# 4500-B

# BORON

Approved by Standard Methods Committee, 2000. Editorial revisions, 2020.

## 4500-B A. INTRODUCTION

### 1. Occurrence and Significance

Boron (B) is the first element in Group IIIA of the periodic table. It has an atomic number of 5, an atomic weight of 10.81, and a valence of 3. The average abundance of B in the earth's crust is 9 ppm. In soils it is 18 to 63 ppm, in streams it is 10 µg/L, and in groundwaters it is 0.01 to 10 mg/L. The most important mineral is borax, which is used in the preparation of heat-resistant glasses, detergents, porcelain enamels, fertilizers, and fiberglass.

The most common form of boron in natural waters is $H_3BO_3$. Although boron is an element essential for plant growth, in excess of 2.0 mg/L in irrigation water, it is deleterious to certain plants and some plants may be affected adversely by concentrations as low as 1.0 mg/L (or even less in commercial greenhouses). Drinking waters rarely contain more than 1 mg/L B. Generally, less than 0.1 mg/L concentrations are considered innocuous for human consumption. Seawater contains approximately 5 mg/L B, and this element is found in saline estuaries in association with other seawater salts.

The ingestion of large amounts of boron can affect the central nervous system. Protracted ingestion may result in a clinical syndrome known as borism.

### 2. Selection of Method

Preferably, perform analyses by the inductively coupled plasma method (Section 3120). The inductively coupled plasma-mass spectrometric method (Section 3125) also may be applied successfully in most cases (with lower detection limits), even though boron is not specifically listed as an analyte in the method.

The curcumin method (4500-B B) is applicable in the 0.10- to 1.0-mg/L range, while the carmine method (4500-B C) is suitable for the determination of boron concentration in the 1- to 10-mg/L range. The range of these methods can be extended by dilution or concentration of the sample.

### 3. Sampling and Storage

Store samples in polyethylene bottles or alkali-resistant, boron-free glassware.

## 4500-B B. CURCUMIN METHOD

### 1. General Discussion

*a. Principle:* When a sample of water containing boron is acidified and evaporated in the presence of curcumin, a red-colored product called rosocyanine is formed. The rosocyanine is taken up in a suitable solvent and the red color is compared with standards visually or photometrically.

*b. Interference:* $NO_3^-$-N concentrations above 20 mg/L interfere. Significantly high results are possible when the total of calcium and magnesium hardness exceeds 100 mg/L as calcium carbonate ($CaCO_3$). Moderate hardness levels also can cause a considerable percentage error in the low boron range. This interference springs from the insolubility of the hardness salts in 95% ethanol and consequent turbidity in the final solution. Filter the final solution or pass the original sample through a column of strongly acidic cation-exchange resin in the hydrogen form to remove interfering cations. The latter procedure permits application of the method to samples of high hardness or solids content. Phosphate does not interfere.

*c. Minimum detectable quantity:* 0.2 µg B.

*d. Quality control (QC):* The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

### 2. Apparatus

*a. Colorimetric equipment:* One of the following is required:

1) *Spectrophotometer,* for use at 540 nm, with a minimum light path of 1 cm.

2) *Filter photometer,* equipped with a green filter having a maximum transmittance near 540 nm, with a minimum light path of 1 cm.

*b. Evaporating dishes,* 100- to 150-mL capacity, of high-silica glass platinum, or other suitable material.

*c. Water bath,* set at 55 ± 2 °C.

*d. Glass-stoppered volumetric flasks,* 25- and 50-mL capacity.

*e. Ion-exchange column,* 50 cm long by 1.3 cm in diameter.

### 3. Reagents

Store all reagents in polyethylene or boron-free containers.

*a. Stock boron solution:* Dissolve 571.6 mg anhydrous boric acid, $H_3BO_3$, in reagent water and dilute to 1000 mL; 1.00 mL = 100 µg B. Because $H_3BO_3$ loses weight on drying at 105 °C, use a reagent that meets ACS specifications, and keep the bottle tightly stoppered to prevent entrance of atmospheric moisture.

*b. Standard boron solution:* Dilute 10.00 mL stock boron solution to 1000 mL with reagent water; 1.00 mL =1.00 µg B.

*c. Curcumin reagent:* Dissolve 40 mg finely ground curcumin and 5.0 g oxalic acid in 80 mL 95% ethyl alcohol. Add 4.2 mL conc HCl, fill to 100 mL with ethyl alcohol in a 100-mL volumetric flask, and filter if the reagent is turbid (isopropyl alcohol, 95%, may be used in place of ethyl alcohol). This reagent is stable for several days if stored in a refrigerator.

*d. Ethyl or isopropyl alcohol, 95%.*

*e. Reagents for removal of high hardness and cation interference:*

1) Strongly acidic cation-exchange resin.

2) Hydrochloric acid, (HCl), 1 + 5.

## 4. Procedure

*a. Precautions:* Closely control such variables as volumes and concentrations of reagents, as well as time and temperature of drying. Use evaporating dishes identical in shape, size, and composition to ensure equal evaporation time because increasing the time increases the intensity of the resulting color.

*b. Preparation of calibration curve:* Pipet 0 (blank), 0.25, 0.50, 0.75, and 1.00 µg boron into evaporating dishes of the same type, shape, and size. Add reagent water to each standard to bring total volume to 1.0 mL. Add 4.0 mL curcumin reagent to each and swirl gently to mix contents thoroughly. Float dishes on a water bath set at 55 ± 2 °C and let them remain for 80 min, which is usually sufficient for complete drying and removal of HCl. Keep drying time constant for standards and samples. After dishes cool to room temperature, add 10 mL 95% ethyl alcohol to each dish and stir gently with a polyethylene rod to ensure the complete dissolution of the red-colored product.

Wash contents of dish into a 25-mL volumetric flask, using 95% ethyl alcohol. Fill to the mark with 95% ethyl alcohol and mix thoroughly by inverting. Read the absorbance of standards and samples at a wavelength of 540 nm after setting the reagent blank at zero absorbance. The calibration curve is linear from 0 to 1.00 µg boron. Make photometric readings within 1 h of drying samples.

*c. Sample treatment:* For waters containing 0.10 to 1.00 mg/L B, use 1.00 mL sample. For waters containing more than 1.00 mg/L B, make an appropriate dilution with boron-free reagent water, so that a 1.00-mL portion contains approximately 0.50 µg boron.

Pipet 1.00 mL sample or dilution into an evaporating dish. Unless the calibration curve is being determined at the same time, prepare a blank and a standard containing 0.50 µg boron and run with the sample. Proceed as in paragraph *b* above, beginning with "Add 4.0 mL curcumin reagent. . . ." If the final solution is turbid, filter through filter paper (Whatman No. 30, or equivalent) before reading absorbance. Calculate the boron content from the calibration curve.

*d. Visual comparison:* The photometric method may be adapted to the visual estimation of low boron concentrations, from 50 to 200 µg/L, as follows: Dilute the standard boron solution 1 + 3 with reagent water; 1.00 mL = 0.20 µg B. Pipet 0, 0.05, 0.10, 0.15, and 0.20 µg boron into evaporating dishes as indicated in paragraph *b* above. At the same time add an appropriate volume of sample (1.00 mL or portion diluted to 1.00 mL) to an identical evaporating dish. The total boron should be between 0.05 and 0.20 µg. Proceed as in paragraph *b* above, beginning with "Add 4.0 mL curcumin reagent. . . ." Compare the color of samples with standards within 1 h of drying the samples.

*e. Removal of high hardness and cation interference:* Prepare an ion-exchange column of approximately 20 cm × 1.3 cm diam. Charge the column with a strongly acidic cation-exchange resin. Backwash the column with reagent water to remove entrained air bubbles. Keep the resin covered with liquid at all times. Pass 50 mL 1 + 5 HCl through the column at a rate of 0.2 mL acid per milliliter of resin in column/min and wash the column free of acid with reagent water.

Pipet 25 mL sample, or a smaller sample of known high boron content diluted to 25 mL, onto the resin column. Adjust the rate of flow to about 2 drops/s and collect the effluent in a 50-mL volumetric flask. Wash the column with small portions of reagent water until the flask is filled to the mark. Mix and transfer 2.00 mL into an evaporating dish. Add 4.0 mL curcumin reagent and complete the analysis as described in paragraph *b* above.

## 5. Calculation

Use the following equation to calculate the boron concentration from absorbance readings:

$$\text{mg/L B} = \frac{A_2 \times C}{A_1 \times S}$$

where:

$A_2$ = absorbance of sample,
$C$ = µg B in standard taken,
$A_1$ = absorbance of standard, and
$S$ = mL sample.

## 6. Precision and Bias

A synthetic sample containing 240 µg/L B, 40 µg/L As, 250 µg/L Be, 20 µg/L Se, and 6 µg/L V in distilled water was analyzed in 30 laboratories by the curcumin method with a relative standard deviation of 22.8% and a relative error of 0%.

## Bibliography

Silverman L, Trego K. Colorimetric microdetermination of boron by the curcumin-acetone solution method. Anal Chem. 1953;25(8): 1264–1267.

Dirle WT, Truog E, Berger KC. Boron determination in soils and plants—Simplified curcumin procedure. Anal Chem. 1954;26(2): 418–421.

Luke CL. Determination of traces of boron in silicon, germanium, and germanium dioxide. Anal Chem. 1955;27(7):1150–1153.

Lishka RJ. Comparison of analytical procedures for boron. J Amer Water Works Assoc. 1961;53(12):1517–1522.

Bunton NG, Tait BH. Determination of boron in waters and effluents using curcumin. J Amer Water Works Assoc. 1969;61(7):357–359.

## 4500-B C. Carmine Method

### 1. General Discussion

*a. Principle:* In the presence of boron, a solution of carmine or carminic acid in concentrated sulfuric acid changes from a bright red to a bluish red or blue, depending on the concentration of boron present.

*b. Interference:* The ions commonly found in water and waste-water do not interfere.

*c. Minimum detectable quantity:* 2 µg B.

*d. Quality control (QC):* The QC practices considered to be an integral part of each method are summarized in Table 4020:1.

### 2. Apparatus

*Colorimetric equipment:* One of the following is required:

*a. Spectrophotometer,* for use at 585 nm, with a minimum light path of 1 cm.

*b. Filter photometer,* equipped with an orange filter having a maximum transmittance near 585 nm, with a minimum light path of 1 cm.

### 3. Reagents

Store all reagents in polyethylene or boron-free containers.

*a. Standard boron solution:* Prepare as directed in 4500-B B.3*b*.

*b. Hydrochloric acid* (HCl), conc and 1 + 11.

*c. Sulfuric acid* ($H_2SO_4$), conc.

*d. Carmine reagent:* Dissolve 920 mg carmine N.F. 40, or carminic acid, in 1 L conc $H_2SO_4$. (If unable to zero the spectrophotometer, dilute carmine 1 + 1 with conc $H_2SO_4$ to replace above reagent.)

### 4. Procedure

*a. Low-level sample concentration:* If a sample contains less than 1 mg/L B, pipet a portion containing 2 to 20 µg B into a platinum dish, make alkaline with 1 N NaOH plus a slight excess, and evaporate to dryness on a steam or hot water bath. If necessary, destroy any organic material by ignition at 500 to 550 °C. Acidify the cooled residue (ignited or not) with 2.5 mL 1 + 11 HCl and triturate with a rubber policeman to dissolve. Centrifuge, if necessary, to obtain a clear solution. Pipet 2.00 mL clear concentrate into a small flask or 30-mL test tube. Treat the reagent blank identically.

*b. Color development:* Prepare a series of boron standard solutions (100, 250, 500, 750, and 1000 µg) in 100 mL with reagent water. Pipet 2.00 mL of each standard solution into a small flask or 30-mL test tube.

Treat the blank and calibration standards exactly as the sample. Add 2 drops (0.1 mL) conc HCl, carefully introduce 10.0 mL conc $H_2SO_4$, mix, and let cool to room temperature. Add 10.0 mL carmine reagent, mix well, and after 45 to 60 min measure absorbance at 585 nm in a cell of 1-cm or longer light path, using the blank as reference.

To avoid error, make sure that no bubbles are present in the optical cell while photometric readings are being made. Bubbles may appear as a result of the incomplete mixing of reagents. Because carmine reagent deteriorates, check the calibration curve daily.

### 5. Calculation

$$\text{mg/L B} = \frac{\mu\text{g B}}{\text{mL sample}} \times \text{D}$$

where:

D = dilution correction (D = 1 for an undiluted sample, 1.25 if concentrated as in 4500-B C4.*a*).
Other values determined by analyst.

### 6. Precision and Bias

A synthetic sample containing 180 µg/L B, 50 µg/L As, 400 µg/L Be, and 50 µg/L Se in distilled water was analyzed in 9 laboratories by the carmine method with a relative standard deviation of 35.5% and a relative error of 0.6%.

### Bibliography

Hatcher JT, Wilcox LV. Colorimetric determination of boron using carmine. Anal Chem. 1950;22(4):567–569.