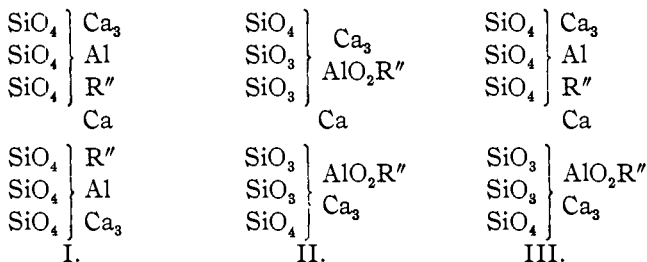


The structural formula suggested by Clarke shows all the aluminium as basic, as shown in formula I. If, on the other hand, it were all to be regarded as acid, this would become formula II. But if the considerations discussed above are valid, then a combination of the two, as shown in formula III, most nearly represents our present knowledge of the constitution of the mineral.



UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

DETERMINATION OF BORIC ACID IN INSOLUBLE SILICATES.

BY EDGAR T. WHERRY AND W. H. CHAPIN.

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Two methods were employed in the estimation of the boric acid, for the investigation described in the previous paper. The first method is really a volumetric procedure and was in this particular study the method applied by Edgar T. Wherry, while the second method, which is a distillation process, was used by William H. Chapin. The comparison of their final results is represented in the table.

Volumetric Method (Wherry).

In entering upon a description of the volumetric process it may be stated at once that in the determination of boric acid in silicates, when distillation is not resorted to, the great difficulty encountered is the separation of the desired constituents from the alumina. If the mineral is fused with alkali carbonate, and extracted with water, boric acid will remain in the residue. If, on the other hand, the fusion is taken up with acid, and ammonium hydroxide added, boron will be carried down with the sesquioxides, even after repeating several times. Precipitation of these oxides by treatment with ammonium chloride, with ammoniacal zinc oxide and with carbon dioxide were tried in this laboratory by Sargent,¹ without success. Morse and Burton² had obtained the boric acid by extracting a sodium hydroxide fusion with alcohol, finally weighing as barium metaborate, but this method did not meet with a favorable reception. Neutralization with potassium

¹ THIS JOURNAL, 21, 858 (1899).

² *Am. Chem. J.*, 10, 154 (1888).

iodide and iodate as suggested by Jones¹ and modified by Stock² was tested on a tourmaline, but failed to yield concordant results. Finally, the use of alkaline earth carbonates to precipitate the sesquioxides suggested itself, and upon being tried was found to give fair satisfaction. Schaak³ had already accomplished the removal of traces of alumina and silica from crude borates with barium carbonate, but had not extended this to insoluble silicates.

The method as finally developed is as follows: Fuse the sample with about 3 grams of sodium carbonate for 15 minutes. Take up with 20 to 30 cc. of dilute hydrochloric acid, adding a few drops of nitric acid to oxidize any ferrous iron. Place in a 250 cc. round-bottomed flask, heat nearly to boiling, and add dry precipitated calcium carbonate in moderate excess. Connect with a return condenser and boil vigorously for about ten minutes. Filter out the precipitate through a small Büchner funnel, washing several times with hot water, but keeping the total volume of liquid below 100 cc.

Return the filtrate to the flask, add a pinch of calcium carbonate and again heat to boiling; then connect with a filter pump, through a splash trap, and continue suction until the boiling has nearly ceased. Cool to the ordinary temperature, filter if the precipitate has a red color, from iron, add four or five drops of phenolphthalein, and run in slowly 0.1 N sodium hydroxide solution until the liquid is strongly pink in color. Introduce about a gram of mannite and shake, whereupon the pink color will disappear. Add sodium hydroxide to end reaction, then another gram of mannite and if necessary more alkali, until a permanent pink color is obtained.

In order to make clear the reasons for the various steps, so that the directions may be intelligently followed, full explanatory notes are here added.

Concerning the amount of the original substance to be operated upon, 0.3 gram is sufficient, if the boron content exceeds 5 per cent. while, if lower, 0.5 gram may be used. It is, however, desirable to keep the alumina-iron precipitate as small as possible.

The acid used to take up the fusion should consist of equal parts of concentrated hydrochloric acid and water. On account of the short fusion, some ferrous iron is likely to escape oxidation, and as this might cause trouble later, it must here be oxidized with nitric acid, or bromine water.

Solutions containing free boric acid should never be boiled openly, because of the volatility of the acid in steam. Before precipitation, therefore, the flask should be heated only until ebullition just begins.

¹ *Amer. J. Sci.* [4], 7, 1899, 147.

² *Compt. rend.*, 130, 1899, 516.

³ *Jour. Soc. Chem. Ind.*, 23, 1899, 699.

When the neutralization point is nearly reached, the calcium carbonate should be added slowly, so that the precipitate will be as granular as possible. For a return condenser a simple glass tube, about 2 cm. wide and 75 cm. long, will be found convenient; the air will cool this sufficiently. The liquid must be boiled for some time both to destroy any calcium bicarbonate formed and to insure complete precipitation of the sesquioxides. In most cases this will require about ten minutes, but frequently, especially when much manganese is present, a longer time seems necessary. Further, in minerals containing considerable iron, it is very difficult to remove all this metal by a single precipitation; a little calcium carbonate should then be added to the first filtrate, and the boiling and filtration repeated.

The filtration of the bulky gelatinous precipitates is by no means a simple operation. Reasonable rapidity has, however, been obtained by the use of an 8 cm. Büchner funnel, covered first by a layer of asbestos and then by a large filter paper, folded around a bottle of slightly less diameter than the funnel. A single stirring with hot water is all the washing required; the bulk of the solution should be kept small, for the end point in the titration is not very sharp if the liquid is too dilute.

All free carbon dioxide must now be removed, and this is accomplished by the use of the filter pump. The introduction of a "splash-trap"¹ is to be recommended, for this will prevent any loss by spattering, and also act as a safety tube in case the liquid tends to boil over.

The action should be continued until the formation of numerous small bubbles gives way to the appearance of occasional large ones, and the temperature has fallen to about 50°. It is then interrupted by pulling off the connecting rubber tube, and after allowing a moment for the splash trap to drain, the flask should be cooled to room temperature by running water over it. In this process there is not the least danger of loss of boric acid.²

The sodium hydroxide used in titration need not be free from carbonate, but must be standardized for the free hydroxide it contains. This is readily accomplished by the method of Winkler—precipitating the carbonate by adding barium chloride to a measured amount of alkali and then titrating slowly with standard acid, using phenolphthalein as indicator. In the operation of the present method the excess of calcium chloride will immediately precipitate all carbonate from the alkali, producing a faint, unobjectionable turbidity or, if suspended carbonate is already present, merely increasing its amount.

The first drop of alkali added should produce, where it strikes the liquid, a distinct pink color (which will, of course, disappear on stirring). If it fails to do so, the presence of calcium bicarbonate, which has escaped de-

¹ A 4-centimeter Reitmair and Stutzer trap was used here.

² Low, *THIS JOURNAL*, 28, 807 (1906). See also Note 5, distillation method.

composition during the process of boiling, is indicated. In this event the solution must be acidified, a slight excess of calcium carbonate added, and the boiling repeated.

The use of mannite as boric acid carrier, first placed on a practical basis by Jones,¹ is much to be preferred to that of glycerol, for only a very small amount is necessary, and the end point is decidedly sharper than with the latter substance. The number of cubic centimeters of alkali required, multiplied by 0.0035, will give directly the amount of free boric acid, B_2O_3 , present in the solution.

The question now arises, does this represent all the boric acid of the original substance? Two assumptions have evidently been made: first, that calcium carbonate will not neutralize free boric acid; and second, that the sesquioxide precipitate will be free from that substance. The first has been tested repeatedly by adding, after completion of the titration as described, some nitrophenol indicator, then acidifying, and finding the difference between the two end points, as described in connection with the second method. The amount of alkali required is practically the same in both cases, so that there is no danger of low results from this source.

The second point, however, requires more consideration. The precipitate as a matter of fact, does tend to retain a small amount of boric acid. The manner in which this is held is not entirely clear. A part of it is evidently mechanically enclosed, for it can be removed by simple boiling with water. But there is also a portion which appears to be combined with the alumina (or iron, as the case may be) and can be extracted only by dissolving the mass in acid, and repeating the whole precipitation process. With some minerals all of the boric acid is obtained after performing this operation three or four times. The following table will serve to show the extent of this effect, and its relation to the constituents present:

	Sample gram.	B_2O_3 , % obtained.	Total %.
Dumortierite, Al_2O_3 , 63%.....	0.5	3.87, 1.12, 0.35, 0.11	5.45
Ludwigite, Fe_2O_3 , 40%.....	0.3	9.93, 0.71, 0.71, 0.52, 0.22	12.80
Danburite, no sesquioxides.....	0.3	23.77, 0.29	24.06
Tourmaline, $Al_2O_3 + Fe_2O_3$, 35%... ..	0.3	8.88, 0.82, 0.23	9.93
Vesuvianite, $4Al_2O_3 + Fe_2O_3$, 20%... ..	0.3	1.75, 0.17	1.92

In most of the minerals examined about one-tenth of the boric acid was retained by the precipitate, as in the last two instances here cited. The proportion was as high as three-tenths only in the single case of dumortierite, while in the iron borates no definite relation could be traced.

Herein, then, lies the weak point of the method; with each reprecipitation the results become less and less certain, so that it is not to be recommended for general use. In the solution of a problem such as undertaken

¹ *Amer. J. Sci.* (4), 7, 147 (1899).

here, the comparative study of vesuvianites, it is, however, not without applicability. For, when the total boric acid does not exceed one or two per cent., reprecipitation is, in general, unnecessary, and it then surpasses any other method, both in simplicity and in rapidity, results which agree perfectly with those of the distillation method being obtainable in less than one hour.

TABLE I.—COMPARISON OF METHODS.

No.	Mineral.	Locality.	Author.	Found.	Chapin.	Wherry.	Average.
1.	Tourmaline (alt.)	Calif.	Schaller	(2.46)	1.22	1.20	1.21
2.	Dumortierite	"	"	5.21, 5.53	5.63	5.59	5.61
3.	Axinite	"	"	6.04	5.97	5.96, 6.00	5.98
4.	Tourmaline (alt.)	"	"	(7.66)	9.16	9.03	9.10
5.	" (black)	"	"	10.61	9.94	9.93	9.94
6.	"	A, Paris, Me.	Riggs	9.02	10.15	10.20	10.18
7.	"	B, " "	"		10.20
					10.28	10.16	10.21
					12.77		
8.	Ludwigite,	Montana	Schaller	13.48	12.89	12.80	12.82
9.	"	Hungary	"	(16.75)	15.72	15.71	15.72
10.	Danburite	Alaska	"	(26.34)	24.03	24.00, 24.06	24.03
					9.38	9.42	9.40
11.	Paigeite	"	"	(20.89)	9.82	9.83	9.83
12.	Hulsite	"	"	(25.27)	10.46	10.42	10.44

Distillation Method (Chapin).

The fact that boric acid can be completely expelled from an acid solution by volatilization as methyl borate has long been made use of in analytical work. The first quantitative methods based upon this principle were those of Gooch¹ and Rosenblatt,² which appeared simultaneously in 1887. According to both methods the solution containing the boric acid was first distilled to dryness, and then methyl alcohol was added in small portions and distilled off, carrying with it the boric acid. Gooch fixed the boric acid in this distillate by pouring over lime, evaporating to dryness, and igniting to constant weight; Rosenblatt used magnesia in place of lime. The forms of apparatus used by these two analysts differed somewhat, that of Gooch being made from a pipette bent into the form of a goose-neck, while Rosenblatt's was simply an Erlenmeyer flask.

In 1893 Thompson³ produced a volumetric method, according to which the boric acid was set free by means of hydrochloric acid, using methyl orange as indicator, and then titrated with sodium hydroxide in presence of glycerol, using phenolphthalein as indicator.

Later, in 1899, Sargent⁴ developed a combination of the Gooch-Rosen-

¹ F. A. Gooch, *Am. Chem. J.*, **9**, 23 (1887).

² Th. Rosenblatt, *Z. anal. Chem.*, **26**, 21 (1887).

³ Thompson, *J. Soc. Chem. Ind.*, **12**, 432 (1893).

⁴ G. W. Sargent, *THIS JOURNAL*, **21**, 859 (1899).

bladt method and the Thompson method, the methyl borate being collected in sodium hydroxide, the boric acid set free by use of hydrochloric acid and methyl orange, and then titrated with sodium hydroxide in presence of glycerol and phenolphthalein.

The latest modifications have been those of Schaak¹ and Low.² They effect the volatilization of the boric acid by running a current of methyl alcohol vapor through the solution. Schaak excludes water and avoids the hydrolytic action by use of concentrated sulphuric acid. The amount of boric acid he determines by the method of Thompson, performing the titration upon the alcoholic distillate as if it were a water solution. His apparatus consists of a Kjeldahl flask attached on the one hand to a distilling flask for supplying a current of methyl alcohol vapor, and on the other to a small condenser.

Low avoids the action of water by use of anhydrous calcium chloride, and determines the amount of boric acid by use of a double titration. The first titration, like Schaak's, is made upon the alcoholic distillate just as it comes from the condenser, but without the use of glycerol. Previous to the second titration the alcohol is distilled off, and carbon dioxide removed by boiling the acid solution under reduced pressure. The boric acid is then titrated according to Thompson's method. Low's apparatus is practically the same as Schaak's. The most characteristic features of Low's modification are the use of *calcium chloride*, the *double titration*, and the removal of carbon dioxide by *boiling under reduced pressure*.

The method outlined in this paper is based principally upon that of Low. In his paper, however, Low speaks of the application of his method only to the analysis of foodstuffs; and in view of the fact that a good method has long been needed in mineral analysis it has been sought to extend the use of the method into that realm. To this end some modifications have been introduced and some additions made where necessity demanded. At other points, also, even where not called for by this new application of the method, changes have been made where they seemed advisable.

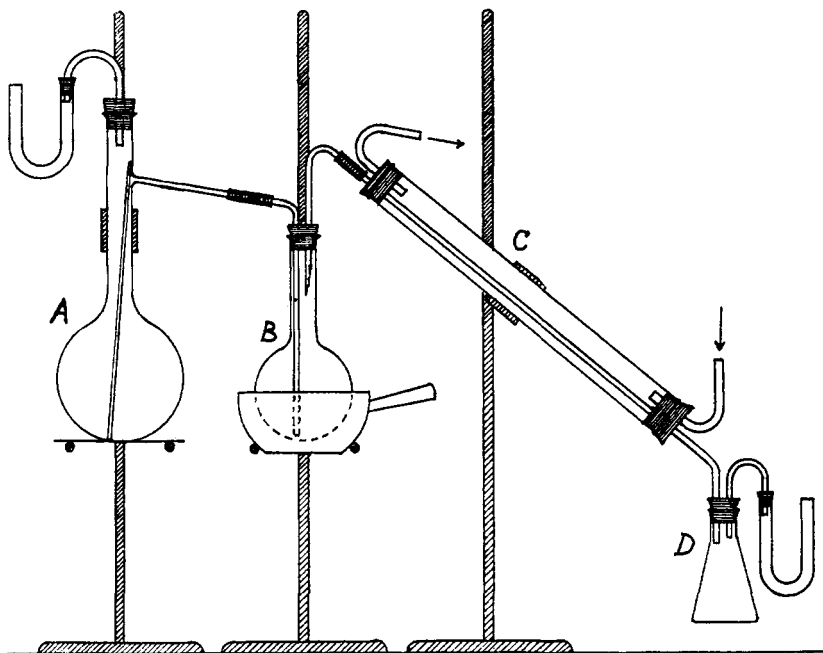
Apparatus.—The form of apparatus used by Schaak and Low needs little improvement. The only changes that have been made are those looking towards greater simplicity and ease of construction. The outfit here shown can be put up in an hour or two, and when once constructed is good for any number of determinations:

A is a 500 cc. round-bottom distilling flask in which the vapors of methyl alcohol are generated. It is supported by a clamp attached to a ring stand, and rests on a wire gauze as shown. It is provided with a "boiling tube"—a long capillary glass tube, 1 mm. internal diameter, having the bore closed at a point 1 cm. from the lower end. This tube

¹ M. A. Schaak, THIS JOURNAL., 23, 699 (1904).

² W. H. Low, *Ibid.*, 28, 807 (1906).

must always be used when boiling the alcohol, as without it it bumps badly. After the alcohol has been boiled it is always necessary to remove the tube and shake out the alcohol before boiling again. The U tube at the top of the flask contains a little mercury. This acts as a trap to prevent explosion in case the outlet tube should become clogged, and also to prevent the liquid from sucking back when the apparatus is cooling down. Obviously the amount of mercury must be a little less than sufficient to balance a column of liquid equal in height to the vertical part of the delivery tube. The stopper in *A* is pure gum, as are also all the other large stoppers used in the apparatus.



B is a 250 cc. round-bottom flask—the “decomposition flask.” It rests in a casserole of water and is supported at the top by the connecting tubes. The tube leading from *A* reaches to within 0.5 cm. of the bottom of *B* and is connected to the side tube of *A* by means of a short rubber connector. A joint is necessary here, as without it the apparatus is too rigid. The outlet tube should be rather wide, and should have a vertical height of not less than 12 cm. The end inside the flask is made jagged to allow the condensed liquid to drop back instead of jumping up the tube. A “splash trap” may be used here, but is neither necessary nor desirable.

C is a condenser made from 3 cm. thin-walled glass tubing. It should be about 40 cm. long. A condenser of this kind is far better than one of the ordinary large ones, and can easily be made in half an hour.

D is a 250 cc. Erlenmeyer flask used as a receiver. The stopper with the bent tube leading to the U-tube always remains attached to the condenser. The receiver hangs free from the bench, being simply pushed on to the stopper until tight. It can thus be taken off and replaced without disturbing the rest of the apparatus. Two or three of these flasks, with necks of the same size, should be provided, so that the receiver may be changed without interrupting the distillation. The small U-tube contains a little water, which acts as a trap to prevent the escape of any uncondensed methyl borate. It is slipped on and off its stopper like the receiver.

E (not shown) is a second condenser like the one here shown. It is connected on the one hand to a flask exactly like *B*, which, however, has a one-hole stopper, and rests completely within a large steam bath. This flask, like the distilling flask *A*, is provided with a "boiling tube." On the other hand the condenser is connected with a receiver like *D*, but without the U-tube. This condensing apparatus is used for distilling off the alcohol after the preliminary titration.

F (not shown) is a filter pump. At the end of the side tube is an "elbow" tube connected to a two-hole rubber stopper of the proper size to fit the flask mentioned in connection with *E*. The second hole of the stopper is closed by means of a glass plug which can be withdrawn to break the vacuum. Midway between the pump and the stopper is a small safety bottle, whose function is to prevent the tap water sucking back into the flask.

Reagents: Para-nitrophenol.—This substance is used as an indicator. It is sensitive to strong acids, very slightly sensitive to carbonic acid, and indifferent to boric acid alone in dilute solution. However, to boric acid in combination with glycerol or mannite it is somewhat sensitive, and therefore cannot be used in neutralizing free mineral acid when this combination is present. Although somewhat sensitive to carbonic acid, it can be used in presence of small amounts of carbonates, the color being simply weakened and not wholly discharged. In acid solution this indicator is colorless, in *neutral* or *alkaline* solution it is yellow. This indicator was used in place of methyl orange in neutralizing free mineral acid, for the reason that the process must be carried out in presence of a large amount of alcohol, by which it is much less affected than methyl orange. Make up by dissolving 1 g. of the solid in 75 cc. of neutral ethyl alcohol, and adding 25 cc. water.

Phenolphthalein.—This indicator is sensitive, not alone to strong acids, but also to weak acids like carbonic and boric. Its sensitiveness to boric acid is, however, not sufficient to permit accurate titration without the addition of some substance like glycerol or mannite by which the acid properties of boric acid are strengthened. Carbonic acid must be gotten

rid of before titrating. Make up by dissolving 1 g. in 100 cc. of ethyl alcohol and diluting to 200 cc. with water.

Hydrochloric Acid.—The only standard solution that will be needed is 0.1 N. This can be prepared in any of the usual ways. The water used should be boiled to free it from carbonic acid.

For the rough work a 1:1 acid is used, and this is well made up in considerable amounts. A dropping bulb should be provided and filled with this acid for use when it is needed in accurate, small amounts.

Sodium Hydroxide.—Two standard solutions of this reagent will be required, 0.5 N and 0.1 N. These should be standardized against pure B_2O_3 .

First prepare a 0.1 N solution of pure B_2O_3 as follows: Take pure orthoboric acid, H_3BO_3 , and fuse it in a platinum dish. While still warm break it into moderately small pieces and quickly introduce into a weighing tube. Weigh out exactly 1.75 grams and dissolve in 250 cc. of hot, *recently boiled* water; cool, and make up to 500 cc. This solution is exactly 0.1 N; that is, in presence of glycerol or mannite 1 cc. is neutralized to the phenolphthalein end point by 1 cc. of 0.1 N sodium hydroxide.

In standardizing the sodium hydroxide against this solution both indicators should be used, so that the end may be the same as that seen in actual titration. Proceed exactly according to the directions for the final titration, only assuming, of course, that the boric acid solution is exactly neutral to para-nitrophenol; that is, is free from mineral acid, which is true. When sodium hydroxide is standardized in this way, the small amount of carbonate always present does no harm, which is not true if it has been standardized in the usual way against a mineral acid, using methyl orange as indicator.

Glycerol.—Commercial glycerin contains fatty acids, which must be neutralized before it can be used. It is not sufficient to neutralize the whole stock and depend upon that, as there seems to be a slow decomposition, possibly of fats, by which more of the acids are generated. Each portion must, therefore, be neutralized just before using. However, it is well to take the whole stock of glycerol and partially prepare it as follows: For each 500 cc. of glycerol add 50 cc. of water to make it less viscid; then add 5 cc. of phenolphthalein solution, and after shaking run in 0.5 N alkali until the pink color of the indicator begins to appear. Now, although this end will not be permanent, all that is necessary, when using, is to measure out the proper amount, and bring up to the end with 0.1 N alkali.

Mannite.—Mannite may be used in place of glycerol if so desired; and indeed it possesses some advantages over that reagent. Being a solid, it is more easily handled; and since it does not increase the bulk of the

solution to which it is added, the end point is sharper. Moreover, it is more likely to be free from acids, and therefore usually needs no preliminary treatment. Comparative experiments show that the results are equally accurate with glycerol and mannite. Choice, therefore, rests simply on convenience.

Methyl Alcohol.—In this case the ordinary commercial alcohol cannot be used. On the other hand it is unnecessary to use that of the highest purity. We have found Kahlbaum's "No. 1" perfectly satisfactory for this work. Of course this may not be of uniform quality, and for that reason it is safest either to run a blank, or assume that it is not quite pure, and redistil over lime. We have tried to use the ordinary commercial alcohol after heating over caustic soda and lime, but find that it does not work well.

The alcohol that has been used and distilled off need not be thrown away. All that is necessary is to dehydrate over lime, and redistil. To accomplish this quickly it should be *heated* in contact with the lime to a temperature at or near its boiling point for several hours, using a return condenser. If not heated it will require several days to dehydrate. The more nearly anhydrous the alcohol is the better it works; that is, the less will be required to volatilize a given quantity of boric acid. This is an essential condition of quick work.

Details of the Method.—In making the analysis of a mineral, the size of the sample to use will depend on the amount of boric acid present. No matter how small the amount, we do not use over 0.5 gram; and only in cases where the amount exceeds 10 per cent. do we use less than that. Where the percentage is high it is best to so limit the size of the sample that the amount of boric acid (B_2O_3) shall not exceed 0.1 gram. Otherwise too long a time will be required for complete volatilization; and the amount of standard soda required will be so large as to very much dilute the solution, and thus render the end points less distinct.

In weighing out the sample it is best to choose some definite amount—0.5, 0.4 or 0.3 gram and weigh it exactly. Weighing in this manner requires no more time, and very much shortens the subsequent calculations. Moreover, it very much lessens the liability to error.

If a flux is required, that, too, should be weighed out to within a milligram or two; and then the amount of acid required to take up the melt can be measured out at once, and there is no danger of having too great an excess.

Proceed, then, with the analysis as follows: If the mineral is soluble in hydrochloric acid weigh out a sample as above indicated into a glazed porcelain crucible, transfer this to the decomposition flask, taking care to keep the neck clean, and treat with not more than 5 cc. of the 1:1 hydrochloric acid (Note 1). Having added the acid, heat the flask gently on a water bath until solution is complete. If the mineral is not completely

soluble in hydrochloric acid it would be safer to treat it as if it were an insoluble silicate, and fuse with a flux.

If the mineral is an insoluble silicate weigh out a sample as above indicated into a platinum crucible. Upon the sample place exactly six volumes of flux ($K_2CO_3 + Na_2CO_3$) and then stir together until the two are intimately mixed. Fuse now in the usual way, and when decomposition is complete allow the melt to cool completely. Without removing the melt from the crucible decompose by means of the 1:1 hydrochloric acid, using 4 cc. for each gram of flux. While this is being done the crucible should stand in a casserole to avoid loss in case the liquid froths up, and the crucible cover should be kept in place as much as possible. Towards the last it may be necessary to heat a little to hasten the action, but care should be taken not to boil (Note 2). When solution is complete, pour the liquid into the decomposition flask, and rinse the crucible with a *very little* water.

To the solution contained in the flask, whether from the mineral alone or its carbonate fusion, add pure anhydrous calcium chloride, using about 1 gram for each cc. of liquid, and running it in through a paper funnel to keep the neck of the flask clean. After a little experience it will not be necessary to weigh out this calcium chloride, as one learns to estimate pretty closely the amount needed. Especially is this true if it be measured out in the same vessel each time.

After twirling the flask about for a moment or two and allowing the chloride to take up the water, connect it up in its place with the rest of the apparatus, raise the casserole beneath it until the flask rests in the water but does not touch the bottom, and then begin the distillation. At this point two things must be remembered: First, the boiling tube must be in the distilling flask and its open end must be free from alcohol; second, the little U tube attached to the receiver must have in it enough water to form a seal.

The decomposition flask is not heated until about 25 cc. of alcohol have condensed in it. After that a small flame is applied to the water bath, and the flask thus kept hot enough to prevent further condensation. Care should be taken not to allow the distillation to proceed too rapidly, or methyl borate may be driven out and lost in spite of the water trap.

When a distillate of about 100 cc. has been collected change receivers, add the contents of the trap to the distillate, and proceed with the preliminary titration, thus: Add a drop of para-nitrophenol, and run in the standard sodium hydroxide solution until the indicator shows that the free mineral acid is neutralized. Next, add 1 cc. of phenolphthalein, and continue the titration until the color of that indicator begins to appear. The end here will not be sharp, but approximate results may be expected. Where the amount of boric acid is small, the end does not appear as soon

as it should, and when the amount is large it appears too soon. The amount of alkali used between the two end points indicates approximately the amount of boric acid in the distillate. Whether to use 0.5 N or 0.1 N alkali depends upon the amount required. If the mineral is likely to contain more than 3 or 4 per cent. of boric anhydride, use the 0.5 N solution. The object, of course, is to keep the distillate as free from water as possible, and thus facilitate the work of dehydration later on.

After completing the titration, add to the distillate *twice* as much alkali as has been used between the two end points, transfer the distillate to the second condensing apparatus, and proceed to distil off the alcohol (Note 3). If the flask is completely within a rapidly boiling steam bath, this distillation should proceed very rapidly.

By the time this portion is in the distilling apparatus, another portion of about 100 cc. will be ready. Unless the alcohol contained water or the amount of calcium chloride added was insufficient, this second distillate should be all that will need to be run off. Therefore, before removing the receiver, stop the distillation. Treat this distillate exactly as the first one was treated, and finally add it to the first already in the condensing apparatus. If the amount of alkali used in titrating the boric acid in this distillate is less than 1 cc. of the 0.1 N solution or 0.2 cc. of the 0.5 N solution, the distillation may be regarded as complete (Note 4).

When the liquid from which the alcohol is being distilled off no longer boils in the steam bath remove it to a casserole, rinsing the flask once or twice, and heat over a direct flame, rotating the casserole in the meantime, until the little remaining alcohol has been boiled out. The residue should now be small—about 25 cc. if 0.1 N alkali was used, and much less if 0.5 N was used. If the volume is less than 25 cc. make up to that amount.

Return the solution to the flask, and add drop by drop with constant twirling 1:1 hydrochloric acid from a dropping bulb until the color of both indicators is discharged, taking care not to add a drop too much. Now put in the boiling tube, heat the flask in the steam bath for a minute or two, and then attach to the filter pump and boil under reduced pressure until the liquid is nearly cold, and only an occasional large bubble appears. By this process all the carbon dioxide is removed from the solution (Note 5). When this is done break the vacuum, cool if necessary under the tap, and then proceed to the final titration. First neutralize the excess of hydrochloric acid by running in carefully 0.5 N sodium hydroxide until the yellow of the para-nitrophenol just appears. Run back to acid reaction with 0.1 N hydrochloric acid, and then again run just to the appearance of the faint yellow, with 0.1 N alkali. The solution is now exactly neutral, since the indicator itself shows this color in neutral

solution. At all odds make sure that the end is reached exactly. One drop of the 0.1 *N* acid should entirely discharge the color.

Now measure out about 40 cc. of the glycerol which has been partially prepared as directed under "Reagents," bring it up to the phenolphthalein end point by means of the 0.1 *N* sodium hydroxide, and then add it to the solution containing the boric acid. Or, if the mannite is used, add about 1 gram here, and then another gram after the titration.

Having added the mannite or glycerol, take the burette reading, and then continue the titration to the phenolphthalein end-point. If mannite was used add the other gram here, and if this causes a disappearance of the end, add more alkali until it reappears (Note 6).

The number of cubic centimeters of the alkali used multiplied by its equivalent in terms of B_2O_3 gives the amount of the latter contained in the solution. If the solution of alkali is exactly 0.1 *N*, this equivalent is 0.0035.

As to the time required for a determination see Note 7.

Notes.—1. The reason for limiting the amount of acid scarcely needs mentioning. The larger the excess, the more will go over with the distillate, and the more of the standard alkali will be required to neutralize it. 5 cc. of the 1:1 acid is sufficient for the solution of any sample of proper size.

2. If a solution of boric acid be boiled at ordinary temperature some of the acid is sure to be carried away with the steam. If such a solution must be boiled a return condenser of some sort should be provided.

3. When sodium hydroxide is added to a solution of boric acid, the first reaction that results may be represented by the following equation:



The phenolphthalein end point appears when this reaction is completed; hence this is the equation which must be used in calculating the value of a standard sodium hydroxide solution in terms of B_2O_3 . But this metaborate, $NaBO_2$, is not stable in boiling methyl alcohol, and for that reason would be decomposed with loss of boric acid upon distilling off the alcohol. However by adding more alkali to such a solution, a second reaction results:



producing the stable orthoborate, from which methyl alcohol may be distilled off with safety.

It should be noted that the second reaction requires for its completion twice as much alkali as the first.

4. With a view to determining the amount of alcohol necessary to be distilled off in order to make sure of volatilizing all the boric acid, and to find whether the complete volatilization was interfered with by

any substance or combination of substances likely to be found in a boron mineral, the following experiments were conducted:

Experiment 1.—10 cc. 0.1 *N* boric acid solution were taken, equal to 0.035 gram B_2O_3 . The following substances were added:

Sodium silicate.....	0.1 gram
Ferrous sulphate.....	1.0 "
Potassium fluoride.....	0.1 "
Sodium carbonate.....	0.01 "
Sodium chloride.....	1.00 "
Calcium chloride.....	10.0 "
Hydrochloric acid.....	2.0 cc. 1:1

Two distillates of 100 cc. each were collected, which in the preliminary titration required respectively 2.2 cc. and 0.4 cc. 0.5 *N* sodium hydroxide for the boric acid content.

The total B_2O_3 found by the final titration was 0.0348 gram.

Experiment 2.—10 cc. boric acid, equal to 0.0350 gram B_2O_3 .

Substances added:

Alum.....	0.5 gram
Sodium silicate.....	0.1 "
Magnesium sulphate.....	0.1 "
Arsenious oxide.....	0.05 "
Manganese chloride.....	0.1 "
Sodium phosphate.....	0.1 "
Sodium chloride.....	0.1 "
Calcium chloride.....	10.0 "
Hydrochloric acid.....	4.0 cc. 1:1

Two distillates of 100 cc. each were collected. The preliminary titration gave respectively 1.9 cc. and 0.5 cc. 0.5 *N* sodium hydroxide. The B_2O_3 found in final titration was 0.0346 gram.

In this case a third distillate of 50 cc. was collected, and found to contain 0.0005 gram B_2O_3 . Total B_2O_3 found 0.0351 gram.

Experiment 3.—10 cc. boric acid equal to 0.0350 gram B_2O_3 .

Substances added:

Ferrous chloride.....	0.2 gram
Ferric chloride-(ous).....	0.2 "
Stannous chloride-(ic).....	0.1 "
Antimonious chloride.....	0.1 "
Zinc chloride.....	0.1 "
Calcium chloride.....	15.0 "
Hydrochloric acid.....	5.0 cc. 1:1

Two distillates of 100 cc. each were collected, requiring in the preliminary titration respectively 1.9 cc. and 0.3 cc. 0.5 *N* NaOH, for the B_2O_3 content. The B_2O_3 found by the final titration was 0.0352 gram.

These experiments show plainly that the substances added neither hindered the complete volatilization of the boric acid nor in any way interfered with its accurate titration afterwards. They also show that it is not safe to stop the distillation until the final distillate requires less than 0.4 cc. 0.5 *N* NaOH.

5. Boiling thus under reduced pressure does not endanger a ponderable loss of boric acid. We have again and again collected the water that

distills off, and tested it for boric acid both qualitatively and quantitatively. In a few cases we have been able to get a very faint test with turmeric paper, but in no case have we found an amount equivalent to 1 drop of 0.1 *N* NaOH. We even collected the distillate from three determinations and tested it all in one portion, but this, too, showed less than the equivalent of 1 drop of 0.1 *N* NaOH.

6. The changes of color that take place during the titration are worthy of mention. When the glycerol or mannite is added to the solution the yellow color due to the para-nitrophenol at once disappears. This is due to the fact that the combination of these reagents with the boric acid forms an acid of sufficient strength to affect the indicator, although boric acid alone does not. As the titration proceeds the color reappears, and grows stronger and stronger, becoming very intense just before the phenolphthalein end appears. The latter will be noticed first as a faint brownish tinge; and then another drop of the 0.1 *N* alkali changes it to an intense brownish red. The brownish tinge marks the real end point, of course.

7. Compared with the time required for other gravimetric determinations the time necessary to carry out this method is not excessive. After apparatus and reagents are ready, a series of determinations at the rate of four a day may be easily run, counting eight hours as a working day.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ATOMIC WEIGHT OF PALLADIUM.¹

By GEORGE I. KEMMERER.

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The atomic weight of palladium has been the subject of no less than twelve separate investigations. The results vary so much that it seemed desirable to give this problem further consideration. Accordingly, thirty-two grams of sheet palladium were purified by the method pursued by Keller and Smith.² From it, salt *A* was prepared. A second sample of metal was purified in the same way as the first but the mercuric cyanide was replaced by ammonium cyanide and ammonium compounds were applied wherever sodium and potassium salts had been used in the first process. All reagents, *e. g.*, water, hydrochloric acid, sodium carbonate, mercuric cyanide, ammonium formate, sulphur dioxide, ammonium thiocyanate, etc., were made pure by well established and generally accepted processes.

The salts studied were:

¹ From the author's Ph.D. thesis.

² *Am. Chem. J.*, **14**, 423 (1892).