A New Method for the Determination of Boron by Spectrophotometry with Pyrocatechol Violet

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(Received December 7, 1960)

For the photometric determination of boron, most of the reagents such as oxyanthraquinones are used in concentrated sulfuric acid media, in another case using curcumin, the sample solution should be evaporated with the reagent solution under carefully controlled conditions for color development. Since these procedures are very tedious and time consuming, it would seem very useful if the color development could be substantiated simply and rapidly in aqueous media.

In previous publications it has been reported that some of the colorimetric reagents such as polyvinylalcohol[1,2], chromotropic acid[3], victoria violet[4,5] and H-resorcinol[6] can be used in aqueous media, and that some reagents are applied to indirect methods. However, many of them are not always applicable to routine work, as they are less accessible reagents, and in the case of chromotropic acid the measurements must be carried out in the ultraviolet region.

Pyrocatechol violet, a kind of sulfophthalein dye, is generally used as a metallochromic indicator for chelatometry and as photometric reagent for many metal ions such as zirconium[7,8], thorium[9], copper[10], bismuth[11], aluminum[12] and yttrium[13]. Patrovský[14] studied the detection of boron, niobium, germanium and tantalum using this reagent.

In this paper the application of the reagent to the determination of boron has been described, and the proposed method is very convenient and useful, because the procedure is carried out in an aqueous medium and the absorbance can be measured in the visible region. In this study, the absorption curves of dilute pyrocatechol violet solutions with various pH values were taken, and the existence of an isosbestic point at 494 mμ was confirmed, various facts including the effect of pH and of the reagent concentration, stability of the color and effect of temperature and of the sort of buffer solutions were examined. The interference of diverse metal ions is masked by adding ethylenediaminetetra-acetate solution as a sequestering agent. Beer's law is obeyed in the range 0.2 to 2.0 p. p. m. of boron at 494 mμ.

Experimental

Apparatus. — Spectrophotometric measurements were made with a Shimadzu quartz spectrophotometer, Model QB-50, with 1 cm. glass 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 ml. of water. One milliliter of the solution corresponds to 100 μg. of boron. Dilute an aliquot of the solution with water, and prepare 10.0 p. p. m. and 5.0 p. p. m. of standard boron solutions.

Pyrocatechol Violet Solution. — Prepare a 2×10^{-3} M aqueous solution (Dotite PV).

Buffer Solutions.—Prepare an ammonium chloride-ammonium hydroxide buffer solution by mixing 8 parts of 0.5 M ammonium chloride solution and 1 part of 0.5 M aqueous ammonia solution, and adjust the pH to 8.55∼8.60. Veronal buffer solution is prepared as follows. To 100 ml. of mixed solution of M/7 sodium diethylbarbiturate and M/7 sodium acetate add 40 ml. of 0.85% sodium chloride solution and 25 ml. of 0.1 N hydrochloric acid, and adjust to pH 8.55∼8.60.

Ethylenediaminetetraacetate Solution. — Dissolve disodium ethylenediaminetetraacetate (dihydrate) in water to make the concentration of 5×10^{-2} M.

Other various salt solutions are prepared from analytical grade reagents.

Measurement of Absorption Spectra of Pyrocatecholviolet. — Twenty milliliters of 10^{-4} M pyrocatechol violet solutions were mixed with 5 ml. of veronal buffer solutions of various pH values and diluted to 50 ml. with water. The absorption spectra of these solutions were measured with water as reference.

Procedure.—Pipet the boron solution containing

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25 μg. or 50 μg. of boron into a 25 ml. measuring flask, add 5 ml. of 2×10^{-3} M pyrocatechol violet solution and 5 ml. of buffer solution at pH 8.55～8.60, and dilute to the mark with water. Measure the absorption at 494 mμ; use a mixed solution containing 5 ml. of pyrocatechol violet and buffer in 25 ml. as reference.

In order to study the effect of diverse salts, color developments were made using 25 μg. of boron with various amounts of 4% salt solutions, and measurements were made for the solution with 50 μg. of several cations.

The effect of the temperature upon the absorbance was investigated as follows. Solutions containing 2.0 p. p. m. of boron were warmed in a water bath at a proper temperature for 15 min., and the absorbance of the solutions was measured against a reference treated similarly. For the solutions containing 1.0 p. p. m. of boron, absorbance and temperature of the warm solutions were measured at proper intervals.

Results

Absorption Spectra of Pyrocatechol Violet Solution.—Fig. 1 shows the absorption curves of 4×10^{-5} M pyrocatechol violet solutions at various pH values. It is found that, as the pH of the solution decreases, a maximum (450 mμ) appears, while when the pH increases absorbance at the absorption maximum (600 mμ) increases, and there is an isosbestic point at 494 mμ. Since the absorbance at the isosbestic point is not affected by the pH value of solutions, and the absorbance of reagent blank is always constant at the wavelength, the use of this isosbestic point is very advantageous for the determination of boron.

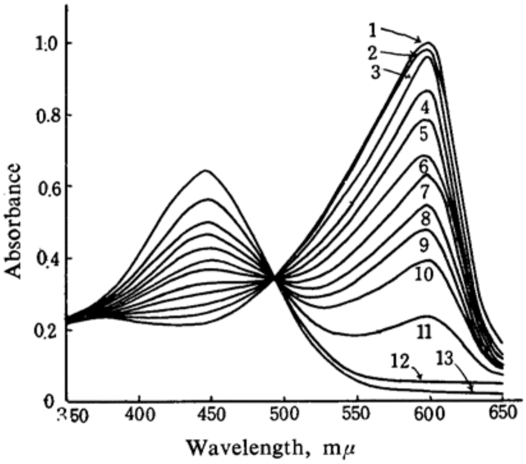

Fig. 1. Absorption spectra of pyrocatechol violet solution at various pH's.

1	pH 9.32	6	pH 8.21	11	pH 7.21
2	8.98	7	8.10	12	5.80
3	8.72	8	7.95	13	4.55
4	8.53	9	7.79		
5	8.41	10	7.63		

Effect of pH.—As shown in Fig. 2, it is found that the maximum absorptions were obtained at pH range of 8.3～8.6.

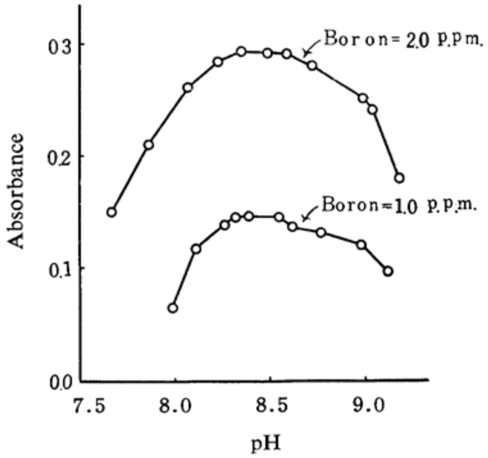

Fig. 2. Effect of pH value.
2×10^{-3} M Pyrocatechol violet soln.; 5.0 ml.,
Veronal buffer soln.; 5.0 ml.,
Measured at 494 mμ

Absorption Spectra of Colored Boron-Pyrocatechol Violet Solution.—Fig. 3 shows the absorption curves of the boron-pyrocatechol-violet solutions, obtained by the standard procedure. The maximum absorption is shown at 484 mμ.

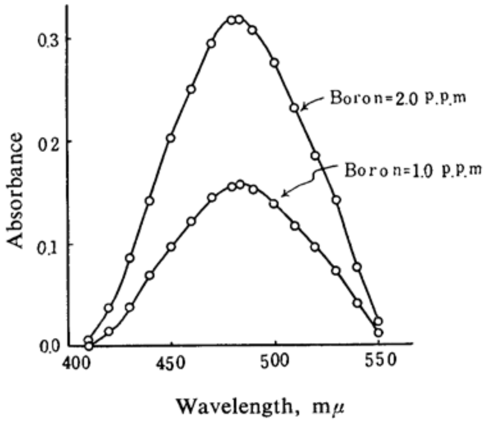

Fig. 3. Absorption spectra of colored boron-pyrocatechol violet solutions.
2×10^{-3} M Pyrocatechol violet soln.; 5.0 ml.
NH_4Cl-NH_4OH buffer soln.; 5.0 ml.

Reagent Concentration.—In order to test the effect of concentration of pyrocatechol violet, a series of the absorbances was measured under various concentrations of the reagent, using the reagent blanks of the same concentration as references. As shown in Fig. 4, 5 ml. of 2×10^{-3} M pyrocatechol violet solution in 25 ml. is the optimum amount.

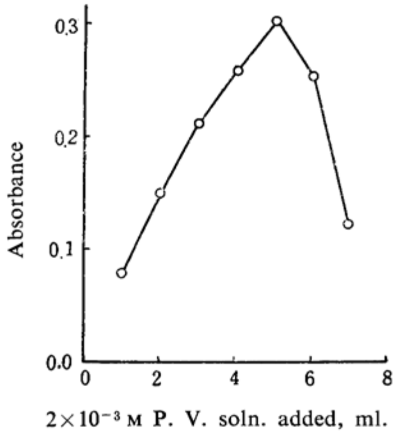

Fig. 4. Effect of pyrocatechol violet concentration.
Boron concentration; 2.0 p. p. m.
NH_4Cl-NH_4OH buffer soln.; 5.0 ml.
Measured at 494 mμ.

Effect of Buffer Solutions. — The effect of buffer solution was tested with varying amounts of 0.5 M ammonium chloride-ammonia buffer solution or veronal buffer solution. At least 2 ml. of both buffer solutions are essential, as shown in Figs. 5 and 6, and 5 ml. is preferable, for the purpose of avoiding the pH change due to the addition of various salts in the following experiments.

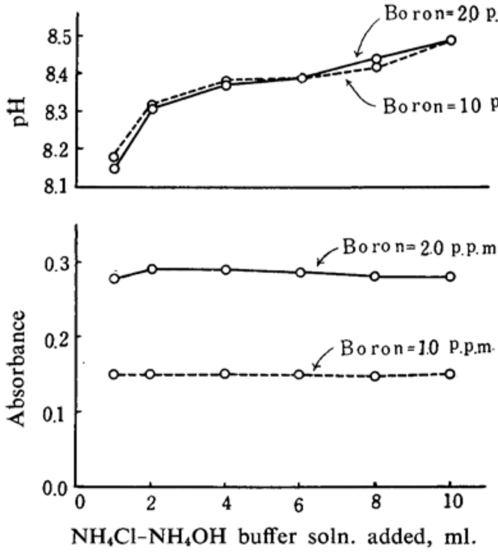

Fig. 5. Effect of buffer solution (I). In the case of ammonium chloride-ammonium hydroxide buffer solution.
2×10^{-3} M Pyrocatechol violet soln.; 5.0 ml.
Measured at 494 mμ

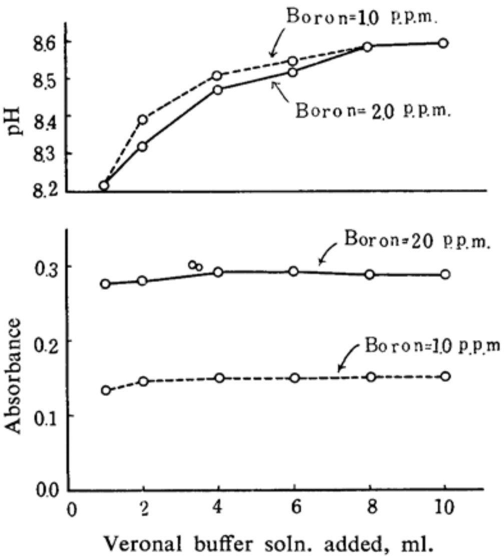

Fig. 6. Effect of buffer solution (II). In the case of veronal buffer solution.
2×10^{-3} M Pyrocatechol violet soln.; 5.0 ml.
Measured at 494 mμ

Color Stability.—Fig. 7 shows that the absorbance of colored solutions is constant for 20 min. Consequently the measurements should be done within 20 min. after color development.

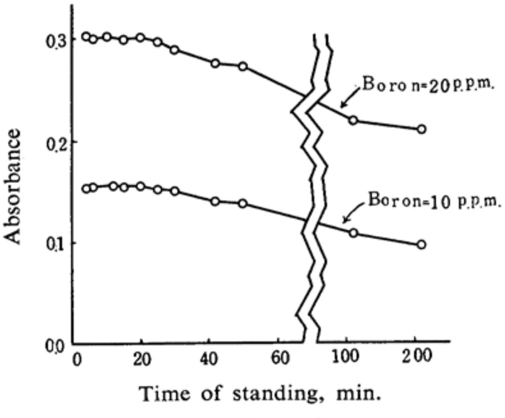

Fig. 7. Color stability of boron-pyrocatechol violet solutions.
2×10^{-3} M Pyrocatechol violet soln.; 5.0 ml.
Veronal buffer soln.; 5.0 ml.
Measured at 494 mμ
Temperature; 26~27°C

Temperature.—It is observed that the absorbance is affected by temperature, that is, the intensity of absorbance increases as temperature is lowered, and there is an apparent linear relationship between absorbance and temperature as shown in Fig. 8. The temperature coefficients are $0.927\times10^{-2}/°C$ for 2.0 p. p. m. and $0.330\times10^{-2}/°C$ for 1.0 p. p. m. of boron.

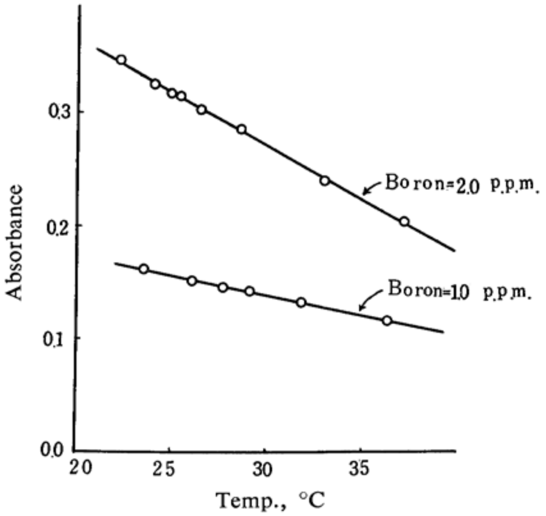

Fig. 8. Effect of temperature.

2×10^{-3} M Pyrocatechol violet soln.; 5.0 ml.
Veronal or NH_4Cl-NH_4OH buffer soln.; 5.0 ml.
Measured at 494 mμ

Stability of Pyrocatechol Violet Solution.—The solution of pyrocatechol violet is stable for more than one month, as shown in Fig. 9.

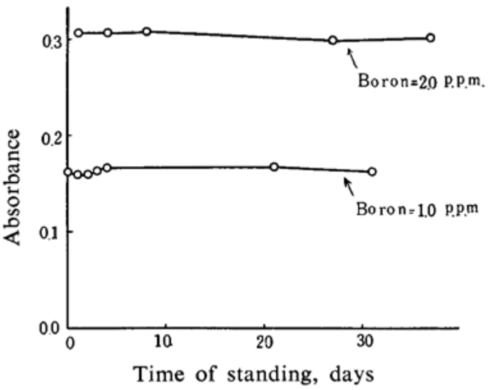

Fig. 9. Stability of pyrocatechol violet solution.

2×10^{-3} M Pyrocatechol violet soln.; 5.0 ml.
Veronal or NH_4Cl-NH_4OH buffer soln.; 5.0 ml.
Measured at 494 mμ

Diverse Salts.—The results are presented in Table I. It was found that the presence of such salts as potassium fluoride, sodium chloride, potassium iodide, sodium sulfate, disodium hydrogenphosphate and potassium sodium tartrate do not interfere even at a concentration of 200 mg. per 25 ml. But sodium sulfite

TABLE I. EFFECT OF DIVERSE SALTS

Salt	Added, mg.				
	0	40	80	120	200
KF	0.159	0.150	0.156	0.158	0.158
NaCl	0.164	0.163	0.155	0.151	0.145
KI	0.159	0.158	0.151	0.152	0.150
Na_2SO_4	0.153	0.155	0.158	0.156	0.153
$Na_2HPO_4\cdot12H_2O$	0.156	0.154	0.155	0.157	0.152
Na_2SO_3	0.154	0.106	0.099	0.088	0.074
KNO_3	0.153	0.171	0.183	0.181	0.181
$KNaC_4H_4O_6\cdot4H_2O$	0.155	0.150	0.157	0.152	0.152
$56Na_2O\cdot44SiO_2$	0.156	0.156	0.156	0.159	0.158
$NaHCO_3$	0.153	0.154	0.154	0.155	0.156

TABLE II. EFFECT OF DIVERSE METAL IONS

Ion	Added, mg.				
	EDTA none		5×10^{-2} M EDTA 0.5 ml. added		
	0	50	100	200	500
Magnesium	0.164	0.125	0.163	0.165	0.166
Zinc	0.158	0.091	0.161	0.155	0.157
Copper(II)	0.159	0.095	0.154	0.152	0.162
Aluminum	0.156	−0.308	−0.009	−0.377	−0.705
Lead	0.152	0.162	0.154	0.150	0.153
Manganase(II)		0.030	0.160	0.157	0.158
Nickel		0.070	0.159	0.153	0.150
Cobalt(II)		−0.015	0.155	0.152	0.153
Cadmium		0.125	0.151	0.158	0.155

and potassium nitrate interfere when 40 mg. per 25 ml. are present.

Diverse Metal Ions.—As shown in Table II, the following ions interfere seriously: Magnesium, zinc, copper(II), manganase(II), nickel, cobalt(II), cadmium and aluminum. Since these cations form stable chelates with ethylenediaminetetraacetate, when disodium salt of ethylenediaminetetraacetate is present in concentration of 10^{-3} M, they are masked effectively and do not interfer even at the concentration of 20 p. p. m. However, the interference of aluminum can not be eliminated.

Calibration Curve.—Measurements were made for the solutions containing various amounts of boron. Beer's law is obeyed up to 2.0 p. p. m. of boron as shown in Fig. 10. The sensitivity of this method was 0.006085/μg. and the mean error was 1.59%. Standard deviation was 0.002528 in absorbance for ten reproducible measurements for each 1.0 p. p. m. of boron.

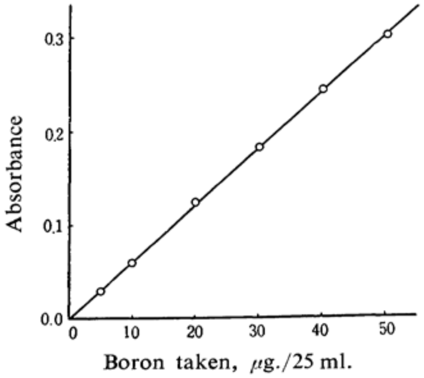

Fig. 10. Calibration curve.

2×10^{-3} M Pyrocatechol violet soln.; 5.0 ml.
NH_4Cl-NH_4OH buffer soln.; 5.0 ml.
Measured at 494 mμ
Temperature; 26~27°C.

Discussion

The proposed new photometric method for the determination of boron by using pyrocatechol violet as a color reagent is simple in procedure as compared with the other methods.

From Fig. 1, considerations can be made as follows. Because pyrocatechol violet is a tetrabasic acid and consequently can release four protons, it may be formulated as H_4F, the absorption band with peak at 450 mμ can be considered as belonging exclusively to H_3F^-, and the peak at 600 mμ must be due to H_2F^{2-} form.

As shown in Fig. 3, for the spectrophotometric measurements it is desired to choose the maximum wavelength at 482 mμ, but because the absorbance of pyrocatechol violet solution is not affected by pH value at the isosbestic point 494 mμ it is preferable that the isosbestic point be chosen for the determination of boron, although photometric sensitivity is lowered slightly.

The proposed method has the feature of no preliminary separation of diverse ions, because many of them may be masked by ethylenediaminetetraacetate. This method can thus effectively be used for the determination of boron in such samples as metals, metallic oxides and alloys.

In this procedure, however, color intensity is considerably affected by temperature, so the absorption measurements must be done under constant temperature. Fortunately the effect of temperature difference will be corrected, provided that the calibration curves are made simultaneously.

Investigations for the effects of other diverse salts and metal ions and also the determination of boron for many metallic samples are now proceeding in this laboratory.

The author is indebted to Dr. Yuroku Yamamoto, Kyoto University, for his guidance and to Dr. Isao Muraki, Chief of the 5th Department of our Institute, for his useful suggestions.

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