



Designation: D 4691 – 02

Standard Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry¹

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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 D 3919 or specialized procedures such as the gaseous hydride method for arsenic (Test Methods D 2972) and selenium (Test Methods D 3859), and the cold vapor technique for mercury (Test Method D 3223).

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 *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.

2. Referenced Documents

2.1 ASTM Standards:

- D 1129 Terminology Relating to Water²
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits²
- D 1193 Specification for Reagent Water²
- D 2972 Test Methods for Arsenic in Water²
- D 3223 Test Method for Total Mercury in Water²
- D 3370 Practices for Sampling Water from Closed Conduits²
- D 3859 Test Methods for Selenium in Water²
- D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry²
- D 4453 Practice for Handling of Ultra-Pure Water Samples²
- D 5810 Guide for Spiking into Aqueous Samples²
- D 5847 Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis³
- E 178 Practice for Dealing with Outlying Observations⁴
- E 520 Practice for Describing Detectors in Emission and Absorption Spectroscopy⁵
- E 863 Practice for Describing Flame Atomic Absorption Spectroscopy Equipment⁵

3. Terminology

3.1 Definitions:

3.1.1 For definition of terms used in this practice, refer to Terminology D 1129.

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. Atomic

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² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol 11.02.

⁴ Annual Book of ASTM Standards, Vol 14.02.

⁵ Annual Book of ASTM Standards, Vol 03.06.

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 *detection limit, n*—a function of the sensitivity and the signal to noise ratio in the analysis of a specific element for a given set of parameters. The detection limit is determined statistically as some multiple, usually two or three times the standard deviation of the signal to noise ratio.

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

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

3.2.7 *nebulizer, n*—as used in atomic absorption, that portion of the burner system where the sample solution is converted into fine mist.

3.2.8 *optimum concentration range, n*—defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. The range varies with the characteristic concentration of the instrument and the operating conditions employed.

3.2.9 *sensitivity, n*—sometimes referred to as the characteristic concentration. It is that concentration of the analyte which produces an absorbance of 0.0044 absorbance units (1 % absorption) when compared to the analytical blanks.^{6,7,8} The characteristic concentration varies 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:

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

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.

3.2.10 *spectral bandwidth, n*—related to the observed dispersion between absorption bands. It is expressed as the exit slit multiplied by the observed separation of two emission lines divided by the difference in wavelength between these lines.

3.2.11 *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 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:

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

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 interference.

⁶ Bennett, P. A., and Rothery, E., "Introducing Atomic Absorption Analysis," Varian Publication, Mulgrave, Australia, 1983.

⁷ Price, W. J., "Spectrochemical Analysis by Atomic Absorption," John Wiley & Sons, New York, NY, 1983.

⁸ VanLoon, J. C., "Analytical Atomic Absorption Spectroscopy—Selected Methods," Academic Press, New York, NY, 1980.