Designation: D 4691 – ~~96~~02

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

This standard is issued under the fixed designation D 4691; 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 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:*

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[1] This practice is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D 19.05 on Inorganic Constituents in Water.

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D 1129 Terminology Relating to Water[2]
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[2]
D 1193 Specification for Reagent Water[2]
D 2972 Test Methods for Arsenic in Water[2]
D 3223 Test Method for Total Mercury in Water[2]
D 3370 Practices for Sampling Water from Closed Conduits[2]
D 3859 Test Methods for Selenium in Water[2]
D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry[2]
D 4453 Practice for Handling of Ultra-Pure Water Samples[2]
E
D 178 Practice 5810 Guide for Dealing with Outlying Observations Spiking into Aqueous Samples[2]
D 5847 Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]
E 520 178 Practice for Describing Detectors in Emission and Absorption Spectroscopy Dealing with Outlying Observations[4]
E 520 Practice for Describing Detectors in Emission and Absorption Spectroscopy[5]
E 863 Practice for Describing Flame Atomic Absorption Spectroscopy Equipment 45

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 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.

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

3.2.78 *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.

3.2.89 *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

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 03.06. 14.02.

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

[5] *Annual Book of ASTM Standards*, Vol 03.06.

[6] Price, W. J., "Spectrochemical Analysis by

[6] Bennett, P. A., and Rothery, E., "Introducing Atomic Absorption," John Wiley & Sons, New York, NY, Absorption Analysis," Varian Publication, Mulgrave, Australia, 1983.

[7] VanLoon, J. C., "Analytical

[7] Price, W. J., "Spectrochemical Analysis by Atomic Absorption Spectroscopy—Selected Methods," Academic Press, Absorption," John Wiley & Sons, New York, NY, 19803.

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 *Analar 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.

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

A = absorbance of analyte concentration used in the determination.

The characteristic concentration defines the slope of the calibration curve.

3.2.910 *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.

3.2.10 *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:

$$I = I_o 10^{-abc} \tag{2}$$

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 broad-band 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 for about 15 s or more between samples is recommended, depending on the concentration of element in the last sample analyzed. Complete purging of the system is ascertained by aspirating water until the absorbance readout returns to near the baseline.

6.5 The physical properties of solutions being aspirated will not only change the nebulization uptake rate but will, for a variety of reasons, have a significant effect on sensitivity. Organic solvents such as those used in extraction techniques, will usually enhance sensitivity. Solutions with high dissolved solids will usually result in a reduction in sensitivity.

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*—A single or dual channel, single or double-beam instrument having a grating monochromator, photomultiplier detector adjustable spectral bandwidth, wavelength range from 190 to 800 nm, and provisions for interfacing with a strip chart recorder or a suitable data system. Refer to Practice E 863.

7.2 *Burner*—The burner recommended by the manufacturer of the spectrophotometer should be used. For certain elements, a nitrous oxide burner is required.

7.3 *Hollow Cathode Lamps*—Single-element lamps are recommended. Multi-element lamps are available but have a shorter lifespan, are less sensitive, require a higher operating current, and increase the chances of spectral interferences. Electrode-less discharge lamps may also be used.

7.4 *Photomultiplier Tube*—A wide spectral range (160–900 nm) multiplier phototube is recommended. Refer to Practice E 520.

7.5 *Strip Chart Recorder*—A recorder is recommended so that there will be a permanent record and any problems with the analysis such as drift, incomplete atomization, changes in sensitivity, etc., can be easily recognized.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade or better chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available. [9] However, in some cases, these reagents may not be of sufficient purity due to the sensitivity of the technique. It is the responsibility of the user to verify that the purity of reagents used for this technique is sufficient.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D 1193, Type I. 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 adversely affecting the precision and bias of the test method.

[9] *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeia Convention, Inc. (USPC), Rockville, MD.

8.3 *Fuel, Acetylene* (C_2H_2)—Minimum acceptable acetylene purity is 99.5 vol %. Normally the cylinder is changed when the pressure reaches 53 g/m^2(75 psig) if the acetylene is packed in acetone. Some manufacturers recommend different pressures. The analyst should check with the manufacturer for instructions. Prepurified grades use a proprietary solvent and can be used to 25–21 g/m^2(30 psig) before replacement. The analyst should follow the manufacturer's instructions for the use of prepurified grades with proprietary solvents to prevent damage to gas control systems. Avoid introducing these solvents into the instrument or else abnormally high pulsating background noise and possible damage to the instrument's plumbing system may result. To prevent solvent carryover, allow acetylene cylinders to equilibrate for at least 24 h before use after moving.

8.4 *Fuel, Hydrogen* (H_2)—For some elements industrial grade hydrogen may be selected to achieve the desired flame characteristics.

8.5 *Oxidant (Air)*—The source may be a compressor or commercially bottled gas. Condition the air by passing it through a filter element to remove oil, water, and particles. Refer to the manufacturer's guidelines for minimum and maximum delivery pressures.

8.6 *Oxidant, Nitrous Oxide* (N_2O)—For certain elements, industrial or medical grade nitrous oxide may be required to achieve the necessary flame temperature.

8.7 *Stock Standard Solutions*—Stock standard solutions may be purchased as certified solutions or prepared from the American Chemical Society reagent grade materials. Store the solutions in high density polyethylene, glass or TFE-fluorocarbon containers at room temperature. Solutions should be labeled with the preparation and expiration dates. They should be inspected periodically for signs of deterioration.

NOTE 1—Polypropylene may be used for sample collection and storage. However, studies published by at least one atomic absorption spectrophotometer manufacturer indicate severe problems with metal adsorption onto the walls of polypropylene surfaces. The analyst should conduct loss studies with time to determine if adsorption is a problem.

9. Safety Precautions

9.1 The majority of calibration standards and sample types encountered in this practice pose no hazard to the analyst. Use of a hood, protective clothing, and safety glasses are required when preparing solutions where reaction between solvent and solute is exothermic, that is, lanthanum oxide in acid solution. The same precautions are required when diluting strong acids to avoid skin and respiratory contact.

9.2 A permanent ventilation system is required to eliminate the large quantity of hot and sometimes toxic exhaust gases produced by the burner during instrument operation. Since acetylene is a flammable gas proper precautions should be taken when using it. To avoid explosions, never pass acetylene through copper or high-copper alloy (brass, bronze) fittings or piping. If the spectrophotometer is not equipped with a protective shield, the operator's safety glasses must also attenuate the ultraviolet light emitted by the flame.

9.3 Oxidizing gases must be separated from reducing gases by a fire wall.

9.4 Follow manufacturer's operating guidelines carefully when optimizing gas flow rates. If proper caution is not exercised, a dangerous combustion within the gas mixing chamber may result.

9.5 To avoid in-line explosions, do not allow the pressure of acetylene being delivered to the instrument to exceed 10.6 g/m^2 (15 psig). Consideration should be given to including a commercially available flash arrestor in the line of all flammable or combustible gases.

9.6 The standard, 50.800 mm (2 in.) nitrous oxide burner head must be used when N_2O is an oxidant. A flashback will occur if a 101.60 mm (4 in.) burner head is used. The nitrous oxide flame must be lit by first using a combination of air/acetylene, then switching to nitrous oxide/acetylene. The system is shut off by following the procedure in reverse order. Nitrous oxide must never be passed through lines containing residual oil or grease or an explosion may result.

9.7 Check that the drain tube from the gas mixing chamber is filled with water before beginning any analyses. Failure to maintain positive pressure to the chamber may result in an explosion. A safety trap, either looped or valved, is highly recommended. Follow the manufacturer's instructions in maintaining this positive pressure liquid seal.

10. Samples and Sampling Procedures

10.1 *Sample Handling*—For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Containers can introduce errors in the measurement of trace metals by contributing contaminants through leaching or surface desorption or by depleting concentrations through adsorption. Refer to Practice D 4453 for handling of ultra-pure water samples.

10.2 *Sample Collection*—Collect all samples in accordance with Specification D 1192 and Practices D 3370.

10.3 *Sample Containers*—Take care to collect a representative sample in clean glass, high-density polyethylene, polypropylene or TFE-fluorocarbon container. Containers having caps with metal or fiber liners shall not be used.

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

10.5 *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 the

sample as soon as possible, preferably at the time of collection.

10.6 *Sample Storage*—Analyze samples containing trace concentrations of analyte as soon as possible, preferably at the time of collection, although some samples may be stored for up to six months if properly preserved.

11. Calibration and Standardization

11.1 *Instrument Optimization*:

11.1.1 *Lamp Current*—The operating current of the hollow cathode or electrodeless discharge lamp is a critical parameter in the optimization of atomic absorption measurements. The use of excessively high currents shortens lamp life. It can also lead to a reduction in sensitivity. The use of currents that are too low can result in lamp instability, insufficient throughput of energy through the instrument's optical system, and increased signal noise due to increased electrical gain applied to the photodetector. Refer to manufacturer's guidelines for recommendations.

11.1.2 *Spectral Bandwidth*—The selection of optimum bandwidth depends upon the spectrum of the particular element being determined. Refer to the manufacturer's guidelines for recommendations.

11.1.3 *Wavelength*—Set the wavelength of the spectrophotometer for each analyte of interest by following the manufacturer's operating guidelines for desired sensitivity. After the instrument has been allowed adequate time to warm up with the flame burning, check the wavelength and readjust if necessary.

11.1.4 *Burner Height and Alignment*—The position of the light beam through the flame, and burner height are optimized according to the manufacturer's guidelines.

11.1.5 *Flame Conditions*—Flame geometry and temperature are important factors governing atomization and sensitivity. Flame atomic absorption requires that the elements exist in the flame in their atomic state to absorb a discrete level of radiation. If the temperature of the flame is too low to cause dissociation of the salt, or to effect vaporization, little or no absorbance is measured. Alternatively, too high a flame temperature can elevate the electrons so high as to result in ionization. Follow manufacturer's operating guidelines carefully when optimizing gas flow rates since combustion within the gas mixing chamber may occur if proper caution is not exercised. Aspirate a standard of the element to be analyzed and adjust the gas flow rate until the maximum difference in absorbance between the standard and a blank is obtained. When flammable organic solvents are aspirated, flame conditions can change drastically as compared to when aqueous solutions are aspirated. Adjust fuel and oxidant flows to provide optimum flame conditions when aspiration of an organic solvent follows that of an aqueous solution. Allow the system to come to equilibrium for 10 to 15 min prior to final adjustment and commencement of analyses.

11.1.6 *Nebulization Rate*—Optimize the rate at which the sample is drawn up into the nebulizer and spray chamber. If an adjustable glass bead nebulizer is used, adjust it according to manufacturer's guidelines. To optimize the nebulizer, aspirate a solution of an element (such as copper) which is insensitive to changes in flame conditions and adjust the nebulization rate until a maximum absorbance is obtained. The nebulizer can clog easily if particulate matter is present in the samples. Symptoms of this are decreased sensitivity, or dramatically increased noise, or both, especially noticeable at higher concentration levels. To unclog the nebulizer, a thorough cleaning with a small diameter wire is usually sufficient.

11.2 *Calibration Standards*:

11.2.1 Prepare all dilutions of stock solutions for calibration standards at the time of analysis. Some low-level standards may be stable. It is the responsibility of the analyst to determine standard stability for their own specific analytical requirements.

11.2.1.1 Use pipettes with verified limits of bias and precision. Use at least three calibration solutions and one zero standard to generate a suitable calibration curve. The lowest standard concentration shall be less than or equal to the anticipated sample concentrations. The highest standard concentration shall be at the top of the linear range of the analysis. Use a higher concentration standard if a calibration curve is drawn or curvature correction is used. However, do not use a standard that yields an absorbance value greater than 1.0. The remaining solution shall be approximately midway between the upper and the lower limit of sample analyses. Calibration standards should bracket the anticipated sample concentrations. In some analyses the addition of matrix modifiers is recommended. The analyst should refer to the specific test method for this information.

11.3 *Calibration Curve*—Aspirate an aliquot of each calibration standard in turn, in order of increasing concentration. Zero the instrument while aspirating the zero standard. Record the absorbance or concentration measured. Construct calibration curves for each of the elements of interest. Check one calibration standard after a maximum of ten samples and the entire calibration curve at the end of the analyses. Values at each concentration level shall agree within three times the standard deviation (3*s*) of the values in the original curve. If results of the calibration check fall outside of these guidelines, recalibrate the instrument and reanalyze all samples analyzed since the last calibration.

12. Sample Analysis

12.1 Optimize the instrument each day or for each parameter, or both, according to the manufacturer's instructions.

12.2 Prepare all standards for each element of interest according to instructions contained in the specific test method.

12.3 If the absorbance for a given sample exceeds the working range of the system, dilute the sample with an appropriate amount of zero standard and reanalyze.

12.4 After every ten samples and at the end of the analyses, check at least one calibration standard. Analyze the quality control check samples, split samples and spike samples as directed by laboratory quality control procedures (Guide D 5810).

12.5 If standard additions are required, use four equal aliquots of sample. Dilute the first aliquot to a known volume with water

or zero standard. 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 shall be identical. 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 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. To validate the method of standard additions, take the following limitations into consideration:

12.5.1 The absorbance plot of sample and standards shall be linear over the concentration range of concern.

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

12.5.3 The standard addition shall respond in a similar manner as the analyte.

12.5.4 The determination shall be free of spectral interferences and must be corrected for nonspecific background interference.

13. Calculation

13.1 For each analyte of interest, construct a plot of the absorbance measured versus standard concentration. Analyze samples and standards of identical volumes where matrix modifiers or other reagents additions have been made. The analyst should refer to Practice E 178 for dealing with outlying observations.

13.2 An integration system may be used to automatically construct a curve and to provide a direct readout of the concentration of the analyte of interest. In such cases, make a sensitivity check using a standard solution of an element such as calcium or copper. Record and chart the sensitivity within certain limits to ensure instrument performance.

14. Quality Control

14.1 *Quality Control*— Verify the —The following quality control information is recommended for measuring elements in water by Flame Atomic Absorption Spectrophotometry

14.2 The instrument and analytical performance. Perform and chart a sensitivity check of the atomic absorption spectrophotometer daily so that deviations can shall be identified. Also make calibrated using a comparison minimum of the analytical blank or zero standard three calibration standards and reagent water a calibration blank. The calibration correlation coefficient shall be equal to determine background contamination from acids, buffers or other chemicals used in standard preparation. During the sample analysis use several types of quality control samples greater than 0.990. In addition to verify analytical performance. These include:

14.2 *Quality Control Check Samples* —After the initial calibration curve is established, analyze blank, a calibration blank shall be analyzed at the quality end of the batch run to ensure contamination was not a problem during the batch analysis.

14.3 An instrument check samples standard shall be analyzed at a minimum frequency of two levels of concentration within 10 % throughout the working range. If the concentration batch analysis. The value of either the instrument check sample falls outside standard shall fall between 80 % and 120 % of the predetermined limits, analyze true value.

14.4 Two method blanks shall be prepared ensuring that an adequate method blank volume is present for a fresh aliquot minimum of sample. If problems persist, check seven repetitive analyses. The standard deviation of the entire calibration curve. If the calibration curve method blank is satisfactory, prepare new check samples and reanalyze.

14.3 *Split Samples*— Analyze one set of split samples for every ten samples. Ideally, used to determine the minimum detectable concentration of each sample to be analyzed and control in duplicate the batch.

14.5 A Laboratory Control Standard shall be unknown to the analyst, separated by time and space.

14.4 *Laboratory Spikes*—Prepare and analyze laboratory spikes. The addition analyzed with each batch of sample at a minimum frequency of 10 %.

14.6 If the QC for the sample batch iks not within the established control limits, reanalyze the samples or qualify the results with the appropriate flags, or both (Practice D 5847).

14.7 Blind control samples should be approximately double submitted by an outside agency in order to determine the anticipated concentration level. laboratory performance capabilities.

15. Precision and Bias

15.1 Precision and bias statements are included with each individual test method for which the technique is applicable.

16. Keywords

16.1 atomic absorption spectrophotometry; flame