Designation: D4691 – 17

Standard Practice for
Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry[1]

This standard is issued under the fixed designation D4691; 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 general considerations for the quantitative determination of elements in water and waste water by flame atomic absorption spectrophotometry. Flame atomic absorption spectrophotometry is simple, rapid, and applicable to a large number of elements in drinking water, surface waters, and domestic and industrial wastes. While some waters may be analyzed directly, others will require pretreatment.

1.2 Detection limits, sensitivity, and optimum ranges of the elements will vary with the various makes and models of satisfactory atomic absorption spectrometers. The actual concentration ranges measurable by direct aspiration are given in the specific test method for each element of interest. In the majority of instances the concentration range may be extended lower by use of electrothermal atomization and conversely extended upwards by using a less sensitive wavelength or rotating the burner head. Detection limits by direct aspiration may also be extended through sample concentration, solvent extraction techniques, or both. Where direct aspiration atomic absorption techniques do not provide adequate sensitivity, the analyst is referred to Practice D3919 or specialized procedures such as the gaseous hydride method for arsenic (Test Methods D2972) and selenium (Test Methods D3859), and the cold vapor technique for mercury (Test Method D3223).

1.3 Because of the differences among various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead the analyst should follow the instructions provided by the manufacturer of a particular instrument.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversion to inch-pound units that are provided for information only and are not considered standard.

1.5 *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.* For specific hazard statements see Section 9.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2972 Test Methods for Arsenic in Water
D3223 Test Method for Total Mercury in Water
D3370 Practices for Sampling Water from Closed Conduits
D3859 Test Methods for Selenium in Water
D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry
D4453 Practice for Handling of High Purity Water Samples
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E178 Practice for Dealing With Outlying Observations
E520 Practice for Describing Photomultiplier Detectors in Emission and Absorption Spectrometry
E863 Practice for Describing Atomic Absorption Spectrometric Equipment (Withdrawn 2004)[3]

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

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *absorbance, n*—the logarithm to the base 10 of the reciprocal of the transmittance (*T*). $A = \log_{10}(1/T) = -\log_{10} T.$

3.2.2 *absorptivity, n*—the absorbance (*A*) divided by the product of the sample path length (*b*) and the concentration (*c*). $a = A/bc.$

3.2.3 *atomic absorption, n*—the absorption of electromagnetic radiation by an atom resulting in the elevation of electrons from their ground states to excited states.

3.2.3.1 *Discussion*—Atomic-absorption spectrophotometry involves the measurement of light absorbed by atoms of interest as a function of the concentration of those atoms in a particular solution.

3.2.4 *continuing calibration blank, n*—a solution containing no analytes (of interest) which is used to verify blank response and freedom from carryover.

3.2.5 *continuing calibration verification, n*—a solution (or set of solutions) of known concentration used to verify freedom from excessive instrumental drift; the concentration is to cover the range of calibration curve.

3.2.6 *detection limit, n—in atomic absorption,* a function of the sensitivity and the signal–to–noise ratio in the analysis of a specific element for a given set of parameters.

3.2.6.1 *Discussion*—The instrument detection limit is determined statistically as some multiple, usually two or three times the standard deviation of the signal-to-noise ratio.

3.2.7 *laboratory control sample (LCS), n*—a solution with the certified concentration(s) of the analytes.

3.2.8 *monochromator, n*—a device used for isolating a narrow portion of the spectrum by means of a grating or prism.

3.2.9 *nebulizer, n—in atomic absorption*, the burner-system portion where the sample solution is converted into fine mist.

3.2.10 *optimum concentration range, n*—a limited concentration range, that may be extended downward with scale expansion (used to measure very small concentrations) or upward by using a less sensitive wavelength or by rotating the burner head.

3.2.10.1 *Discussion*—The range varies with the characteristic concentration of the instrument and the operating conditions employed.

3.2.11 *sensitivity, n*—the analyte concentration (sometimes referred to as the characteristic concentration) that produces an absorbance of 0.0044 absorbance units (1 % absorption) when compared to the analytical blanks.[4,5,6]

3.2.11.1 *Discussion*—The characteristic concentration var-

ies with instrumental conditions and atomization efficiency, as well as other factors and should be determined as conditions change. The characteristic concentration is determined by the following equation:

$$\text{characteristic concentration} = C \times 0.0044/A \qquad (1)$$

where:
C = concentration of the analyte, and
A = absorbance of analyte concentration used in the determination.

The characteristic concentration defines the slope of the calibration curve.

3.2.12 *spectral bandwidth, n*—the observed dispersion between absorption bands.

3.2.12.1 *Discussion*—This bandwidth is expressed as the exit slit multiplied by the observed separation of two emission lines divided by the difference in wavelength between these lines.

3.2.13 *spectrophotometer, n*—an instrument that provides the ratio, or a function of the ratio, of the radiant power of a beam as a function of spectral wavelength.

4. Summary of Practice

4.1 In flame atomic absorption spectrophotometry, a standard or sample solution is aspirated as a fine mist into a flame where it is converted to an atomic vapor consisting of ground state atoms. The flame provides energy to the ground state atoms allowing them to absorb electromagnetic radiation from a series of very narrow, sharply defined wavelengths. Light (from a hollow cathode lamp or other source) consisting of the characteristic monochromatic radiation generated by excitation of the element of interest is passed through the flame. Light from the source beam is isolated by the monochromator and measured by the photodetector. The amount of light absorbed by the analyte is quantified by comparing the light transmitted through the flame during nebulization of a known concentration of the analyte to light transmitted during nebulization of a solution that does not contain any measurable concentration of the analyte.

4.2 An atomic absorption spectrophotometer may have a single or double beam system. The advantages of a single beam system are that the lamp used as a light source can be operated at much lower currents than those used in a double beam system, thereby minimizing the problem of line broadening. This provides for increased sensitivity and longer lamp life. The disadvantage of single beam instruments is that a longer warm-up time is required and there is no means of correcting for changes in intensity of the light source without continually zeroing the instrument between measurements.

4.3 The thermal energy provided by the flame causes the dissociation of metallic elements from their compounds and the reduction of the elements to the ground state. The richness or leanness of the flame may have a bearing on sensitivity. The variation in hydrocarbon content of the flame will have an effect on the number of atoms reduced to the ground state. The compounds of some elements, especially refractory elements such as aluminum or molybdenum are highly resistant to

[4] Bennett, P. A., and Rothery, E., *Introducing Atomic Absorption Analysis*, Varian Publication, Mulgrave, Australia, 1983.

[5] Price, W. J., *Spectrochemical Analysis by Atomic Absorption*, John Wiley & Sons, New York, NY, 1983.

[6] VanLoon, J. C., *Analytical Atomic Absorption Spectroscopy—Selected Methods*, Academic Press, New York, NY, 1980.

thermal decomposition and therefore require a higher temperature flame than less refractory elements such as iron or copper. This is the reason that the nitrous oxide-acetylene flame is required for these elements.

4.4 The amount of light absorbed in the flame is proportional to the concentration of the element in solution. The relationship between absorption and concentration is expressed by Beer's law:

$$I = I_o 10^{-abc} \qquad (2)$$

where:

I = transmitted radiant power,
I_o = incident radiant power,
a = absorptivity,
b = sample path length, and
c = concentration of absorbing species within the path of the light beam, mg/L.

4.5 The atomic absorption spectrophotometer is calibrated with standard solutions containing known concentrations of the element of interest. A calibration curve is constructed for each analyte from which the concentration in the unknown sample is determined.

5. Significance and Use

5.1 Elemental constituents in water and wastewater need to be identified to support effective water quality monitoring and control programs. Currently, one of the most widely used and practical means for measuring concentrations of elements is by atomic absorption spectrophotometry.

5.2 The major advantage of atomic absorption over atomic emission is the almost total lack of spectral interferences. In atomic emission, the specificity of the technique is almost totally dependent on monochromator resolution. In atomic absorption, however, the detector sees only the narrow emission lines generated by the element of interest.

6. Interferences

6.1 Background absorption is caused by the formation of molecular species from the sample matrix that scatter or absorb the light emitted by the hollow cathode or electrodeless discharge line source. Without correction, this will cause the analytical results to be erroneously high. If background correction is not available, a non-absorbing wavelength should be checked or the matrix of the standards and blank matched with the sample constituents. Background correction is usually not necessary unless the solids concentration of the sample is very high (>1 %), or the analysis is being carried out at very short wavelengths (<210 nm), or both. Preferably high solids type samples should be extracted. Three approaches exist for simultaneous background correction: continuum source, Zeeman, and Smith-Hieftje. There are different benefits for each of these background correction methods. The analyst should consult the manufacturer's literature for applicability to analytical requirements.

6.1.1 *Continuum Source*—The continuum source procedures involve the use of a hydrogen or 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 passed through the flame atomizer and alternately read. 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 significantly affected only by the background absorption. The effect of the background is virtually 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 Chemical interference is the most frequently encountered interference in atomic absorption spectrophotometry. A chemical interference may prevent, enhance, or suppress the formation of ground state atoms in the flame. For example, in the case of calcium determinations, the presence of phosphate or sulfate can result in the formation of a salt that hinders proper atomization of the solution when it is aspirated into an air-acetylene flame. This decreases the number of free, ground state atoms in the flame, resulting in lowered absorbance values. This interference can be eliminated by use of a nitrous oxide-acetylene flame. Likewise, aluminum can cause a similar interference when measuring magnesium. The addition of appropriate complexing agents to the sample solution is a technique intended to reduce or eliminate chemical interferences, and it may increase the sensitivity of the test method.

6.3 Alkali and alkaline earth metals, Groups I and II, such as sodium and potassium may undergo ionization in the air-acetylene and nitrous oxide-acetylene flames resulting in a decrease in ground state atoms available for measurement by atomic absorption. In the presence of an excess of an easily ionizable alkali element such as cesium, however, ionization of the alkali element will occur first and may minimize ionization of the element of interest.

6.4 If a sample containing low concentrations of the element being measured is analyzed immediately after a sample containing high concentrations, sample carryover may sometimes occur resulting in elevated readings. High concentrations are evidenced by marked flame coloration, a concentration reading higher than that of the highest standard, or, a large fluctuation in the energy gage, or all of these conditions. To prevent this type of sample interference, routine aspiration of reagent water