (419).

6.12.5 *Standard Additions*—Analyze the sample by method of standard additions while noting the precautions and limitations of its use. See 12.4.

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7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*—Single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, wavelength range from 190 to 800 nm, and simultaneous background correction.

7.2 *Hollow-Cathode Lamps*—Single-element lamps are preferred but multi-element lamps may be used. Electrodeless discharge lamps may also be used when available, and are preferred for elements such as As, Se, Sb.

7.3 *Graphite Tubes*—Graphite tubes should be compatible with furnace device. Pyrolytically coated graphite tubes are recommended.

7.4 *Data System*—Data are collected using internal microprocessor or external desktop computer systems. Data can be stored on disks, transmitted to central servers, or printed in hard copy. Data may be evaluated and processed using the instrument's dedicated systems to determine analyte concentrations. Users of this practice may use a strip chart recorder to obtain sample and calibration data, if desired.

7.5 Automatic sampling should be used. Studies have shown that the coefficient of variation for aqueous samples varies from 0.4 to ~~1.6~~1.6 %, depending upon the metal and concentration (**520**).

8. Reagents and Materials

8.1 *Purity of Reagents*—It is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society as a minimum when such specifications are available.[4] The high sensitivity of graphite furnace atomic absorption spectrophotometry may require reagents of a higher purity. Stock standard solutions are prepared from high-purity metals, oxides, or nonhydroscopic reagent grade salts using water and ultrapure nitric acid. Sulfuric, hydrochloric, and phosphoric acids are to be avoided wherever possible as they produce an adverse effect on many elements. A lesser grade of nitric acid and reagents 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type I of Specification D1193. Other reagent water types may be used, provided it is first ascertained that the water is of sufficiently high purity to permit its use without lessening the bias and precision of the determination.

8.3 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-μm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

8.4 *Nitric Acid* (sp gr 1.42)—Distilled ultrapure concentrated nitric acid (HNO_3). [5]

8.5 *Standard Solution, Stock* (1 mL = 1 mg element)—Prepare each stock solution at a concentration of 1000 mg of the element per liter. Commercially available standard solutions of appropriate known purity may also be used.

8.6 *Argon,* standard, welders grade, commercially available. Nitrogen, argon with 5 % hydrogen, and hydrogen may also be used if recommended by the instrument manufacturer. The analyst should be aware that moisture present in some grades of inert gas may cause interference. The use of dry or moisture-free inert gas is suggested.

9. Samples and Sampling Procedures

9.1 *Sample Handling*—For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus that the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by: (*a*) contributing contaminants through leaching or surface desorption, or (*b*) by depleting concentrations through absorption. Thus, the collection and treatment of the sample prior to analysis requires particular attention (see 6.8).

9.2 *Sample Collection*—Collect all samples in accordance with Practices D3370.

9.3 *Sample Containers*—Store the sample in a clean glass, linear polyethylene, polypropylene, or TFE-fluorocarbon container.

9.4 *Sample Size*—Sample size must be sufficient to allow for the determination. In general, use microliter sample aliquots for the analysis. However, when sample processing or multiple analyses, or both, are required, larger sample volumes may be necessary.

9.5 *Sample Preservation*—In most cases, samples are preserved by adding HNO_3 to a pH of less than 2. However, certain metals may require a different type of preservation. The analyst should refer to the specific method for guidance. If only dissolved elements are to be determined, filter the sample through a 0.45-μm membrane filter before adding acid. Filter and preserve as soon as possible, preferably at the time of collection.

NOTE 1—Alternatively, the filtration and pH may be adjusted in the laboratory if the sample is returned within 14 days. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

9.6 *Sample Storage*—Analyze samples containing trace concentrations of analyte as soon as possible, preferable at the time of collection. The holding time for the samples may be calculated in accordance with Practice D4841.

10. Preparation of Atomic Absorption Spectrophotometer

10.1 *Furnace Device*—Mount the furnace device in accordance with the instructions provided by the instrument manufacturer.

10.2 Turn on the instrument and allow the warm-up as instructed by the instrument manufacturer.

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[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[5] Commercially available Spectrograde or Utrex grade of acids have been found satisfactory for this purpose.

11. Calibration and Standardization

11.1 Initially set up the instrument in accordance with the manufacturer's specifications. Because of the differences between the various makes and models of satisfactory instruments, no detailed operating instructions can be given. Instead, the analyst should follow the instructions provided by the manufacturer for optimizing the drying temperature and time, the charring/ashing temperature and time, and the atomization temperature (or setting) and time.

11.1.1 With electrothermal (or furnace) atomization, background correction becomes of great importance especially at wavelengths less than 350 nm. This is because certain samples, when atomized, absorb or scatter light from the hollow-cathode lamp. This condition can be caused by the presence of gaseous molecular species, salt particles, or particulate matter 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. Background correction is discussed in 6.1.

11.1.2 Some analytical equipment provides for the interruption of the inert or sheath gas flow during the atomization step. This interruption has the advantage of reducing to a minimum the convection of the sample out of the optical beam, and therefore increasing sensitivity. At the same time, gas interruption also increases the unwanted matrix material in the optical beam, usually an undesirable condition. In general, the "gas-interrupt" option should not be used unless the absolute maximum analytical sensitivity is required and the increase in "background" or matrix signal is not harmful. Analyze both samples and standards using identical gas flow conditions. Systems not having "gas-interrupt" features will not necessarily have lower sensitivities.

11.2 Prepare calibration standards by diluting stock solutions at the time of analysis. For best results, prepare these calibration standard solutions daily, or as required, and discard after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. Analyze at least three working standards containing concentrations of each element that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. Space the calibration standards evenly in concentrations from 0 to 20 % greater than the highest expected value. Prepare the calibration standards with the same acid and at the same acid concentration as will result in the sample to be analyzed either directly or after processing.

11.3 Beginning with the blank and working toward the highest standard, analyze the solutions and record the readings.

11.4 Using the electronic data system on the instrument, construct an analytical curve by plotting the absorbances of standards versus their concentrations. Verify an acceptable correlation coefficient for the standard curve. Read results directly in concentration units.

11.4.1 Prepare a new analytical curve for each new series of samples.

12. Samples Analysis Procedure

12.1 Inject a measured aliquot of sample into the furnace device, dry, char/ash, and atomize. If the concentration found is greater than the highest standard, dilute the sample to the same acid concentration and reanalyze or extend the standard curve by analyzing additional calibration standards. The use of multiple injections improves accuracy and helps to detect furnace pipetting errors. It is strongly recommended that the same volume of sample be injected as was used for preparation of the analytical curve.

12.1.1 When the sample to be analyzed contains little or no suspended particles, prior digestion of the sample may not be required. The analyst is responsible for determining the need for sample digestion. The analyst should be aware that digestion would provide for a more uniform matrix and possibly lessen matrix effects for the sample containing dissolved organic material.

12.2 To verify the absence of interference, if necessary, or to minimize interferences, follow the procedureprocedures as given earlier in 6.1.16.12.

12.3 Analyze a check standard after approximately every ten sample injections 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, and a conservative estimate is that a tube will last at least 150 firings. A pyrolytic coating extends that estimate by a factor of about three.

12.4 If the method of standard additions is required (6.2.56.12.5), use four equal aliquots of sample. Dilute the first aliquot to a known volume with water. Add different known amounts of the test element to each of the second, third, and fourth aliquots before they are diluted to the same volume with water, so that the final solutions contain different additions of the analyte. Maintain the concentration of acid and matrix modifiers, if added, at approximately the same level for all four solutions. The volume of all four final solutions must be identical. Using the instrument's software, determine the absorbance of each solution and prepare a graph showing absorbance versus concentration. Scale the vertical axis in absorbance and the horizontal axis in concentrations of the known additions. Scale the abscissa to the left of the ordinate the same as to the right of the ordinate. Plot the absorbances of the four solutions on the graph and extrapolate the resulting line back to zero absorbance. The intercept with the abscissa on the left of the ordinate is the concentration of the unknown. For the method of standard additions to be valid, take the following limitations into consideration:

12.4.1 The absorbance plot of sample and standards must be linear over the concentration range of concern. For best results, the slope of the plot should be nearly the same as the slope of the aqueous analytical curve. If the slope is significantly different, repeat the exercise using a greater sample dilution.

12.4.2 The effect of the interference should remain constant as the ratio of analyte concentration to sample matrix changes.