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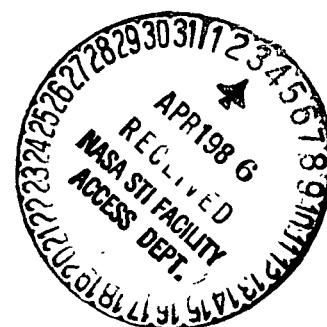
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CONTRIBUTION TO THE PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF BORON TRIOXIDE IN GLASSES

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16. Abstract

The photometric determination is described for boron trioxide in amounts of 0-75 μg B_2O_3 with azomethin H reagent. The yellow colored complex which occurs in a medium held at a pH of 4.5 was measured in light of wavelength 415 nm.

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CONTRIBUTION TO THE PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF BORON TRIOXIDE IN GLASSES

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The determination of small amounts of elements in silicate materi- /193[*]
als is done by most photometric, flame emission, or atomic absorption
methods. In order to determine small quantities of boric oxide in
glass, photometric methods are preferred, because flame emission and
atomic absorption methods do not have the required sensitivity.

The majority of reagents used, such as carminic acid [1] and prob-
ably 1,1-dianthrimid [3] react with borate only in medium of concentrat-
ed sulfuric acid, which makes it undesirable in practice. Furthermore,
such reagents require nonaqueous environments. Curcumine [3] reacts in
an ethanol medium; the methylene blue complex with a tetrafluoroborate
ion is extracted to 1,2-dichloroethane [2]. In determining small am-
ounts of boron, a condensation product of 1-amino-8-naphthol-3,6-disul-
fonic acid with salicyl aldehyde called azomethin H is formed [1],
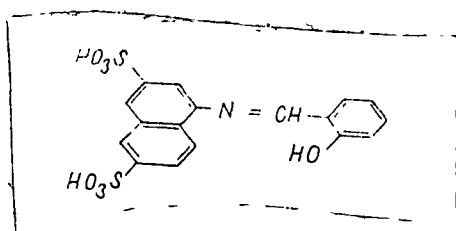which reacts with borate in an aqueous medium [4,5].

Fig. 1.

The yellow-colored complex reagent
with boron has a central, quadruple-
bonded boron atom, and maximum light
transmission has been measured at 415
nm in a medium with pH of 4.5 [4,5].
The complex does not form immediately;
two to three hours must pass before it
can be measured. The reaction is in-
hibited by the presence of a number of ions; those with an inhibiting ef-
fect may include chelate 3, citric acid, tartaric acid, thioglycol, or
an isolated cation as a converter [10]. A work [6] has been published
on determining boric oxide in glass, in which all the factors affecting
the determination were tested. It was confirmed that the optimum pH for

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[*]Numbers in the margin indicate pagination in the foreign text.

the reaction is 4.5. Measurement was done at a wavelength of 415 nm, and the inhibiting effect of several cations encountered in glass may be screened by an addition of a solution of chelate 1 and chelate 3. The time to maximum color was determined to be four hours.

Dempír [7] used a solution of ammonium acetate, citric acid, and chelate 3 for screening and controlling pH. In our test, a buffer solution of ammonium acetate and acetic acid was used, and a solution of chelate 3 and citric acid was used as a screening solution. Both solutions were made up to a pH of 4.5.

Equipment and Reagents

A spectrophotometer or photometer with a filter with maximum light transmission at 415 nm (blue filter) and a 1-cm thick cell were used. The pH meter was of glass and had a saturated calomel electrode. All the reagents were of Analytical Grade.

Azomethin H

A solution of 29 g of 1-amino-8-naphthol-3,6-disulfonic acid in 1 liter of distilled water is made up to a pH of 1.5 and heated to 50°C, and 32 ml of salicyl aldehyde are slowly added while stirring constantly. After two hours, the mixture of left to stand overnight. The purified azomethin is drawn off into a Büchner funnel, washed twice with alcohol and ether, and dried for two hours at 90°C.

The solution is prepared by dissolving 1 g of azomethin and 3 g of ascorbic acid in 100 ml of distilled water and then filtered. The solution always has to be prepared fresh.

Note

Since the purity of the reagent has a great influence on the value of the blind experiment, it is recommended that prepurified 1-amino-8-naphthol-3,6-disulfonic acid and freshly redistilled salicyl aldehyde be used. The reagent is kept in the cold and dark, preferably in a de-

siccator.

Buffer Solution

80 ml of glacial acetic acid and 20 ml of distilled water are mixed. To the solution are added 50 g of ammonium acetate, and after it dissolves, the pH of the acetic acid or ammonia is made up to 4.5.

Screening Solution

20 g of chelate 3 and 10 g of citric acid are dissolved in 450 ml of distilled water, and this is made up to a pH value of 4.5 with acetic acid or sodium hydroxide. The solution is carried out in a reserved 500-ml flask, and it is filled to the top graduation.

Basic Boron Solution

1.776 g of boric acid are dissolved in distilled water. The solution is carried out in a reserved 1000-ml flask, and it is filled to the graduation mark. 1 ml of the solution contains 1 mg of B_2O_3. In order to plot a calibration curve, the basic solution is diluted such that 1 ml of solution contains 10 µg of B_2O_3.

Principal Determinations

To test the path of the reaction, a matheod after [6] was selected whereby the solutions made as in the preceding section were used to correct the pH and for screening.

To reserved flasks made of non-borate glass were pipetted aliquot portions of the diluted basic B_2O_3 solution in the amount of 0.75 µg of B_2O_3. 5 ml of the buffer solution and 5 ml of the screening solution were added and thoroughly mixed. Finally, 5 ml of the axomethin H solution were added, the flask was filled to the graduation, and the solution was mixed thoroughly. The solution was left in the dark for four hours and was then measured against a blind solution in light of wavelength 415 nm. The absorbance values measured for the respective concentrations of B_2O_3 were trasnferred onto millimeter paper, and the cal-

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ibration curve was plotted (Fig. 2). It is apparent from the figure that a straight-line dependence is valid only for the quantities 0-80 µg B_2O_3/25 ml. The dependence of absorbance values was further tested when certain concentrations were processed in accordance with the method above, and absorbance was measured at various time intervals. The dependence is represented in Fig. 3 and shows that the solution must be left for a period of four hours before measuring. This length of time agrees with the data presented in [6].
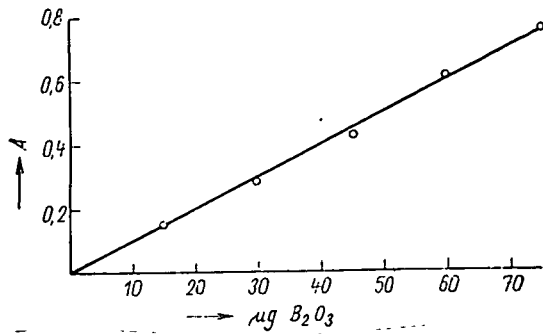

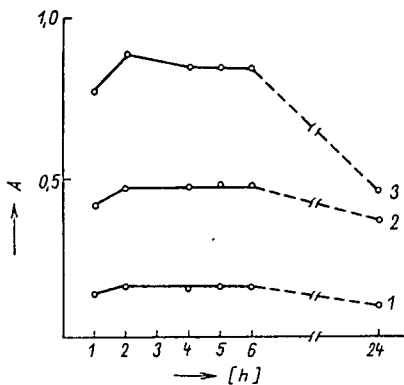Fig. 2. Absorbance of the complex as a function of the amount of B_2O_3 determined.

Fig. 3. Time dependence of the complex absorbance.

Curve 1: 15 µg B_2O_3
Curve 2: 50 µg B_2O_3
Curve 3: 80 µg B_2O_3

Operating Procedure

Into a platinum dish were placed quantities of the sample which contained 2-4 mg of boric acid. A six-fold quantity of non-aqueous sodium carbonate was added, and it was well mixed. The dish was covered and the contents were melted over a gas burner. In parallel with the sample, a blind test was run by a chemically identical method. When the melt was homogeneous, the dish was removed from the flame and allowed to cool. To the cooled melt were carefully added several milliliters of hot distilled water, and this was heated several minutes in a water bath. Then to the covered dish was added 5 ml of hydrochloric acid, [HCl] = 6 mol/liter, for each gram of sodium carbonate, and this was heated in a water bath until it was destructively melted. Then the contents of the dish were put in a 250-ml beaker made of non-borate glass, 25 ml of the screening solution were added,

it was heated to 40-50°C, and after cooling, the pH was corrected to 4.5 with sodium hydroxide, [NaOH] = 10 mol/liter. The solution was made in a reserved 250-ml flack; it was filled with distilled water to the graduation mark and mixed.

Into a reserved 25-ml flask were pipetted 5 ml of the reserve solution, and 5 ml of the buffer solution, 5 ml of the screening solution, and 5 ml of the azomethin solution were added. After adding each reagent, the contents of the flask were thoroughly mixed. Then the solution was filled with distilled water to the graduation mark and mixed again.

The solution was then left in the dark for four hours and was measured against the blind solution in light of wavelength 415 nm in a 1-cm cell. The quantities of boric oxide were read for the measured absorbance values from the calibration curve, and its content was calculated according to the equation

$$X = \frac{0.005 \, m}{m_i} \qquad (1)$$

where X = the content of boric oxide, in percent

   m = the quantity of boric oxide, read from the calibration curve, in µg

   m_1 = input of sample, in g

Conclusions

In order to test this method, "synthetic glass" was analyzed first which was prepared so that the reserved amount of the basic boron solution was added to the input of the pulverized sodium-calcium-silicate glass. The contents of the dish were then boiled in a water bath until dry, a corresponding amount of non-aqueous sodium carbonate was added to the evaporate, and the procedure was thereafter executed as in the preceding section. Each determination for a single concentration was carried out five to ten times, an arithmetic average was calculated, standard deviation was estimated, and a Student's t-test was run for significance level $\alpha = 0.05$ [8]. The results are presented in Table 1.

It follows from Table 1 that the results of the determination are not bound by systematic error ($t < t_k$), and the errors which occur are only found once.

By using the same method, the B_2O_3 contents were determined in two standard glasses: NBS - SRM No. 92 (glass with a 0.70% B_2O_3 content) and the No. 3 standard glass of the Scoiety of Glass Technology (a leaded glass with a 0.20% B_2O_3 content), with the following results:

TABLE 1.   DETERMINATION OF BORIC OXIDE CONTENT

% B_2O_3	0.30	0.80	1.50
$\bar{x}$ % B_2O_3	0.28	0.85	1.48
s	0.06	0.10	0.15
ν	5	8	10
t	0.87	1.49	0.45
t_k	2.57	2.31	2.23

SRM No. 92 - 0.70% B_2O_3:

$\bar{x} = 0.69$, s = 0.09, t = 0.25, $t_k = 2.57$, $\nu = 5$

SGT No. 3 - 0.20% B_2O_3:

$\bar{x} = 0.18$, s = 0.09, t = 0.34, $t_k = 2.36$, $\nu = 7$

The values for the estimate of standard deviation are very good and /195 vary only a little. In applying this method, the following hypotheses must be formed.

Select input such that the boric oxide content in 5 ml of the solution leads to absorbance corresponding to the approximate center of the calibration curve. The calibration curve must be plotted for each measurement. Maintain a constant pH value and time required to color the complex. The method is rapid, reliable, and very well suited for those boric oxide contents whose determinations are not possible by the usual reserve method [9].

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