THE DETERMINATION OF BORON
IN ORGANOBORON COMPOUNDS

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Submitted to the faculty of the Graduate School of
the Oklahoma Agricultural and Mechanical College
in partial fulfillment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY
May, 1956

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ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Paul Arthur for his help and guidance throughout this research.

He also wishes to acknowledge the financial aid given by the Research Foundation of the Oklahoma Agricultural and Mechanical College.

DEDICATION

This thesis is dedicated to my parents with whose help College was begun, and to my wife and Carol with whose patience and understanding it was finished.

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INTRODUCTION AND HISTORY

To determine the boron content of an organoboron compound by combustion, three steps are of importance. First, the compound must be decomposed by some method. Second, the boron liberated by the decomposition must, if necessary, be separated from interfering substances and be in a form which is easily handled for determinations. Third, the method of determination should be simple and rapid for convenience.

Decomposition of Organoboron Compounds.

For the first step, the decomposition of the organoboron compound, there are two approaches: wet combustion of the compound, or dry fusion.

Wet Combustion. Several methods are available for the wet combustion, some of which, however, are for specific compounds only. The method of Abramson and Kahane (1) in which a weighed sample of the compound is digested with a mixture of nitric, perchloric, and sulfuric acids is a general approach. However, the methods of Branch, Yarbroff, and Bettman (18), and Mel'nikov (45) are only for specific compounds or for a specific series of compounds. The method of Roth (53) may be used for most easily decomposed compounds. The compound is placed in a distillation apparatus with sulfuric acid and methanol. The methyl borate which is formed is distilled and the distillate caught in 0.1N sodium hydroxide. Since this distillation procedure is used for separation, it will be discussed later.

For compounds such as the borines which would react violently if treated with sodium peroxide, Snyder, Kuck, and Johnson (61) devised the following as an alternative for their fusion method. A capsule containing the sample was placed in a flask to which was added 0.5 ml. of concentrated sodium hydroxide and 10 ml. of 5% hydrogen peroxide. After warming slightly, more sodium hydroxide and 30% hydrogen peroxide were added and the solution refluxed. An ignition to convert any organic acids formed to carbonates was used, followed by a titration of the boric acid. They claim that this method may also be used for the aliphatic boronic acids. A similar approach was used by Booth and Kraus (16) in which they substituted hydrochloric or sulfuric acid for the sodium hydroxide used in the decomposition. A rather drastic, but effective, method was that of Bowlus and Nieuwland (17) in which the compound was heated to 200° C. in a sealed tube with fuming nitric acid.

Dry Fusion. The fusion method is the one most generally used for decomposing organoboron compounds. Bertrand (7) and Roth (53) both fused the compound with sodium carbonate, dissolved the melt in hydrochloric acid, and followed with a titration procedure. A similar approach was made by Burke (20) who used a Parr bomb for the carbonate fusion rather than a platinum crucible. The Parr bomb has also been used by Pflaum and Wenzke (50), and by Snyder, Kuck, and Johnson (61). The fusion mixture of Pflaum was composed of sodium carbonate, potassium chlorate, and sugar while Snyder used sodium peroxide, potassium chlorate, and sugar. For the determination of boron in borine compounds, Conrad and Vigler (21) used a Parr oxygen bomb with an oxygen pressure of 500 lbs. per square inch.

The Chapin Distillation Method.

The previously mentioned distillation method of Chapin (65) is quite widely used, not only for the decomposition of organoboron compounds, but also whenever it is necessary to separate boron from some interfering element as zinc, lead, aluminum, iron, or nickel (57), or from ash as in the analysis of agricultural products. In essence, the method consists of placing a hydrochloric acid solution of the sample in a flask to which is added anhydrous calcium chloride. The sample flask is connected to a second flask containing methanol, and to a condenser in a manner analogous to that used in a steam distillation. The methyl borate which is distilled is hydrolyzed to boric acid and the acid solution is then titrated in the receiver. In many instances, the procedure is simplified by adding methanol directly to the flask containing the sample.

Quantitative Determination of Boron.

Colorimetric. After the sample is decomposed and, if necessary, the boron separated from contaminants, the boron may be quantitatively determined by either of two principal methods. For very small amounts of boron, 0.1 mg. or less, colorimetric methods are usually used. A number of useful color producing reactions have been found and several modifications of each method may be found in the literature. The most commonly used color producing agents are turmeric (7, 30), quinalizarin (42, 60), and 1,1'-dianthrimide (24, 28).

Titrimetric. The second principal method, useful for boron contents greater than 0.1 mg., is the titration of boric acid. Boric acid is a very weak acid and as such is difficult to titrate directly. Two indicators have been found, however, which give color changes in the correct pH range of 11 to 12. They are tropeoline 0 (37, 52) and nitramine (39). A pH meter could also be used, but the curves obtained are very poor; and, in view of the better methods available, it is very seldom used for this type of titration.

The most common method of titration involves the use of a "complexing" agent as mannitol, glycerol, or invert sugar. In 1842, Biot (9) reported that a solution of boric acid becomes more acidic after the addition of sugars. Klein (36), in 1878 pointed out that boric acid solutions become more acidic on the addition of sugars or certain polyalcohols. Since that time, there have been many investigations of the processes involved and of substances which will effect this phenomenon. Boeseken and his co-workers (12, 13, 14, and 15) have worked for over twenty years on this problem and have published extensively. Many others have worked with mannitol, glycerol, or other specific compounds in trying to elucidate the complexing process (2, 3, 4, 6, 24, 27, 40, 44, 47, 51, 56, and 64).

In 1925, Kolthoff (40) suggested that mannitol, fructose, and probably also other polyhydric alcohols form multibasic complex acids in which 1 molecule of polyvalent alcohol combines with more than 1 molecule of boric acid. The composition of the complexes is apparently dependent on the ratio of boric acid to polyvalent alcohol in solution. Gilmour (27) has said that the complex requires 3 moles of sugar to 1 of boric acid. Ageno (3), however, said the complex is formed in a 1:1 ratio. Others (23, 47, and 64) have claimed that they have isolated solid compounds of boric acid and certain sugars and alcohols.

In 1930, W. D. Bancroft and H. L. Davis (4) published a paper in which they presented all the known evidence for the formation of complexes and/or compounds of boric acid and the various alcohols and sugars. In discussing the evidence, they gave reasonsfor their expressed belief that the conclusion reached by each author was erroneous and explained further how the facts could be interpreted in quite a different manner. In summarizing their paper, they expressed the opinion that the increased acidity of the solutions is due to a change in the nature of the solvent resulting in an increased dissociation of the boric acid.

It seems clear from this, therefore, that the matter is as yet far from settled. The arguments presented by Bancroft, however, are quite convincing as opposed to those presented by many other workers.

Problems in the Use of Polyhydroxy Compounds.

Quantity. Irrespective of the mechanisms involved in increasing the acidity of a boric acid solution by the addition of a sugar, two very important problems are involved in the actual use of such an agent. The first problem is the quantity of mannitol to use. The same question arises with glycerol or fructose, but since mannitol is the most commonly used today and was used in this work, only it will be considered. Kolthoff and Stenger (39), also Kolthoff and Sandell (38), recommend using 0.5 to 0.7 g. per each 10 ml. of solution. Hillebrand, Lundell, Bright, and Hoffman (31), on the other hand, recommend 1 to 3 g. Hollander and Rieman (32) indicate that the mannitol concentration should be about 0.35 moles per liter at the end of the titration. These amounts are in general accord with the recommendations of Schäfer (56). Using 20 ml. of 0.0925 molar boric acid, he added increasing amounts of mannitol and plotted the curves of pH vs. milliliters of added base. With each increase in mannitol concentration, the initial pH, as well as the pH at the end point, was lowered and the vertical portion of the curve became longer. He found, however, that increasing the mannitol concentration beyond 0.3 to 0.5 molar had no advantages and therefore recommended that the concentration be in this range. This is generally accepted at present.

Starting and End Point pH. The second problem is that of selecting an indicator for the end point of the titration and, if a base or a mineral acid is present in the original solution, of choosing the proper pH to which the solution should be adjusted before adding mannitol. From a list of twenty-five different procedures, it is found that in sixteen the titration is carried to a phenolphthalein end point of about pH 8.4 and in five to an α-naphtholphthalein end point of pH 7.2 to 8.6. An end point of around pH 8.5 is in agreement with the end point found on the curves by Schäfer (56) when a mannitol concentration of 0.3 to 0.5 moles per liter is used.

The pH at which mannitol is added is quite varied. Indicators with a pH change interval of 3.3-4.6 are used as well as indicators which change in the pH interval of 5.2-6.8. The most commonly used initial indicators, however, are methyl red (4.2-6.3) and methyl orange (3.3-4.4). It appears that in recent years the use of methyl red has been the more common. An article by Dodd (22) contains considerable information on the results obtained with the various indicators.

In many cases the base is standardized against borax, boric acid, or boric oxide to account for any errors of pH adjustment; however, most of the literature references give no details on the standardization. A few specify the use of potassium acid phthalate (10, 29). It is the belief of the writer, however, that in most of the cases, standardization is made with some boron compound.

Identical pH Methods.

The difficulty of determining the correct initial and final pH values is circumvented by the identical pH method developed by Foote (25). In this method mannitol is added at a pH of 7.6 and the solution is then titrated to a pH of 7.6. Of course, the base must be standardized in exactly the same manner as it is to be used. Other pH's which have been used are 6.90 (43), 6.30 (33), and 8.0 (11). In each of these cases, an indicator or a pH meter is used for the adjustment.

Soon after Foote published his method, Wilcox (66) developed a method using the identical pH principle but determining the end points by means of a null indicator composed of silver chloride and quinhydrone electrodes. The null point was reached around a pH of 7.3. The method has since been modified using other electrodes (54, 63, and 67).

Effect of Neutral Salts.

It should be mentioned that neutral salts have been found to have an activating effect on boric acid solutions. Schäfer and Sieverts (55) found that the acid strength is increased on the addition of enough calcium chloride to saturate the solution. Tanino (62) used sodium chloride and obtained an end point by comparing colors with standards of sodium borate and phenolphthalein or methyl orange. Recently, Shiskido (59) published his results on the addition of various salts and the magnitude of their effects.

SCOPE OF INVESTIGATION

The purpose of this investigation was to develop and test a method for the determination of boron in organoboron compounds. It was necessary to investigate three points in order to develop the method: first, the decomposition of the compounds by heat in a stream of oxygen using a modified carbon and hydrogen train; second, the quantitative removal from the combustion tube of the boric oxide formed by the combustion; and third, the best conditions for the titration of the boric acid solution formed by washing the boric oxide from the combustion tube.

REAGENTS AND MATERIALS

Standard Carbon Dioxide-Free Sodium Hydroxide.

One-liter quantities of approximately 0.02N sodium hydroxide were prepared by adding 1.25 ml. of 16N base, from which insoluble carbonate had been removed by filtration, to one liter of freshly boiled water. The solution was stored in a polyethylene bottle and protected from the atmosphere by a drying tube filled with Ascarite and Dehydrite. A latex rubber tube connected the storage bottle to the buret for filling purposes. The solution was standardized against potassium acid phthalate (Fisher P-243). A second sodium hydroxide solution, used for rough adjustment of the pH of the boric acid solution, was prepared in the above manner but was not standardized. It was approximately 0.1N.

Distilled Water.

A 6-gallon polyethylene bottle was used to store distilled water, thus preventing the leaching of boron from glassware during the storage period. A titration blank was run each time new base was prepared or the storage bottle was filled.

Mannitol.

Fisher Certified Reagent grade mannitol was used for all boron titrations.

Sodium Tetraborate Decahydrate.

Crystalline sodium tetraborate decahydrate was prepared by recrystallization of the powder (Mallenkrodt Analytical Reagent grade) from water. A ratio of 50 ml. of water to 15 g. of borax was used and the temperature was maintained below 55° C. to prevent formation of the pentahydrate. The damp crystals were washed with two portions each of alcohol and ether (each portion being 5 ml. per 10 g. of crystals) (34). The crystals were stored in a desiccator over water saturated with sodium chloride and sucrose (46).

Nitrogen.

Commercial tank nitrogen (water pumped) was used to exclude carbon dioxide from the titration beaker. The gas was passed through a 1N sodium hydroxide solution to remove any carbon dioxide present, then through distilled water to remove any base which might have been carried over as spray.

Oxygen.

Commercial tank oxygen was used for combustion of the organoboron compounds.

Phenylboric Oxide.

The method of Seaman and Johnson (58) was used to prepare phenylboric acid from phenylmagnesium bromide and methyl borate. The acid was placed in a vacuum desiccator over activated alumina until it reached constant weight indicating that 1 mole of water had been removed producing the oxide.

The oxide melted at 206-207° C. in an evacuated sealed tube and at 227-228° C. on a Fisher-Jones melting point apparatus (literature value: 190° C.) (48).

p-Phenetyl Boric Acid.

The method of Bean and Johnson (5) as described by Branch, Yarbroff, and Bettman (18) was used to prepare this compound. It was recrystallized from water giving very short needles which, when heated rapidly gave a melting point of 151-153° C. (literature value: 150 and 159° C. for the acid and 171° C. for the anhydride). When the Fisher-Jones melting point apparatus was used, the temperature was raised very slowly and a cloudiness appeared around the crystals at 120-130° C. -- probably indicating loss of water. The crystals then gave a very sharp melting point at 171-172° C.

p-Phenoxyphenyl Boric Acid.

The compound was prepared by the method of Bean and Johnson (5) as described by Bettman, Branch, and Yarbroff (8) by reacting *p*-phenoxyphenylmagnesium bromide with *n*-butyl borate. It was recrystallized from 25% alcohol and gave needles melting at 138-140° C. on the Fisher-Jones melting point apparatus (literature value: 123-124° C.).

n-Butyl Borate.

The method of Johnson and Tompkins (35) was used to prepare the liquid from boric acid and *n*-butanol. The product was vacuum distilled and a heart cut used for the analysis.

Tri-α-naphthylboron.

The Grignard reaction of boron trifluoride-etherate and α-bromonaphthalene as described by Brown and Sujishi (19) was used. Its melting point (*in vacuo*) was 203-204° C. (literature values: 203-205° C. (41) and 206-207° C. (19)).

APPARATUS

The furnace used to heat the platinum stars in the combustion tube was a Sargent No. S 36400 resistance furnace. It provided a maximum temperature of about 900° C.

In Figure 1 is shown the burner used to burn the samples. It was constructed with a cylindrical casing (A) of aluminum, closed with ends (B) of transite. The burner coil (C) was made from 23 feet of B. and S. gauge No. 20 nichrome wire which had a resistance of 0.66 ohms per foot. The area (D) between the coil and the casing was filled with Celite Analytical Filter Aid (Johns-Manville Co.) for insulating purposes. Contact with a Variac was made by means of the connectors (E).

The combustion tube, purchased from the Hanovia Chemical and Mfg. Co., Newark, New Jersey, was made of clear fused quartz. This tube was 100 cm. long and 8 to 9 mm. I.D. The exit end was drawn to a tip 2 cm. long and 4 mm. O.D.

The 300-ml. round bottom flask used for refluxing water in the combustion tube was made from heavy clear quartz and purchased from the Thermal American Fused Quartz Co., Dover, New Jersey. Boron-free flasks (Corning Glass Co. No. 74280) were tried but found to be very sensitive to thermal shock and for this reason were not used.

The seamless platinum cylinder used in the combustion tube was 25 cm. in length and 6 mm. I.D. It was constructed of 0.003-0.004 inch platinum sheet by The American Platinum Works, Newark, New Jersey.

The platinum contact stars were purchased from the Fisher Scientific Co. (Catalogue No. 20-836).

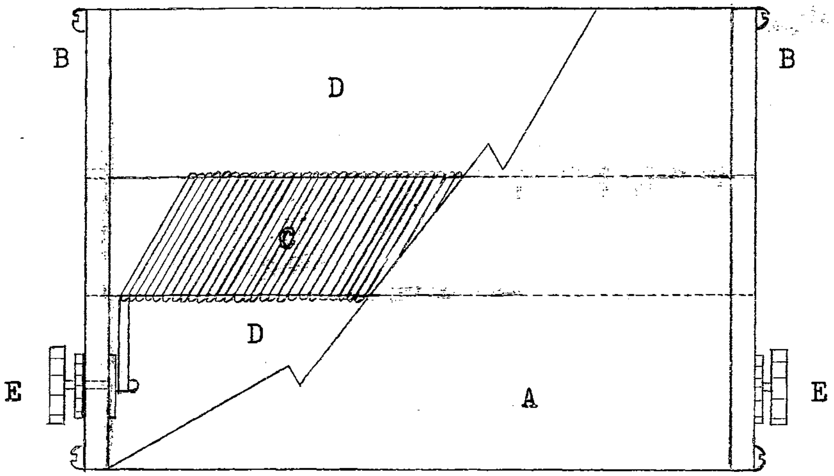

Figure 1

Sample Burner

A. Aluminum shield
B. Transite ends
C. Wire coil
D. Celite insulation
E. Variac connections

The buret, which was used for titrating the boric acid solutions, was of 10-ml. capacity graduated in 0.02-ml. divisions with a drain time of 360 seconds. A three-way stopcock was used for filling and draining the buret. The top of the buret was fitted with an Ascarite-filled drying tube to protect the base from atmospheric carbon dioxide.

The titration cell, shown in Figure 2, was composed of a 100-ml. quartz beaker (A) covered with a No. 14 rubber stopper (B). The stopper was hollowed out on the under side so as to fit rather tightly over the beaker. Holes were provided in the stopper for the pH meter electrodes (C and D), the nitrogen inlet (E), and the tips of the 0.1N and 0.02N sodium hydroxide burets (F and G).

A line-operated Beckman pH meter, model H2, was used throughout the experimental work.

The thermocouple used to calibrate the sample burner Variac was a model 525A1 Tomcometer (Thermo Electric Mfg. Co., Dubuque, Iowa).

The magnetic stirrer was a Magnestir manufactured by Labline, Inc., Chicago, Ill. The stirring bar was covered with Teflon.

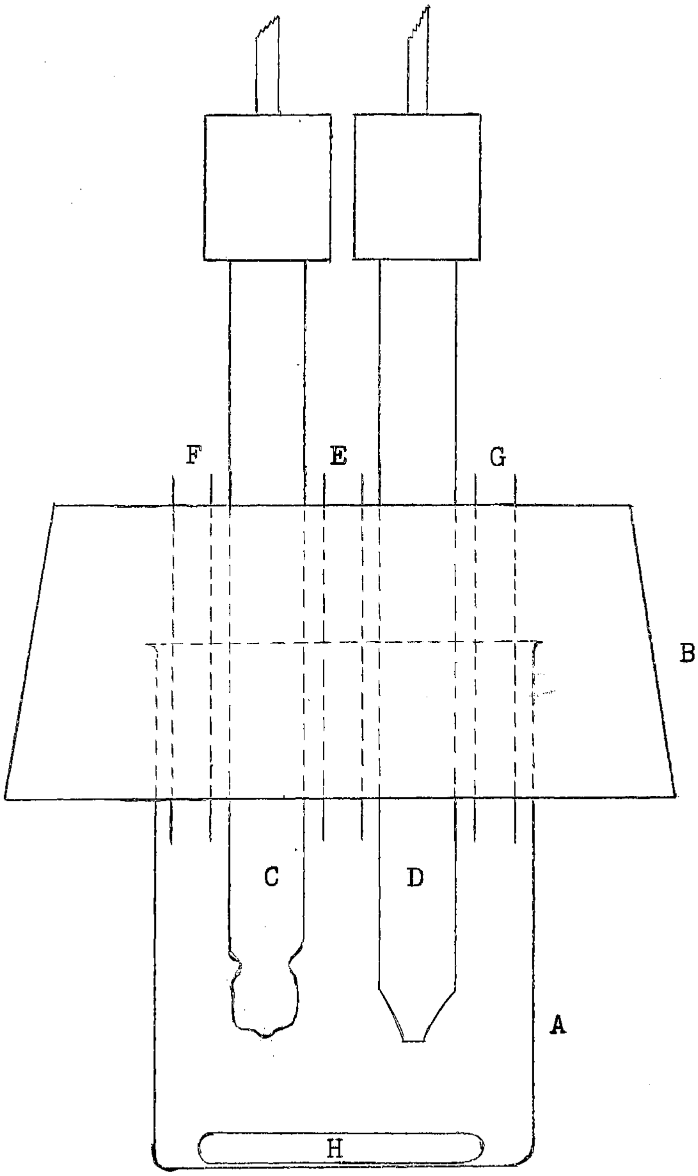

Figure 2

Titration Cell

A. Quartz beaker
B. Rubber stopper
C. Glass electrode
D. Calomel electrode
E. Nitrogen inlet
F. 0.1N Sodium hydroxide buret
G. 0.02N Sodium hydroxide buret
H. Magnetic stirrer bar

EXPERIMENTAL PROCEDURE AND RESULTS

The first compound on which the combustion method of analysis was tried was phenylboric oxide. Several runs were made but the results were not only quite poor in accuracy, but showed very large differences among individual runs. The procedure used in these determinations was simple and its use was continued with modifications.

The sample, contained in a platinum boat, was placed in the combustion tube approximately 7 inches from the stationary furnace (Figure 3), the latter being adjusted to a temperature of 750° C. With the oxygen flow rate adjusted to 5 ml. per minute, the sample was burned using, in general, the procedure of Niederl and Niederl (49) for carbon and hydrogen determinations. The sample burner, adjusted to 750±25° C., was placed about 5 cm. in front of the boat and slowly moved toward the stationary furnace. With 5 minutes employed to reach the boat, the sample burner was then allowed to remain over the boat for another 5 minutes. The burner was then moved slowly toward the stationary furnace taking 5 minutes for the passage. The burner was returned to its starting position and the process repeated using 5 minutes to reach the furnace. After the second pass had been made, the temperature of the burner was raised to 1000° C., and the area from the furnace to, and including, the boat heated. This heating was for 30 minutes to 1 hour or until the black residue, which formed in the boat and in front of the stationary furnace and which is believed to be unburned carbon coated with boric oxide, had disappeared. The tube then was removed from the furnaces, its inlet end was stoppered and the tube was placed in an upright position within the coils of a nichrome wire heater. The area which contained 25 to 30 ml. of water and 1 drop of concentrated hydrochloric acid was then heated. The temperature of

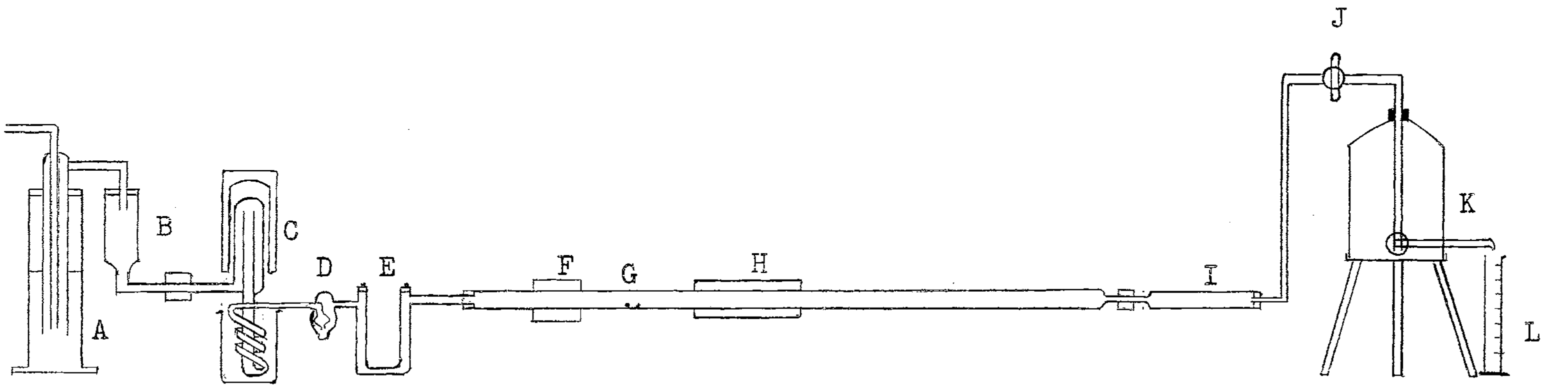

Figure 3

Combustion Train

A. Pressure regulator
B. Drying tube
C. Pre-heater
D. Bubble counter

E. U-tube, drying
F. Sample burner
G. Sample boat
H. Stationary furnace

I. Glass wool packed tube to provide back pressure
J. Stopcock
K. Mariotte bottle
L. Graduated cylinder

the water was raised and held for 20 minutes just below the boiling point. At the end of this time the water was emptied into a steamed quartz beaker, boiled for 2 minutes, then quickly cooled. The magnetic stirring bar was added, and the beaker was placed in position for titration with nitrogen flowing over the surface of the solution. A 0.1N sodium hydroxide solution was added until the pH showed a very sharp rise on the addition of 1 drop of the base. Approximately 5.5 g. of mannitol was added and the solution titrated with 0.01N sodium hydroxide, both the pH and the quantity of base added being recorded at suitable intervals. The end point was taken as the point of greatest pH change per unit quantity of base added.

Modification of Combustion Method.

The results using the above procedure were quite poor; so several different combustion techniques were tried. The one found to give the best results consisted of placing the boat 3 to 4 inches from the stationary furnace, setting the sample burner at 950° C. just in front of the boat, and leaving it in this position until all the sample had volatilized and the vapors moved toward the furnace. The sample burner was then moved slowly toward the furnace and, on reaching it, the temperature raised to 1000° C. As previously, the area was heated for 30 minutes or until the black residue had disappeared.

Investigation of Mannitol Titration.

Exact Neutralization of Hydrochloric Acid. While using this method it was noted that the percentage of boron found varied considerably with the pH at which the mannitol was added. The titration was investigated by placing 5 or 10 ml. of a boric acid solution, containing 0.0609 mg. of boron per milliliter, in a quartz beaker together with 5 ml. of 0.1N hydrochloric acid and 30 ml. of water. The solution was boiled for 2 minutes and then quickly cooled in an ice bath to 26±3° C. The stirring bar was added and the beaker placed in position for titration. The relationship between the 0.1N acid and 0.1N base having been previously determined, enough base was added to just neutralize the hydrochloric acid. The mannitol was then added and the solution titrated with the 0.01N base. As previously, the end point was taken as the maximum pH rise per unit quantity of base added.

Neutralization to a Predetermined pH. It was soon seen that the above method of adjusting the pH prior to adding the mannitol was not too reproducible and gave erratic results. On the basis of this information, it was decided to make a series of runs in which the pH was adjusted to predetermined values. Three such series were run using pH adjustments of 5.5, 6.0, 6.5, 7.0, 7.5, and 8.0 with borax solutions of concentrations such that each sample contained 0.2704, 0.7099, and 1.355 mg. of boron. Borax was used in place of boric acid because it was felt the crystallization and storage procedures used would give a very pure product.

The results of this investigation were not as informative as had been hoped. However, by noting the pH at the theoretical end point for each adjusting pH for the various solutions, it was decided that an adjusting pH of 6.0 and an end point pH of 7.8 were the most mutually satisfactory.

Use of Predetermined Adjusting and End Point pH.

A few boric oxide samples were then run using the procedure originally outlined but using the adjustment and end point pH's mentioned above, as well as the modified combustion technique. In precision, the results improved considerably, but they were still quite far removed from the theoretical value.

Since the combustion of the samples seemed to proceed smoothly, it was felt that the error remained with the titration procedure. Five borax solutions were made up of strengths such that the samples used contained 4.5679, 2.7407, 1.3704, 0.9136, and 0.4568 mg. of boron. These samples were placed in a beaker, 5 ml. of 0.1N acid and 30 ml. of water added, the solution boiled, cooled, and placed in position for titration. The pH was adjusted to 6.0, mannitol added, and the solution titrated with the 0.01N base. The end point was taken as the quantity of base necessary to reach a pH of 7.8.

The results of this series were tabulated and found to be reproducible but low in value. The plots of pH vs. milliliters of base were re-examined and other tables prepared in which the pH was read at increasingly higher values. The optimum value was found to be 8.40 as shown in Table 1. The results were improved considerably by this modification but were still too far in error to be acceptable. A few runs were then made using samples containing 4.5679 and 0.9136 mg. of boron, adjusting the pH at which the mannitol was added to lower values. It may be seen in Table 2 that a pH of 5.20 to 5.40 was best for the two concentrations tried.

Modification of Reflux Technique.

It was recognized quite soon in this research that recovery of the boric oxide by heating water in the combustion tube was incomplete. Consequently, it was decided to attempt to remove the oxide by setting the combustion tube upright, with a water jacket around its upper end, so water boiling in a flask would reflux in the combustion tube and continuously wash down into the flask any combustion products.

The apparatus employed is illustrated in Figure 4. This new procedure gave much better washing and was far easier to control than

Table 1

Percentage Error Found
When Using Various pH Values for the End Point

Mg. Boron (Theory)	pH 7.8	pH 8.2	pH 8.4	pH 8.6
4.5679	- 3.31	- 2.78	- 2.58	- 2.57
2.7407	- 2.54	- 1.93	- 1.71	- 1.75
1.3704	- 1.19	- 0.91	- 0.47	- 0.61
0.9136	- 0.92	- 0.52	- 0.38	- 0.78

Table 2

Percentage Error Found
When Adjusting to Various pH Values Before Adding Mannitol

Mg. Boron (Theory)	pH 5.8	pH 5.5	pH 5.2
4.5679	- 2.11	- 1.17	- 1.02
0.9136		- 0.63	+ 0.21

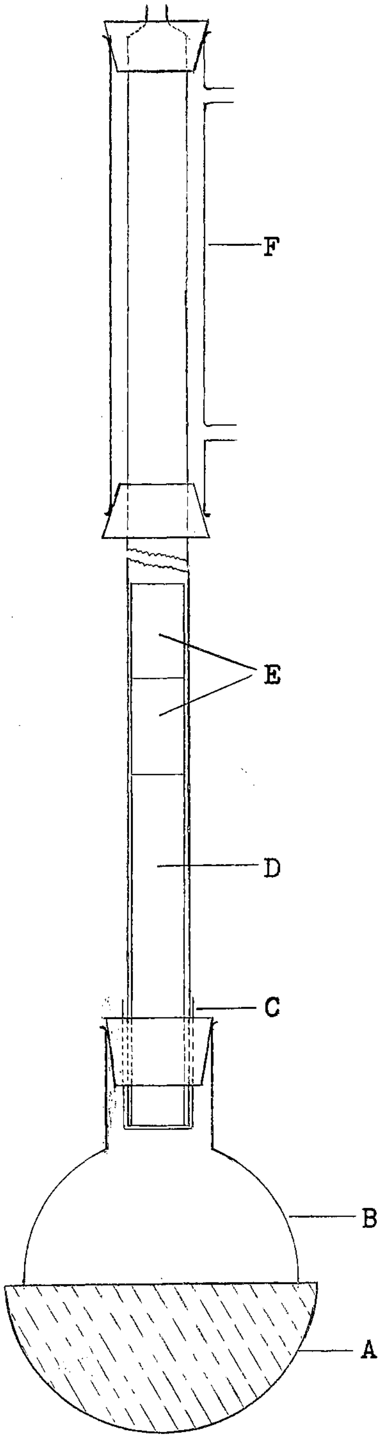

Figure 4

Reflux Apparatus

A.	Heating mantle	D.	Platinum tube
B.	Quartz flask	E.	Platinum stars
C.	Platinum retaining wire	F.	Water jacket

the previous one. Since it was desired to eliminate all possible sources of error, boron-free flasks were used to boil the reflux water (26). These flasks were found to be very sensitive to thermal shock, however, and were abandoned in favor of quartz flasks. The combustion tube was refluxed for 1 hour with 25 to 30 ml. of water added through the exit end of the combustion tube. After refluxing, the boric acid solution was cooled in the flask with an ice bath, then quantitatively transferred to a quartz beaker and titrated. A second 1-hour refluxing was made and the result of the titration of this solution subtracted from the first. It was thought that this "blank" would cancel any sources of error from rubber stoppers, slight acidity or basicity of mannitol, etc.

Fusion of Boric Oxide into Quartz.

The results using this method were much closer to the theoretical but were still a little low. Since the quartz combustion tube was by now in rather poor condition, a new one was prepared. In the first run it was noticed that a glazed spot remained on the inner surface of the tube even after several hours of refluxing. The spot was in the same location as the black area which had to be burned off at 1000° C. A second run was made with the tube rotated 180° to see if a second glazed area would appear. It was found, as previously, where the black area had been burned off. With the results having been low in each determination, it was felt that the error was due to boric oxide being fused into the quartz at the 1000° C. temperature employed.

In an attempt to eliminate the fusion of the oxide into the quartz, the tube was coated in the combustion area with several very thin layers of platinum. The layers were formed by employing a solution of platinum chloride in a mixture of turpentine and butanol. This solution was then applied to the tube with a cotton swab in as uniform a layer as possible. Air was drawn slowly through the tube, and the coated area was very slowly heated until the volatile fractions of the turpentine and the butanol were distilled off. The blackened area was then strongly heated leaving a very thin layer of platinum.

One run was made with the combustion tube coated in this manner. The result was a little high but indicated that the new approach was at least partially successful. Since the platinum coating peeled in the area which had been subjected to the 1000° C. temperature, a platinum tube was obtained to cover the combustion area. The relative positions of the stars, platinum tube, etc. in the combustion tube are shown in Figure 5.

Modification of Reflux Time and Blank; Final Adjustment of pH.

In view of the high result obtained using the platinum-coated tube and the initial pH of 5.20, it was felt that by adjusting the pH to 5.40, better results might be obtained. At this lower pH, any hydrochloric acid still present would be titrated as boric acid thus giving an erroneously high value for the boron percentage. Also, the refluxing periods were increased to 2 hours to more nearly insure removal of any fused boric oxide. From the sum of the two titrations was subtracted a blank. This blank was obtained by placing approximately 50 ml. of distilled water in a quartz beaker together with 5 ml. of hydrochloric acid. After boiling 2 minutes then cooling, it was titrated using mannitol, etc.

A number of runs were made on the phenylboric oxide using these modifications, the results of which are shown in Table 3.

Experiments with Tri-α-naphthylboron.

Before synthesizing any new compounds, two runs were made on tri-α-naphthylboron. This compound had been stored for about a year and because

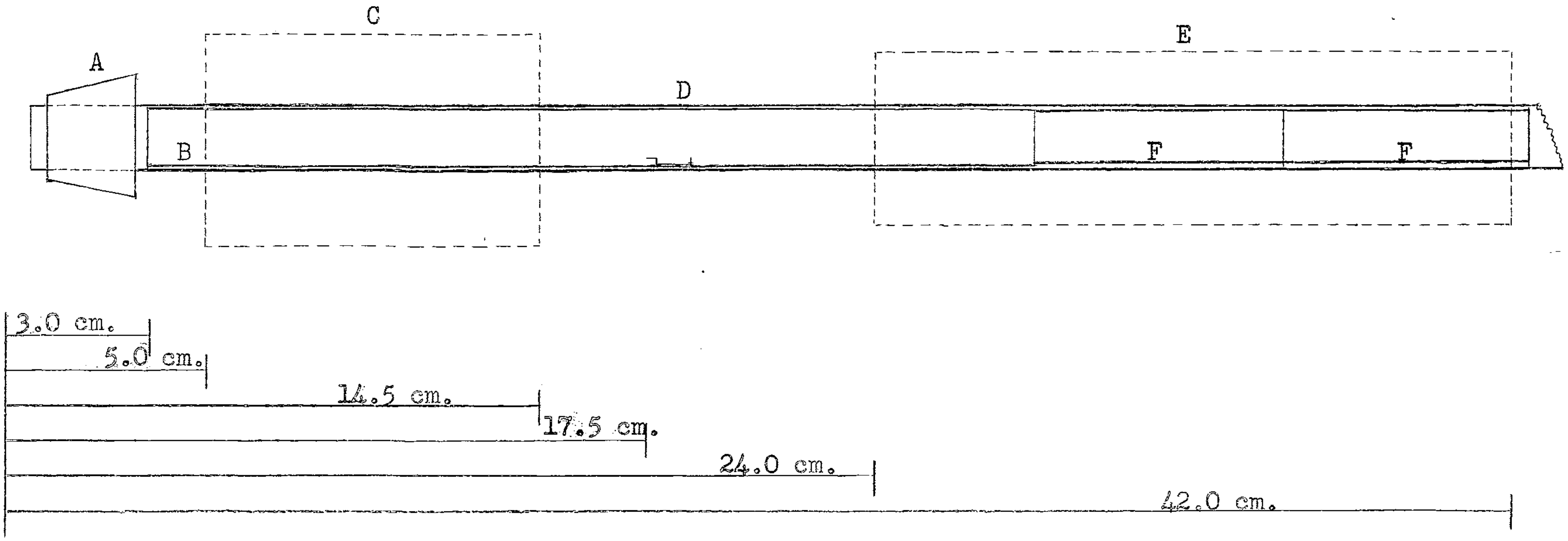

Figure 5

Placement of Platinum Ware and Sample Boat in Combustion Tube

A. Rubber stopper
B. Platinum tube
C. Sample burner
D. Sample boat
E. Stationary furnace
F. Platinum stars

Table 3

Phenylboric Oxide
Theoretical Boron: 10.41%

Sample (mg.)	Mg. Boron (Theory)	Mg. Boron (Exp.)	Boron % (Exp.)
14.754	1.536	1.550	10.51
14.627	1.523	1.516	10.36
16.488	1.716	1.735	10.52
11.691	1.217	1.243	10.63
12.674	1.319	1.303	10.28
		Average:	10.46
		Average deviation:	0.11

of a low melting point and an odor of naphthalene, its purity was questioned. However, it was thought that the runs might be of interest from a combustion standpoint because of the relatively low boron percentage of 2.76. The first run was made with the combustion procedure used on the phenylboric oxide. The result was that a large amount of brown distillate, which proved very difficult to burn without its distilling out of the combustion tube, condensed just beyond the stationary furnace. On the second run the oxygen flow was lowered to 3 ml. per minute and the sample burner, with its temperature reduced to 450° C., was placed about 2 inches from the boat. A small coil of platinum foil was placed inside the platinum tube just in front of the stationary furnace and heated to dull redness with a Bunsen burner. It was hoped that this high temperature decomposition center would give better combustion than the platinum stars alone. The sample burner was advanced slowly taking an hour to reach the furnace. On reaching the furnace the temperature of the burner was raised to 1000° C. and the area heated for half an hour.

When this method was used, there was no brown distillate beyond the furnace; however, the experimental boron percentage was quite high indicating that the compound had partially decomposed. Since there was very little of the compound left, experiments with this substance were discontinued in favor of others.

<u>p-Phenetylboric Acid</u>.

<u>Use of Increased Furnace Temperature</u>. In the first runs on this compound, the incomplete burning experienced with the tri-α-naphthylboron was encountered. One run was made with the stationary furnace at 875° C. as opposed to the usual 750° C. The result obtained was very close to the theoretical in spite of the fact that a considerable amount

of brown distillate which appeared beyond the furnace had to be burned off. In order to burn this distillate, the combustion tube was slowly backed into the stationary furnace until the residue disappeared.

Use of Heated Platinum Coil. It was felt that in a good combustion only water and boric oxide crystals should be visible beyond the furnace. Three runs were then made using the heated platinum foil described for the burning of tri-α-naphthylboron. In each case, though no distillate appeared, the boron percentages were low. Since boric oxide when heated strongly and allowed to cool forms a very hard mass, it was believed that such a mass was being formed at the platinum coil and the refluxing procedure was not removing it. To check the point, the tube was refluxed for 2-hour intervals and the reflux water titrated. In each case the value obtained was considerably higher than that found with distilled water. This procedure was repeated until the tube gave a blank equal to that obtained from the distilled water.

The phenetylboric acid runs were begun again using the following combustion procedure. The sample burner was placed 7/8 to 1 inch from the boat and adjusted to 450° C. With an oxygen flow of 3 ml. per minute, the burner was slowly advanced until water was seen condensing beyond the furnace. The burner was not moved further until the condensation appeared to stop. This process was continued until the stationary furnace was reached. The burner temperature was then raised to 1000° C. and the area heated for 30 minutes.

It was found in making these runs that an initial refluxing of 2 hours followed by a 30-minute refluxing was sufficient. It is possible that an initial refluxing of 1 hour would be permissable providing no fused boric oxide was present on the tube.

Using this method, the results shown in Table 4 were obtained. Occasionally, however, a small amount of the distillate would appear if the oxygen flow became too slow or the burner was advanced too rapidly. If the amount of the distillate was small and if it was burned off by backing the tube into the furnace, little or no error was introduced.

Final Technique for Removal of Carbon Dioxide. It should be noted in Table 4 that the average deviation, 0.03%, is considerably smaller than that obtained with the phenylboric oxide, 0.11%. It may be recalled that in the phenylboric oxide runs, the reflux water was cooled in the quartz flask then poured into a quartz beaker for titration. It had been suggested that this might be a source of error due to carbon dioxide being absorbed by the solution. In the runs on phenetylboric acid, the reflux water was cooled in the quartz flask only enough to enable the operator to pour the water into a quartz beaker. The 5 ml. of hydrochloric acid was then added to the beaker and the solution boiled for 2 minutes. At the end of the boiling period, the covered beaker was placed in ice and cooled as rapidly as possible. When the solution had reached a temperature of 28-29° C., the beaker was placed in position and the usual titration procedure carried out.

p-Phenoxyphenylboric Acid and n-Butyl Borate.

The runs of the p-phenoxyphenylboric acid and the n-butyl borate were made using the combustion technique and the boiling procedures just outlined. The results of these runs are shown in Tables 5 and 6.

Because of the ease of hydrolysis and volatility of n-butyl borate, the following procedure was necessary in weighing out the samples. The platinum boat was placed in a micro weighing piggy, counterbalanced with another piggy to avoid buoyancy errors, and weighed. The boat was then removed from the piggy and 3 to 4 drops of the borate added by means of

Table 4

p-Phenetylboric Acid
Theoretical Boron: 6.52%

Sample (mg.)	Mg. Boron (Theory)	Mg. Boron (Exp.)	Boron % (Exp.)
13.638	0.889	0.882	6.47
17.773	1.159	1.164	6.55
12.212	0.796	0.798	6.54
17.469	1.139	1.143	6.54
16.391	1.069	1.069	6.52
		Average:	6.51
		Average deviation:	0.03

Table 5

p-Phenoxy Phenylboric Acid
Theoretical Boron: 5.07%

Sample (mg.)	Mg. Boron (Theory)	Mg. Boron (Exp.)	Boron % (Exp.)
17.572	0.891	0.883	5.02
20.230	1.166	0.999	4.94
20.832	1.056	1.052	5.05
20.705	1.050	1.055	5.09
17.528	0.889	0.897	5.12
		Average:	5.07
		Average deviation:	0.05

Table 6

n-Butyl Borate
Theoretical Boron: 4.70%

Sample (mg.)	Mg. Boron (Theory)	Mg. Boron (Exp.)	Boron % (Exp.)
23.273	1.094	1.084	4.66
21.318	1.002	0.996	4.67
22.049	1.036	1.025	4.65
16.308	0.767	0.761	4.67
23.229	1.092	1.092	4.70
		Average:	4.67
		Average deviation:	0.01

a dry eye dropper. As quickly as possible, the boat was replaced in the piggy and its weight determined. The piggy containing the boat was taken immediately to the combustion train where the boat was placed immediately in the tube, and the entrance end was closed by a rubber stopper containing the oxygen inlet tube. With the oxygen flow adjusted to 3 ml. per minute, the stationary furnace was turned on and allowed to come to temperature. The sample burner was then turned on and the combustion was made in the manner previously outlined.

Outline of Final Accepted Procedure.

The procedure in its final form is outlined below for convenience and clarity.

1. A sample containing between 0.8 and 1.5 mg. of boron is weighed in a platinum weighing boat.

2. The boat is placed in the combustion tube and pushed to a point approximately 2.5 inches from the stationary furnace. The tube should have been swept with oxygen prior to introducing the boat and the stationary furnace adjusted to 850° C. For solids with low melting points or for liquids, it is better to turn the furnace on after the boat is in position since the platinum tube will conduct considerable heat and a premature burning may occur.

3. The sample burner is placed about 1 inch from the boat and its temperature is adjusted to 450° C. It is allowed to remain in this position for several minutes, then slowly moved forward until condensation of water vapor is noticed beyond the furnace. When no new condensate seems to be forming, the burner is again moved and this process continued until the stationary furnace is reached. At this point there will normally be considerable water vapor condensed on the tube and a small band of boric oxide crystals formed at a point approximately 1 inch from the furnace.

4. The temperature of the burner is then raised to 1000° C. and the burner is left in position for 30 minutes. The boat is located so that it is well inside the area heated by the burner.

5. At the end of the 30-minute heating, the burner and furnace are turned off, the combustion tube removed and allowed to cool. The boat is slid from the tube into the quartz flask and the platinum retaining wire (see Figure 4) moved into a position such that the platinum ware will not slide from the tube when it is placed in an upright position.

6. The water condenser is placed on the tube and the tube set in an upright position in the quartz flask. The rubber stopper should fit tightly in the flask so that no water vapor can escape.

7. Water is then flushed through the tube until 25 to 30 ml. are collected in the flask. The heating mantle is turned on and the water refluxed for 2 hours.

8. At the end of the reflux period, the mantle is removed and a pan of ice water placed around the flask until it is cool enough to handle. The flask is removed and the boric acid solution quantitatively transferred to a clean quartz beaker. The flask is again placed in position, water is added, and the whole is refluxed for a 30-minute period.

9. Five ml. of 0.1N hydrochloric acid is added to the beaker, the latter is covered with a watch glass, and the solution is boiled for 2 minutes. It is then placed in ice water and cooled to room temperature.

10. The stirring bar is added and the beaker is placed in position for titration with nitrogen flowing over the surface of the solution.

11. The pH of the solution is adjusted to 5.40, 2 g. of mannitol is added, and the resulting solution is titrated with 0.02N sodium hydroxide. A pH of 8.40 is taken as the end point.

12. The solution resulting from the second refluxing is treated in the same manner.

13. From the sum of the two titrations is subtracted the value of a water blank. The net result is then used for determining the percentage of boron in the sample.

SUMMARY

It has been shown that micro samples of organoboron compounds can be burned by a modified micro combustion procedure; the boric oxide formed by the combustion can be quantitatively removed by refluxing water in the tube; the resulting boric acid solution can be titrated with sodium hydroxide using mannitol as a complexing agent with an initial pH (before adding mannitol) of 5.40 and an end point pH of 8.40. Best results are obtained when the boron content of the solution is between 0.8 and 1.5 mg.

With due care given to the combustion technique and the titration, excellent results have been obtained on four organoboron compounds.

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