

THE QUANTITATIVE ESTIMATION OF BORIC ACID IN TOURMALINE.¹

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INTRODUCTION.

NOTHING of the constitution of this mineral is understood. In fact, exceedingly little is known concerning the structure of much less complex minerals. Structural formulas have been proposed, but these are conjectures only.

The problem that confronts the chemist undertaking to throw light upon the constitution of any of the products of nature's laboratory, is a very difficult one. No mode of attacking the problem has ever been devised. Substitutions, syntheses, and decompositions cannot be made as with organic bodies. There is no means of estimating the size of the molecule. The question of determining which elements are linked together in many instances seem unanswerable. Again, many elements are capable of existing in two conditions; this complicates the problem still further. Before attempting to answer these questions, however, the composition of the body must be known.

In a careful review of the literature of mineralogy, it will be noticed that in many cases some constituent of a mineral has been determined by difference, owing probably to the fact that no good direct method of estimating it existed at that time. Every chemist feels the necessity of directly determining any constituent. It is especially desirable that this be done in the analyses of complex substances. It may happen that many years have elapsed since the analysis of the mineral was made. Since then the old methods probably have been shown to be inaccurate, hence a redetermination is desirable. Owing to the difficulty of estimating boric acid, Rammelsberg, in numerous instances, in his analyses of tourmaline, obtained it by difference.

Boric acid constitutes from six per cent. to twelve per cent. of this mineral. Silica and alumina are its common associates from which it is separated with great difficulty. Since the time

¹ From the author's thesis presented for the Ph.D. degree, 1898.

of Rammelsberg, many methods have appeared, but few have been found applicable to insoluble borates or borosilicates; with tourmaline, they have proved tedious or unreliable. A chronological review of the various methods for the determination of this acid may be interesting. At least, it will show the condition in which the quantitative determination of boric acid rests at the present time.

HISTORICAL RÉSUMÉ.

Probably the first work that was done toward the quantitative determination of boric acid, was that of Arfvedson,¹ By heating a mixture of borax and calcium fluoride with sulphuric acid, he volatilized the boron as fluoride; the sodium sulphate resulting from this treatment was dissolved out with water, evaporated to dryness, weighed, and the boric acid calculated.

Berzelius² attempted the determination by precipitating boron as potassium borofluoride. Berzelius also used Arfvedson's method with success, but in place of the calcium fluoride and sulphuric acid, he took hydrofluoric and sulphuric acids. In 1828, Menil³ endeavored to estimate boric acid by means of the silver salt, $3\text{Ag}_2\text{O} \cdot \text{B}_2\text{O}_3$, but met with little success. Gay Lussac,⁴ in the year 1830, called attention to the titration of borax by a sulphuric acid solution with tincture of litmus as the indicator. The reaction is: $\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{B}_2\text{O}_3$. The liquid changes color only when free sulphuric acid is present. This was the first volumetric method proposed.

Rose⁵ was the first to volatilize boric acid as the ethyl ester and obtain its amount by difference. This was in 1850, but as early as 1732, Claude Geoffrey knew that boric acid imparted a characteristic green color to the alcohol flame and in 1818, Stro-meyer⁶ mentioned the volatility in an alcoholic solution and the characteristic green color given to the burning liquid. Rose, in his paper, gave a second method, in which a weighed amount of sodium carbonate was added to the borate, evaporated to dryness, and ignited until there was no further evolution of carbon

¹ *K. Vetensk. Acad. Handb.*, (1822), 22, and *Schweigg. Jour.*, 8, 7.

² *Lehrbuch*, 3, Aufl. 84; *Pogg. Ann.*, (1824), 2, 118.

³ *Jsb. d. Chem. und Phys.*, 2, 364.

⁴ *Ann. Chem. et Phys.*, 40, 398.

⁵ *Pogg. Ann.*, 80, 261.

⁶ *Ibid.*, 61, 179.

dioxide. The residue of sodium carbonate and boron trioxide was weighed and from this the boric acid calculated.

Berzelius' method gave poor results, owing to the solubility of the precipitate of potassium borofluoride in alcohol, with which it was washed to free it from potassium fluoride. Weber¹ tried modifying the method of Berzelius, in order to avoid the formation of the large quantity of fluoride, but did not succeed. Rammelsberg² found that if the alcohol used for washing the precipitate was free from water, potassium fluoride contaminated the precipitate, and that alcohol containing water dissolved some of the potassium borofluoride. Schweitzer³ estimated the base and determined the boric acid by difference, by evaporating the base with hydrochloric acid until all the acid was expelled and estimating the chlorine as silver chloride.

In 1856, Kraut⁴ showed that a borax solution boiled with ammonium chloride, reacted according to the following equation: $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{NH}_4\text{Cl} = 2\text{NaCl} + 2\text{B}_2\text{O}_3 + 2\text{NH}_3$, and the ammonia could be caught in a standard acid solution, and thus the boric acid determined. This same year, the method of Stromeyer⁵ appeared. He added to the solution of the borate two equivalents of potassium hydroxide to one equivalent of boron trioxide contained in the borate, then an excess of hydrofluoric acid and evaporated to dryness. The residue he dissolved in a twenty per cent. solution of potassium acetate, and filtered through a weighed filter, using a gutta percha funnel. The precipitate was washed first with a solution of potassium acetate to remove potassium fluoride, then with alcohol, dried at 100° C., and weighed. Upon applying this method to a silicate, Stromeyer obtained 97.5 per cent. of all the boron trioxide.

Where the boric acid content was approximately known, Schaffgotsch⁶ added to the solution a weighed amount of sodium carbonate, in which not less than one and not more than two equivalents of sodium oxide (Na_2O) to two equivalents of boron trioxide were contained. After evaporation to dryness

¹ Pogg. Ann., 80, 276 (1850).

² Ibid., 80, 466 (1850).

³ Pharm. Centrbl., Nr. 24, 390, and Fresenius' Anleitung zur quant. Analyse, 6 Aufl., (1875), I, 424.

⁴ Henneberg's Jour. für Landwirtsch., 4, 112; abs. by Ztschr. anal. Chem., (1863), 73.

⁵ Ann. Chem. (Liebig), 100, 82.

⁶ Pogg. Ann., (1859), 107, 427.

and ignition, the residue was sodium oxide and boron trioxide, the weight of which, less the weight of the sodium oxide taken, gave the boron trioxide. This method is essentially the same as that of Rose.

Marignac¹ in a solution containing alkali salts only, estimated the boric acid thus: After the addition of magnesium chloride, ammonium chloride, and ammonia, he evaporated the solution to dryness in a platinum dish. The residue after ignition was taken up with water and the insoluble portion removed; the filtrate was made ammoniacal, evaporated to dryness, ignited, the residue taken up with water, and the insoluble portion filtered off as before. This was repeated three times. The insoluble portions were ignited and weighed as magnesium pyroborate; the magnesia was determined by dissolving the pyroborate in nitric acid and precipitating as magnesium ammonium phosphate, and from this the boric acid was obtained by difference. Insoluble borates were fused with sodium carbonate, the melt extracted with water, and the solution acidified with hydrochloric acid; ammonia was then added and the whole concentrated to a small volume. Any precipitate that formed was filtered off; any lime present was removed as oxalate. The solution was then supposed to contain the borate together with alkali salts and was ready for the treatment with magnesium chloride solution. In regard to this method, Marignac himself says: "If good results are obtained, it is due to a balancing of errors."

Rose² substituted sodium metaborate for the sodium carbonate used in his earlier method. By fusing boric acid with calcium chloride in the presence of sodium and potassium chlorides, Ditte³ obtained the salt $\text{CaO}, \text{B}_2\text{O}_3$, which crystallized from the fusion in needles and was insoluble in cold water. He utilized this salt for the estimation of the acid. In 1877, Berg⁴ precipitated from an alcoholic solution $\text{BaO}, \text{B}_2\text{O}_3, 4\text{H}_2\text{O}$. The precipitation was fairly completed, enabling him to determine boron trioxide in borax and obtain results within one tenth per cent. to three-tenths per cent. of the theoretical amounts.

¹ *Ztschr. anal. Chem.*, (1862), 1, 405.

² *Handb. der analyt. Chemie*, 6 Aufl, 2, 721 (1871).

³ *Compt. rend.*, 80, 490 and 561 (1875).

⁴ *Ztschr. anal. Chem.*, 22, 25.

Smith¹ precipitated manganese borate, $MnO \cdot 2B_2O_3$, from a borax solution in the presence of alcohol and determined the excess of manganous sulphate added, by evaporating the filtrate from the manganese borate to dryness, taking up with water and titrating the manganese according to Volhard.

In applying this method to a silicate, the latter was fused with sodium carbonate, the melt extracted with water and the solution digested with ammonium sulphate to throw out silica and alumina. After removing these, a known amount of manganous sulphate solution with an equal volume of alcohol was added; the precipitate was removed and the manganese in the filtrate determined as above. In a tourmaline, the percentage of boric acid found by Marignac's method was ten per cent., while that found by Smith's method was nine and seven-tenths per cent. Bodewig² tried the method of Smith upon a silicate, but obtained no result.

With some success, Bodewig used Stromeyer's method in the determination of the free acid, but upon applying it to a silicate, he experienced considerable difficulty in obtaining a solution of the borate free from silica. To accomplish this, the procedure of Berzelius (use of an ammoniacal zinc oxide solution) was resorted to with a fair degree of success.

The method of Gooch and Rosenblatt appeared simultaneously in 1887. Gooch³ evaporated the solution of free boric acid to dryness with a weighed amount of lime and ignited to constant weight. The increase in weight represented boron trioxide. Rosenblatt⁴ used magnesia in place of lime. Both Gooch and Rosenblatt showed that boric acid could be completely expelled from the concentrated acid solution of a borate as the methyl ester. To accomplish this, Gooch used an apparatus consisting of a large pipette bent at one end of the bulb at a right angle and at the other like a goose neck; the end of the pipette extended into a condenser. Insoluble borates were fused with sodium carbonate; the melt was extracted with water and the solution evaporated to dryness in the bulb of the pipette, which was immersed in a paraffin bath. The residue was made acid with nitric or acetic

¹ *Am. Chem. J.*, (1882-83), 4, 279.

² *Ztschr. anal. Chem.*, 23, 149 (1884).

³ *Am. Chem. J.*, 9, 23.

⁴ *Ztschr. anal. Chem.*, 26, 21.

acid and the distillation with methyl alcohol begun; the methyl alcohol was added in portions of ten cc. The distillate was poured into a platinum dish, containing a weighed amount of lime, evaporated to dryness and ignited to constant weight; the increase in weight represented boron trioxide.

The apparatus used by Rosenblatt was more simple than that used by Gooch. It consisted essentially of an Erlenmeyer flask connected with a condenser. Rosenblatt's method differed from Gooch's only in that the ester was caught in an ammonium carbonate solution, then poured into a dish containing a weighed amount of magnesia, and evaporated to dryness.

Morse and Burton,¹ to a concentrated borax solution of small volume, added sulphuric acid to acid reaction using tropaeoline OO as the indicator. After the addition of anhydrous copper sulphate, the resulting mass was extracted with absolute alcohol; this alcoholic solution was run into an excess of standard barium hydroxide. The excess of barium hydroxide was changed to carbonate, the whole evaporated to dryness and weighed as barium carbonate and barium metaborate, from which the boric acid was calculated. Insoluble borates were decomposed by fusion with sodium hydroxide in a nickel crucible. The extract of the fusion was evaporated to a small bulk and treated as the borax solution. By this procedure, Morse and Burton obtained from a tourmaline the following percentages of boron trioxide: 10.03 per cent., 10.08 per cent., and 10.11 per cent. Dr. Riggs obtained from the same tourmaline by a different method 10.15 per cent., 10.00 per cent., and 10.31 per cent. By means of a solution of baryta, Will² titrated boric acid.

Krüss and Moraht³ in the analysis of beryllium borate, gave the method of Stromeyer preference. To the salt of the alkali metal, Parmentier⁴ added an excess of hydrochloric acid or sulphuric acid. After dividing the solution into two equal parts, he added to one methyl orange and titrated the excess of hydrochloric or sulphuric acid; to the other, litmus was added and the total acidity determined. The difference gave the boric acid.

¹ *Am. Chem. J.*, 10, 154 (1888).

² *Arch. d. Pharm.*, 225, 1101; abs. by *Ztschr. anal. Chem.*, 28, 100 (1889).

³ *Ann. Chem. (Liebig)*, 259, 184 (1890).

⁴ *Compt. rend.*, 113, 41 (1891).

Reischle¹ stated, that the color reaction of the litmus was so indistinct that he could obtain no results.

In 1893, Thompson² noticed that a boric acid solution containing thirty per cent. of glycerol could be titrated with sodium hydroxide with phenolphthalein as the indicator. Starch, glucose, and cane-sugar could be substituted for glycerol. In borax the acid was set free by hydrochloric acid using methyl orange as the indicator and the boric acid titrated by a solution of sodium hydroxide with glycerol and phenolphthalein. Thompson applied this method to boracite.

As the commercial method of estimating boron trioxide in boronatrocalcites, Le Roy³ gave the following: Decompose the mineral with dilute sulphuric acid and hydrochloric acid in a flask connected with a reflux condenser; remove the insoluble residue and precipitate the iron and aluminum as hydroxides by caustic soda. After the removal of these, the solution is made acid with hydrochloric acid and boiled to expel carbon dioxide; upon cooling, it is made up to a known volume. Twenty cc. of this solution are titrated with standard alkali and Porrier orange III, until the shade produced corresponds to the yellowish red caused by the same amount of orange III in twenty cc. of water. Another volume of twenty cc. is now titrated with alkali using orange II as the indicator, until the color is a dark red. The difference between the two titrations indicates the boric acid present.

Schwarz⁴ suggested Congo red as an indicator to be used with hydrochloric acid. Hefelmann⁵ gave litmus the preference. Hefelmann recommends the expulsion of the boric acid by heating with ammonium fluoride and the estimation of it by difference.

Barthe⁶ used the method of Thompson with success as did also Hönig and Spitz.⁷ Insoluble silicates were fused by the latter with sodium and potassium carbonates. The melt was dissolved in water and as much ammonium chloride added as equaled the carbonates used in the fusion. The solution was then boiled

¹ *Ztschr. anorg. Chem.*, 4, 111 (1893).

² *J. Soc. Chem. Ind.*, 12, 432.

³ *Ibid.* (1893), 867.

⁴ *Pharm. Ztg.*, 32, 562 (1894).

⁵ *Pharm. Centralhalle (N. F.)*, 1894, 9, 116.

⁶ *J. Pharm. Chem.*, 29, 163 (1894).

⁷ *Ztschr. angew. Chem.*, (1896), 550.

and the precipitated silica removed. The last traces of silica were removed by Berzelius' method. After concentration to a small volume, the liquid was made acid with hydrochloric acid, boiled a few minutes to expel carbon dioxide and titrated. By this procedure, the percentage of boron trioxide found in a "Gasglühlicht-cylinder" was 5.12 per cent., while that found by difference was 5.34 per cent.

Hönig and Spitz also applied the reaction made use of by Kraut ($\text{Na}_2\text{B}_4\text{O}_7 + 2\text{NH}_4\text{Cl} = 2\text{NH}_3 + 2\text{NaCl} + 2\text{B}_2\text{O}_3$) to "Boraxkalk." The results obtained differed 0.10 per cent. to 0.30 per cent. from those gotten by their first method. In 1897, Kraut¹ employed Gooch's method successfully for the analysis of colemanite and pandermite. The apparatus used in the distillation of the ester was, however, more simple than that of Gooch. Schneider and Gaab² distilled the boric acid with alcohol and evaporated the distillate with a weighed amount of sodium carbonate.

By shaking with ether, Bellocq³ removed boric acid from other salts, and upon the evaporation of the ethereal extract obtained the trioxide.

Thaddeeff⁴ applied the Berzelius-Stromeyer method, somewhat modified, to borax. His modification consisted in adding to the potassium acetate solution containing the potassium borofluoride, 100 cc. of alcohol, 0.805 sp. gr., and allowing it to stand twelve to fourteen hours before filtering. The precipitate was washed with alcohol of the same specific gravity. By this means, results varying from 0.08 per cent. to 0.40 per cent. of the theoretical were obtained. Thaddeeff also volatilized boric acid as the methyl ester which was caught in a solution of potassium hydroxide. From this potassium borofluoride was precipitated. To facilitate the volatilization of the ester, Thaddeeff used a current of air. By this procedure, he obtained results varying from 0.01 per cent. to 0.40 per cent. of the theoretical.

INVESTIGATION.

From this review, it is apparent that, while boric acid in borax, soluble borates, and minerals not requiring fusion with alkalis

¹ *Ztschr. anal. Chem.*, 36, 165.

² *Pharm. Centralhalle*, 37, 672 (1897).

³ *Rev. Int. falsific.*, 9, 119; abs. by *Ztschr. anorg. Chem.*, 380 (1897).

⁴ *Ztschr. anal. Chem.*, 36, 568 (1897).

for their decomposition, is estimated with a fair degree of success, this acid, where fusion is required, is not determined with the desired accuracy. Minerals containing silica and alumina usually require fusion with sodium carbonate or caustic soda for their decomposition. The extract from this fusion is supposed to contain all the boric acid together with silicate and aluminate of soda. Digestion with ammonium chloride or sulphate is generally resorted to for the removal of the latter two. The solution is then ready for treatment according to any method applicable to borax.

The methods of Gooch, Stromeyer, and Marignac have been universally used. If Marignac's method is adopted, results are obtained about which there is more or less uncertainty. If Stromeyer's method is used, the potassium borofluoride weighs more than it should, owing to fluosilicate.¹ To avoid this silica, Wöhler² recommends evaporating the hydrochloric acid solution of the fusion to dryness, in a flask connected with a condenser, adding the distillate to the residue and filtering off the silica. By this means, silica is entirely removed, but alumina and other bases are yet to be separated, and in the removal of the alumina as hydroxide, there is a tendency on the part of the precipitate to retain boric acid.³ In the use of Gooch's method the trouble is met in weighing the lime.

It is evident from the foregoing, that the quantitative determination of this acid, where it exists in such combination as it does in tourmaline, is not attended with the most desirable results. With the hope of obtaining a more accurate and more rapid method and of casting some light, perhaps, upon the constitution of this mineral, this investigation was undertaken.

The isolation of the acid is evidently necessary for its successful determination. Its separation from these two associates, silica and alumina, is difficult, and alkalies apparently increase this difficulty; hence it was thought, if the tourmaline could be decomposed by heating with metallic magnesium or fusion with carbonates other than those of the alkalies, the isolation of the boric acid would be more readily accomplished; or if the tourmaline was fused with alkali carbonates, possibly it could be

¹ Fresenius' Quant. Chem. Anal., 424.

² (*Handb. der Mineral Analyse*, under Datholite.)

³ Wöhler : *Ann. Chem. Pharm.*, 141, 268.

completely removed from these objectionable associates in an acid solution.

Since the volumetric method of Thompson seemed to offer the most rapid and accurate means, I decided to investigate it, with the view of utilizing it for the determination of the isolated boric acid.

DETERMINATION OF BORIC ACID IN BORAX BY THE
METHOD OF THOMPSON.

One-tenth normal hydrochloric acid solution was prepared and standardized by precipitating the chlorine with silver nitrate.

I. Ten cc. hydrochloric acid solution gave 0.1430 gram silver chloride = 0.035358 gram chlorine.

II. Ten cc. hydrochloric acid solution gave 0.1440 gram silver chloride = 0.035605 gram chlorine.

	Chlorine. Gram.
Average	0.035481
Theory	0.03545
Difference.....	0.000031

For this hydrochloric acid solution a tenth-normal caustic soda solution was prepared. A borax solution, ten cc. of which contained one gram of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, or 0.03659 gram of B_2O_3 , was prepared from recrystallized borax. As nearly all glycerol is likely to be acid owing to fatty acids, it was found best to add a very small amount of water to the glycerol, then phenolphthalein, shake well, and introduce sodium hydroxide until a faint pink tinge appeared. This neutralized glycerol was kept in a well-stoppered bottle.

For the estimation of boric acid in the latter, a number of cubic centimeters of the borax solution were introduced into an Erlenmeyer flask, a few drops of methyl orange added and tenth-normal hydrochloric acid run in from a burette until all the boric acid was free; fifty cc. of the glycerol were added, together with a few drops of phenolphthalein, and the titration with tenth-normal caustic soda begun. According to the reaction $2\text{B}_2\text{O}_3 + 4\text{NaOH} = 4\text{NaBO}_2 + 2\text{H}_2\text{O}$, one cc. of tenth-normal alkali is equivalent to 0.0035 gram of boron trioxide.

The following table shows the value of this method :

No.	Taken.		Found.		Per cent.
	Borax solution O. cc.	B ₂ O ₃ . Gram.	$\frac{N}{10}$ NaOH. cc.	B ₂ O ₃ . Gram.	
1	10	0.03659	10.4	0.0364	36.40
2	10	0.03659	10.5	0.03675	36.75
3	10	0.03659	10.4	0.3640	36.40
4	20	0.07318	21.0	0.0735	36.75
5	20	0.07318	20.9	0.07315	36.57
6	25	0.09147	26.1	0.09135	36.54
7	25	0.09147	26.1	0.09135	36.54
8	15	0.05488	15.7	0.05495	36.63
9	15	0.05488	15.7	0.05495	36.63
10	15	0.05488	15.6	0.0546	36.40

The atomic weights used were :

Oxygen = 16.00	Boron = 10.95
Silver = 107.97	Chlorine = 35.45
Sodium = 23.05	

The theoretical percentages of the constituents of crystallized borax are :

	Per cent.
Sodium oxide	16.26
Boron trioxide	36.59
Water	47.15

Having proved the volumetric method of Thompson to give reliable results with borax, the problem of isolating the boric acid in tourmaline was taken up.

DECOMPOSITION OF TOURMALINE BY HEATING WITH METALLIC MAGNESIUM.

Two-tenths of a gram of brown tourmaline (No. 2) were heated to expel the water, mixed with half a gram of magnesium powder, the whole placed in a porcelain crucible and covered with a thick layer of thoroughly dried salt. It was then heated for thirty minutes and allowed to cool. The contents, which had the appearance of amorphous silicon, together with any parts of the crucible to which the contents adhered, were powdered, placed in a porcelain boat, and chlorine passed over the same. The chlorine and any volatile portion were caught in two U-tubes containing water; later, heat was applied and gradually raised to a dull red, where it was held until the contents of the boat became quiescent. The heat was then gradually withdrawn.

After four days, most of the chlorine had gone from the U-tubes, leaving the contents exceedingly acid. Sodium carbonate sufficient to neutralize the acid was added, and the solution evaporated almost to dryness. After making acid and expelling the carbon dioxide by drawing air through the solution for fifteen minutes, the excess of acid was neutralized by sodium hydroxide with methyl orange as the indicator, and the boric acid titrated with the following results:

No.	Weight of mineral. Gram.	$\frac{N}{10}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.2000	5.0	0.0175	8.75
2	0.2000	2.5	0.00875	4.357
3	0.2000	1.2	0.0042	2.10
4	0.2000	2.0	0.007	3.50
5	0.2000	1.5	0.00525	2.625

No. 4 was allowed to stand two days before treating the contents of the U-tubes. Very little acid was present. Nos. 2, 3, and 5 were allowed to stand but a few hours before treating. Little acid was present and the chlorine was removed in each instance before the addition of the sodium carbonate, by drawing air through the tubes. It might be added, that the time of heating the mineral with the magnesium powder was varied from fifteen minutes to an hour, and in every case the contents of the crucible had the appearance of amorphous silicon.

This procedure is evidently not a success; just why, I do not know, but am inclined to believe that the boron chloride was not completely broken up when it came in contact with the water saturated with chlorine, but was carried on out with the escaping gas. It may have been that the mineral was not completely decomposed by the magnesium, but from all appearances the magnesium had entirely reduced it. At any rate, this procedure was abandoned, and the fusion of the mineral with the alkaline earth carbonates undertaken.

DECOMPOSITION OF TOURMALINE BY FUSION WITH CALCIUM CARBONATE.

Some of the very finely powdered mineral was fused with a mixture of eight times its weight of precipitated calcium carbonate and its own weight of ammonium chloride, at a low red heat for one hour, as in the J. Lawrence Smith fusion for

the alkalis; when cool the fusion was powdered, placed in a platinum dish, covered with water, and an amount of sodium carbonate introduced slightly in excess of that required. After digesting for half an hour the solution was allowed to cool and the insoluble portion was removed. To the filtrate sulphuric acid to almost neutral reaction was added. The precipitate which formed was filtered off and the solution made slightly acid. For fifteen minutes air was drawn through the solution to remove the carbon dioxide, after which the excess of acid was neutralized with caustic soda, with methyl orange as the indicator, and the boric acid titrated.

In this instance half-normal sodium hydroxide was used in the titration of the boric acid. One cc. of a half-normal alkali solution is equivalent to 0.0175 gram of boron trioxide. The results are shown in this table:

No.	Weight of mineral. Gram.	$\frac{N}{2}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.3000	2.4	0.0420	14.00
2	0.3000	2.8	0.0490	16.33
3	0.3000	3.7	0.06475	21.58

The decomposition of the mineral was complete, because all the portion insoluble in water, except silica, dissolved in hydrochloric acid. Upon allowing the titrated solutions to stand, in every case a precipitate of alumina separated. Thinking that during the boiling of the fusion with soda some alumina was dissolved, I used barium carbonate in the place of the soda and decomposed the fusion by boiling with sodium sulphate, with the hope of avoiding the solution of alumina.

That this was not a success is shown by the following:

No.	Weight of mineral (No. 2). Gram.	$\frac{N}{2}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.3000	1.5	0.02625	8.75
2	0.3000	3.3	0.05775	19.25
3	0.3000	4.3	0.07525	25.08
4	0.3000	2.6	0.0455	15.16
5	0.3000	2.1	0.03675	12.25
6	0.3000	1.85	0.3237	10.79

In every instance, after titration, a copious precipitate of alumina came down upon boiling with hydrochloric acid and adding an excess of ammonia. It is very likely that in the

digestion of the fusion with sodium sulphate, barium carbonate becomes barium sulphate and sodium carbonate is formed; this then dissolves the alumina.

I thought that possibly this alumina might be eliminated completely by adding a small quantity of ammonium sulphate to the sodium sulphate solution free from the insoluble portion, and digesting with a reflux condenser; the ammonia could easily be expelled by boiling with an excess of alkali. This was done and the following results obtained:

No.	Weight of mineral (No. 2).		$\frac{N}{2}$ NaOH.	B_2O_3 .	Per cent.
	Gram.		cc.	Gram.	
1	0.5000		2.6	0.0455	9.10
2	0.5000		2.25	0.03937	7.87
3	0.5000		2.00	0.0350	7.00

Upon testing after the titration, alumina was found. The insoluble portions of some of these fusions were fused with sodium carbonate, and the boric acid therein, determined by distillation with methyl alcohol—a method which will be given later—and the following amounts found:

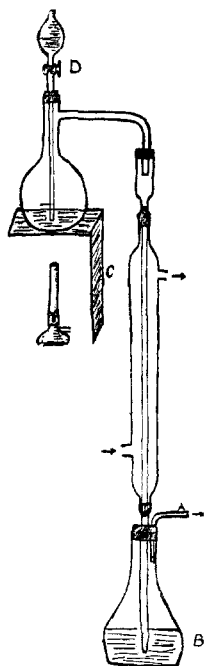
No.	Weight of mineral (No. 2).		$\frac{N}{2}$ NaOH.	B_2O_3 .	Per cent.
	Gram.		cc.	Gram.	
2	0.3000		1.1	0.01925	6.41
3	0.3000		0.6	0.0105	3.50
1	0.5000		1.0	0.0175	3.50
2	0.5000		1.1	0.01925	3.85
3	0.5000		1.4	0.0245	4.90

From this it appears that the decomposition of tourmaline by fusing the mineral with calcium or barium carbonate, is not a success; nor is it a success with datolite, as the following show:

No.	Weight of mineral.		$\frac{N}{2}$ NaOH.	B_2O_3 .	Per cent.
	Gram.		cc.	Gram.	
1	0.5000		4.6	0.0805	16.10
2	0.3000		2.8	0.0490	16.33

The decompositions were complete, but some boric acid had remained with the insoluble portions.

Tourmaline to be completely decomposed must be fused with alkalis. Then if boric acid is to be cleanly removed from the alumina, it must be done in an acid solution. The methods of Gooch and Rosenblatt are the only means of accomplishing this



and directly estimating the boric acid; but the process as practiced by Gooch or Rosenblatt is rather slow. Thaddeeff lessened the time necessary for the complete removal of the boric acid as the methyl ester, by using a current of air. By utilizing the discovery of Gooch and Rosenblatt and the volumetric method of Thompson, I thought a rapid and accurate method could be devised.

THE VOLATILIZATION OF THE BORIC ACID
AS THE METHYL ESTER AND SUBSE-
QUENT TITRATION.

To diminish the time required for the complete volatilization, an apparatus, the plan of which is here shown, was constructed. A weighed amount of fused borax was placed in the bulb, moistened with sulphuric acid, ten cc. of commercial wood alcohol added, and the distillation begun. The distillate was caught in the flask B, which contained twenty-five cc. of tenth-normal caustic soda, into which the condenser tube extended about one inch. When nearly all the alcohol had distilled over, air was drawn through the whole apparatus for a few minutes, by attaching a suction-pump to A and opening the stopcock at D sufficiently far to let the air gently bubble through the solution in B. This operation was repeated until fifty cc. of wood alcohol had been added and distilled off into the sodium hydroxide. The flask was disconnected; twenty-five cc. of tenth-normal hydrochloric acid were introduced, then 100 cc. of glycerol with a few drops of phenolphthalein and the titration of the boric acid with tenth-normal alkali begun. By this procedure the following results were obtained:

No.	Taken.		Found.		
	Weight of borax. Gram.	B ₂ O ₃ . Gram.	$\frac{N}{10}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.1000	0.06924	23.00	0.0805	80.50
2	0.1000	0.06924	22.80	0.0794	79.80

The theoretical percentages of the constituents of fused borax are:

	Per cent.
Sodium oxide	30.76
Boron trioxide	69.24

The amount of alcohol in each case being the same and the results obtained agreeing so closely, I concluded that the alcohol was the cause of the high percentages. Upon evaporating the distillate obtained as above and igniting, a black charred mass was left, which, however, was easily burned. This showed either that some organic compound had been formed in the distillation of the alcohol from the sulphuric acid or existed as an impurity in the alcohol and was carried over during the distillation. If the substance were acetic acid or formic acid, the sodium salt would be formed, which when treated with hydrochloric acid would regenerate the acid and thus increase the amount of sodium hydroxide required.

To ascertain whether a formate was produced, some pure methyl alcohol was distilled with sulphuric acid. The distillate which was caught in caustic soda, was concentrated, the alkali neutralized with nitric acid and silver nitrate added. The odor of formic acid was distinctly perceptible upon neutralizing the sodium hydroxide, and upon adding the silver nitrate and boiling, silver separated. When the ester comes in contact with the alkali, the probable reaction is: $B(OCH_3)_3 + NaOH + H_2O = BOONa + CH_3OH$. The heating of methyl alcohol with sulphuric acid in the air seems to react thus: $CH_3OH + O_2 = H_2O + HCOOH$.

To destroy this organic acid, the distillate was evaporated to a small volume, carbon dioxide rapidly run through to insure the formation of borax, the evaporation then continued to dryness and the residue ignited until all the carbon was consumed. When cool, hydrochloric acid was added in slight excess and the carbon dioxide removed by drawing air through the solution for a quarter of an hour. The excess of hydrochloric acid was neutralized and the boric acid titrated with half-normal sodium hydroxide.

No.	Taken.		Found.		Per cent.
	Weight of borax. Gram.	B ₂ O ₃ . Gram.	$\frac{N}{10}$ NaOH. cc.	B ₂ O ₃ . Gram.	
1	0.2000	0.13848	9.0	0.1575	78.75
2	0.2000	0.13848	8.2	0.1435	71.75
3	0.1000	0.06924	4.0	0.0700	70.00

These results are too high and variable, so pure methyl alcohol was substituted for the commercial article and about sixty cc. were used each time. The boric acid was titrated in this instance with tenth-normal caustic soda. It will be noticed that sometimes tenth-normal alkali was used in the titration, and at other times half-normal. Either gave good results in the titration of boric acid in borax, but with half-normal sodium hydroxide, the end-reaction was more pronounced.

No.	Taken.		Found.		
	Weight of borax. Gram.	B ₂ O ₃ . Gram.	$\frac{N}{10}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.5000	0.3462	97.5	0.34125	68.25
2	0.2000	0.13848	39.5	0.13825	69.13
3	0.3000	0.20772	58.8	0.2038	68.60

According to these reactions: $4B(OH)_3 + 4NaOH = 4BO.ONa + 8H_2O$ and $4BO.OH + 4NaOH = 4BO.ONa + 2H_2O$, the treatment with carbon dioxide was unnecessary and was dispensed with in the following determinations:

No.	Taken.		Found.		
	Weight of borax. Gram.	B ₂ O ₃ . Gram.	$\frac{N}{10}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.2000	0.13848	39.8	0.1393	69.65
2	0.3000	0.20772	59.4	0.2079	69.30
3	0.4000	0.27696	79.3	0.2775	69.36
4	0.2000	0.13848	39.6	0.1386	69.30

The theoretical per cent. of acid in fused borax is 69.24. This shows that this method is a good one, applied to borax. The next thing was to apply it to tourmaline.

A brown tourmaline, marked (No. 2), from McAfee, New Jersey, on analysis gave the following:

	Per cent.
Silica	33.72
Boric acid	10.00
Alumina	25.88
Ferric oxide	1.82
Ferrous oxide.....	3.23
Lime	6.92
Magnesia	14.07
Loss on ignition	1.80
Potassium oxide	0.20
Sodium oxide	2.52

In this instance, the boric acid was estimated according to

Marignac's method. The tourmaline was fused with potassium and sodium carbonates; the fusion was taken up with water, evaporated almost to dryness, then transferred to the distilling bulb together with the insoluble oxides. The distilling bulb instead of resting on an asbestos pad, was immersed to half the depth of the bulb, in a glycerine bath. The temperature of the bath was raised to 135° C. and the contents of the flask rapidly evaporated to dryness by the aid of a current of air. This required about an hour. The glycerine bath was allowed to cool down to 50° C. and a flask containing sodium hydroxide was substituted for the one previously used to catch the distillate. The contents of the bulb were made decidedly acid and the distillation with methyl alcohol commenced. The remainder of the operation was the same as with borax.

The following table shows the results of this method :

No.	Weight of mineral (No. 2). Gram.	$\frac{N}{10}$ NaOH. cc.	B_2O_3 . Gram.	Per cent.
1	0.5000	16.0	0.0560	(11.20)
2	0.5000	16.0	0.0560	(11.20)
3	1.0000	31.0	0.1085	(10.85)
4	1.0000	22.4	0.0784	(7.84)
5	1.0000	27.4	0.0959	9.59
6	0.5000	13.6	0.0476	9.52
7	0.5000	13.7	0.04795	9.59

In Nos. 5, 6 and 7, the fusion was allowed to cool completely and by rolling the crucible between the fingers with gentle pressure, the fusion dropped out. It was placed in the distilling flask, the crucible rinsed with sulphuric acid (1 : 1), and the washings added. Sulphuric acid and water sufficient to break the mass up into a mushy state, were poured over it and the distillation with methyl alcohol conducted as with the others. By the procedure used in these latter determinations, the entire time consumed was about five hours.

A black tourmaline which gave, according to Marignac's method, 9.87 per cent. of boric acid, treated by the above method gave the following :

No.	Weight of mineral. Gram.	$\frac{N}{2}$ NaOH. cc.	B_2O_3 . Gram.	Per cent.
1	0.5000	2.9	0.05075	10.15
2	0.5000	2.9	0.05075	10.15

From datolite, the following percentages were obtained :

No.	Weight of mineral. Gram.	$\frac{N}{2}$ NaOH. cc.	B_2O_3 . Gram.	Per cent.
1	0.5000	5.50	0.09625	19.25
2	0.5000	5.55	0.097125	19.43

Another sample of a brown tourmaline marked No. 4 gave these results :

No.	Weight of material. Gram.	$\frac{N}{2}$ NaOH. cc.	B_2O_3 . Gram.	Per cent.
1	0.5000	2.80	0.0490	9.80
2	0.5000	2.90	0.05075	10.15
3	0.5000	2.85	0.04988	9.976
4	1.0000	5.70	0.09975	9.975

In each of the preceding determinations the residue in the distilling bulb was tested for boric acid, but none was found. These results show this to be a good method of estimating boric acid wherever it is associated with silica and alumina. The time consumed is considerably less than that required by other methods, and the complete isolation of the boric acid is accomplished. The construction of the apparatus required by this method is an objection, a very slight one, however.

It occurred to me that possibly a more simple method might be found in that proposed by Smith.¹ With this in view I took up the method of Smith for investigation.

ESTIMATION OF BORIC ACID BY THE METHOD OF SMITH.

A borax solution, one cc. of which contained 0.004 gram of $Na_2B_4O_7$, a potassium permanganate solution containing zinc sulphate, one cc. of which was equivalent to 0.0018705 gram of manganese, and a manganous sulphate solution containing 0.005228 gram of manganese in each cubic centimeter, were prepared. To a volume of the manganous sulphate solution, a known portion of the borax solution, with an equal quantity of alcohol, was added. As soon as the precipitate settled it was filtered off by means of a Gooch crucible and a suction-pump. The filtrate containing the excess of manganous sulphate was evaporated to dryness, the residue gently ignited and when cool dissolved in water. A few drops of a saturated solution of sulphur dioxide were added to aid in dissolving the residue.

¹ *Am. Chem. J.*, 4, 279.

The liquid was then transferred to a flask and brought to boiling. The titration of the manganese according to Volhard's method was now made, and from this the boric acid calculated by the reaction $\text{MnSO}_4 + \text{Na}_2\text{B}_4\text{O}_7 = \text{MnB}_4\text{O}_7 + \text{Na}_2\text{SO}_4$.

No.	Borax solution. cc.	Borax. Gram.	MnSO_4 solution. cc.	Manganese. Gram.	KMnO_4 . cc.	Excess of Mn.	B_2O_3 . Per cent.	Volume alcohol.
1	10	0.04	5	0.02614	8.0	0.014964	71.03	15
2	10	0.04	5	0.02614	8.0	0.014964	71.03	15
3	10	0.04	5	0.02614	8.2	0.015338	68.33	10
4	10	0.04	10	0.05228	22.1	0.041338	68.91	10
5	15	0.06	10	0.05228	18.9	0.035354	71.71	15
6	15	0.06	10	0.05228	19.2	0.035914	69.38	15
7	25	0.10	15	0.07842	27.3	0.051065	69.54	20
8	25	0.10	15	0.07842	27.3	0.051065	69.54	20
9	25	0.10	25	0.13071	55.3	0.10344	69.30	25
10	20	0.08	20	0.10456	43.5	(67.68)	20

The precipitate of $\text{MnO} \cdot 2\text{B}_2\text{O}_3$ was dissolved off the filter by a warm aqueous solution of sulphur dioxide, transferred to a flask, brought to boiling, and the manganese then titrated with potassium permanganate according to the method of Volhard. This was done with each precipitate with the following results:

No.	KMnO_4 . cc.	Gram Mn with $2\text{B}_2\text{O}_3$.	B_2O_3 . Per cent.	Total Mn determined.	Difference from amount taken.
1	6.0	0.011223	71.31	0.026187	0.000046 plus.
2	6.0	0.011223	71.31	0.026187	0.000046 plus.
3	5.8	0.010849	68.94	0.026187	0.000046 plus.
4	5.9	0.011036	70.11	0.052374	0.000052 plus.
5	9.0	0.016834	71.31	0.052188	0.000094 minus.
6	9.0	0.016834	71.31	0.052188	0.000466 plus.
7	14.5	0.027122	68.94	0.078187	0.000236 minus.
8	14.7	0.027496	69.89	0.078561	0.000138 plus.
9	14.6	0.027310	69.41	0.130750	0.000045 plus.
10	15.0	0.028057	71.31

This shows that boric acid in borax may be successfully estimated either by the titration of the excess of manganous sulphate, which is Smith's method, or by titration of the manganese combined with boron trioxide.

For the estimation of boric acid in a tourmaline, Smith digested the extract of the sodium carbonate fusion with an amount of ammonium sulphate equivalent to the carbonate. The precipitate that formed was removed and the filtrate concentrated to twenty-five cc., after which it was treated as the borax

solution. This I did, but upon adding the manganous sulphate obtained no precipitate, and upon testing with litmus, found the liquid acid. This corroborates Bodewig's statement.¹ Another fusion was made and the extract evaporated to a volume of twenty cc., then transferred to a flask connected with a reflux condenser, and digested with ammonium sulphate. The precipitate was removed and the filtrate and washings concentrated to a volume of twenty-five cc. To the solution, which was faintly ammoniacal, a known volume of manganese sulphate, with an equal volume of alcohol, was added. As soon as the precipitate had settled it was filtered off and washed with alcohol and water (one to one). The filtrate was evaporated to dryness and the residue ignited; when cool, it was taken up with water and a drop of aqueous sulphur dioxide added. The liquid was brought to boiling and the manganese titrated with potassium permanganate. Two determinations gave respectively 23 per cent. and 28.12 per cent. of boric acid.

There is no doubt but that in the ammoniacal solution manganic hydroxide is formed and carried down with the manganese borate. I dissolved this precipitate in aqueous sulphur dioxide, and attempted to remove the manganese from the boron trioxide, in order to titrate the boron trioxide with sodium hydroxide, but could find no means of separating the two without volatilizing some boric acid or introducing harmful reagents.

My attention was next turned towards the method used by Hönig and Spitz², for the determination of boric acid in a "Gasglühlichtcylinder," with the hope of obtaining a simple method applicable to tourmaline.

THE HÖNIG AND SPITZ METHOD OF DETERMINING BORIC ACID IN INSOLUBLE SILICATES.

The extract of the fusion of a brown tourmaline was digested with an amount of ammonium chloride, equivalent to the carbonate used in the fusion, and the precipitated alumina and silica filtered off. An ammoniacal zinc oxide solution was added, and the whole boiled until all the ammonia was expelled. The zinc oxide, with any silica it carried, was removed and the filtrate concentrated to a small volume. After being made

¹ *Ztschr. anal. Chem.*, 23, 143.

² *Ztschr. angew. Chem.* (1896), 551.

slightly acid with hydrochloric acid, the solution was boiled for fifteen minutes in a flask connected with a reflux condenser; when cooled the condenser was washed out with water (the washings going into the flask), and after neutralizing the excess of hydrochloric acid, the titration for boric acid was made. The results obtained were very high, and in every instance after titration, a white precipitate which proved to be alumina and zinc oxide, separated. This further shows that boric acid cannot be separated from alumina by digestion with ammonium salts and that the removal of zinc oxide by this means is a difficult task. The following course was then pursued. After the addition of ammonium chloride, the extract of the fusion was evaporated to dryness, the residue gently ignited to expel the ammonium chloride and when cool taken up with water. Any insoluble matter was removed, a small amount of sodium carbonate added and the whole boiled for a few minutes. When cool, the carbon dioxide was expelled by adding hydrochloric acid and boiling, and the boric acid titrated after neutralizing the excess of hydrochloric acid. Tenth-normal sodium hydroxide was used with the following results:

No.	Weight of mineral (No. 2). Gram.	$\frac{N}{10}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.2000	4.5	0.01575	7.875
2	0.5000	10.5	0.03675	7.35
3	0.5000	11.2	0.0392	7.84

These results are lower than those previously obtained in the same sample (page 875), and are due to the volatilization of some of the boric acid during the ignition necessary to completely expel the ammonium salts, and it may be that some of the acid is lost in the boiling with the ammonium salt. In commenting on the method of Smith, Bodewig¹ says that some of the boric acid resulting from the decomposition of the borax by the ammonium salt, would be volatilized in the boiling; upon testing the escaping vapor, he found it alkaline, while the solution at the same time was acid.

To determine just how much boric acid was volatilized in this way, I decomposed a solution 200 cc. in volume, containing one gram of Na₂B₄O₇, by distilling with ammonium chloride; the

¹ *Ztschr. anal. Chem.* (1884), 143.

solution was distilled to one-fourth its volume. The distillate contained 0.02275 gram of boron trioxide, equivalent to 2.275 per cent. of the borax or 3.29 per cent. of the total boric acid. This shows the necessity of avoiding the boiling of an ammoniacal boric acid solution.

The digestion with ammonium chloride, using a reflux condenser to prevent the loss of boric acid, was tried, but it was impossible to get rid of the silica, alumina, and ammonium salt in this manner. Evaporation to dryness and ignition seemed to be the only way to make the silica and alumina insoluble and destroy the ammonium salt.

THE USE OF LIME TO PREVENT THE VOLATILIZATION OF BORIC ACID DURING EVAPORATION.

It occurred to me that the loss of boric acid during the evaporation to dryness and subsequent ignition, might be avoided by the addition of lime. Therefore, after digesting the extract of the fusion with ammonium chloride in a flask connected with a reflux condenser, and removing the precipitate, I added lime obtained by the ignition of precipitated calcium carbonate, evaporated the whole to dryness in a platinum dish and ignited strongly. Soda in excess of the amount required by the lime, and twenty-five cc. of water were added and the whole digested for half an hour. When cool, the precipitate was removed and well washed with cold water. After concentrating the filtrate and allowing it to cool, sulphuric acid was carefully added to almost the neutral point; the precipitate that formed was filtered out, the solution made just acid and the boric acid then titrated.

The following table shows the results obtained from the brown tourmaline (No. 4), which according to the previous method (page 876) contained 9.97 per cent. of boric acid:

No.	Weight of mineral (No. 4). Gram.	$\frac{1}{2}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.5000	2.9	0.05075	10.15
2	0.5000	3.0	0.0525	10.50
3	0.3000	1.6	0.0280	9.33
4	0.3000	1.75	0.03062	10.21

In these determinations the insoluble oxides were re-fused and the extract of the fusion added to that of the first.

To ascertain whether the $\text{CaO.B}_2\text{O}_3$, formed upon the addition of lime to the ammoniacal boric acid solution, was completely decomposed by the boiling with sodium carbonate, a weighed amount of borax was subjected to the same treatment as the extract of the fusion. That the $\text{CaO.B}_2\text{O}_3$ was entirely decomposed by the boiling with soda, is proved by this table.

No.	Taken.		Found.		
	Volume of solution. cc.	Weight of borax. Gram.	B_2O_3 . Gram.	$\frac{\text{N}}{2}\text{NaOH}$. cc.	B_2O_3 . Gram.
1	10	0.01	0.006924	0.4	0.007
2	10	0.01	0.006924	0.4	0.007
3	20	0.02	0.013848	0.8	0.014

A black tourmaline, in which, as previously shown, the boric acid amounted to 10.15 per cent., yielded 9.92 per cent. when subjected to the above treatment.

Datolite gave the following:

No.	Weight of mineral. Gram.	$\frac{\text{N}}{2}\text{NaOH}$. cc.	B_2O_3 . Gram.	Per cent.
1	0.5000	5.4	0.0945	18.90
2	0.3000	3.3	0.05775	19.25

This same datolite, according to the method on page 876, contained 19.25 per cent. of boric acid.

By using barium hydroxide in place of the lime and sodium sulphate instead of the carbonate, the following results were obtained from the brown tourmaline (No. 4):

No.	Weight of mineral. Gram.	$\frac{\text{N}}{2}\text{NaOH}$. cc.	B_2O_3 . Gram.	Per cent.
1	0.3000	1.3	0.02275	7.58
2	0.3000	1.8	0.0315	10.50
3	0.3000	1.6	0.0280	9.33
4	0.2770	1.5	0.02625	9.49
5	0.5000	2.6	0.0455	9.10
6	0.5000	2.4	0.0420	8.40

In this series, the insoluble oxides were not re-fused, but were dissolved in sulphuric acid and subjected to distillation with methyl alcohol, etc., whereupon the following percentages were obtained:

No.	$\frac{N}{2}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.2	0.0035	1.16
2	0.1	0.00175	0.58
3	0.1	0.00175	0.58
4	0.05	0.000875	0.29
5	0.1	0.00175	0.58

Upon igniting the distillate of No. 6, the characteristic green flame of boron was obtained. If these percentages are added to those previously obtained, it will be noticed that it makes the boric acid found in Nos. 3, 4, and 5 respectively 9.92 per cent., 9.80 per cent., and 9.45 per cent. These numbers agree fairly closely with those obtained from the same tourmaline by the method described on page 876. From the foregoing, the necessity of re-fusing the insoluble oxides in order to entirely remove the boric acid is apparent.

This method, while not giving results as reliable as that in which the boric acid is volatilized as the methyl ester, yet answers fairly well and avoids the use of complicated apparatus: the time is lessened very little if at all. If the digestion with ammonium chloride could be avoided, that is if the alumina could be separated from the boric acid by some other means, the evaporation to dryness and ignition might be unnecessary and thus the time shortened. In looking for a means of accomplishing this object, I happened upon the reaction $2\text{AlO.ONa} + \text{CO}_2 + 3\text{H}_2\text{O} = \text{Al}_2(\text{OH})_6 + \text{Na}_2\text{CO}_3$ which is made use of in the manufacture of soda from cryolite. Hoping by this means to separate the alumina from the boric acid, I conducted carbon dioxide into the boiling solution of the sodium carbonate fusion free from the insoluble oxides. The separation, however, was not complete, as the following show:

No.	Weight of mineral. Gram.	$\frac{N}{2}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.5000	12.0	0.2100	42.00
2	0.3000	10.0	0.1750	58.33

The solutions, after titration, were found to contain large amounts of alumina.

By passing carbon dioxide through a cold solution of sodium aluminate, Day¹ completely separated all the alumina from the

¹ *Am. Chem. J.*, 19, 718.

soda. I then passed carbon dioxide through the cold fusion extract, as shown in this table :

Time of conducting CO ₂ through the solution. Hours.	Volume of solution. cc.			
2.5	200	a precipitate formed.		
2.0	300	"	"	"
1.0	350	"	"	"
2.0	500	no	"	"

7.5 total time. Temperature of solution 1° C.

The solution was then evaporated to a small volume, and after the expulsion of all the carbon dioxide, titrated for boric acid.

No.	Weight of mineral (No. 4). Gram.	$\frac{N}{2}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
I	0.3000	1.95	0.03413	11.34

After titration, upon boiling with hydrochloric acid and adding ammonia, a precipitate of alumina was obtained which weighed 0.0039 gram, equivalent to 1.3 per cent. of the mineral.

This procedure was then repeated with the following results :

Time of conducting CO ₂ through the solution. Hours.	Volume of solution. cc.			
2.0	300	a precipitate formed.		
4.6	400	"	"	"
1.0	500	no	"	"

7.0 total time. Temperature of solution, 1° C.

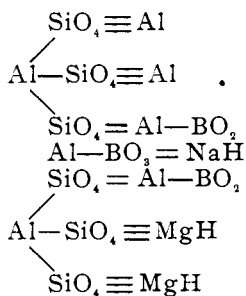
The treatment was as in the former case and 12.77 per cent. of boric acid was found. Upon testing the titrated solution for alumina, 0.0075 gram, equivalent to 1.5 per cent. of the mineral, was obtained.

In all attempts to determine the boric acid in tourmalines containing much alumina great difficulty has been experienced in separating the alumina from the boric acid and alkali carbonate. In following out Marignac's method, alumina is always found with the magnesium borate, magnesium chloride, and silica. The tenacity with which boron oxide and alumina hold to one another in other than acid solutions, is extremely great, as has already been demonstrated and is further shown by the following experiment :

0.1733 gram of aluminum, corresponding to 0.32565 gram of aluminum trioxide, was dissolved in hydrochloric acid and the

excess of acid expelled; 2.019 grams of fused borax and 1.0 gram of sodium carbonate dissolved in water, were added to the aluminum chloride and the whole boiled one hour. These proportions were taken from the equation $3\text{H}_2\text{O} + 3\text{Na}_2\text{B}_4\text{O}_7 + \text{Al}_2\text{Cl}_6 = \text{Al}_2(\text{OH})_6 + 6\text{NaCl} + 2\text{B}_2\text{O}_3$. The precipitated alumina was well washed, dissolved in hydrochloric acid, reprecipitated by ammonia, ignited, and weighed. It equaled 0.2906 gram, or 89.23 per cent. of all the alumina present in the solution. The washings, after boiling to expel the ammonia, were added to the filtrate. The volume of the solution then equaled 400 cc., and when cooled to 1°C . carbon dioxide was conducted through it for fifteen hours. The precipitate was removed and treated as the first; it amounted to 0.0332 gram, or 11 plus per cent. of all the alumina. This with the former percentage equals 100.23 per cent. Carbon dioxide, passed through two hours longer, caused no further precipitation, yet upon acidifying, then adding ammonia, a precipitate was obtained which amounted to 0.0051 gram of aluminum trioxide, or 1.56 per cent. The total amount of aluminum trioxide was 0.32565 gram, while that estimated equaled 0.3289 gram. This excess is due beyond a doubt to the contamination of the precipitates with boric acid, although in all except this last instance the precipitates were dissolved in hydrochloric acid and reprecipitated by ammonia.

The obstinacy with which aluminum trioxide and boron trioxide cling together, it seems to me, would indicate the existence of a salt of aluminum and boron in this alkaline solution. This would also favor the view held by Clarke (Bulletin 125, United States Geological Survey), which he expresses in his structural formula for tourmaline.



The alumina, as is seen, links the boric acid to the silica. This view, I think, is further strengthened by the fact that calcium or barium carbonate, fused with borax, then boiled with sodium carbonate or sulphate, gave up all the boron trioxide to the alkali, while tourmaline, heated with calcium or barium carbonate, then boiled with carbonate or sulphate of soda, yielded to the alkali but a portion of the boric acid; the alumina most likely held the remainder.

SUMMARY.

In order to avoid the introduction of alkalies, which, as it has been shown, are objectionable, new methods for the decomposition of the mineral were attempted. The first of these was the heating of the mineral with metallic magnesium and subsequently volatilizing the boron by heating in a stream of chlorine. From all appearances, the decomposition of the mineral was complete, but in the treatment with chlorine, either the boron was partially retained by the other chlorides formed at the same time, or if it was entirely volatilized as the chloride, it was not decomposed when it came in contact with the water saturated with chlorine. By using a large volume of water this difficulty might be avoided, but if the chlorine is removed by drawing air through the solution, some boric acid would be carried out with it. Again, if alkali is added, hypochlorite of the alkali would be formed, and this, when neutralized, would free chlorine, which again would likely carry with it boric acid, or the hypochlorous acid formed would cause trouble in the titration.

By fusing the mineral with calcium carbonate, also with barium carbonate, a complete decomposition was obtained, but the separation of the boric acid was incomplete. Some of the boric acid was held by the alumina, which was re-fused to yield it to the alkali with which the fusion was digested. This must be the case, since calcium or barium carbonate fused with borax, then boiled with sodium carbonate or sulphate, gave up all the boron trioxide. This strengthens the idea that the boron, which is so constant a quantity in tourmalines, is linked through the aluminum to the silica, probably as an aluminum meta-borate, as Clarke suggests.

The mineral was then fused with alkali carbonates, and by volatilizing the boron from an acid solution as the methyl ester, the boron was successfully isolated and its estimation made by the volumetric method of Thompson. The use of a current of air with the apparatus described, shortens the time required for the volatilization of the ester, very materially. As has been shown, impure methyl alcohol prevents the complete volatilization of the boric acid. The results obtained by this method are reliable, and the method is capable of very wide application. The great affinity that alumina has for boric acid, has been pretty thoroughly demonstrated in the foregoing work, and the most successful means of overcoming this affinity and completely separating these two, is by volatilizing the boric acid from an acid solution. If an acid or ammoniacal borax solution is boiled, there is the likelihood of a very appreciable loss of boric acid; by this method there is no boiling of acid or ammoniacal solutions. These facts, and the brief time required for its performance, recommend this method for the estimation of boric acid in all silicates.

Could boric acid be separated from manganese, without volatilization, its estimation in silicates could be accomplished through the salt $MnO \cdot 2B_2O_3$. As has already been proved, the method is successful when applied to borax. If the attempt is made to remove the manganese with alkali, the precipitation is incomplete; if ammonium sulphide is used, the difficulties encountered are well known, and if the manganese is precipitated from an acid solution, boric acid is volatilized.

As has been shown, the volatility of boric acid in ammonia is very appreciable, hence any method in which an ammoniacal boric acid solution is boiled in the open, is unreliable, unless some substance is introduced to bind the acid. I have used lime for this purpose, and found it to fulfil its end.

By re-fusing the insoluble oxides with alkali carbonate, it is possible to separate the boric acid. However, I do not believe the separation is complete even then, but that the amount of boric acid left after the first fusion is so diluted by the second, that what remains with the insoluble oxides may be neglected. By twice fusing and digesting the extract with ammonium chloride with a reflux condenser, then evaporating the solution

to dryness with lime in a platinum dish and igniting the residue, the silica and alumina are made insoluble; then digestion with sodium carbonate gives borax in which the boric acid is readily titrated by the method of Thompson. This method works very well with alumina containing silicates; with datolite, better results were obtained. It avoids the use of complicated apparatus and requires for its execution about four hours. With silicates decomposable by digestion with acids¹ it seems to me, this would be the method.

The obstinacy that is encountered in separating alumina from boron trioxide in an alkaline solution, calls to my mind a point which I think is worthy of some attention. In the complete analysis of minerals, such as tourmaline, it is customary to evaporate the hydrochloric acid solution of the fusion to dryness, remove the silica and precipitate the iron and alumina from the filtrate as hydroxide by ammonia. Although these hydroxides have been dissolved in hydrochloric acid and reprecipitated, yet considerable difficulty is experienced in obtaining two determinations from the same sample that agree. This trouble I believe to be due to boric acid, which does not go off in the evaporation to dryness with hydrochloric acid. If this be true, this difficulty might be eliminated by the addition of methyl alcohol during the evaporation with hydrochloric acid.

The facts to which I have called attention in the latter part of this paper, argue strongly for the formula proposed by Clarke to represent the structure of tourmaline. But, as I have said, we know nothing of the magnitude of the molecule, hence such representations are surmises only. Until some means of ascertaining the size of the mineral molecule has been devised, such formulas will have to be looked upon with doubt.

BIBLIOGRAPHY.

- Gilbert's *Annalen der Physik*, 61, 179.
K. Vetensk. Acad. Handb., (1822), 22.
Schweigg. *Jour.*, 8, 7.
Lehrbuch, 3 Aufl., 84, Pogg. *Annalen.*, 2, 118.
Jsb. d. Chem. u. Phys., 2, 364.
Ann. Chem. et Phys., 40, 398.
Pogg. *Annalen*, 80, 262.

¹ Wöhler: *Chem. News*, (1867), 255. and Handb. der Mineral Analyse, under Datolite.

- Pogg. *Annalen*, 80, 276.
 Pogg. *Annalen*, 80, 466.
Ann. Chem. (Liebig), 100, 82.
Pharm. Centrbl., 24, 390.
 Pogg. *Annalen*, 107, 427 and *Fres. Quant. Anal.*, 6 Aufl., 1, 424.
Ann. Chem. (Liebig), 98, 28.
 Henneberg's *Jour. f. Landwirthsch*, 4, 112 and *Ztschr. anal. Chem.*
 (1863), 73.
Ztschr. anal. Chem., 1, 405.
Ann. Chem. u. Pharm., 141, 268.
Handb. der analyt. Chem., 6 Aufl., 2, 723.
Compt. rend., 80, 490 and *Ztschr. anal. Chem.*, (1875), 36.
Ztschr. anal. Chem., 22, 25.
Ztschr. anal. Chem., 23, 143.
Ztschr. anal. Chem., 25, 202.
Am. Chem. J., 4, 279.
 Menshutkin, *Analyt. Chemie, Russische*, 5 Aufgabe, (1883), 356.
Am. Chem. J., 10, 154.
Ztschr. anal. Chem., 26, 18.
Am. Chem. J., 9, 23.
Arch. d. Pharm., 225, 1101 and *Ztschr. anal. Chem.*, 28, 100.
Ann. Chem. (Liebig), 259, 184.
Compt. rend., 113, 41.
Ztschr. anorg. Chem., 4, 111.
J. Soc. Chem. Ind., 12, 432.
Pharm. Centralhalle, 9, 116.
Pharm. Ztg., 32, 562.
J. Pharm. Chem. (5), 29, 163.
J. Am. Chem. Soc., 16, 418, (1894).
J. Am. Chem. Soc., 19, 385, (1897).
Pharm. Centralhalle, 37, 672.
Rev. Int. falsific, 9, 119 and *Ztschr. anorg. Chem.*, (1897), 380.
Ztschr. angew. Chem., (1896), 549.
Ztschr. anal. Chem., (1897), 568.
Ztschr. anal. Chem., (1897), 165.
Ann. Chem. et Phys., 4, 6184.
Chem. News, 58, 175.
Bulletin 148, U. S. Geol. Survey.
Chem. News, (1867), 255.
Chem. News, (1883), 309.
J. Soc. Chem. Ind., 12, 867.