Designation: 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*

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

3.2.2 *platform or similar device, n*— a flat, grooved or ungrooved piece of pyrolytic graphite (which is inserted in the graphite 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

[1] This practice is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

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

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

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.

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