



**GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION**

**PREPARATION OF BORON TRIBROMIDE (PART I) AND
ITS PURIFICATION (PART II)**

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**BHABHA ATOMIC RESEARCH CENTRE
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ABSTRACT

In Part I of this report, studies on the preparation of boron tribromide by the action of bromine on elemental boron have been described in detail. It had been found that the most suitable temperature for this preparation was 700°C. The bromination product at this temperature contained about 96% of boron tribromide. Kilogram quantities of the bromide were prepared by this method.

In Part II, the subsequent purification of crude bromide by fractional distillation is described. Using a quartz distillation column a product of 99.99% purity was obtained in a single distillation.

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1. INTRODUCTION

The use of boron tribromide as a dehydrating catalyst and as an intermediate for the preparation of organo-boron compounds is well known for the past many years. Its application as a powerful demethylating reagent for aromatic ethers has recently been reported⁽¹⁾. With the rapid development of electronics industry, it has assumed greater importance as a source for high-purity boron for use as a semiconductor and as a dopant in silicon and germanium. For the preparation of ultra-pure boron, boron hydrides which contain the most desirable percentage of boron appear to be the best choice and attempts have been made to prepare the element by their thermal decomposition^(2, 3). However, their explosive nature and handling problems cause difficulties in the application of this method. The boron halides therefore appear to be the best starting materials. The selection of the suitable halide is governed by a number of factors such as their preparation and purification, decomposition temperature, handling problems and storage. In view of these considerations boron trifluoride is not favoured because of its high thermal stability, low boiling point (-101°C) and highly corrosive decomposition products. Boron trichloride^(4, 5) is also less favourable because of the same factors as in the case of boron trifluoride. Boron tribromide and triiodide are quite suitable since they have the most desirable physical properties (BBr_3 : B. P., 90.6°C , M. P., -45°C ; BI_3 : B. P., 210°C , M. P., 43°C) suitable for purification by standard

techniques and require low temperatures for their decomposition. The bromide is however preferred on account of its higher boron content by weight and of higher yields (90-100%) as compared to iodide⁽⁶⁾ where only 62-63% yield is obtained.

1.1 Selection of the process

A survey of literature suggests the possibility of adopting one of the following methods for the synthesis of boron tribromide.

(1) Action of bromine on elemental boron at elevated temperatures⁽⁷⁻¹⁰⁾
The combination takes place in the temperature range 420-900°C. The product is purer the lower the temperature⁽¹¹⁾.

(2) Bromination of boron carbide⁽¹²⁾ between 950-1000°C.

(3) Halogen exchange of boron trifluoride or potassium fluoborate with aluminium bromide⁽¹³⁾.

(4) Reaction of boron with silver bromide⁽¹⁴⁾. Boron tribromide is formed by the following reaction:-



The reaction has to be carried out in high vacuum since the Gibbs free energy values at normal pressures are positive upto 1000°C.

(5) Reaction of bromine with an intimate mixture of boric oxide and carbon at 250°C⁽¹⁵⁾.

Synthesis of boron tribromide by methods (1) and (5) appears to be quite simple and convenient for its preparation even on a large scale. However, in the case of method (5) we have observed that formation of boron tribromide by brominating a mixture of boric oxide and carbon is not feasible even upto 800°C. The reaction was not carried out at higher temperatures,

since the quartz reaction tube gets brominated. Hence the preparation of boron tribromide by bromination of elemental boron has been studied in detail and the present report deals with these studies.

2. EXPERIMENTAL

2.1 Apparatus

A schematic diagram of the experimental set up is given in Fig. 1. The reaction tube (A) is of transparent quartz (32 mm bore and 36" length) having a bromine dispersion tube (B) and an outlet (C) for the bromide. Boron in the form of pellets is kept over the bromine dispersion tube. Bromine is fed dropwise from the container (F) at the desired rate into the R. B. flask (D), pre-heated by isomantle (E) to vaporise bromine. The flask is attached to the reaction tube through a ground glass joint. Vapours of bromine are led over the charge by passing argon through the inlet (G). The charge is heated by introducing the reaction tube into a tubular furnace (H), the temperature being controlled within $\pm 10^{\circ}\text{C}$ by using a temperature controller and measured by a chromel-alumel thermo-couple. The bromides distilled through the outlet (C), and are led through water condensers(I & I') before being finally collected in the receiver(J), cooled by cold air*. A concentrated sulphuric acid bubbler(L) acting as a guard against any moisture getting into the system either by diffusion or back suction is connected to the second condenser(I').

2.2 Materials

Boron powder (B. D. H.) used for bromination contained 85-86 percent elementary boron. Magnesium was the principal impurity. Besides this, it contained small quantities of silicon, iron, calcium, aluminium and manganese (Table I). The powder was pelleted (~ 10 mm dia and 11 mm thick) under a pressure of about 1000 kg/cm^2 .

Chemically pure bromine is distilled after drying over concentrated

*Cooling the receiver by cold water has to be strictly avoided as any accidental breakage of the receiver containing boron tribromide may lead to violent explosion.

sulphuric acid. Commercial argon and nitrogen are dried over soda lime and concentrated sulphuric acid. They were purified from oxygen by passing over heated (600°C) copper turnings.

2.3 Procedure

Boron pellets are kept over the bromine dispersion tube and the equipment is assembled as shown in Fig. 1. The system was then flushed with pure and dry argon, and the furnace as well as the isomantle switched on. The temperature of the furnace is maintained at about 400°C and that of the isomantle at about 150°C . Any trace of moisture in the assembly is removed by playing a hot flame. Temperature of the furnace is then gradually increased and maintained at the desired value using a temperature controller. Bromine from the reservoir is introduced at the required rate, the rate being regulated by a stop-cock. Vapours of bromine are carried by the argon which was passed at the rate of about 40 cc/min., the rate being measured by a rotameter. Bromides formed distilled over and collected in the receiver(J). On completion of the reaction, the system is flushed to remove bromine by continuing argon at the same temperature for about half an hour. Heating is then discontinued and the temperature allowed to fall to about 100°C in argon atmosphere. The product is then transferred to another container and sealed.

A charge of 75 grams of boron (pellet form) per batch is used during the studies for determining the different parameters. The flow rate of bromine is established for each temperature by observation of the colour of the product. A coloured product indicated that all the bromine was not being used up in the reaction and therefore the flow rate should be diminished. The maximum rate of flow of bromine for a colourless product is taken as the flow rate for that temperature.

3. RESULTS AND DISCUSSIONS

3.1 Effect of formation temperature on purity of boron tribromide

Preliminary experiments indicated that boron tribromide obtained by brominating boron at 850-900°C was not satisfactorily pure. Therefore in order to find an optimum temperature from purity point of view, bromination was carried out at lower temperatures (400-800°C) and purity of the product determined. The distribution of metallic impurities in the product obtained at different temperatures is shown in Table I. The bromide obtained between 400 to 600°C was reasonably pure whereas beyond 600°C the purity decreased gradually and at 850°C the product was found to contain only 87.4 percent boron tribromide, the main impurities being magnesium bromide and silicon bromide. Magnesium bromide was due to the presence of magnesium to the extent of 4.18 percent in the starting material, whereas the bulk of silicon bromide came from the quartz reaction tube.

Assuming equilibrium conditions in the reactor, approximate thermodynamic calculations for estimating the completeness of the reaction of bromine with various impurities could give an explanation to these results. The ΔF values for bromides have been taken from Wicks and Block⁽¹⁶⁾ (Table II). It is evident that excepting carbon all impurities in boron will react to completeness at all temperatures between 400-800°C. However, it was observed (Table I) that there was a marked trend in the purity and the product obtained at lower temperatures was purer. Since this cannot be predicted on the basis of the thermodynamic data; it is believed that the activation energy of the reaction between bromine and the impurities must be the controlling factor. The present experimental set up also helps

Table I

ANALYTICAL RESULTS OF THE HYDROLYSED PRODUCT OF BBr_3 SAMPLES PREPARED AT VARIOUS TEMPERATURES

Impurities in Boron metal (%)		Si	Mg	Ca	Al	Fe	Mn	C	Ti	W	Sn	Pb	Cu	Cr	Mo	Co	Ni
		0.3	4.18	0.35	0.33	0.3	0.14	0.13				Not estimated					
Impurities in the hydrolysed product		Impurity on H ₃ BO ₃ basis															
No.	Reaction Temp. °C	Si	Mg & Ca	Al	Fe	Mn	C	Ti	W	Sn	Pb	Cu	Cr	Mo	Co	Ni	
1	850	3.4*	7500	1900	3300	300	568	270	160	< 10	100	100	75	< 10	< 10	50	
2	800	1.8*	4100	320	780	25	200	240	150	< 10	50	< 5	< 10	< 10	< 5	< 5	
3	700	3400	2000	220	530	25	99	180	100	< 10	100	< 5	< 10	< 10	< 5	< 5	
4	600	400	400	140	450	5	90	250	150	< 10	10	< 5	< 10	< 10	25	< 5	
5	500	100	480	100	410	< 5	110	100	100	< 10	10	< 5	< 10	< 10	25	< 5	
6	400	100	370	90	140	< 5	125	50	50	< 10	< 10	< 5	< 10	< 10	25	< 5	

*Values on weight percentage basis. All other values in ppm.

TABLE II

 ΔF_T° VALUES OF BROMIDES (CAL. /MOLE)Formation : $M + Br_2 \rightarrow MBr_n$

Temp. °K	CaBr ₂ B. P. : 810°C	TiBr ₄ B. P. : 230°C	AlBr ₃ B. P. : 268°C	MgBr ₂ B. P. : 1227°C	SiBr ₄ B. P. : 153°C	MnBr ₂ B. P. : 1027°C	FeBr ₃ B. P. : 627°C	BBr ₃ B. P. : 90.6°C	CBr ₄ B. P. : 189.5°C
298°	-157,500	-142,000	-123,300	-120,000	-89,300	-85,100	-60,410	-57,200	+5,000
500°	-150,350	-132,000	-116,800	-111,000	-	-79,000	-37,000	-49,100	+15,400
700°	-143,000	-	-	-102,000	-	-73,000	-	-46,300	+20,700
1000°	-133,500	-	-	- 92,450	-	-64,000	-	-42,300	+29,700

some extent in retaining the non-volatile bromides on the cooler portions. It was observed that large amount of a white solid product was collected on the cooler portion of the reactor and on the outlet tube for the bromides. This was qualitatively analysed and found to be mainly magnesium bromide.

3.2 Rate of bromination of boron at different temperatures

During the studies on the bromination of boron at various temperatures (400 to 800°C), it was observed that the rate of formation of boron tribromide (as seen from the colourless liquid being collected in the receiver) was not constant throughout the experiment. On commencement of the reaction the rate of formation of the bromide was considerably low and it gradually increased as the reaction proceeded and was continuous only after about four hours. This may be due to the fact that impurities like calcium, aluminium, iron and magnesium present in boron were being brominated preferentially in the initial stage. This view is well substantiated by the thermodynamic data (Table II).

Therefore in order that the rate studies be more meaningful, the bromination at each temperature was carried out for eight hours. The rate of formation of the bromide at different temperatures is given in Table III. From the variation in the amount of the product obtained at different temperatures it is clear that the reaction rate increased with increasing temperature. The amount of the product obtained at 400°C was 10 grams/hour where as it was 73 grams/hour at 800°C. It was not advisable to carry out the reaction beyond 800°C since, as stated before, it was found that the quartz reaction tube got attacked by bromine. This not only contaminated the product with silicon but also shortened the life of the reaction

TABLE III

TEMPERATURE DEPENDENCE OF THE RATE OF
BROMINATION REACTIONS

Boron charge	= 75 grams
Packed density of boron	= 0.51 gm/cm ³
Reactor diameter (I. D.)	= 3.2 cm
Duration of experiment	= 8 hours
Argon flow rate	= 2.4 litres/hour

	Temperature °C	Bromine flow rate grams/hour	Product obtained grams/hour	BBr ₃ content in the product %
1.	400	12	10	99.4
2.	500	25	22	99.0
3.	600	45	40	96.5
4.	700	70	63	95.4
5.	800	80	73	92.0

tube. Even at 800°C appreciable amount of silicon was found in the product (Table I). The yield of the product on the basis of bromine consumption in the temperature range 400-800°C was between 83 to 88 percent.

3.3 Choice of temperature for the preparation of boron tribromide

While selecting the optimum temperature for the preparation of boron tribromide on a large scale, the rate of formation and purity of the bromide has to be taken into consideration. From this point of view 600 and 700° appear to be competitive, since the rate of formation and purity of the product at these temperatures were 40 grams/hour, 96.5%; 63 grams/hour and 95.4% respectively. Although the purity of the product obtained at 600°C is slightly better, the yield at this temperature is quite low. Therefore 700°C appears to be the optimum temperature for the large scale preparation of boron tribromide where a greater yield with product

of comparative purity is obtained.

3.4 Preparation of boron tribromide on large scale

For the preparation of boron tribromide on kilogram scale, 400 grams of boron in pellet form was taken for bromination at 700°C in a quartz tube of 55 mm I. D. The packed height of boron in the tube was 25 cm, and packed density was 0.64 grams/cm^3 . Bromine was passed at the rate of about 175 grams/hour and the flow rate of carrier gas (argon) was maintained at about 5 litres/hour. The reaction was discontinued when the product was getting coloured with free bromine, indicating that all the bromine was not being used up in the reaction. The break through of bromine occurred after 28 hours when 4.5 kilograms of the product was obtained. During this period 1.63 litres of bromine was used up. The yield of the product on the basis of bromine consumption was 91 percent, whereas 55 percent of boron was used up during the reaction. Boron tribromide content in the product was found to be 96 percent.

3.5 Nitrogen as a carrier gas

From the literature survey on the preparation of boron tribromide, it is found that almost all the authors have invariably used helium or argon as the carrier gas for bromine in the preparation of boron tribromide. In our studies also, argon was used for this purpose. However, in view of the high cost of argon and helium the possibility of using a cheaper ambient like nitrogen was considered especially for the purpose of large scale preparation. Since boron and other metals form nitrides at elevated temperatures, the formation temperature of nitrides of boron and other impurities present in boron were considered (Table IV).

TABLE IV
FORMATION OF NITRIDE BY THE REACTION
BETWEEN METAL AND NITROGEN

Nitride	Temp. of formation
BN	> 1200°C
Si ₃ N ₄	1300°C
AlN	800°C
Mg ₃ N ₂	560°C
Ca ₃ N ₂	500°C

It is seen that some nitrogen will probably be used up in the formation of nitrides of calcium, magnesium, aluminium etc. without affecting the main course of the reaction. The results of bromination experiments carried out at 700°C (the optimum temperature for boron tribromide preparation) in presence of nitrogen and argon are compared in Table V. The results show that nitrogen can be used in place of argon or helium in this preparation

TABLE V

RESULTS OF BROMINATION OF BORON IN PRESENCE OF ARGON
AND NITROGEN

Boron charge = 75 grams
Packed density of boron = 0.51 gms/cm³
Reactor diameter (I.D.) = 32 mm.
Rate of flow of carrier gas = 2.4 litres/hour

Parameters	Argon	Nitrogen
Bromine flow rate	60 grams/hour	60 grams/hour
Time required for break-through of bromine	14 hours	14 hours
BBr ₃ obtained	810 grams	800 grams
Yield on the basis of bromine consumption	91%	90%
Boron used up	55%	53%
BBr ₃ content in the product	95.4%	96%

PART II

4. PURIFICATION OF BORON TRIBROMIDE

Boron tribromide required in semiconductor technology for doping purpose should preferably be 99.99% pure⁽¹⁷⁾. Its purification by fractional distillation has been reported by several workers^(18-20, 6). Zone melting technique using low temperature bath has also been tried but was found to be unsuccessful⁽²¹⁾. Therefore fractional distillation is the best choice for the purification of boron tribromide.

Medcalf⁽¹⁸⁾ reported the purification of boron tribromide in fused silica distillation column having an efficiency equivalent to 30 plates and a reflux ratio of the order of 15. During distillation dry purified helium or argon gas was allowed to flow through the distillation unit to ensure that no air was pulled into the system during distillation. Powell et al⁽¹⁹⁾ purified technical grade boron tribromide by fractional distillation on a 55 theoretical plate column packed with 'Fenske' helices. The bromide obtained was of 99.5% purity. Starks and Bedford⁽²⁰⁾ reported the purification of crude boron tribromide by fractional distillation in a 150 cm long transparent fused quartz column. A minimum of three distillations were used to produce boron tribromide in which the only spectroscopically detectable impurity was silicon (1-5 ppm). Ivanov et al⁽⁶⁾ conducted fractional distillation of boron tribromide in an 'Oldershov' sieve plate column of 32 mm diameter having 25 real plates. Experiments showed that in the first distillation sufficiently pure boron tribromide, having silicon tetrabromide less than 0.01% was obtained. The distillation was carried out using a reflux ratio within the limits 5-20.

4.1 Calculation of distillation parameters

The boron tribromide content of the crude product used in the present work was about 96 percent. The major impurity was silicon, most probably as silicon tetrabromide although the probability of other bromides of silicon cannot be ruled out. In addition Fe, Al, Mg, Ca, S, Ti etc. were also present as bromides or oxybromides. The physical properties of these bromides are listed in Appendix A. For the calculation of experimental parameters such as number of theoretical plates, reflux ratio etc., so as to design a suitable rectification column, the removal of silicon tetrabromide, which is a major impurity in crude boron tribromide has been taken into consideration. SiBr₄-BBr₃ system is also a good choice for such calculations because of the high volatility of SiBr₄ and also because it is known to form an ideal solution with boron tribromide⁽²²⁾.

4.2 Number of theoretical plates and reflux ratio

The relative volatility, α , for SiBr₄-BBr₃ system was calculated from the published vapour pressure data for the system⁽²²⁾,

$$\alpha = \frac{P_{\text{BBr}_3}}{P_{\text{SiBr}_4}}$$

The average value of α , obtained by taking geometric mean from two terminal values of α (i.e., those corresponding to the boiling points of the components) was 5.5. The minimum number of theoretical plates, N_{min} , required at total reflux were calculated from Fenske's equation⁽²³⁾.

$$N_{\text{min}} + 1 = \frac{\log \left(\frac{x_D}{1 - x_D} \right) \left(\frac{1 - x_W}{x_W} \right)}{\log \alpha_{\text{av}}}$$

where X_D is mole fraction of the BBr_3 in the distillate, X_W is mole fraction of the BBr_3 in the residue and α_{av} is average value of relative volatility.

For calculation purposes the initial feed composition was fixed at 95 mole percent of BBr_3 and all other concentrations were taken as mole percentages.

The minimum reflux ratio, R_{min} was calculated using the following equation⁽²⁴⁾.

$$R_{min} = \frac{1}{\alpha_{av}-1} \left(\frac{x_D}{x_W} - \frac{\alpha(1-x_D)}{(1-x_W)} \right)$$

The operating reflux ratio R_o was taken as $\frac{3}{2} R_{min}$ ⁽²⁵⁾. The number of theoretical plates required at the operating reflux ratio was calculated from the graph of $\frac{N_o - N_{min}}{N_o + 1}$ versus $\frac{R_o - R_{min}}{R_o + 1}$ where R_o and N_o are the operating reflux ratio and theoretical plates respectively⁽²⁶⁾. The required number of theoretical plates were computed by taking into consideration the plate efficiency as 70 percent. The results of the calculations showing the required number of theoretical plates for varying residue compositions and distillate purity at operating reflux ratio are given in Table VI. Assuming that all the SiBr_4 in the mixture will remain in the residue along with about five percent of BBr_3 , the conditions for distillation were fixed as, number of theoretical plates 25; and reflux ratio 10.

Load and column dimensions : The distilled product, (BBr_3) usually gets coloured on storage and handling due to decomposition. Therefore it is not considered advisable to store it in bulk quantity. In order to keep the distilled product colourless it is preferable to distil the bromide directly into the glass ampoules of the required capacity (50 to 75 grams). Therefore an hourly distillate take off rate of 80-100 grams of the bromide was considered practical. The load on the column (the amount of material that passes through

TABLE VI
THEORETICAL PLATES AND REFLUX RATIO REQUIREMENTS

Feed composition (BBr ₃)	Residue composition after distillation (BBr ₃)	Distillate purity % (BBr ₃)	N min	R min	Ro	Theoretical plates at Ro	Number of actual plates
95%	10%	99.9	5.4	2.22	3.33	10.8	1
		99.99	6.7	2.22	3.33	13.4	18
		99.999	8.1	2.22	3.33	16.2	22
95%	5%	99.9	5.8	7.64	11.46	11.6	16
		99.99	7.2	7.64	11.46	14.4	20
		99.999	8.5	7.64	11.46	17.0	23
95%	1%	99.9	6.8	60	90	13.5	18
		99.99	8.1	60	90	16.2	22
		99.999	9.5	60	90	19.0	26

the column and condenses in unit time, i. e., the sum of distillate and reflux, must be kept in the range of 900-1100 grams per hour at the intended reflux ratio of 10. In order to calculate the column diameter for the intended load, one must know the limiting velocity of the vapour in the column. This velocity depends upon the packing to be employed. This was calculated using the equation⁽²⁷⁾,

$$\mu_1 = \sqrt{\frac{C_u d_p g}{Q_R}}$$

where μ_1 = limiting velocity in meter/sec. $Q_R = \frac{Q_V}{Q_L}$ = density of vapour / density of liquid at operating pressure. C_u = constant depending upon the type of packing employed. d_p = diameter of the packing unit in meters. g = acceleration due to gravity (9.81 m/sec²). The packing units to be used in the distillation column were 4 mm x 4 mm transparent quartz 'Rashig' rings having a wall thickness of about 1 mm. The value for C_u was taken as 0.01 (ref. 27). The limiting velocity thus calculated was 0.34 m/sec. It is customary in distillation experiments to load the column to about 50-70 percent of the calculated limiting velocity. Therefore taking the vapour velocity as 0.20m/sec, the cross-sectional area of the column was calculated from the equation⁽²⁸⁾,

$$A = \frac{0.0228 V \cdot T}{u} \text{ cm}^2$$

where A = cross-sectional area. V = amount of vapors in gm moles/hour. T = distillation temperature °K. u = selected vapour velocity cm/sec. The cross-sectional area was found to be 2.323 cm². The diameter of the column was therefore 17.2 mm.

In order to obtain the height of the distillation column, the height equivalent to a theoretical plate (HETP) for the intended column packing is needed. Since this data is not available in literature for the quartz 'Raschig' rings, it was experimentally determined using standard procedure⁽²⁹⁾. The HETP was found to be ~ 8.0 cm. Therefore the column height needed was $25 \times 8 = 200$ cms.

4.4 Apparatus and procedure

The distillation assembly used is shown schematically in fig. 2. It consists of a boiler flask (A) (one litre capacity), distillation column (B), a swinging funnel type distillation head (C) and the receiver (D). The boiler flask is electrically heated by an isomantle and the input heat to the boiler is controlled by a voltage regulator. The distillation column is of transparent quartz (O. D. 18 mm) with standard joints and packed with 4 mm x 4 mm transparent quartz 'Raschig' rings of about 1 mm wall thickness. The total packed height is 200 cms. The distillation column is surrounded by an electrical heat compensating jacket. A small iron core sealed inside a glass tube is attached to the 'swinging funnel' of the distillation head. An electromagnet (E) attracts the funnel when actuated by an electronic timer thus allowing the condensed liquid from the condenser to flow to the receiver. The on and off timings set on the timer help to set and control the desired reflux ratio. The stopcock used in the distillation head has a teflon plug in order to avoid use of any lubricants. All standard joints in the distillation head and column are used either dry or with teflon sleeves. The boiling point of the distillate is read with the thermometer (F). Dry nitrogen gas is allowed to flow through the distillation unit to ensure that no air or moisture is pulled into the system

during the distillation. The commercial nitrogen gas is dried by bubbling it through concentrated sulphuric acid and then passing it through packed columns of silica gel and phosphorus (V) oxide.

For carrying out distillation, all the apparatus in perfectly dry condition, is assembled as shown in fig. 2 and dry nitrogen made to flow through the apparatus. The boiler flask and the distillation column are heated to about 90°C by regulating the input voltage of the isomantle and heat compensating jacket. The distillation head and receiver assembly are also heated occasionally by an open flame. After about three hours of heating the apparatus is slowly brought to room temperature while the nitrogen gas continues to flow through the apparatus. The boron tribromide charge of about one kilogram is transferred to the boiler flask and brought to boiling by controlled heat input to the isomantle. The heat supplied is gradually increased such that flooding occurs throughout the packed length of the column. This is done in order to ensure that the packing in the column is uniformly wetted. The flooding condition is maintained for 20-25 minutes and then gradually the input is decreased. At this point the heat compensating jacket is switched on. The load is adjusted to about 900-1100 gm/hr by the heat supply to the boiler flask. The distillation column is maintained at total reflux for about 3 hours to attain equilibrium, after which the required reflux ratio is adjusted by means of the electronic timer. The first fraction of the distilled product ($\sim 10\%$) consisting of some free bromine, a highly coloured intermediate mixture of $\text{BBr}_3\text{-Br}_2$ and low boiling impurities is rejected. The middle fraction ($\sim 70\text{-}75\%$) is either collected in a round bottom receiver flask or directly in pyrex glass ampoules (50-75 grams) and sealed. The last fraction (remaining in the boiler flask)

which contains high boiling impurities and some boron tribromide is discarded.

4.5 Analysis

The boron tribromide samples (~ 2 ml) are hydrolysed carefully with distilled de-ionized water in a platinum dish. This operation is carried out in a suitably covered enclosure inside the fumehood. The hydrolysed product is slowly evaporated to remove excess of water. This is repeated 2-3 times with additional quantity of water to obtain a residue free from HBr. The dry residue mostly boric acid, is analysed spectrographically for metallic impurities.

5. RESULTS

The crude boron tribromide invariably contains, in addition to small amount of free bromine, impurities such as Si, Mg, Ca, Fe, Al, Ti etc., as their bromides. Among these, silicon tetrabromide was present to the extent of 3-5 percent; mainly due to the corrosion of reaction vessel. The spectrographic analysis of samples obtained from pure fractions in four distillation batches are given in Table VII. Since these analysis were carried out on the basis of boric acid obtained after hydrolysis of boron tribromide, the actual level of impurities in the purified bromide would be approximately one-fourth the tabulated values since the molecular weight of boric acid (61.83) is nearly one-fourth of boron tribromide (250.54). Silicon which is the major impurity in the crude product has been reduced to < 10 ppm (average) after a single distillation. The traces of metallic impurities such as Ca, Mg, Fe etc. found in the boric acid obtained by the hydrolysis of purified BBr_3 are attributed to have crept in through water during the hydrolysis although distilled de-ionized water was used for this purpose. It is only reasonable to assume that the level of these impurities in the purified product will be much lower.

TABLE VII

SPECTROGRAPHIC ANALYSIS OF H_3BO_3 OBTAINED AFTER THE HYDROLYSIS OF BBr_3 *

Batch No.	Sample No.	Pb	Mn	Cr	Al	Fe	Ca	Mg	Si
I	1	<5	<5	7	<10	10	25	14	<25
	2	<5	<5	8	<10	<10	<25	13	25
II	1	<5	<5	-	<10	<10	<25	16	30
	2	<5	<5	-	<10	12	<25	17	35
III	1	<2	<5	<10	<10	15	<20	30	45
	2	<2	<5	<10	<10	<10	20	12	35
IV	1	<5	<5	<10	<10	25	30	15	45
	2	<5	<5	<10	<12	25	30	17	35

* All values in PPM.

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APPENDIX A

PHYSICAL DATA OF SOME OF THE IMPURITIES
EXPECTED IN CRUDE BORON TRIBROMIDE

Compound	Boiling point °C	Melting point °C	Density 25°
1. S ₂ Br ₂	57	-46	2.629
2. COBr ₂	64.5	-80	2.44
3. SOBr ₂	139.7	-50	2.68
4. SiBr ₄	153.2	5.4	2.77
5. PBr ₃	172	-40.5	2.85
6. GeBr ₄	185.9	26.1	3.13
7. CBr ₄	189.5	48.9 ^α 90.1 ^β	-
8. POBr ₃	192	55.56	2.8
9. SnBr ₄	203	32	3.35
10. AsBr ₃	221	32.8	3.54
11. TiBr ₄	233	39	2.6
12. AlBr ₃	255-270	98	3.01
13. CaBr ₂	810	760	3.35
14. CuBr ₂	1318	483	5.05
15. MgBr ₂	1227	695	3.72
16. MnBr ₂	1027	698	4.39
17. FeBr ₂	927	684	4.64
18. FeBr ₃	627	227	-
19. PbBr ₂	918	360	6.67

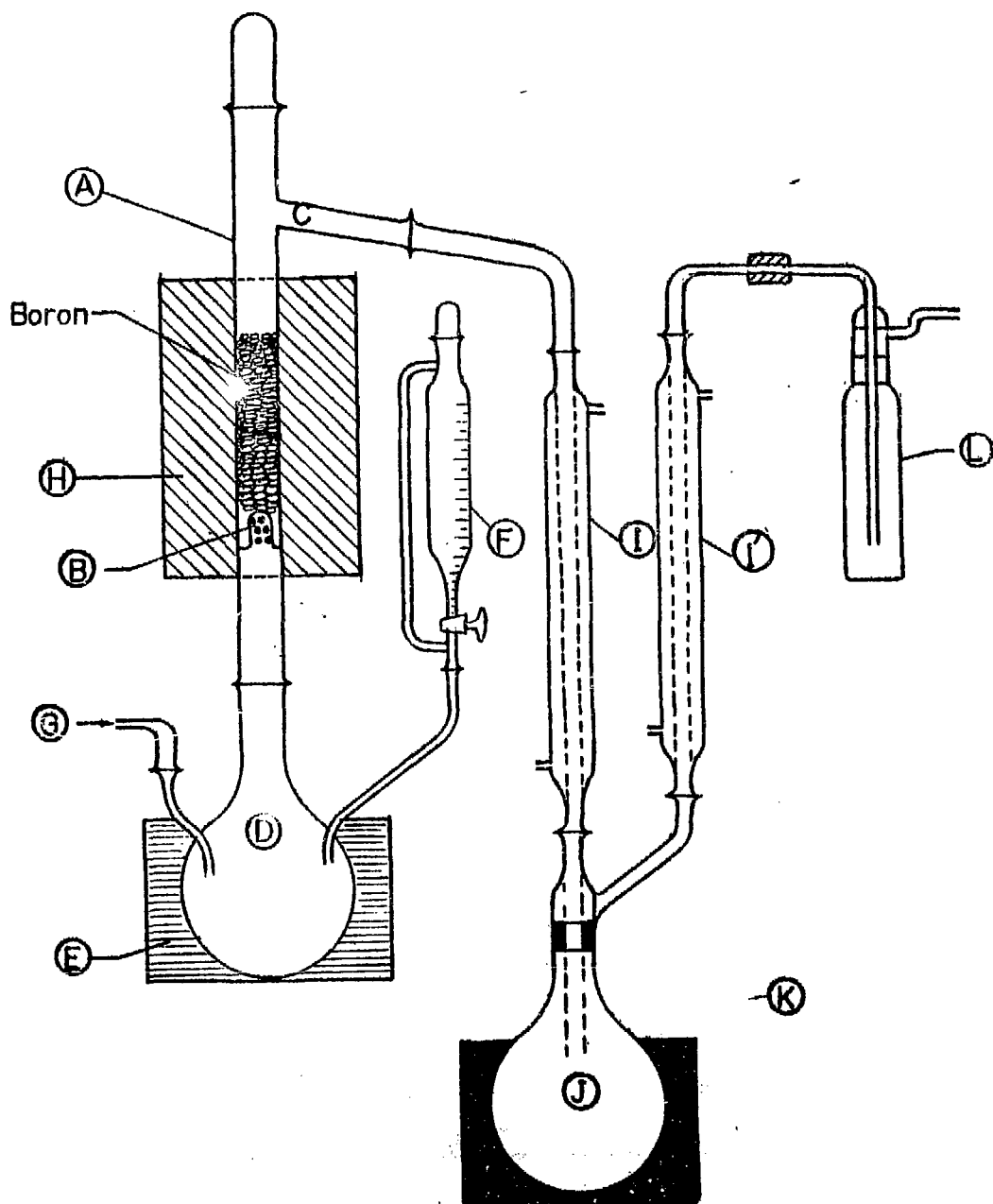
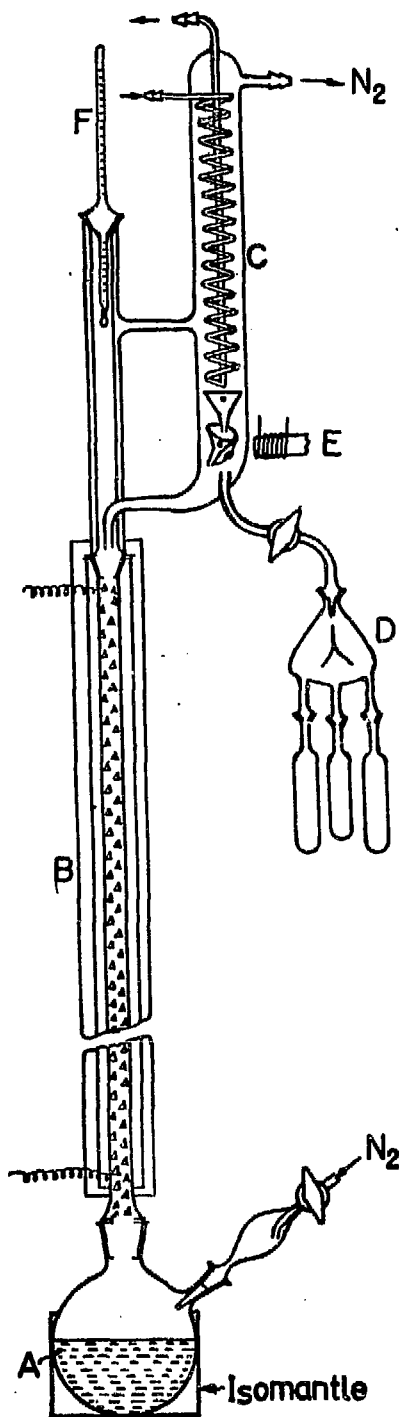


Fig.I. Experimental assembly for the preparation of Boron tribromide.

A-Reaction tube, B-Bromine dispersion tube; C-Outlet for bromide, D-Bromine boiler; E-Isomantle; F-Bromine reservoir; G-Inlet for argon; H-Furnace; I & I'-Water condensers; J- BBr_3 receiver; K-Support for the receiver; L-Sulphuric acid bubbler.



- A - Boiler flask
- B - Distillation column
- C - Distillation head
- D - Receiver
- E - Electromagnet
- F - Thermometer

Fig. 2. Distillation assembly.

