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Designation: **D 4191 – 9703**

Standard Test Method for Sodium in Water by Atomic Absorption Spectrophotometry¹

This standard is issued under the fixed designation D 4191; 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 This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water. Current edition approved ~~Dec. Jan. 10, 1997; 2003~~, Published ~~December 1998; January 2003~~. Originally published as ~~D 4191 – 82~~; approved in 1982. Last previous edition approved in 1997 as D 4191 – 937.

1. Scope*

1.1 This test method covers the determination of low amounts of sodium in waters² having low solids content. The applicable range of this test method is from 0.20 to 3.0 mg/L when using the 589.6-nm resonance line. This range may be extended upward by dilution of an appropriate aliquot of sample or by use of the less-sensitive 330.2-nm resonance line (see Test Method D 3561). Many workers have found that this test method is reliable for sodium levels to 0.005 mg/L, but use of this test method at this low level is dependent on the configuration of the aspirator and nebulizer system available in the atomic absorption spectrophotometer as well as the experience and skill of the analyst. The precision and bias data presented are insufficient to justify use of this test method in the 0.005 to 0.20-mg/L range.

1.2 This test method has been used successfully with spiked reagent water. It is the analyst's responsibility to assure the validity of the test method to other low dissolved solids matrices.

1.3 *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:

D 1066 Practice for Sampling Steam³

D 1129 Terminology Relating to Water³

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits³

D 1193 Specification for Reagent Water³

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water³

D 3370 Practice for Sampling Water from Closed Conduits³

D 3561 Test Method for Lithium, Potassium, and Sodium Ions in Brackish Water, Seawater, and Brines by Atomic Absorption Spectrophotometry⁴

~~E 60 Practice~~

D 5810 Guide for Photometric and Spectrophotometric Spiking into Aqueous Samples³

² Platte, J. A., and Marcy, V. M., "A New Tool for the Water Chemist," *Industrial Water Engineering*, May 1965.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 11.02.

~~D 5847 Practice for the Writing Quality Control Specifications for Standard Test Methods for Chemical Water Analysis of Metals⁵~~

~~E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers⁶³~~

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

4. Summary of Test Method

4.1 Sodium is determined by flame atomic absorption spectrophotometry. The sodium content is determined by aspirating the low solids sample directly with no sample pretreatment.

5. Significance and Use

5.1 Sodium salts are very soluble, and sodium leached from soil and rocks tends to remain in solution. Water with a high ratio of sodium to calcium is deleterious to soil structure.

5.2 Sodium is not particularly significant in potable water except for those persons having an abnormal sodium metabolism, but water supplies in some areas contain sufficient sodium to be a factor in the planning of sodium-free diets.

5.3 The use of sodium salts is common in industry; therefore, many industrial wastewaters contain significant quantities of sodium. For high-pressure boiler feed-water even trace amounts of sodium are of concern.

6. Interferences

6.1 In the analysis of low-solids water, interferences are usually negligible.

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer* for use at 589.6 nm.

NOTE 1—The manufacturer's instructions should be followed for all instrumental parameters. Wavelengths other than 589.6 nm may be used only if they have been determined to be equally suitable.

7.2 *Sodium Hollow-Cathode Lamps*—Multielement hollow cathode lamps are available and also have been found satisfactory.

7.3 *Oxidant: Air*, which has been passed through a suitable filter to remove oil, water, and other foreign substances is the usual oxidant.

7.4 *Fuel: Acetylene*—Standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders can affect analytical results. The cylinder should be replaced at 50 psig (345 kPa) to avoid acetone carryover.

7.4.1 **Caution**—“Purified” grade acetylene containing a special proprietary solvent rather than acetone should not be used with poly(vinyl chloride) tubing as weakening of the tubing walls can cause a potentially hazardous situation.

7.5 *Pressure-Reducing Valves*—The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the operating pressure of the instrument by using suitable valves.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁵ Other grades 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.

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⁵ “Reagent Chemical, American Chemical Society Specifications,” Am. Chemical Soc., Washington, DC. For suggestions on the testing of ASTM reagents not listed by the American Chemical Society, see “Analar Standards, Vol 03-05, for Laboratory Chemicals,” BDH Ltd., Poole, Dorset, U.K., and the “United States Pharmacopeia.”

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⁶ Supporting data are available from ASTM Standards, Vol 03-06, Headquarters. Request RR: D19-1080.

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 bias and precision of the test method. Type II water was specified at the time of round robin testing of this test method.

8.3 *Sodium Solution, Stock* (1.0 mL = 1.0 mg Na)—Dry sodium chloride to constant weight at 105°C. Dissolve 2.5418 g of the dry sodium chloride (NaCl) in water and dilute to 1 L with water.

NOTE 2—Certified sodium stock solutions are commercially available through chemical supply vendors.

8.4 *Sodium Solution, Standard* (1.00 mL = 0.1 mg Na)—Dilute 100.0 mL of sodium stock solution to 1 L with water.

9. Sampling

9.1 Collect the samples in accordance with the applicable ASTM test method as follows: Practices D 3370, Practice D 1066, and Specification D 1192.

10. Standardization

10.1 Prepare 100 mL each of a blank and at least four standard solutions to bracket the expected sodium concentration range of the samples to be analyzed by diluting the standard sodium solution (8.4) with water. Prepare the standards each time the test is to be performed. Select the standards to give zero, middle, and maximum points for an analytical curve.

10.2 Aspirate the blank and the standards and record the instrument readings. Aspirate water between standards.

10.3 Prepare an analytical curve by plotting the absorbance versus concentration for each standard on linear graph paper. Alternatively, read directly in concentration if this capability is provided with the instrument.

11. Procedure

11.1 Aspirate each sample and determine its absorbance or concentration. Aspirate water between samples.

12. Calculation

12.1 Calculate the concentration of sodium in the samples, in milligrams per litre, by either referring the absorbance obtained for each sample to a prepared analytical curve (10.3) or reading directly in concentration if the capability is provided with the instrument.

12.2 If an aliquot of diluted sample was analyzed, multiply the concentration of sodium, in milligrams per litre, by the appropriate dilution factor.

13. Precision and Bias ⁶

13.1 The overall and single-operator precision of this test method for eight laboratories, which include a total of twelve operators analyzing each sample on three consecutive days, within its range for reagent water varies with the quantity being measured according to Table 1-1.

NOTE 3—Only reagent water was used to obtain the precision statement since this test method is designated for the determination of low amounts of sodium in low-solids water.

13.2 Recoveries of known amounts of sodium (from sodium chloride) in the series of prepared standards for the same laboratories and operators were as given in Table 1.

13.3 Precision and bias for this test method conforms to Practice D 2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D 2777 – 98, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

14. Quality Control

14.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing sodium.

14.2 Calibration and Calibration Verification:

TABLE 1 Determination of Bias for Sodium in Reagent Water by Atomic Absorption

Amount Added, mg/L	Amount Found, mg/L	S_i	S_o	Bias %
0.20	0.184	0.053	0.024	-8.0
1.20	1.25	0.094	0.028	+ 4.17
2.70	2.81	0.129	0.081	+ 4.07

14.2.1 Analyze at least three working standards containing concentrations of sodium that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

14.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within $\pm 15\%$ of the known concentration.

14.2.3 If calibration cannot be verified, recalibrate the instrument.

14.3 *Initial Demonstration of Laboratory Capability:*

14.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

14.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of sodium. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps. The replicates may be interspersed with samples.

14.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. If a concentration other than the recommended concentration is used, refer to Practice D 5847 for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

14.4 *Laboratory Control Sample (LCS) :*

14.4.1 To ensure that the test method is in control, analyze a LCS containing a known concentration of sodium with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within $\pm 15\%$ of the known concentration.

14.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.5 *Method Blank:*

14.5.1 Analyze a reagent water test blank with each batch. The concentration of sodium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of sodium is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.6 *Matrix Spike (MS):*

14.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of sodium and taking it through the analytical method.

14.6.2 The spike concentration plus the background concentration of sodium must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

14.6.3 Calculate the percent recovery of the spike (*P*) using the following formula:

$$P = 100 [A(V_s + V) - B V_s] / C V \quad (1)$$

where:

- A* ≡ analyte concentration (mg/L) in spiked sample,
- B* ≡ analyte concentration (mg/L) in unspiked sample,
- C* ≡ concentration (mg/L) of analyte in spiking solution,
- V_s* ≡ volume (mL) of sample used, and
- V* ≡ volume (mL) added with spike.

14.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D 5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 4—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D 5810 for additional information.

14.7 *Duplicate:*

14.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

14.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an *F* test. Refer to 6.4.4 of Practice D 5847 for information on applying the *F* test.

14.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

14.8 Independent Reference Material (IRM):

14.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

15. Keywords

145.1 analysis; atomic absorption; sodium; water

SUMMARY OF CHANGES

This section identifies the location of selected changes to these test methods that have been incorporated since the last issue. For the convenience of the user, Committee D19 has highlighted those changes that may impact the use of these test methods. This section may also include descriptions of the changes or reasons for the changes, or both.

- (1) The QC section was added to the test method.
- (2) Section 13.3 was added.

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