Designation: D4192 – 15

Standard Test Method for Potassium in Water by Atomic Absorption Spectrophotometry[1]

This standard is issued under the fixed designation D4192; 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 test method covers the determination of low amounts of potassium in waters[2] having low solids content. The applicable range of this test method is 0.20 to 4.0 mg/L when using the 766.5-nm resonance line. The range may be extended upward by dilution of an appropriate aliquot of sample or by using the less-sensitive 404.4-nm resonance line. Many workers have found that this test method is reliable for potassium levels to 0.02 mg/L, but use of this test method at this low level is dependent on the configuration of the aspirator and nebulizer systems available in the atomic absorption spectrophotometer as well as the skill of the analyst. The precision and bias data presented are insufficient to justify use of this test method in the 0.02-mg/L range.

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

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

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 a specific precautionary statement, see 8.6.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
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
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
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 Potassium is determined by flame atomic absorption spectrophotometry. The potassium content is determined by aspirating the low solids sample directly with no sample pretreatment.

5. Significance and Use

5.1 Potassium occurs in rocks in a form that is not easily solubilized; therefore, the potassium content of natural waters is usually low. Most natural waters contain less than 20 mg/L of potassium, but waters containing several hundred milligrams per litre are occasionally found. Potassium is essential to animal nutrition, but a concentration of 1000 to 2000 mg/L in stock water is regarded as the extreme limit permissible.

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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 D19.05 on Inorganic Constituents in Water.

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

[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.

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

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 766.5 nm.

NOTE 1—The manufacturer's instructions should be followed for all instrumental parameters. Wavelengths other than 766.5 nm may be used only if they have been determined to be equally suitable.

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

7.3 *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 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 where such specifications are available.[4] 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*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D1193, 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 *Potassium Solution, Stock* (1.0 mL = 1.0 mg K)—Dry potassium chloride to constant weight at 105°C. Dissolve 1.907 g of the dry potassium chloride (KCl) in water and dilute to 1 L with water.

NOTE 2—Certified potassium stock solutions of appropriate known purity are commercially available through chemical supply vendors.

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

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

8.6 *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 345 kPa (50 psig) to avoid acetone carry over. (**Warning—**"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.)

9. Sampling

9.1 Collect the samples in accordance with the applicable ASTM standard as follows: Practices D3370 and Practice D1066.

10. Standardization

10.1 Prepare 100 mL each of a blank and at least four standard solutions to bracket the expected potassium concentration range of the samples to be analyzed by diluting the standard potassium solution 8.4 with water. Prepare the standards each time the test is to be performed or as determined by Practice D4841. Select the standards to give zero, median, and maximum points for an analytical curve.

10.2 Analyze at least four working standards containing concentrations of potassium that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. Aspirate the blank and the standards and record the instrument readings. Aspirate water between standards.

10.3 Read directly in concentration if this capability is provided with the instrument or prepare a linear analytical curve by plotting the absorbance versus concentration for each standard on linear graph paper.

11. Procedure

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

12. Calculation

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

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

13. Precision and Bias[5]

13.1 The overall and single-operator precision of this test method for eight laboratories, which included a total of twelve

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

Amount Added, mg/L	Amount Found, mg/L	S_t	S_o	Bias %
0.15	0.164	0.037	0.014	+ 9.33
1.50	1.62	0.085	0.044	+ 8.00
3.00	3.03	0.179	0.062	+ 1.13

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[4] *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 *Annual 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.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1081. Contact ASTM Customer Service at service@astm.org.

operators analyzing each sample on three consecutive days, within its range for reagent water varies with the quantity being measured according to Table 1.

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

13.2 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

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

13.4 Precision and bias for this test method 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 – 13, 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 potassium .

14.2 *Calibration and Calibration Verification:*

14.2.1 Analyze at least four working standards containing concentrations of potassium that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument (see 10.2). 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 ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

14.2.3 If calibration cannot be verified, recalibrate the instrument.

14.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

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 potassium. 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.

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 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 To ensure that the test method is in control, analyze a LCS containing a known concentration of potassium with each batch (laboratory-defined or twenty 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 ±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 laboratory-defined batch. The concentration of potassium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of potassium 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 laboratory-defined batch by spiking an aliquot of the sample with a known concentration of potassium and taking it through the analytical method.

14.6.2 The spike concentration plus the background concentration of potassium 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 known concentration (mg/L) in spiked sample,
B = analyte known concentration (mg/L) in unspiked sample,
C = known concentration (mg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

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 4—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 laboratory-defined 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 analysis; atomic absorption; potassium; water

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D4192 – 08) that may impact the use of this standard. (Approved Feb. 1, 2015.)

(1) 8.3 was modified to clarify the purity of the commercial standards.
(2) Section 10 was modified with standard and calibration information and to use a computer.
(3) Section 13 was modified to allow for direct reading instruments.
(4) 14.2.4 and 14.6.3 were modified.