

THE DETERMINATION OF CARBON, HYDROGEN AND NITROGEN  
IN ORGANOBORON COMPOUNDS AND OF BORON AND  
CARBON IN BORON CARBIDES

By

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### Dedication

This work is dedicated to my wife. With her understanding the work was begun, with her patience it was continued and through her perseverance it was finished.

Also, it is dedicated to my parents, who started it all.

## TABLE OF CONTENTS

Chapter		Page
I.	INTRODUCTION AND HISTORY . . . . .	1
II.	SCOPE OF INVESTIGATION . . . . .	4
III.	REAGENTS AND MATERIALS . . . . .	5
IV.	APPARATUS . . . . .	11
V.	EXPERIMENTAL PROCEDURE AND RESULTS . . . . .	15
	Determination of Carbon and Hydrogen . . . . .	15
	Determination of Nitrogen . . . . .	28
	Determination of Carbon and Boron in Boron Carbides . . . . .	32
VI.	DISCUSSION . . . . .	47
VII.	SUMMARY . . . . .	52
VIII.	BIBLIOGRAPHY . . . . .	53

## LIST OF TABLES

Table	Page
1. Data Supplied on Boron Carbide Samples . . . . .	8
2. Comparison of Results with Various Techniques . . . . .	23
3. Determination of Carbon . . . . .	25
4. Determination of Hydrogen . . . . .	25
5. Determination of Carbon . . . . .	26
6. Determination of Hydrogen . . . . .	26
7. Analysis of Pyridine-boron Trifluoride . . . . .	29
8. Determination of Nitrogen . . . . .	33
9. Determination of Carbon in Boron Carbide . . . . . Sample C/B = .25	35
10. Results with the Induction Furnace of Durbin and Winget . . Sample C/B = .25	35
11. Determination of Boron and Carbon in Boron Carbides . . . .	45

## LIST OF FIGURES

Figure	Page
1. Sample Burner . . . . .	12
2a. Combustion Tube Packings - Non-nitrogenous Compounds . . . .	16
2b. Combustion Tube Packings - Amine-boron Trifluoride Compounds.	16
3a. Aspirator . . . . .	18
3b. Complete carbon and Hydrogen Combustion Train . . . . .	18
4a. Tube Packing for the Dumas Nitrogen Determination . . . . .	30
4b. Dumas Nitrogen Apparatus . . . . .	30
5. Pedestal with Sample Disk . . . . .	38
6. Combustion Tube for Leco Furnace with Pedestal and Disk . . .	39
7. Combustion Train used for the Analysis of Boron Carbides . .	41
8. Reflux Apparatus . . . . .	43

## INTRODUCTION AND HISTORY

Carbon and hydrogen in organic compounds may be determined by burning samples in a combustion tube in a stream of oxygen or air, passing the gaseous products over suitable oxidizing catalysts, and collecting the carbon dioxide and water. The method of measuring the carbon dioxide varies: it may be determined volumetrically in a suitable gasometer: it may be passed into a basic solution and titrated, or it may be absorbed by soda lime or a solid suspension of sodium hydroxide and weighed. Water is usually absorbed by a drying agent and weighed.

Carbon itself can also be determined by means of what is known as the "wet" method - i. e., by oxidizing the sample with oxidizing solutions. There are many mixtures of oxidizing agents used for this type of analysis, e. g. potassium and silver dichromates in concentrated sulfuric acid or chromic oxide in concentrated sulfuric acid. The gases produced by this wet oxidation are further catalytically combusted in a stream of oxygen, then absorbed in a suitable titration vessel or measured manometrically.

Total carbon may also be determined by the Parr bomb method. In this method, the sample is mixed with sodium peroxide and fused. The product is taken into solution, made acid and the carbon dioxide distilled and titrated.

When certain organoboron compounds, particularly those containing boron linked to carbon, are burned at the usual combustion



temperatures (700-800°C.) a black residue remains after combustion and the resulting carbon values are low. Thus, Ainley and Challenger (1) reported low carbon results for derivatives of phenylboric acid, "owing to the fusion of boric oxide round particles of unburned carbon during the combustion". Similarly, when the Parr peroxide total carbon bomb was used by Seaman and Johnson (27) for the analysis of phenylboric acid and its derivatives, they reported low carbon values and noted that there always were "a few specks of unoxidized carbonaceous material in the fused mass".

Yabroff and Branch (37) carried out combustions in a tube containing two parts copper oxide and one part lead chromate in an atmosphere of air. Copper was used at the end of the tube to reduce oxides of nitrogen. The carbon percentages were always low and it was suggested that this was due to the "occlusion of charred particles by the boric oxide formed".

Cook, et al (4) obtained erratic results for carbon while Snyder, et al (29) who used a semimicro procedure, stated that the combustion must take place over the catalyst if acceptable results are to be obtained. In a later paper, however, Snyder and Wyman (31) reported that they were unable to analyze substituted naphthaleneboronic acids by a dry combustion procedure.

In 1937, H. Roth (23) published a paper on the micro-elementary analysis of organoboron compounds. He, with others, (5, 22) postulated that there are two reasons for low carbon values obtained with dry combustion procedures: the formation

of boron carbide, and the occlusion of carbon in the residual boric acid melt. Mixing the sample with copper oxide did not alleviate this difficulty. By mixing the compound with vanadium pentoxide and then burning, however, he was able to obtain acceptable results for salts of the chelates of hydroxy organic acids and boric acid and also for the  $\beta$ -diketone boron difluorides. Nitrogen determinations by the Dumas method were not acceptable even when vanadium pentoxide was used, but Kjeldahl determinations yielded good results.

Morgan and Tunstall (16) mixed their samples of  $\beta$ -diketone boron difluorides with powdered copper oxide and obtained acceptable results.

Carbon in boron carbide has been determined by combustion in a stream of oxygen with the sample under a layer of lead oxide and lead filings (6, 15, 25). Wet oxidation procedures with chromic oxide-sulphuric acid mixtures have also been used (12). Glasser (7) determined carbon by a combustion procedure employing a Lindberg carbon determinator. In all cases, a separate sample was oxidized by fusion or wet oxidation and the boron determined by titration with base after the addition of mannitol. (6, 7, 15, 26)

## SCOPE OF INVESTIGATION

The purpose of this research was to develop a new micromethod for, or adapt an existing one to, the determination of carbon, hydrogen and nitrogen in organoboron compounds and to test it on compounds of the types which are reported to give low results. Also, it was our purpose to investigate the possibility of simultaneously determining boron and carbon in boron carbides.

A consideration of the possible procedures led to the conclusion that some modification of the micromethods developed by Pregel (21) and by Niederl and Niederl (17) would be most promising; for the basic techniques are already known to a large number of analysts, and such methods have been widely applied to organic compounds in general. It was hoped that the employment of higher temperatures would drive these combustions to completion, especially if temperatures high enough to volatilize boric oxide were used.

## REAGENTS AND MATERIALS

Dehydrite (anhydrous magnesium perchlorate).

This was purchased from A. H. Thomas Co., Philadelphia, Pa. and used as the water absorbent in carbon combustions.

Ascarite (sodium hydroxide-asbestos absorbent).

This, in 8-20 mesh form, was also purchased from the A. H. Thomas Co., Philadelphia, Pa. and used as the carbon dioxide absorbent in the carbon combustions.

Carbon Dioxide.

The carbon dioxide used for the Dumas determination of nitrogen was an especially purified quality of tank carbon dioxide obtained from the Ideal Dry Ice Mfg. Co., Ada, Oklahoma. It was found necessary to bleed a new tank slowly for several hours before acceptable blanks could be obtained.

Phenylboric Acid and Phenylboric Oxide.

Phenylboric acid was first prepared by the method of Seaman and Johnson (27) from phenylmagnesium bromide and methyl borate. It was found, however, that the acid very readily dehydrated to the oxide and that it was difficult to be sure that the product was not a mixture of the two. Consequently, part of the product was converted to phenylboric oxide by placing it in a vacuum desiccator over activated alumina until the product reached constant weight. The remainder was recrystallized from water and dried on the filter by drawing air through the mass for two

hours. Tests of the resulting phenylboric acid indicated that this was sufficient to dry it but not enough to cause appreciable dehydration to the oxide. The acid had a melting point of 213-5°C. (literature values 216°C. (9) and 215.5-219°C. (27)); the oxide melted at 206-7°C. (literature value, 190°C. (14)).

#### Tri- $\alpha$ -naphthylboron.

This compound was prepared from boron trifluoride and  $\alpha$ -bromonaphthalene by the Grignard reaction as described by Brown and Sefeshi (3). Its melting point (in vacuo) was 203-4°C. (literature values, 203-5°C. (11), and 206-7°C. (3)).

#### n-Butylboric Acid.

This was produced by the reaction of n-butylmagnesium bromide and methyl borate at -75°C. as described by Snyder, et al (29). The product, after recrystallization from toluene, was dried in a stream of nitrogen at room temperature for 10-14 hours and then analyzed. Immediate analysis and great care in handling were found necessary owing to the fact that this compound dehydrates readily and undergoes autooxidation on exposure to air (30).

#### Acetanilide-boron Trifluoride.

Ten grams of acetanilide was dissolved in 80 ml. of chloroform and the resulting solution was poured into an excess of boron trifluoride in diethyl ether. The needle-like crystals which appeared after 10 minutes were filtered and washed, while wet, with ether. They were then stored in vacuo over calcium chloride for 48 hours before analysis. The product melted, with decomposition, at 143-9°C. (literature value, 133°C. with decomposition (32)).

### Pyridine-boron Trifluoride.

Boron trifluoride was passed through 10 g. of pyridine dissolved in 20 ml. of benzene (2, 34). The precipitate which appeared after some time was washed with benzene, dissolved in acetone and reprecipitated with ether. The solid product was stored in a desiccator over sulfuric acid.

### Miscellaneous Amine-boron Trifluoride Complexes.

The following amine-boron trifluoride compounds were obtained through the courtesy of Dr. P. L. Pickard of Oklahoma University: benzylamine-boron trifluoride, o-chloroaniline-boron trifluoride, diethylamine-boron trifluoride, and o-bromoaniline-boron trifluoride.

### Boron Carbides.

Samples of various boron carbides were obtained through the courtesy of Dr. P. W. Gilles of Kansas University, who also provided the information shown in Table 1.

### Standard Carbon Dioxide-free Sodium Hydroxide.

A solution approximately 0.05N was prepared by taking 3.1 ml. of 16N sodium hydroxide from which insoluble carbonate had been filtered and diluting it to one liter with carbon dioxide-free distilled water. The resulting solution was kept in a one-liter stoppered polyethylene bottle, protected from the atmosphere by means of a drying tube filled with Ascarite and Dehydrite. A delivery tube of latex rubber inserted in the stopper was used to fill the burette. The solution was then standardized against potassium acid phthalate (Merck No. 73353), and against a standard sodium borate decahydrate solution.

Table 1. Data Supplied on Boron Carbide Samples

Sample No.*	Production Conditions			Particle Size	Extra Phases***	
	C/B**	Crucible	Temp. (°C.)			Time (min.)
1	0.25					
3	0.20	graphite	1900	120	-325 mesh	graphite, Al <sub>2</sub> O <sub>3</sub> (both very faint)
5	0.15	graphite	2060	120	-400 mesh	none
6	0.10	graphite	1960	120	-400 mesh	Al <sub>2</sub> O <sub>3</sub>
7	0.108	tantalum	2115	60	-400 mesh	Al <sub>2</sub> O <sub>3</sub>
8	0.05	graphite	2070	30	-400 mesh	Boron?
9	0.05	graphite	2000	15	-400 mesh	Boron?
11	0.00	graphite	2090	8	-400 mesh	Boron?

\* Numbers are those used by Dr. Gilles.

\*\* Atomic ratio of unsintered mixture.

\*\*\* As identified from x-ray diffraction powder pattern. According to Dr. Gilles, all the samples probably contain Al<sub>2</sub>O<sub>3</sub> as a contaminant since they were ground in an Al<sub>2</sub>O<sub>3</sub> mortar. Also, sample 11 which is listed as free from carbon is suspected to contain appreciable carbon because of pickup from the graphite crucibles used for the annealing.

A second solution approximately 0.1N was made and standardized in a similar manner.

#### Sodium Borate Decahydrate.

Sodium borate decahydrate was obtained by recrystallization of the powder (Mallenckrodt Analytical Reagent) from water in the ratio of 50 ml. water to 15 g. borax, the temperature being kept below 55°C. to eliminate formation of the pentahydrate. The damp crystals were washed with two portions of ethyl alcohol followed by two portions of ether (each portion being 5 ml. per 10 g. of crystals) (8). They were then stored in a desiccator over a solution saturated with both sodium chloride and sucrose. (13).

#### Mannitol.

The mannitol used in the boric acid titration was Fisher Certified Reagent grade.

#### Nitrogen.

The nitrogen used in the titrations to prevent entrance of carbon dioxide from the air, was a commercial tank (water pumped) type purchased from Linde Air Products Co., New York, N. Y. It was purified by passage through 1N sodium hydroxide to remove any carbon dioxide and then through a water trap.

#### Distilled Water.

Each batch of distilled water was found to have a slightly different titration blank. Quantities of the water, therefore, were stored in a large 6-gallon polyethylene bottle. This also excluded any possible error from the leaching of boron from glassware during the period of storage.



Oxygen.

A commercial tank type of oxygen, purchased from Linde Air Products Co., New York, N. Y. was used for the carbon and hydrogen determinations.

Boron Trifluoride.

The boron trifluoride used for the synthesis of amine-boron trifluoride compounds was a commercial tank type purchased from The Matheson Co., Inc., Joliet, Illinois.

Packing Materials.

In preparing the materials used for packing the combustion tubes, the suggestions of Niederl and Niederl were followed (20).

Boron-free-glass Chips.

Damaged boron-free glassware purchased from E. H. Sargent & Co. (S-33857) was broken in a mortar to a suitable size and used in the combustion tube to prevent the boric oxide smoke from escaping.

## APPARATUS

A line-operated Beckman pH meter, Model H2, was used for all titrations. The solution was stirred with a magnetic stirrer (Magne Stir, Labline Inc., Chicago).

A Sargent No. 3-36400 (E. H. Sargent & Co.) resistance furnace was used for determination of carbon and hydrogen in non-nitrogenous compounds, while a Sentry electric furnace No. 23815 (The Sentry Co., Foxboro, Mass.) capable of reaching 1400°C., was used for those compounds containing nitrogen and also for some experiments on the determination of carbon in boron carbide.

The heater used to burn the sample is shown in Figure 1. The outside cylindrical casing (A) and the cover (B) are constructed of aluminum with ends (E) of Transite. The heater coil (C) is made of 18 feet of nichrome wire B. and S. No. 20 (0.67 ohm per ft.); the space between the coil and aluminum shell is filled with Celite (D) to provide heat insulation. It was connected through a 5-ampere ammeter to a 500-watt Variac at points (F), and calibrated by means of a thermocouple placed within the combustion tube.

An experimental induction furnace, constructed by Durbin and Winget (36), was borrowed from the Oklahoma A. & M. Department of Physics and used for preliminary studies with boron carbide. The oscillator circuit of this furnace was rewired to be symmetrical, since unbalanced parasitic oscillations were causing unequal loading of the tubes. At the same time, the circuit was modified to

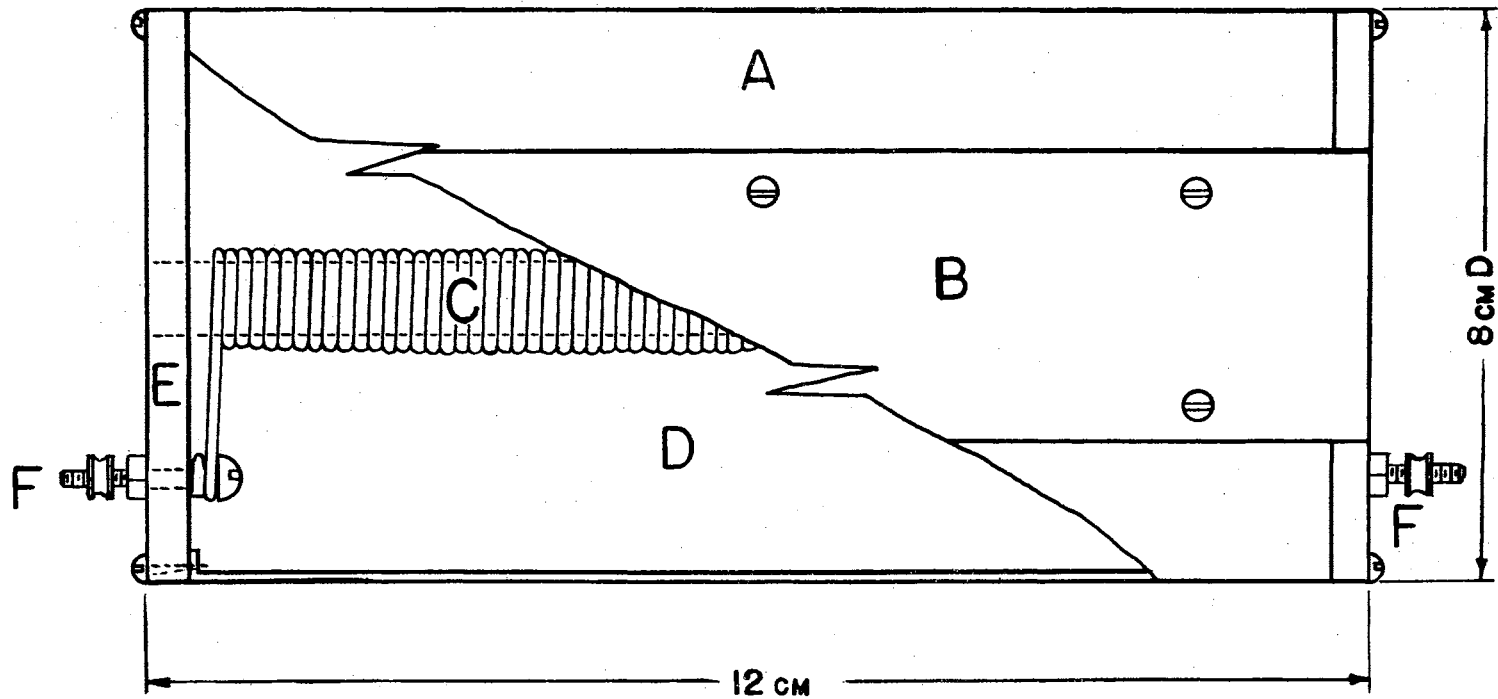


Figure 1. Sample Burner

handle larger power tubes (Eimac 250TH). A 5-volt, 30-ampere filament transformer was substituted for the 10-volt transformer used with the original T-155 oscillator tubes. The grid resistor was replaced with a 500-ohm 50-watt fixed resistor in series with a 1000-ohm 50-watt variable one. The total resistance thus could be varied according to the plate voltage used; however, most experiments were conducted at a plate voltage of 4000 volts and a grid resistance of 1180 ohms. The grid current or feedback was obtained by tapping into the tank coil; the amount of current was determined by the number of turns tapped. A setting of 2 turns was found to give a grid current of 150 ma. when the set was detuned. On tuning to resonance with the variable tank capacitor, the grid current decreased to 93 ma. (the operating current for the tubes at 4000 volts) and the plate current increased to a maximum of 320 ma. Transfer of power to the secondary or work circuit was accomplished by a single turn of 1/4" copper tubing about the tank coil. Closer coupling caused overloading with consequent cessation of oscillation. A work coil was constructed of 1/4" copper tubing with couplings to allow water to flow through the coil for cooling. This inductor consisted of two coils; the inner one of 7/8-inch diameter and 13 turns in 4 3/4", and the outside coil of 1 3/4-inch diameter and 13 turns in 4 1/4". These were connected in such a way as to result in addition of the inductance. In this way, a larger inductance per unit length and diameter was achieved and closer electrical coupling could be obtained with the work (i. e., the

platinum combustion boat). The operating or resonant frequency was 4-6 mc. A more detailed description of the construction of this furnace may be obtained from the thesis of J. C. Winget (35).

A Leco high-frequency induction furnace, Model IH-10C, Serial No. 1H-10-173 (Laboratory Equipment Corporation, St. Joseph, Michigan) was used for the final experiments with the boron carbides.

Temperatures in the induction furnaces were measured with an optical pyrometer (Pyrometer Instrument Co., New York, Serial No. 6355).

## EXPERIMENTAL PROCEDURE AND RESULTS

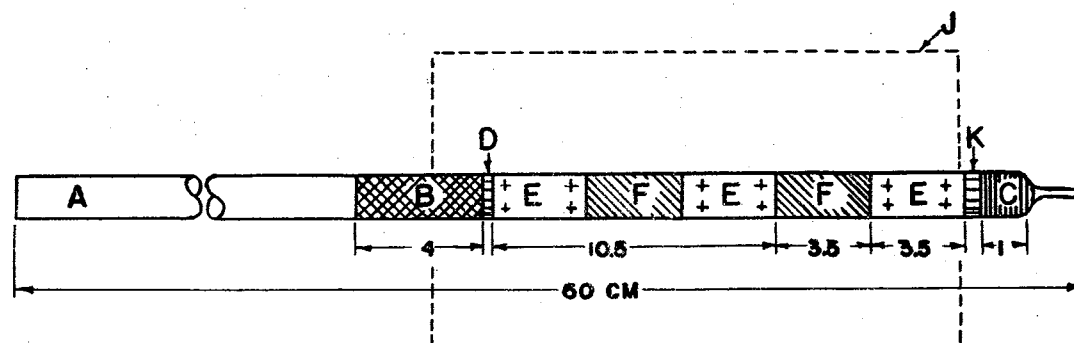
### Determination of Carbon and Hydrogen.

The combustion tubes used for the determination of carbon and hydrogen in organoboron compounds (Figure 2a and 2b) were made of clear fused quartz, 1.0 cm. O. D., and drawn to a 3-mm. tip at their exit ends. The "simple band" filling (Figure 2a) is that described by Niederl and Niederl (19) but the "combination band" filling (Figure 2b) which was employed for the amine-boron trifluoride complexes was modified to include a 6.0-cm. band of fine silver wire, B. and S. No. 30, placed after the platinum gauze to remove halogen. After a large number of runs had been made, this silver wire was found to be badly discolored. The quartz tube at this point was so weakened that a section had to be cut out, the remaining parts washed, fused together, and the resulting tube re-packed. The increase in the number of alternate bands of copper oxide and platinized asbestos was done to accommodate the increase in heating area provided by the Sentry furnace.

The packed portion of the tube was heated to  $750 \pm 25^\circ\text{C}$ . and a separate sample burner (Figure 1) was used to burn the sample at  $1000-1100^\circ\text{C}$ .

A schematic diagram of the assembled train used for compounds containing nitrogen is given in Figure 3b. When nitrogen is not present, the heating mortar (I) is eliminated and the tube shown in Figure 2a is used.

A. Non-nitrogenous Compounds



B. Amine-boron Trifluoride Compounds

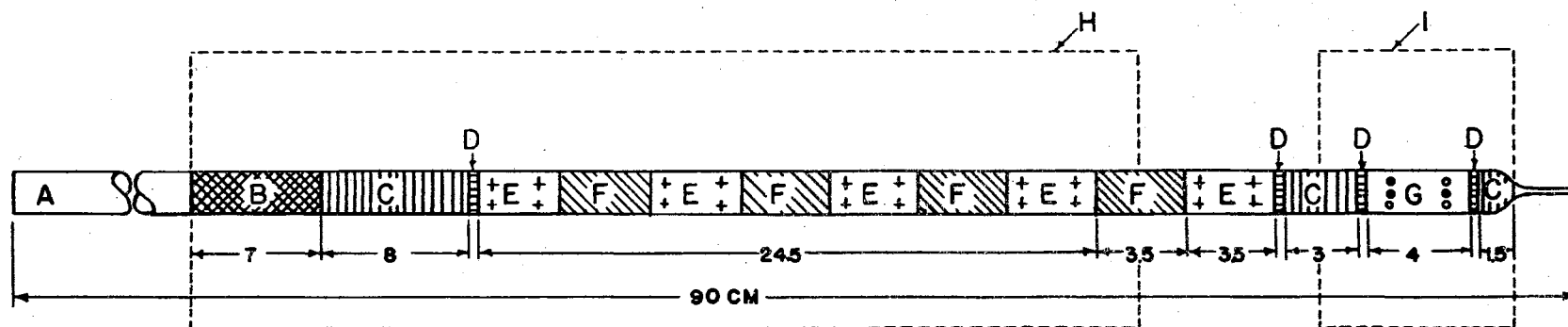


Figure 2. Combustion Tube Packings

## Legend for Figure 2a and 2b

- A - Quartz combustion tube, 1.0 cm. O. D., with 3-mm. O. D. tip.
- B - Platinum gauze.
- C - Silver wire, B. and S. No. 30 wound loosely around a 3-mm. glass rod to form rolls to fill the tube.
- D - Asbestos plugs (1-2 mm. thick).
- E - Copper oxide.
- F - Platinized asbestos.
- G - Lead peroxide pellets.
- H - Sentry electric furnace No. 23815, the Sentry Company, Foxboro, Mass.
- I - Heating mortar (filled with p-cymene, B. P. 175-178°C.).
- J - Sargent furnace, No. S-36400.
- K - Asbestos choking plug (4-6 mm. thick).



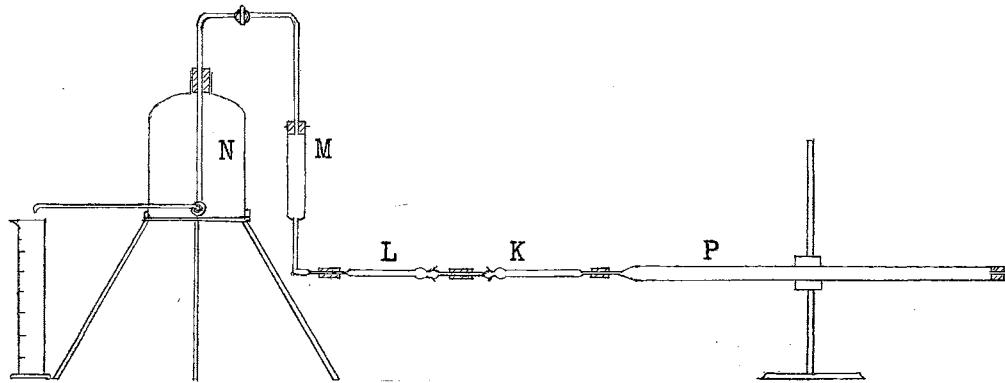


Figure 3a. Aspirator

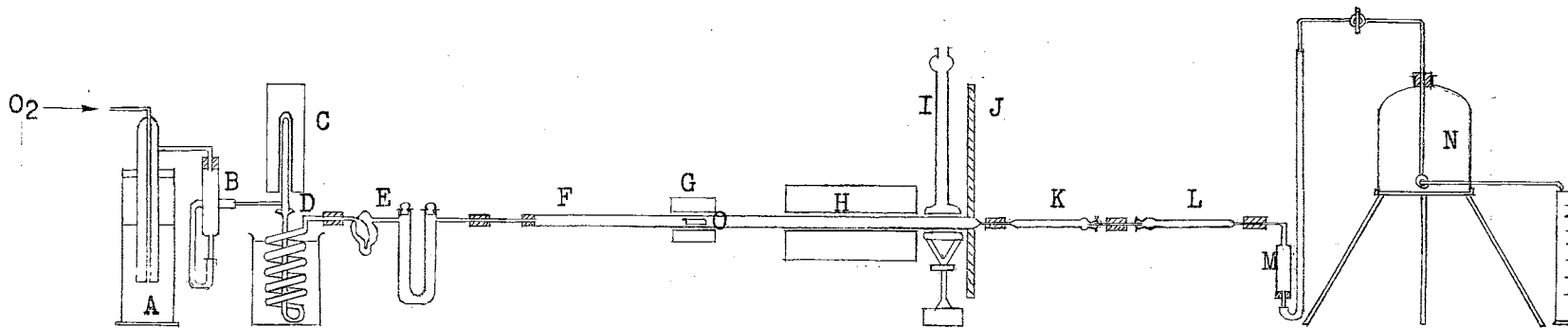


Figure 3b. Complete Carbon and Hydrogen Combustion Train

## Legend for Figure 3a and 3b

- A - Pressure regulator
- B - Drying tube
- C - Electric heater
- D - Preheater
- E - Bubble counter and U-tube
- F - Combustion tube
- G - Sample burner
- H - Furnace
- I - Heating mortar (filled with p-cymene, B. P. 175-178°C.)
- J - Baffle
- K - Water absorption tube
- L - Carbon dioxide absorption tube
- M - Safety tube
- N - Mariotte Flask
- O - Platinum boat
- P - Tube filled with Ascarite and Dehydrite

The oxygen pressure is fixed by the pressure regulator (A). The drying tube (B) removes any water from the oxygen which is then passed over hot copper oxide contained in (D) (to oxidize any organic impurities in the oxygen), and then cooled. It is then passed through a bubble counter and U-tube (E). Here, the speed of the oxygen passing through the combustion tube is observed with the bubble counter, and the carbon dioxide and water from the organic impurities are removed by the Dehydrite and Ascarite contained in the U-tube. The sample, in a platinum boat (O) is placed in the combustion tube (F) where it is burned with the sample burner (G). The resulting gases are passed through the packed portion of the tube, the latter being heated by furnace (H) to a temperature of  $750 \pm 25^{\circ}\text{C}$ . The heating mortar (I) is used when lead peroxide is a part of the packing. Lead peroxide, which is used for the absorption of the oxides of nitrogen formed when nitrogen-containing substances are burned, must be maintained at a constant temperature to insure proper moisture balance. The baffle (J) protects the rubber connections of (K) the water absorption tube and (L) the carbon dioxide tube from excessive heating. The safety tube (M) is filled with Dehydrite and absorbs any moisture which may emanate from the Mariotte Flask (N). The purpose of the Mariotte Flask (N) is to measure the volume of oxygen passing through the system and to maintain a slight suction to help overcome the resistance offered by the absorption tubes.

In any combustion it is necessary first to condition the

tube and packing in order to drive adsorbed carbon dioxide from the packing, activate the platinum catalyst, and establish moisture balance. The packing is conditioned by adjusting the furnace to  $750 \pm 25^\circ\text{C}$ ., passing oxygen through the train for 24 hours; and then burning a few benzoic acid samples.

In an actual run, samples were weighed on a microbalance in the platinum boat (O) and placed in the combustion tube (F). The absorption tubes (K and L) were then wiped with damp flannel and dry chamois. After they stood long enough to reach equilibrium with the atmosphere - usually about 15 minutes - the tubes were weighed. These tubes were then connected into the train, the oxygen flow rate was adjusted to 5 ml. per minute with the pressure regulator (A), and heat was applied about 5 cm. in front of the boat (O). With the conventional procedure the heater, at a temperature of about  $750^\circ\text{C}$ . was then moved slowly toward the furnace, taking about 5 minutes to reach the sample, 5 minutes to heat it directly, and 5 minutes more to reach the furnace (H) itself. A second burning was then performed as above, taking only 5 minutes for the whole procedure. The heater was then turned off and the combustion products swept through with 100 ml. of oxygen - the whole procedure consuming about 40 minutes and 200 ml. of oxygen. Finally, the tubes (K and L) were disconnected and 50 ml. of dry carbon dioxide-free air, obtained from the aspirator (Figure 3a) was passed through them. The tubes (K and L) were then wiped and weighed as before.

In order to obtain first-hand information on the normal behavior of boron compounds, a conventional combustion was tried first. A Vycor combustion tube was packed with a simple band filling (Figure 2(a)) and the train assembled. The packing was then conditioned as previously described. The procedure and apparatus were then checked by determining the carbon and hydrogen in purified benzoic acid. When acceptable determinations were obtained, phenylboric oxide was tried. As had been expected, the results for phenylboric oxide were low and a black residue remained in the boat (see Table 2).

It was then decided to change to the previously described quartz tubes since Vycor could not stand temperatures much above the normal combustion temperatures.

The quartz combustion tube was packed as indicated in Figure 2a, and then was conditioned and equilibrated as described earlier. The sample, contained in a platinum boat, was placed 6-7 cm. in front of the platinum gauze (B, in Figure 2a) and the heater (Figure 1) 2-3 cm. in front of the boat. For the analysis of relatively stable compounds such as phenylboric oxide, the heater temperature was adjusted immediately to 1000°C. It was left in its original position for 5 minutes and then was slowly moved to the platinum gauze over a period of 15 minutes. Without further movement of the heater, burning was continued for 10 more minutes or until all black residue was gone. The sample burner was turned off and the remaining gases were then flushed out for a period of 20 minutes more. The oxygen flow rate was maintained at 5 ml. per

Table 2. Comparison of Results with Various Techniques

Compound	Procedure	Carbon		Hydrogen	
		Found (%)	Theor. (%)	Found (%)	Theor. (%)
Benzoic Acid	Conventional	68.88	68.84	5.24	4.95
		68.70		5.51	
Phenylboric Oxide	*	67.42	69.34	5.34	4.82
		67.81		5.24	
Phenylboric Oxide	Conventional (sample layered with V <sub>2</sub> O <sub>5</sub> )	68.65	69.34	7.02*	4.82
Phenylboric Oxide	High heat until residue disappeared	69.46	69.34	5.60	4.82

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\* The high result is probably due to the fact that no precaution was taken to dry the V<sub>2</sub>O<sub>5</sub> before use.

minute throughout the combustion, a total volume of 250 ml. being used. The absorption tubes were then flushed with 50 ml. of dry carbon dioxide-free air, wiped in the usual manner and weighed.

For highly combustible compounds such as n-butylboric acid, the heater temperature was kept at 300-400°C. and the first burning completed as described before in 15 minutes. The heater was then moved back to its starting position and a second pass, requiring a period of 15 minutes with the heater at 1000°C. was used to burn any residue. The remainder of the operation was as described for the phenylboric oxide.

In all, four compounds i.e., phenylboric acid, phenylboric oxide, n-butylboric acid, and tri- $\alpha$ -naphthylboron, were used in testing this procedure (see Tables 3 and 4).

In determining carbon and hydrogen in amine-boron trifluoride complexes such as acetanilide-boron trifluoride, the burning procedure first tried was the same as that described for phenylboric oxide, the combustion tube packing, however, being as illustrated in Figure 2b. The compounds supplied by Dr. Pickard had been tested in his laboratory and seemingly were pure at that time.

Since no evidence of decomposition was visible, it was assumed that they still were pure on reaching this laboratory. The combustion analysis, however, gave poor results (see Tables 5 and 6) and before it finally was found that the samples were impure, several modifications of the procedure were tested in an effort to improve results.

Table 3. Determination of Carbon

Compound	Theor. (%)	No. Det'm.	Experimental		
			Av. (%)	Deviation from Mean Av. Max.	
Phenylboric Acid	59.10	5	59.12	0.06	0.13
Phenylboric Oxide	69.34	5	69.42	0.05	0.07
Tri- $\alpha$ -Naphthylboron	91.87	5	91.68	0.05	0.11
<u>n</u> -Butylboric Acid	47.15	5	47.08	0.05	0.07
Acetanilide-BF <sub>3</sub>	47.33	6	47.24	0.03	0.06

Table 4. Determination of Hydrogen

Compound	Theor. (%)	No. Det'm.	Experimental		
			Av. (%)	Deviation from Mean Av. Max.	
Phenylboric Acid	5.74	5	6.01	0.02	0.03
Phenylboric Oxide	4.82	5	5.14	0.04	0.08
Tri- $\alpha$ -Naphthylboron	5.36	5	5.58	0.08	0.11
<u>n</u> -Butylboric Acid	10.81	5	11.18	0.02	0.03
Acetanilide-BF <sub>3</sub>	4.43	6	4.72	0.13	0.24



Table 5. Determination of Carbon

Compound	Theor. (%)	No. Det'm.	Av. (%)	Experimental Deviation from Mean	
				Av.	Max.
Diethylamine-BF <sub>3</sub>	34.04	6	30.61	0.22	0.27
Benzylamine-BF <sub>3</sub>	48.05	7	45.26	0.08	0.14
<u>o</u> -Chloroaniline-BF <sub>3</sub>	36.88	6	33.70	0.11	0.20
<u>o</u> -Bromoaniline-BF <sub>3</sub>	30.04	6	27.65	0.10	0.20
Pyridine-BF <sub>3</sub>	40.87	5	34.19	0.08	0.19

Table 6. Determination of Hydrogen

Compound	Theor. (%)	No. Det'm.	Av. (%)	Experimental Deviation from Mean	
				Av.	Max.
Diethylamine-BF <sub>3</sub>	7.81	6	7.50	0.25	0.45
Benzylamine-BF <sub>3</sub>	5.14	7	5.02	0.14	0.20
<u>o</u> -Chloroaniline-BF <sub>3</sub>	3.07	6	3.13	0.18	0.23
<u>o</u> -Bromoaniline-BF <sub>3</sub>	2.50	6	2.71	0.13	0.33
Pyridine-BF <sub>3</sub>	3.40	5	3.14	0.03	0.06

Various oxidizing agents were layered on samples of diethylamine-boron trifluoride and combustions carried out at 1000°C. There was no appreciable increase in the carbon values over those obtained by heating the sample alone, when any of the following agents were used: lead, lead oxide, silver wire and silicon dioxide. In no case was there any black residue visible after burning.

Suspicion having been aroused as to the purity of the compounds, efforts to purify by recrystallization were made with no improvement. Finally, pyridine-boron trifluoride was chosen for purity checks. Samples of pure pyridine were weighed out and transferred to the distilling flask of a steam distillation apparatus. Concentrated sodium hydroxide was then added and the pyridine was steam distilled into a known volume of hydrochloric acid. The excess acid was titrated with standard sodium hydroxide using bromphenol blue indicator and the sodium hydroxide titer was then calculated. Since the end point of the titration is not sharp, the procedure was standardized so as to distill over the same volume (100 ml.) each time and each titration was carried to the same indicator color.

Samples of pyridine-boron trifluoride were then weighed out and the pyridine content determined as above. It was assumed in these experiments that the pyridine entity would probably be reasonably intact and that any impurity would be a hydrolysis product of the boron trifluoride portion or else some complex of pyridine and boron trifluoride involving other than the 1:1 mole

ratio (34) e.g., the known 1:2 complex (2). If such were true, it was expected that a corrected theoretical carbon percentage calculated from the determined pyridine content would correspond much more closely to the experimental values determined by combustion of the original complex. This proved to be the case (see Table 7). A similar correction for hydrogen proved less satisfactory, but this could be expected if hydrolysis had occurred.

Further checks based upon nitrogen determinations (see next section) confirmed the conclusion that these compounds were impure. Consequently a new compound, acetanilide-boron trifluoride, which had been reported as quite easily prepared in pure form and as quite stable (32), was prepared and analyzed by the method originally tried with these complexes. The results (see Tables 3 and 4) were quite satisfactory.

#### Determination of Nitrogen.

Nitrogen was determined by the Dumas method (18). The assembled train is shown in Figure 4b. The sample was mixed with powdered copper oxide in a small test tube and introduced into the combustion tube (D) as part of the temporary packing (see Figure 4a). It was burned by heating with the burner (E), the combustion taking place in an atmosphere of carbon dioxide and the nitrogen produced being swept out by means of carbon dioxide. The nitrogen was measured volumetrically over a 50% potassium hydroxide solution in the nitrometer (I), the carbon dioxide and all combustion products, other than nitrogen, being soluble

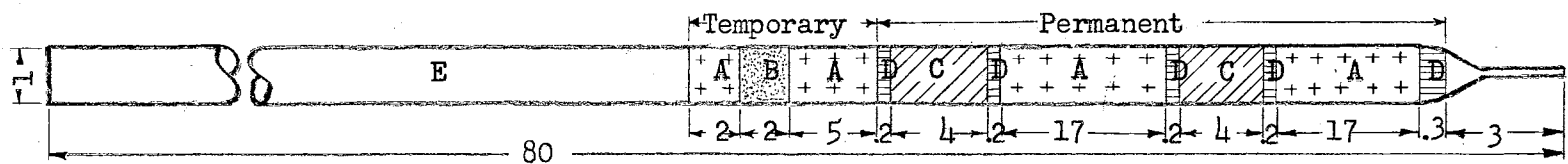
Table 7. Analysis of Pyridine-boron Trifluoride

Compound	Pyridine		Carbon		Hydrogen	
	Theor. (%)	Found (%)	*Corr. (%)	Found (%)	Corr. (%)	Found (%)
Pyridine-BF <sub>3</sub>	53.85					
Pyridine-2BF <sub>3</sub>	36.84					
Sample		45.35	34.42	34.19	2.87	3.14

\* The values for carbon and hydrogen in the columns marked "Corrected" were obtained by using the formula:

$$\frac{5C}{C_5H_5N} \times \% \text{ pyridine (Found)} = \text{Corrected \% C.}$$

$$\frac{5H}{C_5H_5N} \times \% \text{ pyridine (Found)} = \text{Corrected \% H.}$$



All dimensions are in centimeters

Figure 4a. Tube Packing for Dumas Nitrogen Determination

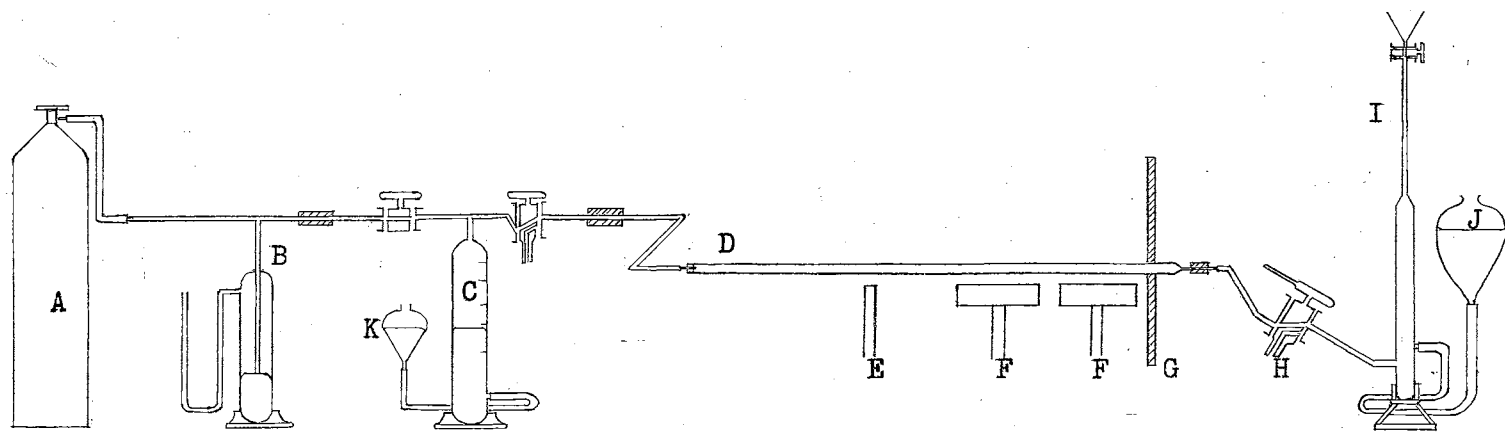


Figure 4b. Dumas Nitrogen Apparatus

## Legend for Figure 4a

- A - Coarse copper oxide
- B - Powdered copper oxide
- C - Copper wool
- D - Asbestos plugs

## Legend for Figure 4b

- A - Carbon dioxide
- B - Safety valve
- C - Gasometer
- D - Combustion tube, Vycor
- E - Sample burner
- F - Heating unit for permanent packing
- G - Baffle
- H - Special stopcock for nitrometer
- I - Nitrometer (filled with 50% potassium hydroxide)
- J - Potassium hydroxide leveling bulb
- K - Mercury leveling bulb

in this solution.

In the conventional tube, the permanent packing is only half as long as indicated in Figure 4a; i. e., it contains only 4 cm. of copper and 17 cm. of copper oxide. This was found to suffice if samples were kept very small (4 mg.) and burning rates very slow; otherwise high nitrogen percentages would be obtained. With the increase in packing, larger samples (up to 10 mg.) could be used and the packing did not need as frequent replacement. It was also necessary to provide a little more free space in front of the sample since the compounds exhibited a tendency to volatilize back against the carbon dioxide stream.

Results on the amine-boron trifluoride complexes are given in Table 8. For comparison purposes, corrected values for carbon, calculated on the assumption that the nitrogen determinations were accurate, and that impurities present did not change the C/N ratio, are included.

#### Determination of Boron and Carbon in Boron Carbides.

Initial experiments with boron carbide were concerned with the determination of carbon alone. The combustion tube was made of alundum, 1.2 cm. O. D. and 100 cm. length, drawn to a 3-mm. tip at its exit end. It contained no packing. The Sentry furnace was used at 1390°C. but the temperature in the tube proved to be only 1000-1100°C. The assembled train is shown in Figure 3a with the elimination of the sample burner (G) and the mortar (I).

The weighed sample in a platinum boat was inserted in the cold portion of the tube, about 40 cm. from the inlet end. After

Table 8. Determination of Nitrogen

Compound	No. Det'm.	Nitrogen Theor. (%)	Nitrogen Found (%)	Deviation from Mean		Carbon Theor. (%)	Carbon* Corrected (%)
				Av.	Max.		
Acetanilide-BF <sub>3</sub>	6	6.90	6.96	.02	.06		
Benzylamine-BF <sub>3</sub>	5	8.01	7.46	.03	.08	48.05	48.60
<u>o</u> -Chloroaniline-BF <sub>3</sub>	6	7.17	6.51	.02	.06	36.88	37.09
Diethylamine-BF <sub>3</sub>	6	9.94	8.69	.05	.08	34.04	35.02
<u>o</u> -Bromoaniline-BF <sub>3</sub>	6	5.84	5.44	.04	.09	30.04	29.68

\* The values for carbon in the column marked "Corrected %" were obtained using the data above and that from Table 5 in the formula:

$$\text{Corrected \%} = \frac{\% \text{ N. by theory}}{\% \text{ N. by experiment}} \times \text{experimental \% carbon}$$



the absorption tubes had been connected, the oxygen flow rate was adjusted to the desired value. Experiment showed 2 ml. per minute to be best, higher rates cooling the samples too much. The whole tube was then moved into the furnace so that the sample was situated in the middle of the furnace heating length. After the prescribed time for complete combustion (which was found to vary from 2 1/2 to 4 hours), the oxygen flow rate was raised to 5 ml. per minute and the final flushing was continued for 20 minutes.

Results from a number of determinations on the same carbide are given in Table 9.

To determine both carbon and boron, an induction furnace was used for heating the sample. Preliminary experiments were conducted using the experimental induction furnace of Durbin and Winget (36). The combustion tube was made of clear fused quartz, with an outside diameter of 2 cm. for 33 cm., tapered to 1 cm. O. D. for 33 cms., then to a 3-cm. tip of 3 mm. O. D.. The whole tube thus had an overall length of 70 cm.. The work coil was placed at a point 40 cm. from the tip. The latter half of the tube of 1.0 cm. O. D. was packed with boron-free-glass chips. The sample holder was made of a half cylinder of 0.008-inch platinum with B. and S. No. 17 platinum wire legs. The sample, weighed in a platinum boat, was placed in this half cylinder, and platinum scrap (about 6 g.) layered over the sample. It was then placed in the combustion tube midway through the work coil. The tube was flushed with 100 ml. of oxygen, the absorption tubes connected, and the oxygen flow rate adjusted to 5 ml. per minute.

Table 9. Determination of Carbon in Boron Carbide - Sample C/B = .25\*

Sample (mg.)	Combustion time (hr.)	Carbon Found (%)	Comments
4.670	2.5	18.85	no black residue
6.060	4.0	18.46	black specks (?)
4.735	4.0	19.09	no black residue

Table 10. Results with Induction Furnace of Durbin &amp; Winget - Sample C/B = .25\*

Weight Sample (mg.)	Combustion time (min.)	Carbon Found (%)	Boron Found (%)	Total (%)	C/B Found
4.580	40	18.60	66.74	85.34	.25
4.130	30	18.46	67.31	85.77	.25

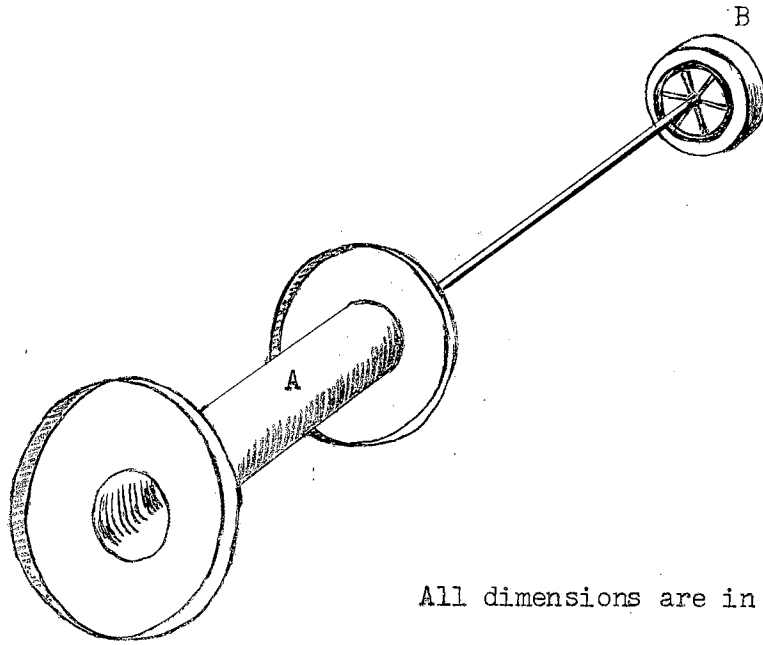
\* These are the ratios used in preparing the carbide (see Table 1).

The furnace was then turned on and the sample burned for 1/2 hour at an average temperature of 1300-1400°C. After a final flushing with 100 ml. of oxygen, the tubes were disconnected, flushed with cleaned air, and weighed in the usual manner. The combustion tube was disconnected, fitted with a cooling jacket, and attached in refluxing position to a quartz flask in which the sample holder and the boron-free-glass chips and 40 ml. of distilled water had been placed. The boric oxide in the combustion tube was then washed out by refluxing for 1 to 2 hours. The resulting boric acid solution was then quantitatively transferred to a 100-ml. quartz beaker for titration.

The titration procedure employed was one which had been tested by Mr. W. Patrick Donahoo in this laboratory. Five milliliters of approximately 0.1N hydrochloric acid was added and the solution boiled for two minutes to expel any carbon dioxide. After cooling to 25°C. in an ice bath and introducing a magnetic stirrer, the pH meter electrodes were placed in it and arranged for titration. The pH was adjusted as exactly as possible to 5.4 with 0.1N sodium hydroxide, the pH meter itself having been calibrated with standard buffers of pH 5.4 and 8.2. Seven grams of mannitol was added and the solution titrated potentiometrically with the standard base to a pH of 8.1 as endpoint. A nitrogen atmosphere was maintained over the surface at all times during the titration. A water blank was then run in exactly the same manner and the blank (ca 0.08 ml. of 0.05N sodium hydroxide) was subtracted from the volume used in the original titration.

The percentage of boron calculated from the results are shown in Table 10.

Final experiments were conducted with a Leco IH-10C high-frequency furnace. Since the boric oxide formed might be expected to react with, or be absorbed in the pores of, ceramics normally employed in this furnace, the ceramic crucibles and crucible supports supplied were eliminated and all-platinum apparatus was substituted (see Figure 5 and 6). The sample was weighed out on a platinum disk (B, in Figure 5) made from 6 g. of platinum gauze. Another piece of gauze or a matrix of thin platinum scrap (ca 5g.) welded together, was placed on top of the sample. The disk was then placed on the holder shown in Figure 5 and raised into the combustion tube (Figure 6). The completed train is shown in Figure 7 minus the oxygen purifier equipment which is the same as previously mentioned. The assembled train with sample in place was flushed out for 15-20 minutes with oxygen at 5-7 ml. per minute. The absorption tubes were attached and the oxygen rate was raised to 30 ml. per minute to counteract the back pressure produced by the sudden heating when the furnace was turned on. The furnace was turned on and the oxygen flow regulated to 5 ml. per minute after the desired temperature of 1300-1400°C. had been attained. The burning time for the sample varied (depending upon the amount of boron present) from 30 to 45 minutes. The train was flushed further with 100 ml. of oxygen after the power was turned off; then the absorption tubes were flushed with air, purified, and weighed in the usual



All dimensions are in centimeters.

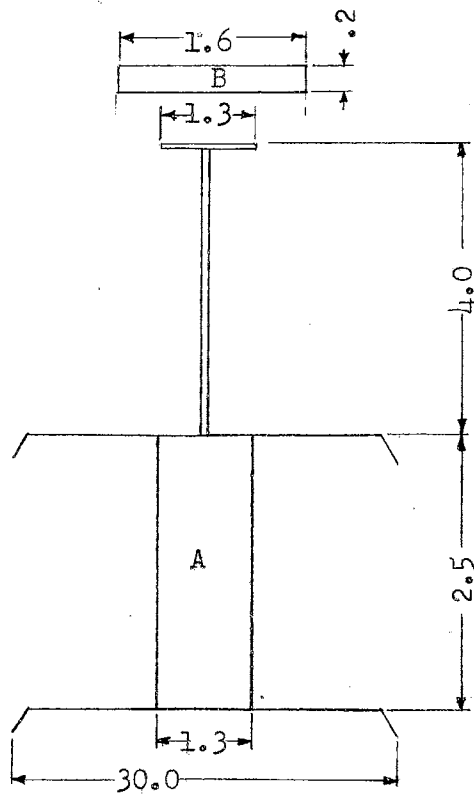


Figure 5. Pedestal with Sample Disk

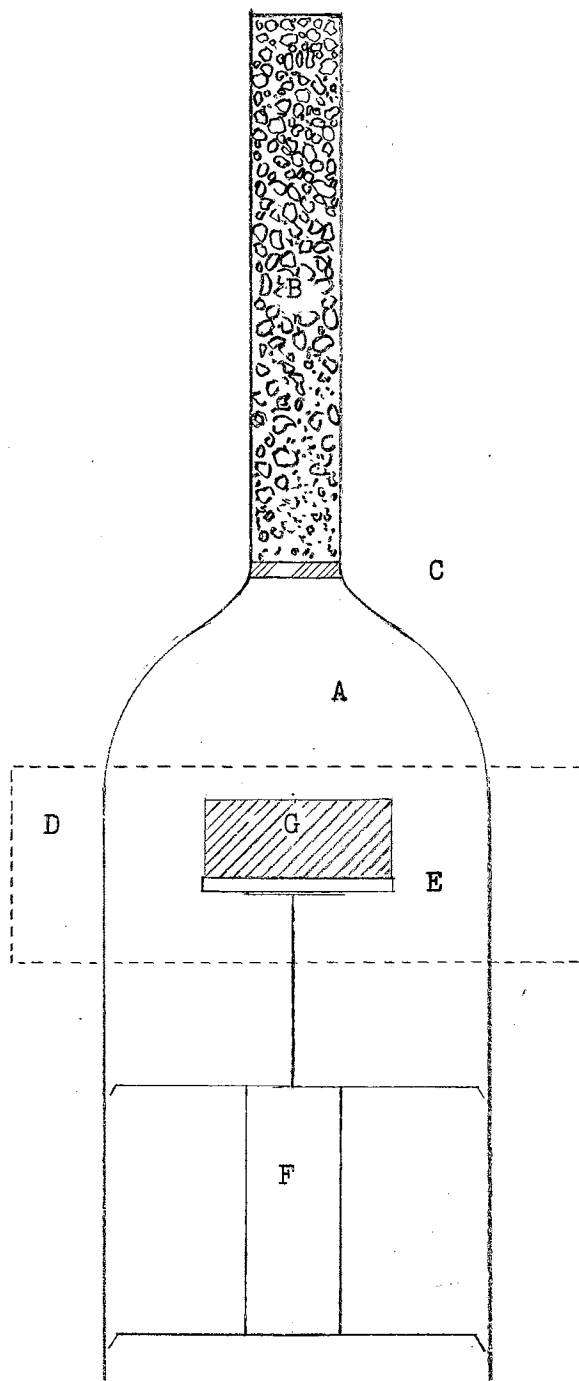


Figure 6. Combustion Tube for Leco Furnace with Pedestal and Disk

## Legend for Figure 5

- A - Pedestal of .008 inch platinum
- B - Sample disk made from 6 g. of platinum gauze

## Legend for Figure 6

- A - Quartz combustion tube
- B - Boron-free-glass chips
- C - Platinum gauze
- D - Furnace coil
- E - Platinum disk (sample disk)
- F - Platinum pedestal
- G - Platinum scrap or gauze

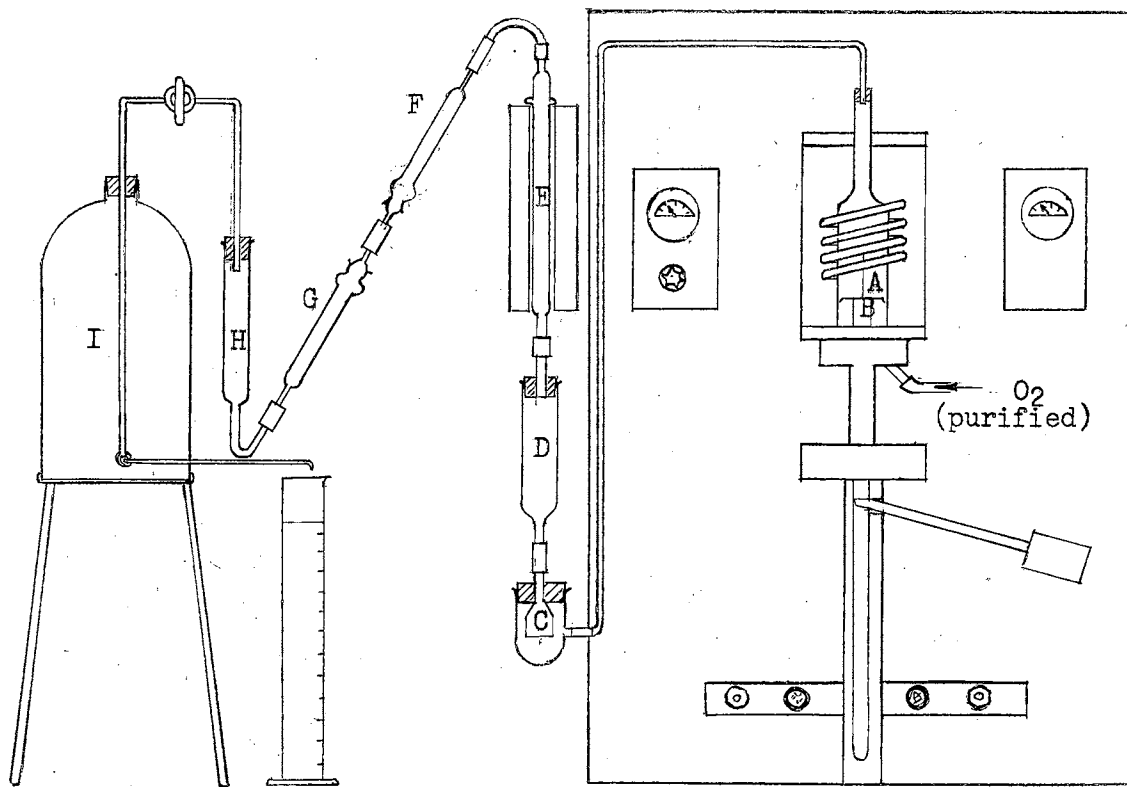


Figure 7. Combustion Train Used for the Analysis of Boron Carbides



## Legend for Figure 7

- A - Quartz combustion tube
- B - Pedestal
- C - Dust trap
- D - Sulfur trap
- E - Copper oxide tube and electric heater (used to insure complete conversion of carbon monoxide to carbon dioxide)
- F - Water absorption tube
- G - Carbon dioxide absorption tube
- H - Safety tube
- I - Mariotte Flask

## Legend for Figure 8

- A - 250-ml. quartz flask
- B - Quartz combustion tube
- C - Quartz tube (11 mm. O. D., length 31 cm.)
- D - Water jacket (pyrex 38 mm. O. D.)
- E - Rubber stoppers
- F - Heating mantel

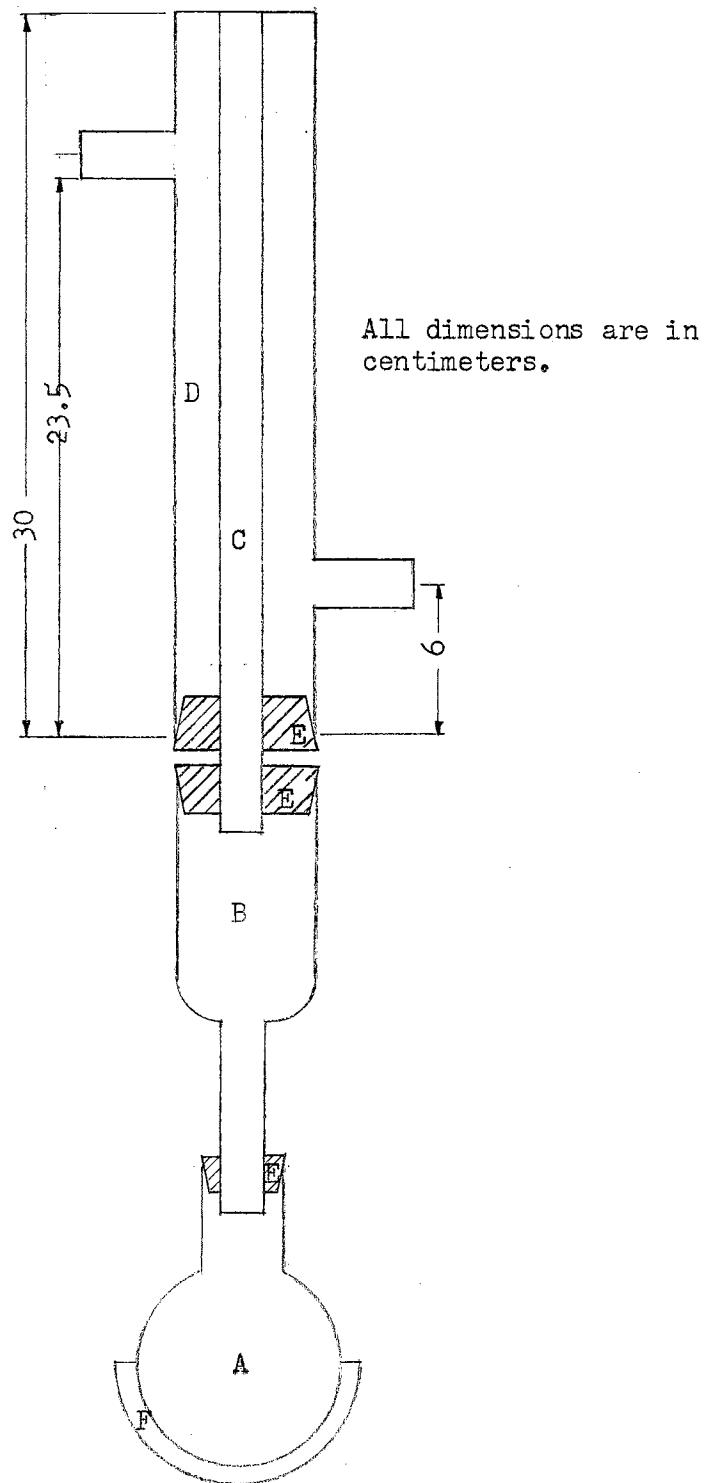


Figure 8. Reflux Apparatus

manner. The whole procedure took about 1 1/2 hours for pre-flushing, burning and final flushing.

The combustion tube was then disconnected. The sample disk and the platinum gauze used to cover the sample, together with the boron-free-glass chips, were placed in the quartz flask (A, of Figure 8). The platinum pedestal was left in the combustion tube (B, of Figure 8). About 40 ml. of distilled water was added, the apparatus being refluxed for two hours. The resulting boric acid solution was quantitatively transferred to a 100-ml. quartz beaker and the boron was determined as before.

To prove that the recovery of boric acid was complete, the procedure was checked using pure boric acid. Two samples of boric acid were weighed out - one on the disk and the other in a quartz beaker. The above combustion procedure was followed, the boron determined, and the results were compared to those obtained by direct titration of the other sample. These results agreed within 0.05%.

The experimental data on a number of samples of carbides are shown in Table 11.

Upon combustion of these carbides in the induction furnace, a black smooth, shiny, deposit formed on the sides of the tube. This deposit was scraped off and dissolved in aqua regia. The resulting solution gave, with potassium chloride and iodide (33), a positive test for platinum. Frequent removal of this coating was necessitated by the fact that when the coating became too heavy, it absorbed too much of the power of the furnace.

Table 11. Determination of Boron and Carbon in Boron Carbides

Sample	No. Det'm.	Carbon (%)	Deviation from Mean		Boron (%)	Deviation from Mean		Sum (%)	Residue (%)	Total (%)	C/B	
			Av.	Max.		Av.	Max.				Theor.*	Found
#1	5	18.37	.11	.23	67.03	.14	.28	85.4	14.7	100.1	.25	.25
#3	6	20.51	.09	.17	77.50	.18	.30	98.01	2.5	100.5	.20	.25
#5	9	17.44	.12	.22	80.65	.19	.30	98.09	1.7	99.78	.15	.19
#6	2	15.02 15.22			78.50 78.50			93.62			.10	.16
#7	2	14.40 14.40			76.00 76.25			90.53			.108	.16
#8	2	12.03 12.05			85.60 85.50			97.59			.05	.14
#9	2	10.50 10.85			86.20 85.80			96.63			.05	.11
#11	2	9.62 9.12			85.00 85.58			94.55			.00	.10

\* These are the ratios used in preparing the carbide (see Table 1).

A colorless water-insoluble, nonvolatile residue was left after burning these boron carbides. Experiments were run to determine the percentage of this residue in three of the samples. A platinum boat was used as the sample holder and was inserted in an alundum tube at 1100°C., and a stream of oxygen passed through. The weight loss of platinum at 1100°C. (ca 0.036 mg. per hour) was determined by weighing the boat after timed intervals at this temperature. A sample was then weighed out into the boat and burned. Since it was suspected that significant quantities of boric oxide also remained in and on the platinum boat, this had to be washed out. Examination of the residue showed it to be sintered into the platinum surface; consequently, gently refluxed water was employed for the removal of the boric oxide. This washing was performed in the reflux apparatus of Figure 8, the boat being removed at times for drying and weighing until constant weight was obtained. This usually took about four hours. After correction for loss of weight of platinum was made, the weight of the residue was calculated. This procedure was naturally subject to a few errors, but as great care as possible was taken to keep these errors small.

Results are included in Table 11, together with total calculated percentages of the carbide constituents.

## DISCUSSION

The preliminary results of our combustion experiments (Table 2) indicated that a higher burning temperature provided a simple means of obtaining acceptable results for carbon in organoboron compounds. This was confirmed by the carbon data in Table 3 which are in excellent agreement with theoretical values. The hydrogen values (Table 4) in every case run high but are still within the average accuracy of this method - which is  $\pm 0.3\%$  (24). A possible explanation of these high hydrogen values may be that with the high burning temperature used, the hot stream of oxygen drives out some of the equilibrium moisture from the packing.

As has previously been mentioned, one of the chief obstacles in testing the new method of determining carbon, hydrogen and nitrogen in amine-boron trifluoride compounds lay in the difficulty of obtaining compounds whose purity could be trusted. Since acetanilide-boron trifluoride had been reported in pure form by Sugden, et al (32) and used for parachor studies, it was thought this compound might be used for a check of the method. The results obtained (see Tables 3, 4 and 8) are very close to the theoretical values.

In view of the difficulty of obtaining other such compounds in the pure state (10, 32) studies, based upon the assumption that impurities would be such as not to change the ratio of carbon to

nitrogen from that in the pure compound, were attempted. It was hoped in this manner to show the validity of the method by assuming that the carbon and nitrogen percentages would change by the same percentage, and that application of a correction factor to the experimental results would give a value close to the theoretical. The results obtained are shown in Table 8.

At first glance, only the acetanilide-boron trifluoride seems to have given good results. A study of Table 8 and a consideration of the factors involved, however, shows that even these results indicate that the new method of determining carbon, hydrogen, and nitrogen in amine-boron trifluoride complexes probably gives, with acceptable accuracy, the actual composition of the substances being employed. Since the percentage of carbon is from three to six times that of the nitrogen in the amines considered, an error of 0.1% in the determination of the nitrogen would mean an error of 0.3% to 0.6% in the corrected carbon percentage. If this is kept in mind, it can be seen that the agreement between the theoretical and corrected experimental values for carbon in benzylamine-boron trifluoride, o-chloroaniline-boron trifluoride, and o-bromoaniline-boron trifluoride is acceptable. With diethylamine-boron trifluoride, the precision of the carbon determination (Table 5) was very poor and the product was undoubtedly of very low purity. A similar correlation on the pyridine-boron trifluoride was attempted but the results were extremely poor. The carbon determinations had been run several weeks previous to the Dumas determination, consequently, there was reason to suspect that

the compound was not in the same state of purity in the two cases.

Since the Dumas nitrogen determination is applicable for all nitrogen in all oxidation states, this was the method used. The slight modifications noted in the "Procedure" produced reliable results if the permanent packing was renewed after every 6-8 determinations. That halogen compounds have a deleterious effect on the packing in the Dumas determination has been noted elsewhere (28).

The results shown in Table 10 indicate that the carbon in boron carbide may be determined by burning at  $1100^{\circ}\text{C}$ . in a stream of oxygen. The time required is rather long, but considering the difficulty of the determination this is still quite acceptable. Further experiments showed that the time of burning increased enormously as the percentage of boron increased and that of the carbon decreased. Raising the temperature to  $1400^{\circ}\text{C}$ . would probably solve this problem but we were interested in determining the boron also. Since the resistance furnace heats the tube as well as the sample, it was felt that at this temperature, the boric oxide would diffuse into or react with the materials of which any known combustion tube is made and would thus become non-recoverable through washing. By using induction heating with quartz tubes, and all-platinum ware, both the carbon and the boron can be recovered.

Unfortunately, the samples of boron carbide obtained were also impure. They were undoubtedly contaminated for the most part with alundum since they were ground to a suitable mesh size



in alundum containers. The attempts to establish this percentage impurity by weighing the residue left after ignition of the sample in a platinum boat, thorough washing, and calculation after correction for the loss of weight of platinum during the heating interval gave surprisingly good results. The loss in weight of platinum was appreciable and since the impurity in most cases was less than 10%, these results were expected to be of questionable accuracy. However, they were useful as a method of estimating the amount of uncombustible residue in the sample.

The amount of residue present was obtained only for samples 1, 3 and 5 since, as previously mentioned, with an increase in boron content, either the burning time or the temperature had to be increased to such an extent that the loss of weight due to the platinum obscured the results. The sample labeled No. 1 (14.7% residue) was grayish in color as contrasted to the other samples which were black.

The most carefully studied carbides, Samples 1, 3, and 5, show excellent precision and quite acceptable (insofar as it can be determined) accuracy. The maximum deviation of the boron analysis is 0.3% and of carbon, 0.2%. These values are remarkably good if one considers that with a 4-mg. sample of 80% boron, a deviation of 0.02 ml. in the titration will cause a 0.3% change in the calculated percent of boron. The carbon determination is even more critical. Here, any combination of errors in weighing either the sample or the carbon dioxide absorbers amounting to 0.03 mg. will cause a 0.2% variation in the calculated value of carbon.

Although precision alone is not a measure of accuracy, it does give an insight into the reliability of the results. This, coupled with the total percentages obtained when the residue is added, presents a strong argument for the methods' being considered accurate.

### SUMMARY

It has been shown that the analysis of organoboron compounds is possible using a conventional micro dry combustion procedure with slight modifications in burning temperature, packing, etc.

Both boron and carbon in boron carbides may be determined simultaneously by burning at  $1400^{\circ}\text{C}.$ , in an induction furnace. The carbon is measured by absorption of the resulting carbon dioxide on Ascarite and the boron by titration of the boric oxide formed.

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