

A Method for Preparing Boron of High Purity

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Commercial boron has a low degree of purity, varying between 65 and 80 % of boron¹. It contains impurities of different kinds, for instance oxides of boron, aluminium, magnesium and iron, borides of aluminium and magnesium, and silicon compounds. Some of the impurities may be removed by treating the boron with acids and potassium hydroxide followed by heat treatment in vacuum, but the product still contains impurities amounting to 5—15 %.

Many methods have been suggested and used to obtain a pure product. These have been reviewed by Laubengayr and his associates². Later Laubengayr *et al.*³ prepared pure crystalline boron by reducing boron tribromide with hydrogen on a hot tungsten or tantalum filament. All the methods described, however, only give very small amounts of boron and in most instances a rather complicated apparatus is necessary. In connection with the studies on metal borides, carried out at this institute, a method for preparing boron of high purity has been worked out. It consists essentially of the vapor phase reduction of boron tribromide with hydrogen in a quartz tube at 750—800° C. The use of a quartz tube has the advantage of giving a much greater hot surface than a filament, and at the temperatures used quartz doesn't seem to be attacked at the reaction. The yield is 1—2 g of boron for each run, but the apparatus can be constructed for greater capacity.

APPARATUS

The apparatus is shown in Fig. 1. It consists of two reaction tubes (1 and 3) with condensation vessels (2 and 4). In the first tube boron tribromide is prepared by the action of bromine on commercial boron at 700° C. The reaction tube is composed of pure fused silica (translucent vitreosil) having a length of 700 mm and a diameter of 10 mm. The glass details are made of Pyrex, sealed to the tube by picein. All of these materials are resistant to the

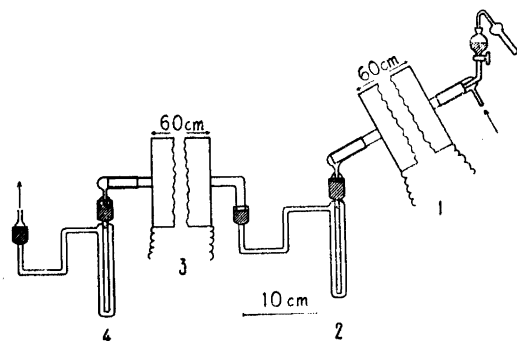


Fig. 1. Apparatus.

1. Furnace with quartz tube for preparation of boron tribromide.
2. Condensation vessel.
3. Furnace with quartz tube for reduction of boron tribromide with hydrogen.
4. Condensation vessel.

vapors of boron tribromide. Ground joints are avoided on the boron bromide side of the apparatus as most stopcock greases are attacked by the vapors, forming a mass which causes the joints to stick together. The connections between different parts of the apparatus are tightened by mercury in a manner, shown in Fig. 2. (Mercury is not attacked by boron tribromide, even at elevated temperatures⁴.) The use of mercury tightenings has the further advantage over ground joints in that they give a less rigid apparatus.

In the second tube (3) (Fig. 1) boron tribromide vapors are reduced by hydrogen to give pure boron. The reduction is carried out in a quartz tube (translucent vitreosil) having a length of 600 mm and a diameter of 10 mm. One end is bent and connected with the condensation vessel (2). The other end of the tube is provided with a Pyrex socket, sealed to the tube by picein and connected to the condensation vessel (4) as shown in Fig. 2. The condensation vessels are made of Pyrex, each having a volume of about 25 ml.

PROCEDURE

As boron tribromide is decomposed even by slight traces of humidity, the apparatus must be carefully dried by a stream of hydrogen, purified by passage over copper at 500° C and dried over cooled silica gel and phosphorous pentoxide. Boron tribromide is prepared by the action of dry bromine on commercial boron* (containing about 75 % of boron) at 700° C, principally according to the method given by Meyer and Zappner⁵. Instead of filling the tube with powdered boron, however, the boron is first pressed to pastilles to avoid subsequent stoppage of the tube. The bromide, having a boiling point of about 90° C, is condensed in vessel (2), cooled by a salt-ice mixture.

* To remove some impurities (iron oxide, part of the boron nitride and so on) the commercial boron is previously treated with hydrochloric acid.

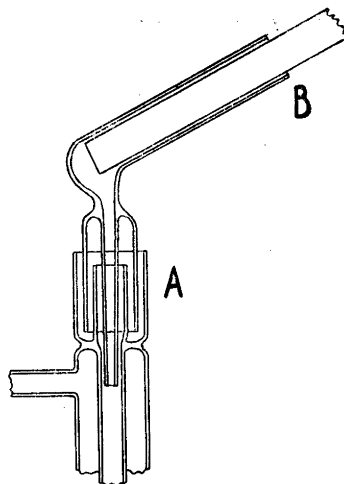


Fig. 2. Connections between different parts of apparatus.

The connections are tightened by means of mercury at A and by means of picein at B.

When 5—10 ml have been obtained, the bromine flow is interrupted and all bromine, remaining in the tube, is carefully driven out by hydrogen. With careful work, the preparation of the bromide takes about half an hour, giving a colourless liquid without any trace of bromine. Then the temperature of vessel (2) is raised to room temperature and the stream of hydrogen regulated to 2—4 bubbles per second. The hydrogen picks up the vapors of the bromide and the mixture is allowed to pass through the second quartz tube (3), where the reduction is carried out at 800° C. The elementary boron is deposited on the wall. At 800° C about half the initial amount of boron bromide has not taken part in the reaction and is condensed in vessel (4). The vessels are then changed and the procedure continued. When the boron bromide has been consumed, a new amount of bromide is prepared and the procedure repeated as above. The amount of commercial boron in tube (1), about 15 g, yields about 75 ml of the bromide. It is more convenient to work with 5—10 ml portions as described rather than preparing the whole amount of bromide at once because of the difficulty in storing the bromide for any longer time. If so stored, part of it often solidifies to a glassy colourless solid. This is probably caused by traces of humidity.

The deposited boron seems to catalyze the reduction. This is shown by Table 1. It thus is advantageous not to remove the boron from quartz tube (3) too early.

Reaction temperatures between 600° and 800° C have been tried, the upper limit depending on the permeability of the quartz tube for hydrogen at higher temperatures. The yield at different temperatures is given in Table 2. It thus seems to be of advantage to work at as high a temperature as possible.

Table 1. Yield of boron, using different amounts of boron tribromide each time starting with a clean reaction tube.

Temperature 800° C, reaction time about 1 hour/ml bromide.

Amount of BBr ₃ ml	Yield g	Efficiency %
5	0.220	39
10	0.550	48
14	1.250	78

For best performance of an apparatus, working continuously and with as small losses of bromide as possible, it would no doubt be necessary to have the hydrogen input in vessel (2). The mixture then should pass a quartz tube, the dimensions of the tube and the composition of the mixture having previously been chosen to give as complete a reaction as possible. The construction of such an apparatus, however, would necessitate a further study of the reaction constants, an investigation which lies beyond the purpose of this work.

PURITY AND PROPERTIES OF BORON

The product obtained is washed with hot water to remove traces of boron tribromide and dried. A yellowish-brown powder is obtained, which reacts vigorously and in an inflammatory way with concentrated nitric acid. To determine the boron content, samples of 50—100 mg were completely oxidized by nitric acid 1 : 1, and boric acid titrated in the presence of mannitol in the usual way. Values between 98.0 and 100.0 % of boron have been obtained with a mean value of 98.9 %. The possible impurities are silicon, oxygen and hydrogen and those metals, present in commercial boron which form easily vaporized bromides, especially aluminium. To determine the content of silicon, aluminium and magnesium, about 400 mg were brought into solution and evaporated in the presence of sulfuric acid. Boric acid was evaporated with methyl alcohol and the silicon content of the insoluble residue determined by the usual method. The value was compared with results, obtained from colorimetric determinations of soluble silicon.⁶ In the filtrate aluminium was precipitated as 8-hydroxyquinolate in slightly acid solution and determined by titration with bromate. Magnesium, if present, should form a precipitate with the same reagent in the filtrate from the aluminium determination if the solution was made slightly alkaline. No precipitate, however, was formed.

Table 2. Yield of boron at different temperatures.

Amount of bromide, used at each preparation 5 ml, reaction time about 1 hour/ml bromide.

Temperature ° C	Yield g	Efficiency %
600	0.003	0.5
650	0.079	14
700	0.110	19
750	0.165	29
800	0.220	39

The results showed, that most of the impurities were concentrated in the first 5 ml of boron tribromide formed by each successive filling of commercial boron in tube (1). If this portion was neglected, a mean value of 0.4 % aluminium and 0.1 % silicon was obtained. The silicon, present in the boron, does not seem to originate from the quartz tube, which after a run of about 150 hours was apparently unattacked. It seems to be generated by the reduction of silicontetrabromide present as an impurity of boron tribromide. A further purification was obtained by distilling the tribromide once in slightly modified vessels. For the purpose of this investigation, however, the purity of the boron was considered to be high enough and for this reason the tribromide was used undistilled.

Oxygen, if present, must form oxides of boron, silicon or aluminium. To determine the content of these oxides, samples of about 100 mg were heated in a stream of dry chlorine¹. In no case was any weighable residue left. To determine the content of hydrogen, samples of 25—50 mg were burnt in oxygen and the water thus formed absorbed by magnesiumperchlorate (anhydron) and weighed. No weighable amounts were obtained.

The mean values of the analyses of the final product are

Boron	98.9 weight %
Aluminium	0.4 » »
Silicon	0.1 » »
Magnesium	less than 0.1 weight %
Oxygen	» » 0.1 » »
Hydrogen	» » 0.1 » »

SUMMARY

A method for preparing boron of high purity by reduction of boron tribromide vapor with hydrogen in a quartz tube is described.

A description of the apparatus is given as well as the yield obtained at different temperatures and for different reaction times.

At 800° C an amount of 1—2 g of boron may be obtained after about 14 hours reaction time and with an efficiency of about 80 % according to the amount of boron tribromide used.

The product has a mean purity of 98.9 %, containing 0.4 % aluminium and 0.1 % silicon as impurities.

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