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ROUTINE DETERMINATION OF BORON IN GLASS

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ABSTRACT

A method for the routine determination of boric oxide in glass, based on the "partition" of boric acid between water and ether in the presence of hydrochloric acid and ethanol, has been developed. A slightly acid solution of the fusion of the glass is shaken with ether and ethanol, and the boric acid in the ether layer titrated. The partition coefficient is 0.403 at $25 \pm 2^\circ$ C. The advantages of this method are its speed and simplicity without material sacrifice of accuracy.

Boric oxide between 0.7 and 16 percent can be rapidly and accurately determined. Lime, magnesia, alumina, soda, iron, and arsenic, in amounts likely to be found in glass, do not interfere. Barium, fluorine, and abnormally large amounts of iron interfere slightly. Zinc interferes seriously.

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I. INTRODUCTION

The methods now used for the determination of boric oxide in glass, silicate minerals, and similar materials are of two general types: those requiring distillation of the boron and those not requiring it. Examples of the former are the Gooch [1],¹ and the Chapin [2] methods; of the latter, the Wherry [3], with its various modifications, and the Mylius [8] methods.

For occasional determinations of boric oxide, the distillation methods are cumbersome because they require a rather elaborate "setup" and a large supply of special reagents. The nondistillation methods can be handled more easily, but the necessary filtrations are time-consuming and the results are probably not as accurate as those obtained by distillation.

Since the determination of boric oxide in commercial glasses has become increasingly necessary in recent years, because of the more frequent use of borax or boric acid in making such glasses, a rapid,

¹ Numbers in brackets refer to references at the end of this paper.

simple, and reasonably accurate method is desirable. In connection with a study of experimental glasses at the National Bureau of Standards, a method possessing these advantages has been developed. It is especially useful if many determinations of boron are to be made on glasses of the same type. It is based on the relative solubility of boric oxide in water and an ether-ethanol mixture and involves a special application of Henry's law—the so-called "partition law." Ether alone proved unsatisfactory because it extracted only traces of boric oxide from the aqueous solution.

II. EXPERIMENTAL STUDY

As boric oxide is reasonably soluble in alcohols, it was decided to use mixtures of absolute ethanol and ether inasmuch as Herz and Kurzer [4] have shown that the partition law applies in the case of mixed solvents. To determine the most effective mixture of ethanol and ether, a series of solutions of boric acid in ethanol-water mixtures was prepared, each solution containing approximately 0.05 g of boric oxide and 1 ml of hydrochloric acid (sp gr 1.18) in 50 ml. One solution contained 5 ml of absolute ethanol in 50 ml of solution, the others 10, 15, 20, 25, and 30 ml, respectively. To each of these solutions in a calibrated 100-ml glass-stoppered graduate were added 50 ml of ether. The liquids were thoroughly mixed by vigorous shaking and allowed to stand until the ether and water layers had separated. The volumes of the layers were read to the nearest 0.1 ml. The concentration of the boric oxide in the ether layer was determined as follows:

A 50-ml portion was pipetted into a 250-ml erlenmeyer flask, two drops of *p*-nitrophenol added and the solution titrated to the *p*-nitrophenol endpoint with 0.5*N* sodium hydroxide. One ml of phenolphthalein was added and the titration continued to the phenolphthalein endpoint. A volume of 0.5*N* sodium hydroxide equal to three times that used between the two endpoints was added and the flask vigorously shaken. Its sides were washed down with distilled water and the volume of the aqueous layer was made up to 40 to 50 ml. The ether and ethanol were quickly removed by first heating on the steam bath and finally by boiling over a free flame. The volume was adjusted to 35 to 45 ml with distilled water, the solution allowed to cool, and then made just acid with 0.5*N* hydrochloric acid to *p*-nitrophenol. After warming on the steam bath, the carbon dioxide was removed by boiling under reduced pressure until cool. The solution was then titrated to the *p*-nitrophenol endpoint with 0.1*N* barium hydroxide, mannitol added, and the boric oxide titrated.

The amount of boric oxide in the total ether layer was calculated from the amount of boric oxide found in the 50-ml aliquot portion and the boric oxide in the water layer was obtained by difference. From the concentration of boric oxide in each layer, the "partition coefficient" $\left(K = \frac{C_{\text{Et}_2\text{O}}}{C_{\text{H}_2\text{O}}}\right)$ was calculated. The values of *K* for the mixtures containing 5, 10, 15, 20, and 25 ml of ethanol were 0.044, 0.100, 0.189, 0.263, and 0.440, respectively. The relation between these values and the volume, *V*, of ethanol added can be expressed by the empirical equation:

$$K = 0.000637V^2_{\text{EtOH}} + 0.032.$$

The addition of 30 ml of absolute ethanol produced complete miscibility. Hence, 25 ml of ethanol was used in the succeeding experiments as that volume gave the maximum value of K and could be conveniently measured by means of a standard pipette. The data in table 1 indicate that the partition coefficient is practically independent of the quantity of boric oxide present, and boric oxide is, therefore, in the same state of association in each of the layers.

The effect of shaking was studied in a series of experiments using a sample containing about 0.05 g of boric oxide. The solutions were shaken by hand three times a minute and about five seconds each time. As the values of K were practically constant for shaking periods ranging from 5 to 30 minutes, it was concluded that, for these clear solutions, equilibrium is reached in less than five minutes. In this series of experiments it was found that the substitution of 95 percent for absolute ethanol caused a decrease in the average value of K from 0.444 to 0.374.

TABLE 1.—Effect of the amount of B_2O_3 on K

B_2O_3 sol. +1ml HCl (sp gr 1.18)+ H_2O =25 ml.
25 ml C_2H_5OH (abs.) and 50 ml $(C_2H_5)_2O$ added.

[Determinations made at room temperature]

Quantities involved	Experiment number—				
	1	2	3	4	5
B_2O_3 added, (g).....	0.01099	0.03297	0.05495	0.08243	0.1099
$(B_2O_3)_{Et_2O}$, (g).....	.00513	.01490	.02488	.03712	.04975
$(B_2O_3)_{H_2O}$, (g).....	.00586	.01807	.03007	.04531	.06015
Et_2O layer, (ml).....	62.4	62.6	63.1	63.2	63.1
H_2O layer, (ml).....	35.2	34.1	34.0	33.7	33.8
$C_{Et_2O} \times 10^4$, (g/ml).....	0.822	2.380	3.943	5.873	7.884
$C_{H_2O} \times 10^4$, (g/ml).....	1.665	5.299	8.844	13.45	17.80
$K' = C_{Et_2O}/C_{H_2O}$494	.449	.446	.437	.443

Average $K = 0.444$.^a

^a The average in this and succeeding tables is adjusted and is obtained by means of the equation:

$$\text{Average } K = \frac{\sum (g B_2O_3 \times K')}{\sum (g B_2O_3)}$$

where K' is the value computed from the analytical data in each experiment.

The effect of variations in temperature, t , on the value of K was investigated, using a 20-minute shaking time and amounts of boric oxide varying from 0.14 to 0.73 g. At 1.5, 10, 21, and 30.5° C the values of K were 0.613, 0.520, 0.453, and 0.409, respectively. The variation of K with temperature is expressed by the equation, $K = 0.668 - 0.0469\sqrt{t}$ (see curve 1, fig. 1).

1. EFFECT OF THE AMOUNT OF FLUX, SODIUM CARBONATE, USED IN DECOMPOSING THE SAMPLE ON THE PARTITION COEFFICIENT

Although 0.5-g samples of most glasses can be completely decomposed after fusion with 1 g of sodium carbonate, if intimately mixed beforehand, tests were made to determine the effect of varying the amount of flux by dissolving 1 g and 2 g of sodium carbonate, respectively, in varying amounts of a standardized aqueous solution of boric acid, and then determining the boric oxide in the ether layer as previously stated. Herz [5] states that sodium chloride decreases

the solubility of boric acid in water, and the sodium chloride equivalent to the amount of sodium carbonate used seems to have a greater effect in decreasing its solubility in the ether-ethanol layer. This can be seen by comparing the values of K in tables 1 and 2. These tables also show that sodium chloride decreases the volume of the water layer.

The effect of temperature variations on the value of K in the presence of sodium chloride was also studied. No work was done in

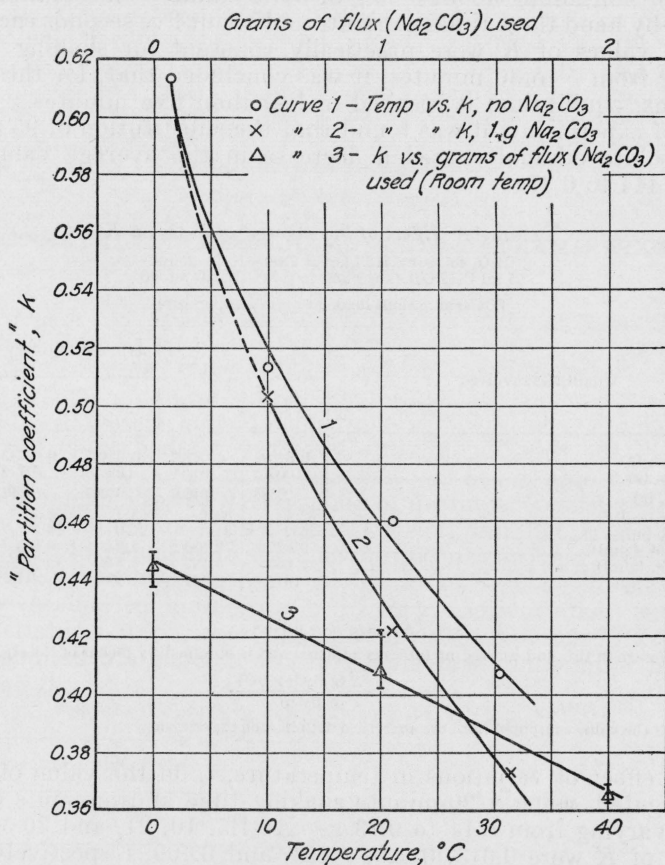


FIGURE 1.—Effect of variations in temperature and in the amount of flux used in decomposing the sample on the "partition coefficient."

the region of 0° C in this case after it was found that the value of K at 10° C fell off rapidly for amounts of boric oxide in excess of about 0.05 g. This did not happen in the experiments carried out at 21° C, so it would seem that there would be no advantage in using a temperature much lower than 20° C for the extractions. At the temperatures of 10, 21, and 31.5° C, K was found to be 0.503, 0.422, and 0.373, respectively, and the variation of K with temperature is expressed by the equation $K=0.673-0.054\sqrt{t}$. In figure 1 the effects of changes in temperature (curve 2) and the amount of flux (sodium carbonate) used on K (curve 3) are graphically shown.

TABLE 2.—Effect of NaCl on *K*

[Determinations at room temperature]

Quantities involved	Experiment number						
	6	7	8	9	10	11	12
Na ₂ CO ₃ added, (g).....	1.000	1.000	1.000	1.000	1.000	2.000	2.000
B ₂ O ₃ added, (g).....	.01075	.02150	.03225	.04300	.05375	.10000	.20000
(B ₂ O ₃) _{Et₂O} , (g).....	.00567	.01144	.01698	.02234	.02798	.05387	.10774
(B ₂ O ₃) _{H₂O} , (g).....	.00508	.01006	.01527	.02066	.02577	.04613	.09226
Et ₂ O layer, (ml).....	71.9	71.6	71.6	71.5	71.6	74.0	74.3
H ₂ O layer, (ml).....	26.3	26.6	26.6	26.6	26.6	23.4	23.1
C _{Et₂O} ×10 ⁴ , (g/ml).....	.789	1.598	2.372	3.124	3.908	7.280	14.50
C _{H₂O} ×10 ⁴ , (g/ml).....	1.932	3.782	5.741	7.767	9.688	19.71	39.94
<i>K'</i>408	.422	.413	.402	.403	.369	.363

Average *K* = 0.408 (1 g of Na₂CO₃).Average *K* = 0.365 (2 g of Na₂CO₃).

2. EXPERIMENTAL WORK ON GLASSES AND INTERFERING ELEMENTS

One-half g samples of NBS Standard Sample 80,² which contains no boron, were fused in a platinum crucible with 1 g of sodium carbonate, cooled, digested in the crucible with varying amounts of a standardized aqueous solution of boric acid, and neutralized with hydrochloric acid (1:1) to the *p*-nitrophenol endpoint. The boric oxide in the resulting mixture (which contained some precipitated silica) was determined as previously outlined. The results obtained show that *K* is constant up to about 0.08 g of boric oxide; above that amount it is definitely low. Consequently, amounts of boric oxide up to 16.00 percent can be conveniently determined by this method. Since the value of *K* obtained in these experiments (0.408) is the same as that obtained when 1 g of sodium carbonate was used (table 2), silica, lime, magnesia, and soda do not interfere when present in amounts equivalent to those in Standard Sample 80.

TABLE 3.—Partial composition of standard samples

Constituents	NBS Standard Samples—			
	80	93	91	92
	%	%	%	%
SiO ₂	74.10	80.600	67.60
R ₂ O ₃42	2.060	6.00
CaO.....	4.65	10.48
MgO.....	3.23	.027	.01
Na ₂ O.....	16.65	4.160	8.46
K ₂ O.....	.04	.16	3.24
B ₂ O ₃	None	12.76	None	0.70
	Ignition loss=0.30	F=5.75

Since commercial glasses may contain appreciable amounts of arsenic, aluminum, barium, zinc, iron, and fluorine, tests were made to determine if these elements interfere. The tests were made by

² The partial composition of Standard Sample 80 of the National Bureau of Standards and of the other standard samples used in this work is given in table 3.

adding appropriate soluble salts, in varying amounts, to fusions of several standard samples of glass, and determining the boron.

Arsenious and arsenic oxides were added in amounts between 0.002 and 0.025 g. Arsenious oxide up to 0.005 g and arsenic oxide up to 0.01 g caused no trouble; above these amounts a plus error resulted in the value of K .

Alumina up to 0.05 g had no effect.

One-hundredth g of barium oxide did not affect the determination of boric oxide in Standard Sample 92, but caused low results on Standard Sample 93. However, the interference of small amounts of barium oxide can be avoided by adding a drop of sulphuric acid (1:1) when decomposing the fusion.

The equivalent of 5 percent of zinc oxide added to Standard Sample 80 gave a titration indicating 3.5 percent of boric oxide. This and other work leads to the conclusions that in the presence of zinc this method cannot be used until it has been removed and also that zinc chloride may lower the partition coefficient.

Iron, in the amounts usually present in glass, gave no trouble; but when it was added in amounts equivalent to 1 percent of ferric oxide the color of the ferric chloride formed from it masked the *p*-nitrophenol endpoint.

The presence of approximately 6 percent of fluorine caused a blank about twice that of the normal blank (0.56 ml of barium hydroxide solution as against 0.27 ml). Furthermore, low values of the partition coefficient were obtained, probably on account of the formation of potassium fluoborate (or possibly sodium fluoborate) which, according to Smith, Hamilton, and Graham [7], is quite insoluble under the conditions of the experiment.

It is evident from curve 2 of figure 1 that the effect of temperature on the partition coefficient cannot be disregarded. A constant-temperature room would insure very satisfactory conditions for making boron determinations by this method and, unless one is available, proper temperature corrections must be made if one wishes to obtain reasonable accuracy. However, for routine work ordinary variations in the temperature of the laboratory will not produce serious errors in the determination of small amounts of boric oxide (up to 8 percent) even if the temperature corrections are not applied. The error gradually increases for increasing amounts of boric oxide until, for 16 percent, it becomes about 0.2 percent (plus or minus, depending on whether the temperature is 2° below or above 25° C).

It can be seen from curve 3 of figure 1 that variations in the amount of flux used in decomposing the glass have a definite effect on K , but the effect is not as great as the temperature effect and is not serious, because a definite weight is much more easily obtained than a constant temperature.

III. RECOMMENDED METHOD OF ANALYSIS

1. REQUIRED REAGENTS

(1) *Para-nitrophenol*.—One gram dissolved in 75 ml of ethanol (95 percent) and made up to 100 ml with distilled water.

(2) *Phenolphthalein*.—One gram dissolved in 100 ml of ethanol (95 percent) and made up to 200 ml with distilled water.

- (3) *Hydrochloric acid, 0.5N.*
- (4) *Sodium hydroxide, 0.5N.*
- (5) *Barium hydroxide, 0.1N.*
- (6) *Ethanol, absolute.*
- (7) *Ethyl ether, free from aldehyde and peroxide (as indicated by test given below).*
- (8) *Mannitol.*

2. ANALYTICAL PROCEDURE

Grind 0.5 g of glass and 1 g of sodium carbonate intimately together in a mortar and transfer to a platinum crucible. Fuse at as low a temperature as possible and only as long as is necessary to effect complete decomposition. Cool, wash the lower surface of the lid, catching the washings in the crucible, and wash down the sides of the crucible with hot distilled water. Disintegrate the melt (with the aid of a platinum wire) on the steam bath and concentrate to about 5 ml. Cool and neutralize most of the alkali with HCl (1:1), guarding against loss of boron both by spattering and volatilization. Add two drops of *p*-nitrophenol, complete neutralization dropwise, add 1 ml of concentrated HCl (sp gr 1.18), and transfer to a calibrated, 100-ml glass-stoppered cylinder. Dilute to 25 ml, add 25 ml of absolute ethanol and 50 ml of ether³ and shake intermittently for 20 minutes, noting the temperature. Allow the layers to separate, record their volumes, and pipette off a 50-ml sample of the ether layer for analysis. To the 50-ml sample, in a 250-ml erlenmeyer flask, add two drops of *p*-nitrophenol and titrate to the *p*-nitrophenol endpoint with 0.5N NaOH. Read the burette, add 1 ml of phenolphthalein, and continue the titration to the phenolphthalein endpoint. Add a volume of 0.5N NaOH equal to three times that used between the two endpoints, and shake the flask vigorously. Wash down the sides with distilled water and make the water volume up to 40 to 50 ml. Boil off the ether and ethanol as quickly as possible,⁴ first on a water or steam bath and finally over the free flame to remove the last traces of ether and ethanol. Adjust the volume with distilled water to 35 to 45 ml, cool, and then make just acid with 0.5N HCl. Warm on the steam bath for about one minute and boil under reduced pressure until cool to remove CO₂. Titrate to the *p*-nitrophenol endpoint with 0.1N Ba(OH)₂, record the burette reading, add mannitol, and titrate the B₂O₃. 1 ml of 0.1N Ba(OH)₂ is equivalent to 0.00348 g of B₂O₃. A blank determination should be made using a glass, preferably of similar composition, but containing no boron.

³ It became evident during the course of this work that the quality of the ether used in this method must be examined at frequent intervals and should be purified if the *p*-nitrophenol endpoint is not sharp or if the sample, after removal of the ether and ethanol and subsequent acidification, shows color. A satisfactory test method is to treat approximately 50 ml of ether, 5 ml of 0.5N NaOH, and about 50 ml of distilled water exactly as a sample would be treated for the removal of ether and ethanol. Upon diluting to 35 to 45 ml and neutralizing with 0.5N HCl to the *p*-nitrophenol endpoint, no color should be evident. For purification, a modification of the method of Palkin and Watkins [6] was used. The ether was first agitated with asbestos impregnated with alkaline permanganate (5 ml of saturated KMnO₄ to 15 ml of 33-percent NaOH) and then slowly siphoned, in a very fine stream, through a column of the alkaline permanganate into a bottle. This bottle also contained asbestos impregnated with alkaline permanganate and was kept in a cool, dark place.

⁴ Long standing on the water or steam bath gives a colored acid solution which has a tendency to mask the *p*-nitrophenol endpoint in the final titration.

The equation for calculating the percentage of B_2O_3 in a 0.5-g sample, is as follows:

$$\text{Percent } B_2O_3 = 4(B_2O_3)_{50Et_2O} \left[V_{Et_2O} + \frac{V_{H_2O}}{K} \right]^5$$

where $(B_2O_3)_{50Et_2O}$ is the grams of B_2O_3 in the 50-ml aliquot portion taken for analysis, and V_{Et_2O} and V_{H_2O} the volumes of the ether layer and water layer, respectively. For routine work, where the temperature does not vary more than 2° from $25^\circ C$, 0.403 may be used as the value of K without significant sacrifice of accuracy; otherwise its value must be calculated from the equation, $K = 0.673 - 0.054\sqrt{t}$ (see table 4).

TABLE 4.—Results obtained with samples containing varying amounts of B_2O_3 , when proper temperature corrections are made

NBS Standard Samples used	B_2O_3 present or added	Extraction temperature	Et_2O layer	H_2O layer	K^1 (calculated)	$B_2O_3^2$ present or added	B_2O_3 found	Difference
Number	g	$^\circ C$	ml	ml		%	%	%
80.....	0.00480	21.5	72.3	25.8	0.423	0.96	1.05	+0.09
80.....	.00959	23.0	72.7	25.2	.414	1.92	2.00	+ .08
80.....	.02467	24.0	72.6	25.4	.408	4.93	4.92	- .01
80.....	.04934	26.0	73.0	25.0	.398	9.87	9.96	+ .09
80.....	.07401	26.0	72.8	25.3	.398	14.80	14.77	- .03
92.....	.06350	24.5	72.7	25.3	.406	.70	.78	+ .08
80 and 93.....	.00629	19.0	72.1	25.5	.438	1.26	1.24	- .02
80 and 93.....	.01257	17.5	72.1	25.8	.447	2.52	2.59	+ .07
80 and 93.....	.02515	18.0	72.7	25.5	.444	5.03	4.97	- .06
80 and 93.....	.03772	25.0	72.4	25.9	.403	7.54	7.67	+ .13
80 and 93.....	.05030	25.0	72.5	25.7	.403	10.06	9.96	- .10
93.....	.06287	27.0	72.6	25.4	.393	12.57	12.58	+ .01

¹ $K = 0.673 - 0.054\sqrt{t}$.

² On the assumption that the "boric oxide present or added" was in 0.5-g sample of glass.

The experimental work on this subject was started by J. F. Klekotka, and the authors acknowledge his assistance and thank him for the part of the work he did.

$$K = \frac{C_{Et_2O}}{C_{H_2O}} \text{ or } C_{H_2O} = \frac{C_{Et_2O}}{K}$$

$$C_{Et_2O} = \frac{(B_2O_3)_{50Et_2O}}{50} \text{ and } C_{H_2O} = \frac{(B_2O_3)_{50Et_2O}}{50K}$$

$$(B_2O_3)_{Et_2O} = C_{Et_2O} \times V_{Et_2O} = \frac{(B_2O_3)_{50Et_2O}}{50} \times V_{Et_2O} \quad (1)$$

$$(B_2O_3)_{H_2O} = C_{H_2O} \times V_{H_2O} = \frac{(B_2O_3)_{50Et_2O}}{50K} \times V_{H_2O} \quad (2)$$

$$\text{The total } B_2O_3 = (1) + (2) = \frac{(B_2O_3)_{50Et_2O}}{50} \left[V_{Et_2O} + \frac{V_{H_2O}}{K} \right]$$

$$\text{Percent } B_2O_3 = \frac{100 \times B_2O_3}{0.5} = 4(B_2O_3)_{50Et_2O} \left[V_{Et_2O} + \frac{V_{H_2O}}{K} \right]^5$$

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