Ultraviolet Spectrophotometric Determination of Boron Using Tiron as a New Reagent

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Previous publications have described how many kinds of colorimetric reagents, such as oxyanthraquinones, flavone compounds, curcumin, etc., have been examined photometrically for boron. In the case of oxyanthraquinones, the colored complexes are formed in a concentrated sulfuric acid medium, while in the case of flavones or curcumin, sample solution should be evaporated with the reagent solution under conditions carefully controlled for color development. Since these procedures are very tedious and time-consuming, it would seem advantageous if the color development could be achieved simply and rapidly in an aqueous medium.

Tiron, disodium 1, 2-dihydroxybenzene-3, 5-disulfonate, was initially proposed as a photometric reagent for iron by Yoe and Jones[1]; thereafter this reagent has been utilized for the determination of titanium[2-7], iron[3,6], cerium[8-10], molybdenum[11,12], uranium[13] and niobium[14] in many kinds of samples.

This compound is expected to be a useful reagent of boron, because it has vicinal hydroxy groups which may be functional groups for boron. As a result of preliminary experiments based upon the above expectation, it was found that tiron could be applicable to the photometric determination of boron. The new photometric method is very convenient and advantageous, because the procedure is carried out rapidly in an aqueous medium and the boron-tiron complex formed is very stable under controlled conditions.

In this paper, the application of the reagent to the new spectrophotometric method for boron is described. The absorption spectra of dilute tiron solutions with various pH values were taken, and the existence of four isosbestic points, at 230, 243, 279 and 293 mμ, was confirmed. Then the absorption curves of mixed solutions of boron and tiron with various pH values against tiron solution as a reference were taken, and the optimum pH value and wavelengths for measurements were found. The effects of the concentrations of a tiron and buffer solution, of diverse salts and of the temperature were examined. It was found that the boron-tiron complex had a mole ratio of 1 : 1 under the proposed conditions, and that Beer's law was obeyed in the range from 0.40 to 3.20 p. p. m. of boron at the wavelengths of both 252 and 306 mμ.

Experimental

Apparatus. — Spectrophotometric measurements were made with a Shimadzu quartz spectrophotometer, model QB-50, using 1.000 cm. quartz transmission cells. A Horiba glass electrode pH meter, model H-3, was used for all pH measurements.

Materials.—*Standard Boron Solutions.*—Dissolve 0.5716 g. of reagent grade boric acid in 1000.0 ml. of water. This solution corresponds to 100.0 p.p.m. of boron. Dilute an aliquot of the solution with water, and prepare 10.0 p. p. m. of a standard boron solution.

Tiron Solution.—Dissolve 3.1422 g. of tiron (Dotite-Tiron) in 1000.0 ml. of water and prepare a 10^{-2}M solution.

Buffer Solution.—Prepare a buffer solution of the Michaelis type by mixing 4 parts of a 0.5 M disodium hydrogen phosphate solution and 1 part of a 0.5 M potassium dihydrogen phosphate solution, and adjust the pH to 7.40~7.50. Various other salt solutions were prepared from the reagents of an analytical grade.

Procedure.—Pipet an aliquot of the boron solution into a 25.0 ml. measuring flask, and add to it 2.0 ml. of a 10^{-2} M tiron solution and 1.0 ml.

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of a buffer solution of pH 7.40~7.50, and dilute it to the mark with water. Mix thoroughly and measure the absorption of the solution at 252 or 306 mμ against a reagent blank.

In order to study the effect of diverse salts, color developments were made using 30.0 μg. of boron in the presence of varying amounts of 2.0% salt solutions.

To ascertain the stability of the color, absorbances of the solution were measured at proper time intervals after color development.

Measurements of the absorption spectra of the dilute tiron solution at various pH values are made as follows: Into a 50.0 ml. measuring flask, pipet 2.0 ml. of a 10^{-3} M tiron solution, and add 5.0 ml. of a buffer solution of 0.5 M disodium hydrogen phosphate-potassium dihydrogen phosphate, 1 M sodium acetate-acetic acid, and or 1 M aqueous ammonia-ammonium chloride to the flask and dilute it to the mark with water. The absorption spectra of these solutions were measured at 5 mμ intervals of wavelength against water as a reference.

Results

Absorption Spectra of Tiron Solution.—As shown in Fig. 1, when the pH of the solution increases, two absorption maxima (260 and 305 mμ) appear, while when the pH decreases, absorbance at the absorption maximum (290 mμ) increases. There are four isosbestic points, at 230, 243, 279 and 293 mμ.

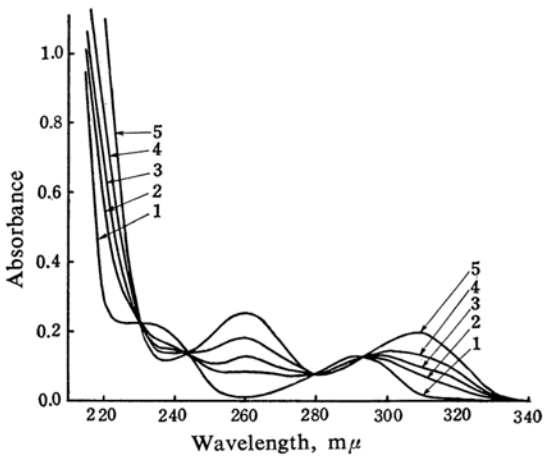

Fig. 1. Absorption spectra of tiron solutions.

Tiron; 4×10^{-5} M
Buffer soln.; 5.0 ml./50.0 ml.
Reference; Water

1 pH=6.00 2 pH=7.51 3 pH=7.85
4 pH=8.01 5 pH=9.52

Absorption Spectra of Boron-Tiron Complex.—Figure 2 shows the absorption curves of boron-tiron solutions. There are two absorption bands in the ultraviolet region, both of which are affected by the pH value of the solution.

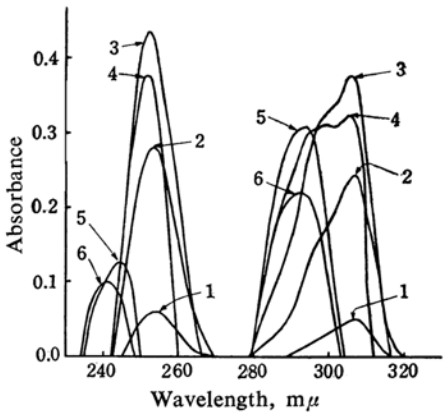

Fig. 2. Absorption spectra of boron-tiron complex.

Boron; 4×10^{-4} M
Tiron; 4×10^{-4} M
Buffer soln.; 5.0 ml./50.0 ml.
References; Blank solns.

1 pH=5.89 2 pH=6.79
3 pH=7.49 4 pH=7.59
5 pH=8.51 6 pH=9.80

Effect of pH.—In Fig. 3, the absorbances at the absorption maxima are plotted against the pH values. It was found that the maximum absorptions were obtained over the pH range of 7.40~7.50. For the photometric measurements, it is advantageous to select the wavelengths of maximum absorption, at 252 and 306 mμ, as is shown in Fig. 4, in which graphs are plotted of the maximum wavelengths against the pH values.

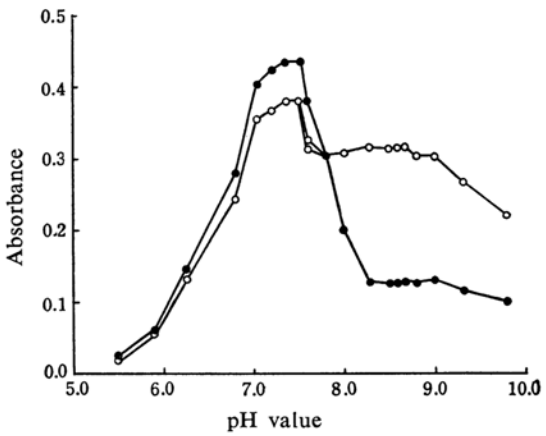

Fig. 3. Relation between absorbances at the absorption maxima and pH values.

Boron; 4×10^{-4} M
Tiron; 4×10^{-4} M
Buffer soln.; 5.0 ml./50.0 ml.
References; Blank solns.

—●— Obtained at 252 mμ
—○— Obtained at 306 mμ

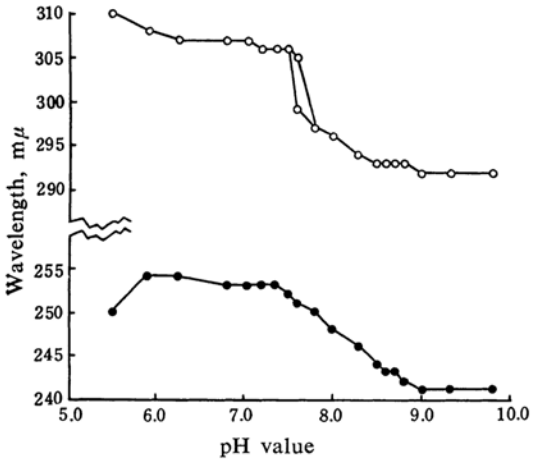

Fig. 4. Relation between wavelengths of maximum absorption and pH values.
Boron ; 4×10^{-4} M
Tiron ; 4×10^{-4} M
Buffer soln. ; 5.0 ml./50.0 ml.
References ; Blank solns.

Reagent Concentration.—In order to find a proper concentration of tiron, the measurement of the absorbances of a series of solutions containing 2.00 or 4.00 p. p. m. of boron with varying amounts of the reagent was undertaken, using the reagent blanks of the same concentration as references. As is shown in Fig. 5, 2.0 ml. of a 10^{-2} M tiron solution in 25.0 ml. is the optimum amount.

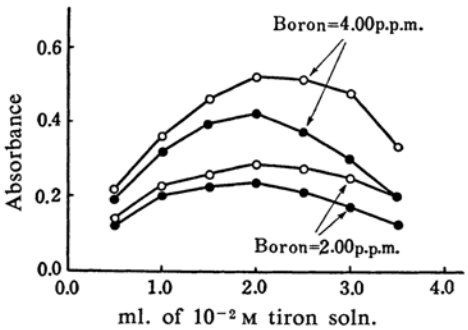

Fig. 5. Effect of concentration of tiron.
Boron ; 4.00 p. p. m. or 2.00 p. p. m.
Buffer soln. ; 1.0 ml./25.0 ml.
References ; Blank solns.
—○— Obtained at 252 mμ
—●— Obtained at 306 mμ

Effect of the Buffer Solution.—The effect of the buffer solution was tested with varying amounts of a 0.5 M disodium hydrogen phosphate-potassium dihydrogen phosphate buffer solution. 1.0~2.0 ml. of the buffer solution is favorable, as is shown in Fig. 6. The addition of 1.0 ml. of the buffer solution is thus adopted in the following experiments.

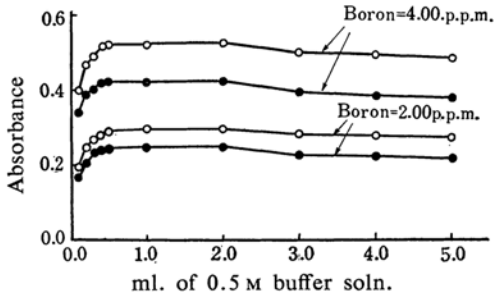

Fig. 6. Effect of concentration of buffer solution.
Boron ; 4.00 p. p. m. or 2.00 p. p. m.
Tiron ; 8×10^{-4} M
References ; Blank solns.
—○— Obtained at 252 mμ
—●— Obtained at 306 mμ

TABLE. I. EFFECT OF DIVERSE SALTS

Boron : 2.00 p. p. m.
Tiron : 8×10^{-4} M
Buffer soln. : 1.0 ml./25.0 ml.
Reference : Blank soln.

Salt	Added mg.	Absorbance at 252 mμ	Absorbance at 306 mμ
—	—	0.285	0.236
NaF	5	0.289	0.239
	10	0.303	0.249
	20	0.312	0.260
	50	0.371	0.306
	100	0.439	0.369
NaCl	5	0.297	0.244
	10	0.300	0.245
	20	0.293	0.236
	50	0.341	0.274
	100	0·360	0.291
Na_2SO_4	5	0.283	0.235
	10	0.284	0.237
	20	0.285	0.236
	50	0.311	0.256
	100	0.329	0.270
Na_2SO_3	5	0.387	0.301
	10	0.478	0.347
	20	0.619	0.436
	50	1.01	0.631
	100	1.37	0.812
$CH_3COONa\cdot3H_2O$	5	0.284	0.238
	10	0.290	0.242
	20	0.294	0.244
	50	0.317	0.257
	100	0.333	0.275
KNO_3	5	0.290	0.241
	10	0.308	0.264
	20	0.340	0.291
	50	0.408	0.365
	100	0.517	0.479

Stability of Absorbance.— The absorbances of the solution of a boron-tiron complex show no appreciable change during about 20 hr., although they decrease slightly after 3 days.

Effect of Temperature.—It is observed that the absorbances are affected by the temperature of the solution; that is, the values of absorbance increase as the temperature falls. The temperature coefficients are 0.00159~0.00176/°C at 252 mμ and 0.00161~0.00176/°C at 306 mμ for 1.00 p. p. m. of boron.

Effect of Diverse Salts.— As is shown in Table I, it is found that sodium sulfate and sodium acetate do not interfere when they are present 20 mg. per 25.0 ml. However, sodium sulfite interferes seriously at a concentration of 10 mg. per 25.0 ml.

Mole Ratio of Boron to Tiron in Solution.— In order to confirm the mole ratio of the boron-tiron complex, two methods were employed, the continuous variation and the slope ratio methods. In the first method, the measurement of the absorbances of a series of solution containing a varying mole per cent of 10^{-2} M boron and 10^{-2} M tiron was undertaken, using as references the reagent blanks of the same concentrations. As is shown in Fig. 7, the maximum absorbance of the complex was obtained when the mole ratio of boron to tiron is 1 to 1.

In the second method, two series of solutions were prepared: one with a varying concentration of boron in the presence of a large, constant amount of tiron, and the other with a varying concentration of tiron in the presence of a large, constant amount of boron. The absorbances of each series of solutions were also measured. Two linear absobance-concentration curves with the same tangential value of the slope were obtained, as is shown in Fig. 8. From the results of these experiments, it is confirmed that the mole ratio of boron to tiron in the complex formed is 1 to 1.

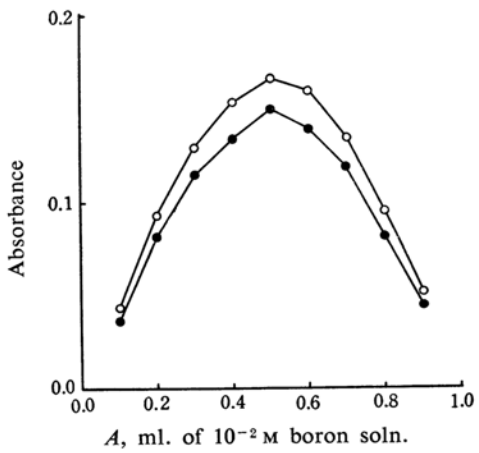

Fig. 7. Determination of mole ratio of boron to tiron by the method of continuous variations.

Boron; 10^{-2} M soln., A ml.
Tiron; 10^{-2} M soln., $(1.0-A)$ ml.
Buffer soln.; 1.0 ml./25.0 ml.
References; Blank solns.

—○— Obtained at 252 mμ
—●— Obtained at 306 mμ

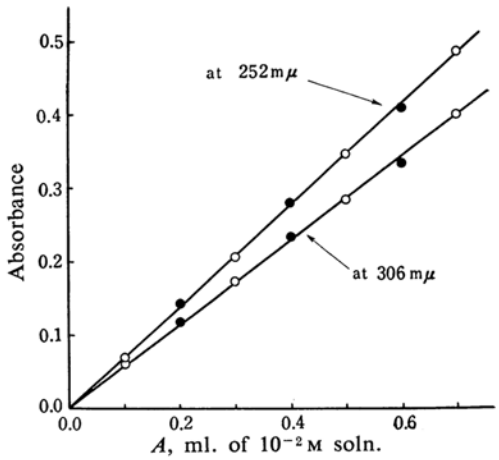

Fig. 8. Determination of mole ratio of boron to tiron by the method of slope ratios.

—●— Boron; A ml. Tiron; 2.0 ml.
—○— Boron; 2.0 ml. Tiron; A ml.

Calibration Curves.—To establish calibration curves, measurements of absorbance readings were made with a number of the boron-tiron solutions containing different amounts of boron; they were plotted against boron content. The results show that Beer's law is obeyed over the range from 0.40 to 3.20 p. p. m. of boron at the wavelengths of both 252 and 306 mμ,

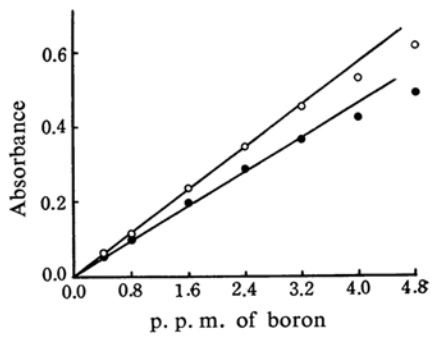

Fig. 9. Calibration curves.

Tiron; 8×10^{-4} M
Buffer soln.; 1.0 ml./25.0 ml.
Reference; Blank soln.
Temperature; 18°C

—○— Obtained at 252 mμ
—●— Obtained at 306 mμ

as in Fig. 9. The sensitivities of this method are 0.17/cm^2 and 0.20/cm^2, and the molar extinction coefficients are 1620 and 1370 at 252 and 306 mμ respectively.

Discussion

The proposed new photometric method for the determination of boron with tiron as a color reagent is more simple and rapid than other methods. As is shown in Figs. 7 and 8, the constitution of the boron-tiron complex has the mole ratio of 1 : 1. Because the measurements of absorbance are made in the ultraviolet region, some obvious interferences with diverse metal ions are to be expected. Therefore, for the determination of boron in many kinds of practical samples, a proper separation of boron is desired. In this procedure, absorbance is affected by the temperature, so the absorption measurements must be done under as constant temperature as possible. Fortunately, the effect of temperature difference can be eliminated, provided that the calibration curves are made simultaneously with the sample analysis. Determination of the boron content of many samples is now proceeding in this laboratory. In this procedure, however, absorbance is very stable for about 20 hr.; this is advantageous for the spectrophotometric measurements.

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