Designation: D 3082 – 92 (Reapproved 1996)

Designation: D 3082 – 03

Standard Test Method for Boron In Water[1]

This standard is issued under the fixed designation D 3082; 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 D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.
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1. Scope*

1.1 This test method covers the determination of boron in water and wastewaters by the curcumin colorimetric-extraction method[2] in concentrations between 0.1 and 1.0 mg/L. The range can be extended by dilution of the sample.

1.2 Only dissolved boron is determined. This test method requires that the water sample be filtered through a 0.45-µm membrane filter before analysis.

1.3 This test method is a colorimetric method that is very sensitive to low concentrations of boron in water and requires a relatively small sample volume for analysis.

1.4 Precision and bias were obtained on natural and wastewaters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

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:*
D 1066 Practice for Sampling Steam[3]
D 1129 Terminology Relating to Water[3]
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[3]
D 1193 Specification for Reagent Water[3]
D 1293 Test Methods for pH of Water[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water[3]
D 3370 Practices for Sampling Water from Closed Conduits[3]
D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents[3]
D 5810 Guide for Spiking into Aqueous Samples[3]
D 5847 Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]
E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[4]
E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[5]
E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[6]

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 When a water sample containing soluble boron is acidified with hydrochloric acid and evaporated to dryness in the presence of curcumin, a red-colored complex called rosocyanine is formed. This colored product is taken up in isopropyl alcohol and is read spectrophotometrically.

[2] This test method is similar to, but not identical with that appearing in *Standard Methods for Examination of Water and Wastewater* , 13th Ed., American Public Health Association, Washington, DC, pp 69–72.
[3] *Annual Book of ASTM Standards*, Vol 11.01.
[4] *Annual Book of ASTM Standards*, Vol 03.05.
[5] *Annual Book of ASTM Standards*, Vol 15.05.
[6] *Annual Book of ASTM Standards*, Vol 03.06.

5. Significance and Use

5.1 Because boron can be both essential and deleterious to plant growth, and because ingestion of large amounts can affect the central nervous system in humans, a method is required to determine its concentration in potable, natural, and wastewaters. This test method provides a means of determining the boron concentration of these waters. The holding time for the samples may be calculated in accordance with Practice D 4841.

5.2 Boric acid is used for chemical shim control of neutron flux in a nuclear reactor. This test method serves to determine if the boron concentration is within acceptable limits.

6. Interferences

6.1 Nitrate concentrations above 20 mg/L begin to interfere. Hardness levels about 100 mg/L as $CaCO_3$ give high results because of the turbidity caused by the insolubility of the hardness salts in isopropyl alcohol. The turbidity can be eliminated by filtering the final solution through a 0.45-µm membrane filter before reading on the spectrophotometer.

6.2 Organic color may be present in the sample that could affect absorbance readings on the spectrophotometer. If an interfering organic color is present in the sample, the following procedure has been found useful in reducing this interference for some matrices. Pipet an appropriate sample aliquot into a platinum dish (Note 1). Make alkaline to litmus with NaOH solution (20 g/L) and add 3 drops in excess. Evaporate to dryness on a steam or hot-water bath. If desired, organic material may be destroyed by ignition at from 500 to 550°C before proceeding. Allow the platinum dish to cool and acidify with 5 mL of HCl (1 + 19). Triturate with a rubber policeman to dissolve the residue, pour the contents into a calibrated centrifuge tube, wash the platinum dish with 3 or 4 mL of water, and add to the centrifuge tube. Dilute to the 10-mL mark. Centrifuge to obtain a clear solution. Perform the same steps on a reagent blank.

NOTE 1—Other types of evaporating dishes may be used but must be checked. Porcelain or ceramic-type dishes may contain boron-fluxing agents.

7. Apparatus

7.1 All laboratory ware used in the performance of this test method must either be plastic or boron-free.

7.2 *Hot-Water Bath*, with temperature control at 55 ± 2°C.

7.3 *Spectrophotometer*, suitable for use in the range of 540 nm. The photometric practices prescribed in this test method shall conform to Practice E 60. Spectrophotometers shall conform to Practice E 275. Measure absorbance using a 50-mm cell.

7.4 *Evaporating Dishes*, 100 to 150 mL capacity.

8. Reagents

8.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[7] 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, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I, II, or III water. Type I is preferred and more commonly used. Type II water was specified at the time of round robin testing of this test method.

NOTE 2—The user must ensure the type of reagent water chosen is sufficiently free of interferences. The water should be analyzed using the test method.

8.3 *Boron Solution, Stock* (1.00 mL = 1.00 mg B)—Dry about 10 g of boric acid (H_3BO_3) crystals in a desiccator containing a silica gel desiccant for 24 h (Note 2). Dissolve 5.719 g of the dry H_3BO_3 in water and dilute to 1 L. Store the solution in a plastic bottle or boron-free container.

NOTE 3—If boric acid is heated, it gradually loses water, changing first to metaboric acid (HBO_2) and finally dehydrating completely to the anhydrous oxide (B_2O_3). It is important therefore that oven drying not be used as a method of drying boric acid.

8.4 *Boron Solution, Standard* (1.00 mL = 0.010 mg B)—Quantitatively dilute 10.0 mL of the stock boron solution to 1 L with water. Store in a plastic bottle or boron-free container.

8.5 *Curcumin Solution*—Dissolve 40 mg of finely ground curcumin [8] and 5 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in 80 mL of isopropyl alcohol. Add 4.0 mL of hydrochloric acid (HCl, sp gr 1.19) and make up to 100 mL with isopropyl alcohol.

8.6 *Hydrochloric Acid* (1 + 19)—Add 1 volume of hydrochloric acid (sp gr 1.19) to 19 volumes of water.

8.7 *Isopropyl Alcohol*.

8.8 *Sodium Hydroxide Solution* (20 g/L)—Dissolve 2 g of NaOH in water and dilute to 100 mL.

9. Sampling

9.1 Collect the samples in accordance with Practice D 1066, Specification D 1192, or Practices D 3370.

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[7] Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary* , U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[8] Curcumin is available through Eastman No. 1179.

9.2 Filter the sample through a 0.45-µm membrane filter as soon as possible after sampling.

9.3 Samples should be collected and stored in polyethylene bottles or alkali-resistant, boron-free glass. No other preservation is required.

10. Calibration and Standardization

10.1 Prepare a series of standard boron solutions to cover the range from 0 to 1.0 mg/L. Make up standards by diluting suitable volumes of the boron standard solution (1.00 mL = 0.010 mg B) to 100 mL.

10.2 Develop the color complex as directed in 11.1 through 11.4. Measure the absorbance of each standard at 540 nm in a 50-mm cell using a reagent blank as the reference solution to set zero absorbance on the spectrophotometer. Plot absorbance versus concentration on linear graph paper. The calibration curve is linear from 0.1 to 1.0 mg/L.

11. Procedure

11.1 Pipet 1.0 mL of a clear, filtered sample containing 0.1 to 1.0 mg/L of boron into an evaporating dish (Treatment of organic interferences discussed in 6.2). Run a blank and at least one standard in conjunction with the unknown sample. Add 4 mL of curcumin solution to each sample and standard, and then, gently swirl to mix contents.

11.2 Place the evaporating dishes in a hot-water bath that is controlled at 55 ± 2°C and evaporate to dryness. Allow 15 min after the contents appear dry before removing. Cool to room temperature.

11.3 Add 10 mL of isopropyl alcohol to each dish and stir with a plastic rod to ensure complete dissolution of the red-colored complex. Wash the contents of each evaporating dish into a 25-mL volumetric flask using isopropyl alcohol. Dilute to the mark using isopropyl alcohol and mix thoroughly.

11.4 If the solution appears turbid, filter through a 0.45-µm membrane filter before reading the absorbance. Measure the absorbance of each sample and standard at 540 nm on the spectrophotometer using the reagent blank to set zero absorbance. Record the boron concentration as indicated by the calibration curve.

12. Calculation

12.1 Calculations are not required, as the boron concentration can be read directly from the calibration curve provided no dilution or concentration of the original sample was made.

13. Precision and Bias [9]

13.1 The overall and single-operator precision of this test method for five laboratories varied with the concentration of boron being measured in accordance with Fig. 1 and Fig. 2. Test method evaluation included a total of seven operators analyzing each sample on three consecutive days, within its range for reagent water and water of choice.

13.1.1 The overall precision for reagent water varies linearly with the concentration of boron being measured, and it may be expressed mathematically as follows:

$$S_t = 0.030\,X + 0.020$$

where:

S_t = overall precision, mg/L and

X = concentration of B, mg/L.

13.2 Recoveries of known amounts of boron (from boric acid) in a series of prepared standards for the five participating laboratories were as given in Table 1.

13.3 Waters of choice arbitrarily selected by participating round-robin laboratories consisted of natural and wastewaters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

~~13.4 The use of five laboratories in~~

13.4 Precision and bias for this test method conforms to Practice D 2777 – 77, which was in place at the time of collaborative ~~study meets~~ testing. Under the ~~requirements~~ allowances made in 1.4 of Practice ~~D 2777 – 77, but does not~~ D 2777 – 98, these precision and bias data do meet ~~the six laboratory~~ existing requirements for interlaboratory studies of ~~Practice D 2777 – 85.~~ 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 boron.

14.2 *Calibration and Calibration Verification*:

14.2.1 Analyze at least three working standards containing concentrations of boron 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.

[9] Supporting data have been filed at ASTM Headquarters. Request RR:D19-1126.

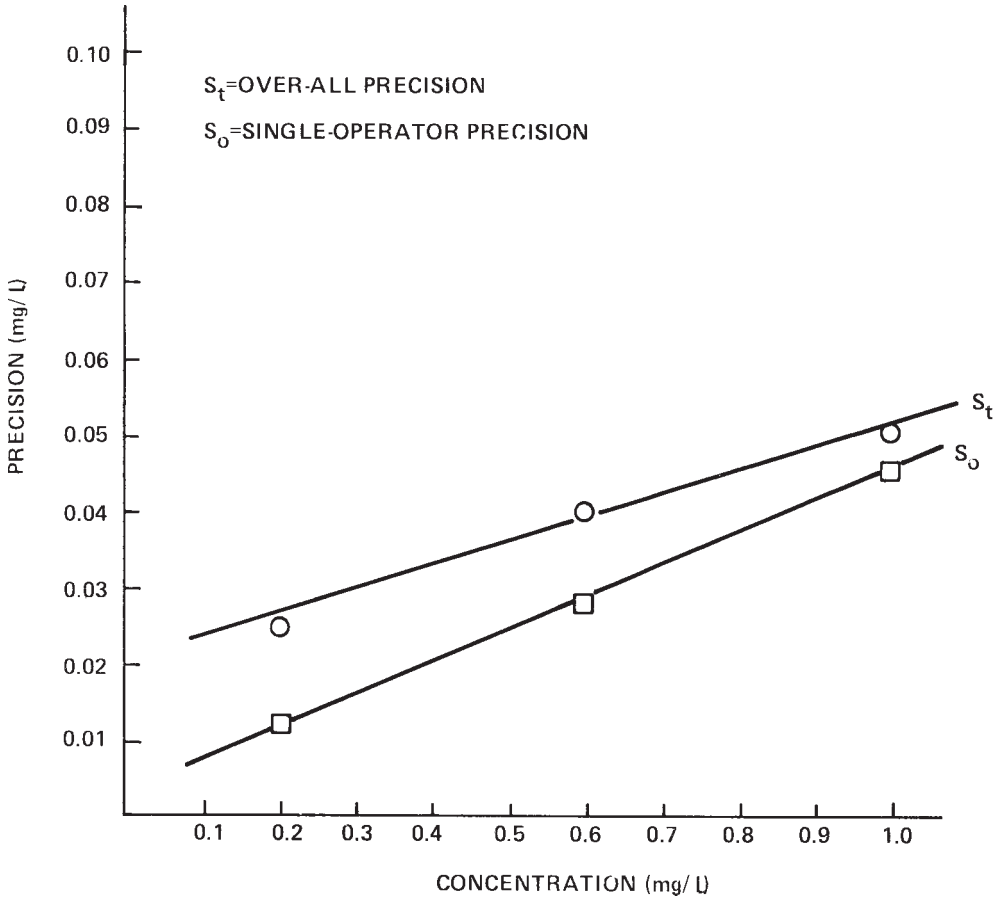

FIG. 1 Interlaboratory Precision for Boron in Reagent Water by Curcumin Colorimetric Method

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, 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 boron. 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 boron 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 ±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 boron found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of boron 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.

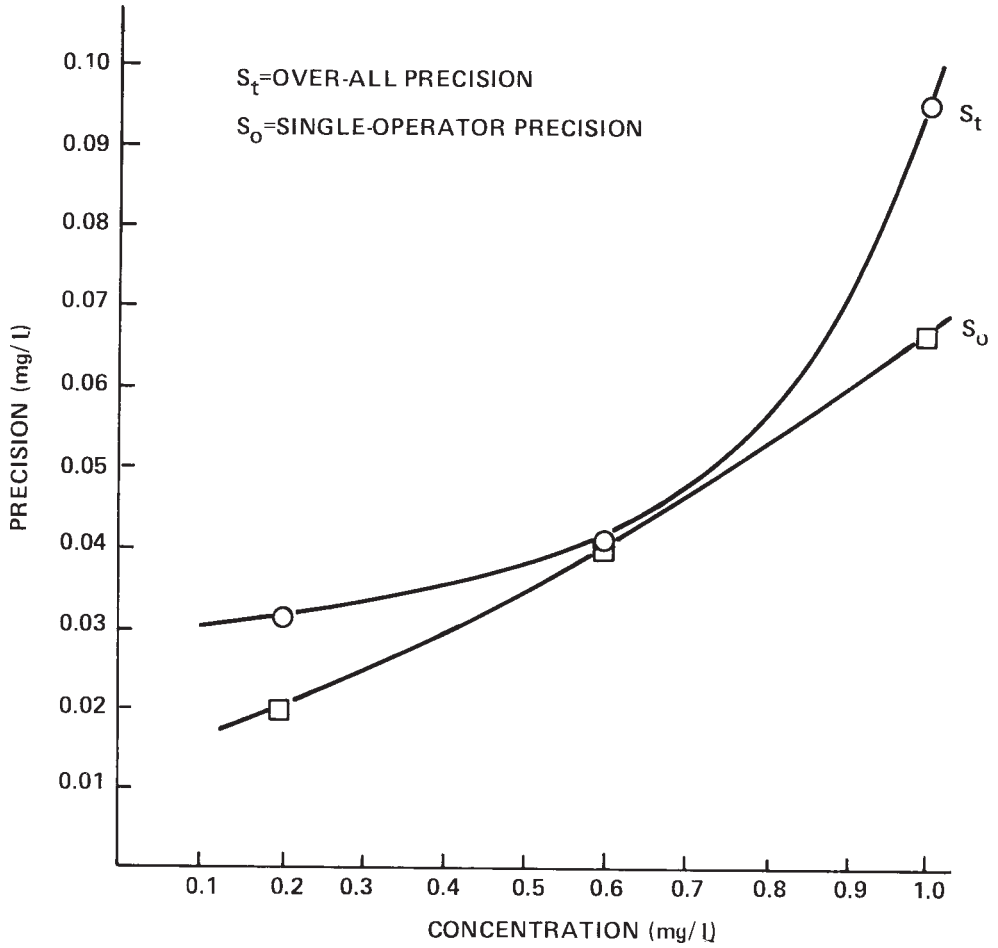

FIG. 2 Interlaboratory Precision for Boron in Natural Water and Waste Water (Combined Data) by Curcumin Colorimetric Method

TABLE 1 Recovery and Precision Data

Amount Added mg/L	Amount Found mg/L	Recovery, %	Bias, %	Statistical Significance (95% Confidence Level)
Reagent H_2O (Type II)				
1.000	0.993	99.3	−0.7	no
0.600	0.581	96.8	−3.2	no
0.200	0.201	100.5	+ 0.5	no
Nonreagent Water (Water of Choice)				
1.000	1.011	101.1	+ 1.1	no
0.600	0.587	97.8	−2.2	no
0.200	0.200	100.0	0.0	no

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 boron and taking it through the analytical method.

14.6.2 The spike concentration plus the background concentration of boron 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) 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

15.1 boron; colorimetric-extraction; curcumin; spectrophotometric; 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 13.4 was added.