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An American National Standard

Standard Test Methods for Beryllium in Water[1]

This standard is issued under the fixed designation D3645; 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 These test methods cover the determination of dissolved and total recoverable beryllium in most waters and wastewaters:

	Concentration Range	Sections
Test Method A–Atomic Absorption, Direct	10 to 500 µg/L	7 to 17
Test Method B–Atomic Absorption, Graphite Furnace	10 to 50 µg/L	18 to 26

1.2 The analyst should direct attention to the precision and bias statements for each test method. It is the user's responsibility to ensure the validity of these test methods for waters of untested 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 specific hazard statements, see Section 12 and 24.4.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D858 Test Methods for Manganese in Water
D1068 Test Methods for Iron in Water
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D1687 Test Methods for Chromium in Water
D1688 Test Methods for Copper in Water
D1691 Test Methods for Zinc in Water
D1886 Test Methods for Nickel in 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
D3557 Test Methods for Cadmium in Water
D3558 Test Methods for Cobalt in Water
D3559 Test Methods for Lead in Water
D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry
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 these test methods, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *total recoverable beryllium, n*—a descriptive term relating to the beryllium forms recovered in the acid-digestion procedure specified in these test methods.

4. Significance and Use

4.1 These test methods are significant because the concentration of beryllium in water must be measured accurately in order to evaluate potential health and environmental effects.

5. Purity of Reagents

5.1 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

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[1] These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] 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**

specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is sufficiently high in purity to permit its use without lessening the accuracy of the determination.

5.2 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.

6. Sampling

6.1 Collect the samples in accordance with Practices D3370. The holding time for samples may be calculated in accordance with Practice D4841.

6.2 Preserve samples with HNO_3 (sp gr 1.42), adding about 2 mL/L, to a pH of 2 or less immediately at the time of collection. If only dissolved beryllium is to be determined, filter the sample, before acidification, through a 0.45-µm membrane filter.

NOTE 1—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

TEST METHOD A—ATOMIC ABSORPTION, DIRECT

7. Scope

7.1 This test method is applicable in the range from 10 to 500 µg/L of beryllium. The range may be extended upward by dilution of the sample.

7.2 The precision and bias data were obtained on reagent water, tap water, salt water, river water, lake water, spring water, and untreated wastewater. The information on precision and bias may not apply to other waters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

8. Summary of Test Method

8.1 Beryllium is determined by atomic absorption spectrophotometry. Dissolved beryllium is determined by aspirating a filtered sample directly with no pretreatment. Total recoverable beryllium in the sample is determined in a portion of the filtrate obtained after a hydrochloric-nitric acid digestion of the sample. The same digestion procedure is used to determine total recoverable cadmium (Test Methods D3557), chromium (Test Methods D1687), cobalt (Test Methods D3558), copper (Test Methods D1688), iron (Test Methods D1068), lead (Test Methods D3559), manganese (Test Methods D858), nickel (Test Methods D1886), and zinc (Test Methods D1691).

9. Interferences

9.1 Aluminum at concentrations greater than 500 µg/L has been reported to depress the beryllium absorbance.

9.2 Sodium and silicon at concentrations in excess of 1000 mg/L have been reported to severely depress the beryllium absorbance.

9.3 Beryllium is slightly ionized in the nitrous oxide-acetylene flame. This ionization is suppressed by adding calcium chloride to give a final concentration of 900 mg/L calcium in all standard and sample solutions.

10. Apparatus

10.1 *Atomic Absorption Spectrophotometer,* for use at 234.9 nm.

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

10.2 *Beryllium Hollow Cathode Lamp.*

10.3 *Pressure Regulators*—The supplies of oxidants and fuel shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable regulators.

11. Reagents and Materials

11.1 *Beryllium Solution, Stock* (1.00 mL = 1000 µg Be)—Dissolve 1.000 g of beryllium metal in a minimum volume of HCl (1 + 1) and dilute to 1 L. (Beryllium is toxic and the solution should be prepared in a well-ventilated hood.) A purchased metal stock solution of appropriate known purity is also acceptable.

11.2 *Beryllium Solution, Intermediate* (1.00 mL = 100 µg Be)—Dilute 10.0 mL of the beryllium stock solution to 100.0 mL with nitric acid (HNO_3, 1 + 499).

11.3 *Beryllium Solution, Standard* (1.00 mL = 1.00 µg Be)—Dilute 5.00 mL of the beryllium intermediate solution to 500.0 mL with nitric acid (HNO_3, 1 + 499).

11.4 *Calcium Solution* (10 g/L)—Dissolve 25 g of calcium carbonate in a minimum volume of HCl (1 + 1) and dilute to 1 L with water.

11.5 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-µm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

11.6 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

NOTE 3—If a high reagent blank is obtained, distill the HCl or use spectrograde acid. (When HCl is distilled, an azeotropic mixture is obtained (approximately 6 *N* HCl). Therefore, whenever concentrated HCl is specified in the preparation of a reagent or in the procedure, use double the amount if distilled acid is used.)

11.7 *Hydrochloric Acid* (1 + 1)—Mix 1 volume of HCl (sp gr 1.19) with 1 volume of water. Always add acid to water.

11.8 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

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[3] *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.

NOTE 4—If a high reagent blank is obtained, distill the HNO_3 or use spectrograde acid.

11.9 *Nitric Acid* (1 + 499)—Add 1 volume of HNO_3 (sp gr 1.42) to 499 volumes of water.

11.10 *Oxidant:*

11.10.1 *Air,* which has been passed through a suitable filter to remove oil, water, and other foreign substances, is the oxidant used prior to switching to nitrous oxide.

11.10.2 *Nitrous Oxide* is the required oxidant.

11.11 *Fuel:*

11.11.1 *Acetylene*—Standard commercially available acetylene is the required fuel. Acetone, always present in acetylene cylinders, can affect analytical results. The cylinder should be replaced at a gage pressure of 517 kPa (75 psi). ("Prepurified" grade acetylene containing a special proprietary solvent other than acetone should not be used with poly (vinyl chloride) tubing as weakening of the walls can cause a potentially hazardous situation.)

12. Hazards

12.1 Due to the high toxicity of beryllium, all sample preparation and digestion steps should be carried out in a well-ventilated hood. Also, the atomic absorption unit should be vented as recommended by the manufacturer.

13. Standardization

13.1 Prepare a blank and at least four standard solutions to bracket the expected beryllium concentration range of the samples to be analyzed by diluting the beryllium standard solution (11.3) with HNO_3 (1 + 499) (11.9). Analyze at least three working standards containing concentrations of beryllium that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument. Prepare the standards (100 mL) each time the test is to be performed or as determined by Practice D4841.

13.2 For total recoverable beryllium, add 0.5 mL of HNO_3 (sp gr 1.42) (11.8) and proceed as directed in 14.2 – 14.6. For dissolved beryllium, proceed with 13.3.

13.3 Add 1.0 mL of calcium solution (11.4) to a 10.0-mL aliquot of each standard and blank solution. Mix thoroughly.

13.4 Aspirate the blank and standards and record the instrument readings. Aspirate HNO_3 (1 + 499) between each standard. (The atomic absorption unit should be vented properly.)

TABLE 1 Overall $S_{(T)}$ and Single-Operator (S_O) Interlaboratory Precision for Beryllium by Flame AAS, Test Method A

	Reagent Water		
Concentration (X), µg/L	15.4	211.0	444.8
S_T	2.7	10.8	21.3
S_O	1.2	4.4	11.9
	Natural Water		
Concentration (X), µg/L	16.9	214.7	444.4
S_T	2.9	7.7	19.2
S_O	2.2	5.4	10.3

13.5 Prepare an analytical curve by plotting the absorbance versus the standard concentration for each standard on linear graph paper. Alternatively, use a direct concentration readout if the instrument is so equipped.

14. Procedure

14.1 Measure 100.0 mL of a well-mixed acidified sample into a 150-mL beaker.

NOTE 5—If only dissolved beryllium is to be determined, start with 14.5.

14.2 Add 5 mL of HCl (sp gr 1.19) (11.6) to each sample.

14.3 Heat the samples on a steam bath or hot plate until the volume has been reduced to 15 or 20 mL, making certain that the samples do not boil. (Perform in a well-ventilated hood.)

NOTE 6—For brines and samples with high levels of suspended matter or total dissolved solids, the amount of reduction is left to the discretion of the analyst.

NOTE 7—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

14.4 Cool and filter the samples through a suitable filter (11.5) (such as a fine-textured, acid-washed, ashless paper) into 100-mL volumetric flasks. Wash the filter paper two or three times with water and adjust to volume.

14.5 Add 1.0 mL of calcium solution (11.4) to a 10.0-mL aliquot of each sample and mix thoroughly.

14.6 Aspirate each sample and determine its absorbance or concentration. Aspirate HNO_3 (1 + 499) between each sample.

15. Calculation

15.1 Calculate the concentration of beryllium in each sample, in micrograms per litre, using the analytical curve described in 13.5.

TABLE 2 Precision and Bias, Atomic Absorption, Direct

Amount Added, µg/L	Amount Found, µg/L	% Bias	Statistically Significant (95 % Confidence Level)
	Reagent Water, Type II		
16	15.4	−3.75	no
220	211.0	−4.09	yes
460	444.8	−3.30	yes
	Selected Water Matrices		
16	16.9	+ 5.60	no
220	214.7	−2.41	yes
460	444.4	−3.39	yes

16. Precision and Bias[4]

16.1 Based on the round-robin results from seven laboratories and ten operators, the following precision and bias statements can be made:

16.1.1 The overall and single-operator precision of this test method, within its designated range for reagent water and selected water matrices, varies with the quantity tested as shown in Table 1.

16.1.2 The bias of this test method is listed in Table 2.

16.2 The precision and bias data were obtained on reagent water, tap water, salt water, river water, lake water, spring water, and untreated wastewater. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

16.3 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.

17. Quality Control

17.1 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 beryllium.

17.2 *Calibration and Calibration Verification:*

17.2.1 Analyze at least three working standards containing concentrations of beryllium that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument (13.1). The calibration correlation coefficient shall be equal to or greater than 0.990.

17.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The absorbance shall fall within 4 % of the absorbance from the calibration. Alternately, the concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

17.2.3 If calibration cannot be verified, recalibrate the instrument.

17.2.4 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.

17.3 *Initial Demonstration of Laboratory Capability:*

17.3.1 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.

17.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing mid-range concentration of beryllium. 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.

17.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable range of bias in 16.1. This study should be repeated until the recoveries are within the limits given in 16.1. 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.

17.4 *Laboratory Control Sample (LCS):*

17.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of berylllium 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 the LCS shall fall within ±15 % of the known concentration.

17.4.2 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.

17.5 *Method Blank:*

17.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of beryllium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of beryllium 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.

17.6 *Matrix Spike (MS):*

17.6.1 To check for interferences in the specific matrix being tested, perform a matrix spike (MS) on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of beryllium and taking it through the analytical method.

17.6.2 The spike concentration plus the background concentration of beryllium 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.

17.6.3 Calculate the percent recovery of the spike (P) using the following calculation:

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

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1043. Contact ASTM Customer Service at service@astm.org.

where:

A = analyte known concentration (µg/L) in spiked sample,
B = analyte known concentration (µg/L) in unspiked sample,
C = known concentration (µg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

17.6.4 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. See Note 8.

NOTE 8—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

17.7 *Duplicate:*

17.7.1 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.

17.7.2 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.

17.7.3 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 with the performance criteria of the test method.

17.8 *Independent Reference Material (IRM):*

17.8.1 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.

TEST METHOD B—ATOMIC ABSORPTION, GRAPHITE FURNACE

18. Scope

18.1 This test method covers the determination of dissolved and total recoverable beryllium in most waters and wastewaters.

18.2 This test method is applicable in the range from 10 to 50 µg/L of beryllium using a 20-µL injection. The range can be increased or decreased by varying the volume of sample injected or the instrumental settings. High concentrations may be diluted but preferably should be analyzed by direct-aspiration atomic-absorption spectrophotometry. ICP-MS may also be appropriate but at a higher instrument cost. See Test Method D5673.

18.3 This test method has been used successfully with reagent water, lake water, river water, well water, filtered tap water, and a condensate from a medium Btu coal gasification process. It is the user's responsibility to ensure validity of this test method to waters of untested matrices.

18.4 The analyst is encouraged to consult Practice D3919 for a general discussion of interferences and sample analysis procedures for graphite furnace atomic absorption spectrophotometry.

19. Summary of Test Method

19.1 Beryllium is determined by an atomic-absorption spectrophotometer used in conjunction with a graphite furnace. A sample is placed in a graphite tube, evaporated to dryness, charred (pyrolyzed or ashed), and atomized. Since the graphite furnace uses the sample much more efficiently than flame atomization, the detection of low concentrations of elements in small sample volumes is possible. Finally, the absorption signal generated during atomization is recorded and compared to standards. A general guide for the application of the graphite furnace is given in Practice D3919.

19.2 Dissolved beryllium is determined on a filtered then acidified sample with no pretreatment.

19.3 Total recoverable beryllium is determined following acid digestion and filtration. Because chlorides interfere with furnace procedures for some metals, the use of hydrochloric acid in the digestion or solubilization step is to be avoided. If suspended material is not present, this digestion and filtration may be omitted.

20. Interferences

20.1 For a complete discussion on general interferences with furnace procedures, the analyst is referred to Practice D3919.

21. Apparatus

21.1 *Atomic Absorption Spectrophotometer,* for use at 234.9 nm with background correction. See Note 9.

NOTE 9—The manufacturer's instructions should be followed for all instrumental parameters.

21.2 *Beryllium Light Source*—Beryllium hollow cathode lamp.

21.3 *Graphite Furnace,* capable of reaching temperatures sufficient to atomize beryllium.

21.4 *Graphite Tubes,* compatible with furnace device. Standard graphite tubes are preferred unless extreme sensitivity is required.

21.5 *Pipettes*—Microliter with disposable tips. Sizes may range from 1 to 100 µL, as required.

21.6 *Data Storage and Reduction Devices, Computer- and Microprocessor-Controlled Devices, or Strip Chart Recorders* shall be utilized for collection, storage, reduction, and problem recognition (such as drift, incomplete atomization, changes in sensitivity, etc.). Strip chart recorders shall have a full scale deflection time of 0.2 s or less to ensure accuracy.

21.7 *Automatic Sampling*—Is recommended if available.

22. Reagents and Materials

22.1 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

22.2 *Beryllium Solution, Stock* (1.00 mL = 1.00 µg Be)—See 11.1.

22.3 *Beryllium Solution, Intermediate* (1.00 mL = 0.100 µg Be)—Dilute 10.0 mL of stock solution and 1 mL of HNO_3 (sp gr 1.42) to 100 mL with water. This standard is used to prepare working standards at the time of the analysis.

22.4 *Filter Paper*—See 11.5.

22.5 *Argon*—Prepurified argon is the support gas. Nitrogen may also be used if recommended by the instrument manufacturer.

23. Standardization

23.1 Initially, set the instrument in accordance with the manufacturer's specifications. Follow the general instructions as provided in Practice D3919. Analyze at least three working standards containing concentrations of beryllium that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument.

24. Procedure

24.1 Clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, by rinsing first with HNO_3 (1 + 1) and then with water. If possible, soak the glassware overnight in HNO_3 (1 + 1).

24.2 Measure 100 mL of each standard and well-mixed sample into a 125-mL beaker or flask.

24.3 If only dissolved beryllium is to be determined, proceed with step 24.6.

24.4 For total recoverable beryllium, add 5 mL of HNO_3 (sp gr 1.42) to 100 mL of standard and sample and heat at 95°C in a steam bath or hotplate, and in a well-ventilated fume hood, until the volume has been reduced to 15 to 20 mL. Make certain that the sample does not boil. See Note 6. See Note 7.

TABLE 3 Precision and Bias, Atomic Absorption, Graphite Furnace

Amount Added, µg/L	Amount Found, µg/L	S_T, µg/L	Bias, µg/L	% Bias	Statistically Significant (95 % Confidence level)
		Reagent Water			
20	22.6	2.5	+ 2.6	+ 13.0	yes
25	24.8	1.9	−0.2	−0.8	no
40	49.2	12.9	+ 9.2	+ 23.0	yes
		Water of Choice			
20	26.2	7.8	+ 6.2	+ 31.0	yes
25	27.6	5.4	+ 2.6	+ 10.0	no
40	43.0	4.7	+ 3.0	+ 7.5	no

24.5 Cool and filter the sample through a suitable filter (22.4) such as fine-texture, acid-washed, ashless paper, into a 100-mL volumetric flask. Wash the filter paper two or three times with water and bring to volume.

NOTE 10—If suspended material is not present, this filtration may be omitted, but the sample must still be diluted to 100 mL.

24.6 Inject a measured aliquot of sample into the furnace device following the directions provided by the particular instrument manufacturer. Refer to Practice D3919.

25. Calculation

25.1 Determine the concentration of beryllium in each sample by referring to Practice D3919.

26. Precision and Bias[5]

26.1 The precision of this test method was tested by ten laboratories in reagent water, lake water, river water, well water, filtered tap water, and condensate from a medium Btu coal gasification process. One laboratory reported data from two operators. Although multiple injections may have been made, the report sheets provided allowed only for reporting single values. Thus, no single operator precision data can be calculated.

26.1.1 The overall precision of this test method, within its designated range for reagent water and selected water matrices, varies with the quantity tested as shown in Table 3.

26.1.2 Recovery and bias data for this test method are listed in Table 3.

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

26.3 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.

27. Quality Control

27.1 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 beryllium.

27.2 *Calibration and Calibration Verification:*

27.2.1 Analyze at least three working standards containing concentrations of beryllium that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument (see 23.1). The calibration correlation coefficient shall be equal to or greater than 0.990.

27.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1110. Contact ASTM Customer Service at service@astm.org.

calibration standards. The absorbance shall fall within 4 % of the absorbance from the calibration. Alternately, the concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

27.2.3 If calibration cannot be verified, recalibrate the instrument.

27.2.4 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.

27.3 *Initial Demonstration of Laboratory Capability:*

27.3.1 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.

27.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing mid-range concentration of beryllium. 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.

27.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable range of bias in 26.1. This study should be repeated until the recoveries are within the limits given in 26.1. 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.

27.4 *Laboratory Control Sample (LCS):*

27.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of berylllium 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 the LCS shall fall within ±15 % of the known concentration.

27.4.2 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.

27.5 *Method Blank:*

27.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of beryllium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of beryllium 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.

27.6 *Matrix Spike (MS):*

27.6.1 To check for interferences in the specific matrix being tested, perform a matrix spike (MS) on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of beryllium and taking it through the analytical method.

27.6.2 The spike concentration plus the background concentration of beryllium 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.

27.6.3 Calculate the percent recovery of the spike (*P*) using the following calculation:

$$P = \frac{100\left[A\,(V_s + V) - BV_s\right]}{CV} \tag{2}$$

where:

A = analyte known concentration (µg/L) in spiked sample,
B = analyte known concentration (µg/L) in unspiked sample,
C = known concentration (µg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

27.6.4 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. See Note 11.

NOTE 11—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

27.7 *Duplicate:*

27.7.1 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.

27.7.2 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.

27.7.3 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 with the performance criteria of the test method.

27.8 *Independent Reference Material (IRM):*

27.8.1 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.

28. Keywords

28.1 atomic absorption; beryllium flame (Method A); furnace (Method B); total recoverable beryllium; water

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3645 – 08) that may impact the use of this standard. (Approved Feb. 1, 2015.)

(1) Revised Section 1 to update the units of measurement statement.
(2) Revised Section 2 to include D5673.
(3) Revised Section 3.
(4) Revised Section 6 to allow for pH of the samples in the laboratory.
(5) Revised Sections 11 and 12 to allow for commercial standards and add information on filter paper.
(6) Revised Sections 13 and 23 with standard and calibration information.
(7) Revised Sections 13, 14, and 24 to add reagent references.
(8) Revised Section 14 to include note about the use of block digestion systems.
(9) Added Section 17 and renumbered the subsequent sections accordingly.
(10) Revised Section 18 to inform the user of the possibility of using an ICP-MS.
(11) Revised Section 21 to replace former Strip Chart Recorder information with Data Storage and Reduction Devices information.
(12) Revised Section 27.

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