Designation: D6071 – 14

Standard Test Method for
Low Level Sodium in High Purity Water by Graphite Furnace Atomic Absorption Spectroscopy[1]

1. Scope*

1.1 This test method covers the determination of trace sodium in high purity water. The method range of concentration is 1 to 40 µg/L sodium. The analyst may extend the range once its applicability has been ascertained.

NOTE 1—It is necessary to perform replicate analysis and take an average to accurately determine values at the lower end of the stated range.

1.2 This test method is a graphite furnace atomic absorption spectrophotometric method for the determination of trace sodium impurities in ultra high purity water.

1.3 This test method has been used successfully with a high purity water matrix.[2] It is the responsibility of the analyst to determine the suitability of the test method for other matrices.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)[4]
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
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

3. Terminology

3.1 *Definitions:*

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

4. Summary of Test Method

4.1 Sodium is determined by atomic absorption utilizing a graphite furnace for sample atomization.

4.2 A sample volume of several microlitres, depending upon the concentration of the analyte, is deposited on a graphite tube housed within an electrical furnace, and the system is heated in an inert gas environment. The sample is evaporated to dryness, ashed (charred or pyrolyzed), and atomized.

4.3 Ground-state atoms are produced during the atomization stage of the temperature program. The ground-state atoms absorb the energy at a specific wavelength produced from a source as they are bombarded by the energy. The amount of energy absorbed is proportional to the concentration of the analyte in the sample.

4.4 The absorption signal produced during atomization is recorded on a chart recorder or stored in microprocessor memory and compared to those standards taken through the same process by means of an analytical curve.

4.5 A general guide for graphite furnace applications is given in Practice D3919.

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

Current edition approved Sept. 15, 2014. Published September 2014. Originally approved in 1996. Last previous edition approved in 2013 as D6071 – 13. DOI: 10.1520/D6071-14.

[2] *RP2712 Sub Program—Grab Sample Method Validation Report Results*, Electric Power Research Institute, Palo Alto, CA, 1987.

[3] 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.

[4] The last approved version of this historical standard is referenced on www.astm.org.

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

5. Significance and Use

5.1 Small quantities of sodium, 1 to 10 µg/L, can be significant in high pressure boiler systems and in nuclear power systems. Steam condensate from such systems must have less than 10 µg/L. In addition, condensate polishing system effluents should have less than 1 µg/L. Graphite furnace atomic absorption spectroscopy (GFAAS) represents technique for determining low concentrations of sodium.

6. Interferences

6.1 No known interferences from other constituents are found in high purity waters.

6.2 For a complete discussion on interferences with graphite furnace procedures, refer to Practice D3919.

6.3 Sodium is a common contaminant in many reagents. The analyst must ensure that the quality of the reagent used in the procedure is sufficiently high to determine trace levels of sodium.

6.4 All plasticware and apparatus must be cleaned and maintained to eliminate high background levels of sodium when determining trace levels.

6.5 Airborne particulates are a potential interference with the analysis of sodium by GFAAS. The user must ensure that all plasticware and other equipment is capped or stored in air tight containers.

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer,* with the capability of setting the following instrumental parameters:

Metal	Wavelength, nm	Slit width (SBW), nm
Sodium	589.0	0.5

NOTE 2—The manufacturer's instructions should be followed for all instrument parameters.

7.2 *Hollow Cathode Lamp,* for sodium.

7.2.1 Multielement hollow cathode lamps may be used if the analyst ensures the necessary sensitivity is available for the low level determination.

7.3 *Graphite Furnace,* capable of reaching temperatures sufficient to atomize the elements of interest. Maximum sensitivity will be obtained when atomization temperatures are reached rapidly.

7.4 *Graphite Tubes,* compatible with the furnace device. Standard graphite tubes of uncoated graphite should be used. When maximum sensitivity is required, the analyst may choose to use pyrolytically coated graphite tubes.

7.5 *Autosampler,* compatible with the graphite furnace device may be used to increase the precision of the injection or dispensing the sample into the graphite tube.

7.6 *Pipets,* microlitre with disposable plastic tips. Sizes may vary from 1 to 100 µL, as required.

7.7 *Flasks,* plastic, volumetric. Sizes may vary from 100 to 1000 mL.

7.8 *Strip Chart Recorder (Computing Device with Display)*—The user must keep a permanent record of the data in addition to instrument problems (drift, incomplete atomization, changes in sensitivity, etc.).

7.8.1 The strip chart recorder with a response of 0.2 s or less for full scale deflection is recommended to ensure accuracy.

8. Reagents and Materials

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.[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.

8.2 *Purity of Water*—Reference to water that is used for reagent preparation, rinsing or dilution shall be understood to mean water that conforms to the quantitative specifications of Type I reagent water of Specification D1193.

8.3 *Sodium Solution, stock (1 mL = 1000 µg Na)*—Dissolve 2.542 g of sodium chloride in water and dilute to 1 L.

8.4 *Sodium Solution, intermediate (1 mL = 10.0 µg Na)*—Dilute 10.0 mL of stock sodium solution from 8.3 to 1 L with water.

8.5 *Sodium Solution, standard (1 mL = 0.05 µg Na)*—Dilute 5 mL of intermediate sodium solution from 8.4 to 1 L with water.

NOTE 3—Alternatively, the analyst may purchase a commercially available standard (1 mL = 1000 µg Na). Additional dilution will be necessary to obtain the stock sodium solution concentration in 8.3.

8.6 *Argon,* 99.99 % pure.

9. Sampling

9.1 Collect the sample in accordance with Practices D1066 and D3370 or Specification D1192.

9.2 Samples should be collected in polystyrene, TFE-fluorocarbon or polypropylene bottles only. Do not use glass or polyethylene containers. The containers should be rinsed with Type I water. The container should be stored prior to use by either air drying and capping or filling with Type I water and capping. For further details, see Practice D4453.

9.3 To avoid the possibility of contamination, samples should not be acidified.

10. Calibration

10.1 Prepare standards for the analytical calibration containing 0.0, 1.0, 5.0, 10.0, and 25.0 µg/L Na by diluting 0, 2, 10, 20, and 50 mL sodium standard solution in 8.5 to 100 mL with water. The 50.0 µg/L intermediate stock solution in 8.5 will be used as the high standard concentration.

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[5] *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.

10.2 Perform an instrument zero without making an injection.

10.3 Set the temperature program (dry, ash/char/pyrolyze, atomize) in accordance with the manufacturer's instructions.

10.3.1 *Sample Size*—Use 10 to 100 µL depending on the graphite tube size, the concentration, and desired detection level required. Use the same injection volume for the blank, standards, and all samples.

10.3.2 *Temperature Program:*

Program stage	Temperature,° C	Time, s
Dry	100	1 to 3 s/µL
Ash/char/pyrolize	800	20.0
Atomize	2300	4.9

10.4 Condition the graphite tube surface prior to initiating the analysis. Condition the furnace by conducting the following steps.

10.4.1 Determine the furnace blank by initiating the atomization program without making an injection. Repeat until the furnace blank reproduces within 10 % of the initial absorbance value obtained.

10.4.2 Condition the graphite tube surface by injecting the 10 µg/L standard. Repeat until the absorbance reproduces within 10 %.

10.4.3 Inject each of the calibration standards. Reproducibility must be within 10 % for each standard concentration.

10.5 Prepare a calibration curve by plotting peak height or peak area versus concentration as µg/L on linear paper if direct concentration readout is unavailable on the instrument.

11. Procedure

11.1 Use volumetric plasticware for the preparation of all standards and samples.

11.2 Rinse all the plasticware and equipment with water prior to use. The analyst may choose to store all plasticware in water or air dry and store in covered containers.

11.3 Analyze the samples as described in Section 10.

NOTE 4—The analyst should cover the sample containers or use a covered autosampler to minimize the possibility of airborne contamination between injections of the samples into the graphite tube.

12. Calculation

12.1 Read the sample concentration directly from the instrument where applicable or from the calibration curve generated in 10.5.

13. Precision and Bias[6]

13.1 The precision and bias for this test method were obtained in accordance with Practice D2777.

13.2 *Precision*—The precision of this test method was determined using high purity water in eight laboratories. The precision may be expressed as follows:

$$S_t = 0.22(X) + 0.88$$

$$S_o = 0(X) + 0.91$$

where:

S_t = overall precision,
S_o = single operator precision, and
X = determined concentration of sodium, µg/L.

13.3 *Bias*—Mean recoveries of known amounts of sodium in prepared series of high purity water were as follows:

Amount added, µg/L	Amount found, µg/L	± Bias	± % Bias	Statistically significant
0.00	0.16	+0.16	—	No
0.00	0.40	+0.40	—	No
1.07	1.03	−0.04	−4 %	No
1.42	1.36	−0.06	−4 %	No
5.65	5.56	−0.09	−2 %	No
7.08	7.14	+0.06	+1 %	No
28.40	28.54	+0.14	0 %	No
35.40	40.41	+5.01	+14 %	No

13.4 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 98, these precision and bias data do meet existing requirements of 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 each element.

14.2 *Calibration and Calibration Verification:*

14.2.1 Analyze five working standards containing concentrations of silica 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.i

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 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, and so forth, 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 each element. 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

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1160. Contact ASTM Customer Service at service@astm.org.

the table in 13.3. This study should be repeated until the recoveries are within the limits given in the table in 13.3. If a concentration other than the recommended concentration is used, refer to Test Method D5847 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 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 98, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

14.4.2 To ensure that the test method is in control, analyze a Continuing Calibration Verification (CCV) standard containing a known concentration of silica with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the CCV after every 10 samples. The CCV for a large batch should cover the analytical range when possible. The CCV must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range CCV shall fall within ±10 % of the known concentration.

14.4.3 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 silica found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of silica 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 silica and taking it through the analytical method.

14.6.2 The spike concentration plus the background concentration of silica 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:

$$P = 100\left[A\left(V_s + V\right) - BV_s\right]/CV \quad (1)$$

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 D5810, 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 5—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 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 D5847 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

15.1 graphite furnace atomic absorption spectroscopy (GFAAS); high purity water; sodium

APPENDIX

(Nonmandatory Information)

X1. TECHNIQUES FOR REDUCING CONTAMINATION

X1.1 Always wear uncolored, unpowdered plastic gloves during all operations. If gloves come in contact with sources of contamination, they need to be replaced.

X1.2 Wash flasks with HCl (1 + 1) immediately before use. If glass pipets are used, rinse with HCl (1 + 1) and rinse several times with water immediately before use.

X1.3 If using an automatic sampler for sample introduction, rinse the sample cups several times with water immediately prior to use. Do not load more than five cups on the sampler at one time. Contamination appears to be a problem if samples are allowed to sit for a period of time prior to analysis.

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D6071 – 13) that may impact the use of this standard. (Approved Sept. 15, 2014.)

(1) Revised 14.4.2.

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