A method for the rapid and routine analysis of boron in plants and aqueous soil extracts
by Donald R McCormick

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University

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ABSTRACT

Plant ash containing boron as boric acid is adjusted with sodium hydroxide to pH 7.6. Mannitol is added, and the solution titrated electrometrically with standard sodium hydroxide until the pH is again 7.6. Amount of sodium hydroxide required is a measure of the quantity of boron present. More than 3.5 mg. phosphorus present as phosphate must be removed, using barium chloride. Other ions do not interfere in concentrations present. Method also applied to soil extracts. Advantages claimed are simplicity, rapidity, and 97 per cent recovery. A number of plant and soil analyses are given.

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I. INTRODUCTION

The analysis of boron in plants and soils has become increasingly important during the past decade. Research carried on during this period gives abundant evidence that boron is an essential element for plant nutrition. Because boron occurs in such minute quantities in plants and soils, its analysis is a difficult one. Most of the procedures for the separation of boron are long and tedious and many require special apparatus not found in an ordinary laboratory.

It is the purpose of this thesis to adapt the Cavanagh[9] electrometric method, as used by Wilcox[55] for the determination of boron in waters, for the determination of boron in plant tissue and aqueous soil extracts.

II. HISTORICAL RESUME

Since 1732, when Claude Geoffrey discovered that boric acid imparts a characteristic green color to an alcohol flame. there has been a voluminous amount of work done on the analysis for boron.

Probably the first work done on the quantitative determination of boron was that of Arfvedson[2] in 1822. He heated a mixture of borax and calcium fluoride with sulphuric acid, volatilizing the boron as the boron fluoride. The boron was determined indirectly by weighing the sodium sulphate which resulted from the reaction.

Berzelius,[8] in 1824, attempted the determination of boron by precipitating it as the potassium borofluoride. Menil,[30] in 1828, attempted to estimate boron by precipitating it as the silver salt, $3\ Ag_2O.B_2O_3$, but he met with little success. In 1830, Gay Lussac[20] called attention to the titration of borax with sulphuric acid using tincture of litmus as the indicator. This method is unique in that it is probably the first volumetric method preposed for the determination of boron. Rose,[38] in 1850, was the first to volatilize boric acid as the ethyl ester, but as early as 1818, Stromeyer[49] had mentioned the volatility of boric acid in an alcoholic solution.

Weber,[52] in 1850, attempted to modify the method of Berzelius[8] by regulating the amount of calcium fluoride used, but he met with little success. Rammelsberg[36] proved the difficulty with the method of Berzelius[8] to be that the potassium borofluoride is soluble in the alcoholic wash solution used.

In 1856, Kraut[23] showed that if a borax solution is boiled with ammonium chloride, ammonia is liberated, which can be titrated with standard acid, thus determining the boron indirectly. Stromeyer,[48] in the same year, modified the method of Berzelius,[8] using instead of alcohol, a 20 per cent potassium acetate solution for washing. He applied this method to an insoluble silicate, obtaining 97.5 per cent of the boron present. This last is significant because up to this time most of the analyses for boron were made on pure boron salts or nearly pure boron-bearing minerals.

Ditte,[14] obtained the salt, $CaO.B_2O_3$, insoluble in cold water, by fusing boric acid with calcium chloride in the presence of sodium and potassium chloride. Along the same line, Berg[5] in 1877, precipitated $BaO.B_2O_3.4H_2O$ from an alcoholic solution.

The first quantitative method, which depended on the volatilization of boric acid as methyl borate appeared simultaneously in the year 1877 in papers by Gooch[21] and Rosenbladt.[39] Both men showed that boric acid can be expelled completely from a strongly acid solution as methyl borate. Gooch[21] poured the methyl borate over a weighed amount of calcium oxide. In the presence of water the methyl borate saponified completely, the free boric acid combining with the calcium oxide to form calcium meta borate which was then ignited and weighed, the increase in weight representing the boron trioxide present. The procedure of Rosenbladt[39] was the same except that he used magnesium oxide instead of calcium oxide.

The property, which boric acid solutions exhibit of becoming more acid on the addition of certain polyatomic alcohols, was first pointed out by Klein[25] in 1878. Thompson,[50] in 1893, noticed that a boric acid solution containing glycerin can be titrated with sodium hydroxide using phenolphthalein as an indicator. Duncan[16] studied the chemistry of the reaction between boric acid and glycerin and isolated anhydrous glycerol boric acid to which he gave the formula $H-C_3H_5OHBO_3$.

Barthe[4] used the method of Thompson[50] with success as did also Honig and Spitz,[22] who used it to determine boron in insoluble silicates after removal of iron and aluminium.

In 1897 Kraut[24] used the method of Gooch[21] successfully for the determination of boron in colemanite and pandermite. In the same year Schneider and Gaab[42] also used Gooch[21] method for determining boron in insoluble silicates, substituting a weighed amount of sodium carbonate instead of calcium oxide. Sargent,[41] in 1899, tested a number of methods including that of Smith,[46] in which the boron is precipitated as $MnO.2B_2O_3$ from an excess of a standard solution of manganous sulphate. The excess Mn ions were determined by Volhard's titration. Sargent[41] concluded that the only method which could be depended upon was that of Gooch.[21] He admits, however, that in the method of Gooch, seven or eight distillations are necessary in order to obtain all the boron, a factor which makes it very time consuming and hence unsuitable for routine boron analyses.

Low,[27] in 1906, working on the determination of boron in meat, made a very important contribution to the distillation method. He found it almost impossible to distill all the boric acid from an aqueous solution without evaporating nearly to dryness. He added anhydrous calcium chloride to remove the water and found that all the boric acid could be distilled as the methyl borate very easily. This procedure is still used today by many investigators.

Wherry,[53] in 1908, used calcium carbonate to precipitate the iron and aluminium in the determination of boron in insoluble silicates. He found that two and sometimes three reprecipitations were necessary to obtain all the boric acid which had been occluded. Chapin[53] in the same year applied with success the method of Gooch,[21] as modified by Low,[27] for the determination of boron in insoluble silicates.

Bertrand and Agulhan[7] determined the boron both spectroscopically and by titration with barium hydroxide, after first having separated the boron as methyl borate.

Congdon and Rosso,[11] in 1924, studied the Gooch,[21] Ashman,[3] Ditte,[14] and Dunstan[17] methods for the determination of boron. They concluded that the method of Dunstan, titration of the boric acid with sodium hydroxide in the presence of glycerin, was the best. However, since they analyzed only pure solutions of boric acid, their results are not applicable to the determination of boron in such complex mixtures as plants and soils.

In 1930 Wilcox[54] modified the Chapin[53] distillation method by using copper flasks and beakers instead of the boron-free glassware previously used. Wilcox reported that the blank titration was reduced materially, which overcame an undesirable feature of the Chapin method.

Scott and co-workers,[43] in 1932, used sodium hydroxide to precipitate the iron and aluminium in insoluble silicates instead of calcium carbonate as employed by Wherry.[53] Scott[43] found that in a sample of tincal, $Na_2B_4O_7.10H_2O$, containing 1.9 per cent iron and aluminium oxides and over

44 per cent boron trioxide, that a loss of 1.15 per cent of boron trioxide occurred by occlusion of the boric acid by the iron and aluminium hydroxides.

Pflaum and Wenzke[34] determined both boron and fluorine in organic boron trifluoride compounds. They noticed that ammonium ions, due to buffer action, interfered in the titration of the boric acid with sodium hydroxide.

Scott and Webb[45] utilized the color reaction of boron with turmeric paper to determine boron in aqueous soil extracts. I have not obtained reliable results with this reaction.

Smith[47] took advantage of the color reaction occurring between boric acid and quinalizarin in concentrated sulphuric acid solutions. Berger and Truog[6] also have worked with the quinalizarin reaction for determining boron in plants and soils. The only disadvantage I can see for the method is its extreme sensitivity. Very small samples must be taken for analysis, not usually a good procedure in analysis of soils and plants. If small amounts of plant material are taken, the sample involved in the final comparison is so small that any slight error at this stage becomes magnified many times in the calculations that follow.

Naftel's[33] method for boron depends on a color reaction which occurs when a solution of boric acid and oxalic acid are evaporated to dryness with curcumin. This method also was utilized for the analysis of boron in plants and soils.

Cook and Millar[12] describe a micro-titration for determining readily soluble boron in soils. They isolate the boron as methyl borate, which in my opinion makes their method too long to be used for routine boron analysis of plants and soils.

III. THEORY AND APPARATUS

The Cavanagh[9] electrometric method has been successfully used by Wilcox[55] for the titration of boron in natural waters. This method combines the greatest simplicity with the highest accuracy. No potentiometer, standard cell, normal electrode, or reference "half cell" is required. Neither is any type of liquid junction involved.

Cavanagh[9] makes application to electrometric titration of the long known principle of the Helmholtz cell, or cell without liquid junction. A familiar example of this type of cell consists of a hydrogen electrode and either a calomel or a silver chloride electrode in a single solution of hydrochloric acid. The e.m.f. of such a cell at a temperature (T) is

$$E=E_o+2RT/F \log_e C$$

where E_o is a constant and C is the concentration of the hydrochloric acid times its activity coefficient.

At a temperature of 16°C the e.m.f. of this cell is

$$E=E_o+0.1147 \log_{10} C$$

For a solution containing hydrogen and chloride ions, the e.m.f. is expressed by

$$E=E_o+0.05735 \log (C_H x C_{Cl})$$

where C_H and C_{Cl} are corrected concentrations or activities.

Using a silver chloride-quinhydrone cell and various concentrations of the two ions, Cavanagh obtained a mean value of 0.4740 for E_o. At the endpoint of the titration the equation may be written

$$E=0.4740+0.05735 \log_{10}(H)+0.05735 \log_{10}(Cl)$$

With this value for E_o, E vanishes in a solution with a pH of 7.62 and a chloride concentration (times the activity coefficient) of 0.209 equivalent per liter. Likewise with a chloride concentration (times the activity coefficient) of 0.108 equivalent, E vanishes in a solution of pH 7.3. The fact that the pH at which E vanishes can be predetermined by adjusting the chloride ion concentration makes it possible to adapt this electrometric method to the direct determination of boric acid.

Wilcox[55] in utilizing this method makes use of an observation of Foote[18] which is essentially the following.

A dilute acid solution of mixed salts containing boron as boric acid is titrated to a neutral point near pH of 7; the solution becomes acid on the addition of mannitol and the quantity of alkali required to titrate back to the same neutral point is an accurate measure of its boron content. In this method the initial and endpoint pH of the boron titration are the same.

APPARATUS

Wilcox[55] gives the directions for making the electrodes. He used platinum wire 1 mm. in diameter and 6 cm. long in making the platinum electrode. This is sealed into a glass tube and external connection made by means of mercury. He makes the silver chloride electrode from a piece of 1 mm. silver wire 10 cm. long. This is made the anode (a piece of platinum wire, the cathode) in a 0.1 N sodium chloride solution and a current of about 2 milliamperes is passed for one hour. In use the electrodes are held parallel by binding posts. Instead of using binding posts, the silver wire was soldered to copper wire, placed in a glass tube and the electrode fastened to the glass by means of Dekotinsky cement. Such an electrode is much sturdier and can be used again and again by cleaning thoroughly in concentrated ammonium hydroxide and replating with silver chloride. Cavanagh[9] states that a number of such electrodes can be made at once and stored in the dark in distilled water. The galvanometer used was ten times as sensitive as that used by Wilcox[55] or $25x10^{-9}$ amperes per division. A tap key and small mechanical stirrer complete the equipment. (Figure 1)

IV. ANALYSIS OF PLANTS

A. Method

The method as finally devised for the determination of boron in plants consists essentially in the electrometric titration of the boric acid, after removal of interfering ions. The details of the electrometric titration have previously been worked out by Wilcox.[55] All plant samples were collected so as to obtain a representative sample. These were dried and ground to a diameter not greater than one millimeter. All samples were analyzed on an air-dry basis.

Although all the solutions used are common laboratory ones, it is deemed advisable to include directions for their making here. These are given below.

1 per cent phenolphthalein--dissolve 1 gram phenolphthalein in 95 per cent alcohol and dilute to 100 ml. with the alcohol.

0.1 per cent Bromothymol Blue--treat 100 mg. of the indicator with exactly 1.6 ml. of 0.1 N sodium hydroxide. Dissolve the paste in water and dilute to 100 ml.

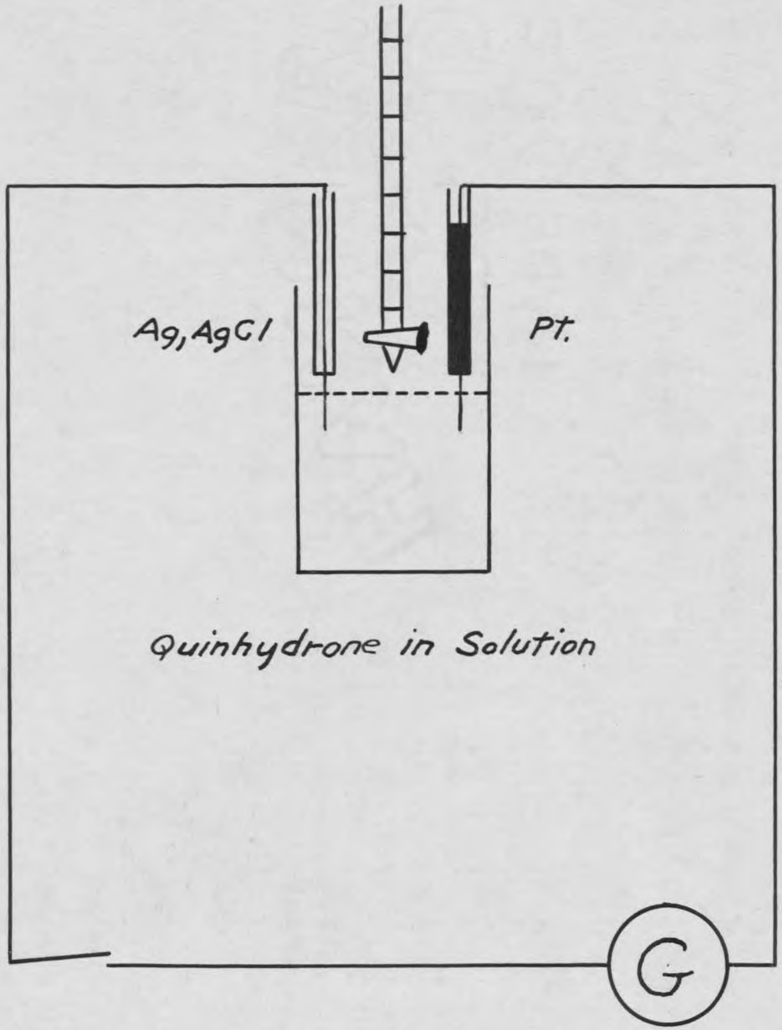

Figure1 Diagram of Apparatus

1.000 N Barium Chloride--dissolve 12.216 grams $BaCl_2 \cdot 2H_2O$ in water and dilute to 100 ml.

2.000 N Sodium Chloride--dissolve 116.90 grams of NaCl in water and dilute to 1000 ml.

Saturated Barium Hydroxide--add an excess of $Ba(OH)_2$ to water and shake until solution is saturated. Keep this tightly stoppered.

Approximately 13 N Sodium Hydroxide--dissolve approximately 550 grams of NaOH in 1 liter of water. Allow to stand until the sodium carbonate has settled out.

Approximately 0.5 N Sodium Hydroxide (carbonate free)--dilute 20 ml. of the 13 N NaOH with water (CO_2 free) to 500 ml.

Standard Sodium Hydroxide (carbonate free)--this base should be of such strength that 1 ml. is equivalent to 0.25 mg. of elemental boron. This is standardized against boric acid using the electrometric titration.

Quinhydrone--this product as obtained from the Eastman Kodak Company is used without further purification.

A precaution is to be noted here in that all solutions should be kept in boron-free containers. Pyrex glass containing about 11 per cent boron trioxide may cause a serious contamination if used in this method. Berger and Truog[6] suggest that common soft glass bottles are usually satisfactory.

The procedure for the determination of boron in plants is as follows: ash 5.000 grams of finely ground air-dry plant material in a platinum or porcelain evaporating dish in an electric muffle for twelve to sixteen hours at a temperature of 350-400°C.

Transfer the ash to a 550 ml. Kavalier beaker of boron-free glass.

Use water to make the transfer. At this point it is advisable to add about 1 ml. of concentrated nitric acid to the dish and loosen the ash with a rubber policeman, bringing the acid in contact with all the inner surface of the dish in order to dissolve or loosen any ash which has not been removed by the water. Add sufficient concentrated HNO_3, 3-5 ml., to render the ash slightly acid. Cover the beaker with a watchglass and heat on a steam plate for fifteen minutes. It is important to keep the beaker covered because according to Scott,[44] boric acid volatilizes with steam. Remove the beaker from the steam plate, cool, and dilute to 100 ml. with water, at the same time rinsing off the watchglass and adding these rinsings to the main solution. Add exactly 12.5 ml. of 1 N barium chloride solution. This should be added very carefully as 0.05 equivalent of the chloride reference ion is obtained from this source. Now add 10 drops of 1 per cent phenolphthalein and make slightly alkaline with 13 N NaOH. Make just acid again with concentrated nitric acid. Now add the barium hydroxide until the solution is alkaline. The phosphate ion present is precipitated as $Ba_3(PO_4)_2$. Some calcium phosphate may also precipitate at this point. The beaker is again covered with a watchglass and the contents heated to boiling. Stir several times and filter while hot, using a retentive but fast filter paper, such as Munktell No. 3. Wash thoroughly with water to a volume of 175-200 ml. This last is very important because efficient washing of the precipitate will lower the amount of boron which is occluded at this point.

To the solution is now added 0.15 equivalent of chloride ion in the form of 18.75 ml. of 2 N sodium chloride solution or 2.192 grams of NaCl depending on the volumes. The volume should be exactly 250 ml. for the electrometric titration. The Kavalier glass beakers were conveniently marked for this volume, by filling them with 250 ml. of water and pasting a thin strip of paper at the water line. The paper strip is then covered with a thin coating of collodion solution to make it a permanent marking. After the addition of the sodium chloride, ten drops of a 0.1 per cent solution of bromothymol blue are added and the solution is made acid to this indicator by using 2-3 drops of concentrated nitric acid. Place in the solution a small strip of ashless filter paper, held to the bottom of the beaker by a stirring rod. This prevents bumping while boiling. Cover the beaker with a watchglass and boil gently 2-3 minutes to remove carbon dioxide. After cooling, remove the piece of filter paper, washing it free of the solution with freshly boiled carbon-dioxide-free water. Make the solution nearly neutral to the bromothymol blue with 0.5 N sodium hydroxide (carbonate free) and then dilute to exactly 250 ml. with carbon-dioxide-free water. Add enough quinhydrone, usually 0.2 grams, to saturate the solution and then introduce the silver chloride and platinum electrodes into the solution along with the stirrer. Adjust the pH with the dilute standard sodium hydroxide until a null point is received on the galvanometer when the circuit is closed by means of a tap key. This is the starting point of the titration and is at a pH of 7.6 with a 0.2 equivalent of chloride ion present. Read the burette, which should be one that delivers about 0.03 ml. per drop, and add 10 grams of neutral mannitol. If boric acid is present, the solution becomes acid as indicated by a deflection in the galvanometer when the tap key is depressed. Now add dilute base until a null point is again reached on the galvanometer. This is the endpoint of the titration. The amount of sodium hydroxide used between the starting and endpoint of the titration is an accurate measure of the amount of boric acid present.

The solution being titrated should not contain over 1.25 mg. of boron, when using standard base of which 1 ml. is equivalent to 0.25 mg. of boron. In other words, the volume of the solution being titrated should not be increased by more than 5 ml. because the chloride ion concentration must be kept as close as possible to 0.2 equivalent per liter. A blank titration should be run using all the reagents. A number of determinations has shown the blank titration to be equal to 0.14 ml. According to Foote[18] the same amount of mannitol should be used for every titration. Also in standardization of the base the same amount of mannitol as employed for the samples themselves should be used.

Because of some occlusion of boron by the precipitate formed in the removal of the phosphates, it is necessary to dissolve the precipitate in 5 ml. of concentrated nitric acid and reprecipitate as before. In samples of high boron content a third precipitation may be necessary.

Wherry,[53] in determining boron in insoluble silicates found that boric acid is occluded by aluminium and iron hydroxides. Some of his results are given below. The numbers 1, 2, 3, 4, and 5 refer to the number of reprecipitations that were necessary in order to get all the boric acid.

From the table, one can see that where the sesquioxides were present to a large extent, four or five reprecipitations were necessary to obtain all the boron. Where the sesquioxides were absent or present only to a small extent, only two precipitations were necessary to obtain all the boron.

SAMPLE	PER CENT B_2O_3 OBTAINED					TOTAL
	1	2	3	4	5	Per Cent
Dumortierite--containing 63% Al_2O_3	3.87	1.12	0.35	0.11	....	5.45
Ludwigite--containing 40% Fe_2O_3	9.93	0.71	0.71	0.52	0.22	12.80
Danburite--containing no sesquioxides	23.77	0.29	....	....	....	24.06
Tourmaline--containing 35% Al_2O_3 + Fe_2O_3	8.88	0.82	0.23	....	....	9.93
Vesuvianite--containing 20% Al_2O_3 + Fe_2O_3	1.75	0.17	....	....	....	1.92

In this work on plants the analyses have shown that in many cases all the boron was obtained after the first precipitation. However, a second precipitation is recommended. In the samples used here, a third precipitation was found to be unnecessary in every case.

B. Removal of Organic Matter

The removal of organic matter constitutes a very important part of any analytical method being used for plant analysis. In the analysis of boron in plants, there are two problems which must be considered. One is the choice of a suitable container in which to ash the plant material, and the other is whether a base should be added to the plant before ashing to prevent loss of boron by volatilization.

Pyrexware, which is used to a large extent in this laboratory for ashing plants, contains about 11 per cent boron trioxide, a fact which prohibits its use in this determination. Berger and Truog[6] used both platinum and porcelain evaporating dishes for this purpose. Platinum, of course, is very satisfactory, but due to its high cost, many laboratories have not the large number of platinum dishes which would be necessary for running numerous samples in routine analysis. It was decided to try to verify the work of Berger and Truog[6] in their use of porcelain dishes. To do so a sample of alfalfa was used, and three ten-gram samples were ashed in porcelain evaporating dishes and three in platinum dishes. The results are given below:

TYPE OF DISH	WEIGHT OF SAMPLE			BORON FOUND		
	1	2	3	1	2	3
	grs.	grs.	grs.	mgs.	mgs.	mgs.
Porcelain	10	10	10	0.256	0.261	0.263
Platinum	10	10	10	0.250	0.258	0.258

It can be seen from these results that porcelain dishes are quite satisfactory.

The second problem, as stated before, is whether or not a base should be added to the plant tissue before ashing to prevent loss of boron by volatilization. Berger and Truog[6] determined the boron in a number of plant samples with and without the addition of potassium carbonate prior to the ashing. They found no significant difference in the boron content of the plants ashed alone and in the presence of potassium carbonate. Foster and Horton[19] have obtained similar results.

To test these findings the boron content of an alfalfa sample was determined, ashing the sample alone and in the presence of sodium carbonate solution. The sodium carbonate solution contained 40 grams of anhydrous Na_2CO_3 per 100 ml.

Three 5-gram samples were ashed alone, and to each of the other three 5-gram samples were added 6 ml. of the sodium carbonate solution, a little water being added to thoroughly wet the sample and to bring the sodium carbonate solution into intimate contact with all the plant tissue. The results are given below:

SAMPLE	WEIGHT	BORON p.p.m.	
		Ashed With Na_2CO_3	Ashed Without Na_2CO_3
Alfalfa	5 grams	18.6	18.1
Alfalfa	5 grams	18.6	18.6
Alfalfa	5 grams	17.4	18.1
	AVERAGE	18.2	18.3

From the above results it is concluded that addition of a base to the sample before ashing to prevent loss of boron is unnecessary. Also, when a base like sodium carbonate is added to plant tissue, it is necessary to raise the ashing temperature to around 600°C while if the sample is ashed alone, a temperature of 350°-400°C is sufficient to give a white or nearly white ash.

C. Removal of Interfering Ions

The advantage of a direct titration of boric acid lies in the fact that it is not necessary to separate boron from other ions.

Foote,[18] who used a direct titration for determining boron in natural waters and soil extracts at low concentration, could see no reason for such a titration failing in solutions containing a higher percentage of salts. Wilcox[55] pointed out that large amounts of phosphates and silicates might interfere in the direct electrometric titration of boric acid. Deerns[13] found that the phosphoric acid in crabs caused a constant error in the determination of boron, about 0.5 per cent too high.

To determine the effect of a number of ions on the direct electrometric titration of boric acid, a grass sample was analyzed for six different elements giving the following results: 0.44 per cent Ca; 0.19 per cent P; 1.50 per cent K; 0.10 per cent Mg; 0.13 per cent S; 1.70 per cent N. A solution was made up containing the above elements in the amounts indicated and also 23.3 mg. Si, corresponding to 0.47 per cent Si was added. The table below shows the element, the amount added, and the source of the element.

ELEMENT	ELEMENT	SOURCE OF ELEMENT
	mgs.	
P	9.5	H_3PO_4
Ca	22.6	$Ca(NO_3)_2 \cdot 4H_2O$
K	75.0	KNO_3
N	85.0	KNO_3; $Ca(NO_3)_2 \cdot 4H_2O$ $Mg(NO_3)_2 \cdot 6H_2O$; HNO_3
S	6.5	Na_2SO_4
Mg	5.0	$Mg(NO_3)_2 \cdot 6H_2O$
Si	23.3	40 per cent solution of Na_2SiO_3

Two samples were titrated electrometrically, starting at a pH of 7.6

and a chloride ion concentration of 0.2 equivalent per liter. The other two samples were titrated starting at a pH of 7.3 and a chloride ion concentration of 0.1 equivalent per liter. It should be remembered that no boron was added to the samples, so if none of the above ions interfere, the titration should amount to a blank titration only. The results are given below:

STARTING pH	Cl IN EQUIVALENT PER LITER	NaOH	AVERAGE	BLANK	TITRE
		ml.			
7.3	0.1	0.53	0.59	0.14	0.45
7.3	0.1	0.64	....	....	....
7.6	0.2	0.45	0.43	0.14	0.29
7.6	0.2	0.40	....	....	....

The conclusion drawn from the above data is that one or more of the ions is increasing the amount of NaOH required. Following Wilcox's[55] suggestion that phosphates may interfere, a solution was made up consisting of the same amounts of the elements as before, only this time leaving out the phosphate ion. On running these samples, the titration amounted to only a blank titration, good evidence that phosphates are the interfering ions.

To determine the concentration of phosphorus, which must be present to interfere, a number of samples ranging in phosphorus content from 0.44 mg. to 4.44 mg. were titrated electrometrically. The phosphorus was added as phosphoric acid, H_3PO_4. The results are tabulated on the next page.

From these data it can be seen that approximately 3.50 mgs. of phosphorus must be present before interference with the titration is noticed. The titrations below all started at a pH of 7.6.

NUMBER	P PRESENT	NaOH REQUIRED
	mgs.	ml.
1	0.44	0.14
2	0.89	0.14
3	1.77	0.14
4	2.66	0.14
5	3.54	0.15
6	4.44	0.25

From the results obtained, it is concluded that removal of phosphorus is necessary since this element occurs in all plant tissue. Other investigators have worked on this before in determining boron in more concentrated solutions in the presence of phosphates. Thomson,[51] determining boron in milk, precipitated the phosphates as $Ca_3(PO_4)_2$ by the use of lime water, taking advantage of the fact that calcium borate is fairly soluble in a weakly alkaline solution while calcium phosphate is not. Both Alcock[1] and Monier-Williams[32] pointed out that it is very difficult to adjust the alkalinity to just the optimum pH in order not to get co-precipitation of the calcium borate along with the calcium phosphate. Both these men also pointed out the fact that in the presence of large amounts of phosphates that low results will be obtained.

Both Robertson[37] and Dodd[15] by adjusting the alkalinity very carefully were able to use Thompson's method with some success. Monier-Williams[32] precipitated the phosphates as magnesium ammonium phosphate, but his procedure is very lengthy. Ross and Deemer,[40] determining boron in fertilizers, removed phosphates as well as iron and aluminium by adding barium chloride solution and making alkaline with barium hydroxide. Lipscomb, Inman and Watkins[26] used the method of Thompson with some success in determining boron in fertilizers. They adjusted the alkalinity by use of saturated calcium hydroxide solution.

Three methods were examined with regard to their ability in removing phosphate without removing boron. The first is that of Thompson[51] precipitating the phosphates as calcium phosphates. One modification was used in that $Ca(NO_3)_2$; $4H_2O$ was used as the source of calcium ion rather than calcium chloride which Mellon and Swim[28] say causes boric acid to ionize, thus giving low results for boron. The procedure tried was as follows: to the solution containing phosphoric acid and boric acid, add 1 gram $Ca(NO_3)_2$; $4H_2O$ and make slightly alkaline to phenolphthalein with 0.5 N sodium hydroxide. Then add 25 ml. of saturated calcium hydroxide solution. Mix well and filter washing six or seven times with warm water. Hot water should not be used due to the decreased solubility of calcium borate at higher temperatures. Add 25 ml. of 2 N sodium chloride to the filtrate, make slightly acid with 1 N sulphuric acid, boil to remove carbon dioxide, cool, and then titrate electrometrically. Samples 1, 2, 3, 4, and 5 were filtered without suction, while samples 6 and 7 were filtered with suction. Suction was tried because the solutions filtered very slowly, and the calcium phosphate dried at the top of the filter paper, making it very difficult to wash. The results are given on following page.

No.	Manner of Filtration	P Present	B Present	B Obtained	Boron Recovered
		mg.	mg.	mg.	Per Cent
1	Without Suction	44.3	0.525	0.160	30.5
2	Without Suction	44.3	0.525	0.165	31.4
3	Without Suction	44.3	0.525	0.010	19.0
4	Without Suction	22.2	0.525	0.251	47.8
5	Without Suction	22.2	0.525	0.010	19.0
6	With Suction	22.2	0.525	0.276	52.6
7	With Suction	22.2	0.525	0.287	54.7

In considering the above data, one can make two assumptions. Either the borate is being co-precipitated as the calcium borate, or the calcium nitrate may have caused the ionization of some of the boric acid. Both would give low results. On running a standard sample of boric acid, no effect of the calcium nitrate on the ionization of boric acid was noted. The conclusion drawn is that this method of removal of phosphates is very unsatisfactory due to co-precipitation of calcium borate along with calcium phosphate.

The second method tried was precipitating the phosphates as ammonium phospho molybdate in slightly acid solution, filtering, washing with 1 per cent solution of potassium nitrate and then determining boron in the filtrate. Upon adding mannitol to this solution, instead of obtaining the normal acid reaction as when boric acid is present, the solution became strongly basic due probably to some complex reaction. This makes the method wholly unsatisfactory for the removal of phosphates.

The third method consisted in precipitating the phosphates as barium phosphate in the presence of barium chloride and hydroxide solutions. This has previously been used by Ross and Deemer[40] in determining boron in phosphate fertilizers. It was necessary to modify this method to be able to use it for analysis of plants. First, instead of making alkaline with barium hydroxide to precipitate the phosphates, it was necessary to use 13 N sodium hydroxide because an excessive amount of $Ba(OH)_2$ would be necessary to neutralize the nitric acid present, causing undesirable dilution of the solution. To remedy this, the 13 N sodium hydroxide was added to bring the solution almost to the neutral point and then barium hydroxide solution was added to slight alkalinity. Also, since the chloride ion concentration must be controlled, it was necessary to add a known quantity of barium chloride solution, part of the chloride concentration coming from this source and the rest of it from the sodium chloride. This method as already given is basically the following: to the acid solution add 12.5 ml. of 1 N barium chloride; almost neutralize with 13 N sodium hydroxide; make slightly alkaline with saturated barium hydroxide; boil, filter while hot and wash thoroughly with hot water. Application of this method to solutions containing both phosphoric acid and boric acid gave the following results:

P PRESENT	B PRESENT	B RECOVERED	RECOVERY
mgs.	mgs.	mgs.	Per Cent
44.3	0.525	0.481	91.6
44.3	0.525	0.481	91.6
22.2	0.525	0.523	99.6
22.2	0.525	0.523	99.6

The preceding results are very satisfactory, especially since 22.2 mgs. of phosphorus in 5 grams of plant material represent 0.44 per cent of phosphorus in the sample, a per cent which is seldom exceeded in ordinary samples.

Several tests were made on the efficiency of the removal of the phosphates by this method. The filtrates from the precipitations of phosphate in an alfalfa sample were tested for phosphate by the colorimetric method where a blue color is developed by the reduction of phosphomolybdate. The intensity of color produced was measured in a photronic color photometer calibrated with a standard phosphoric acid solution. A concentration of 2 p.p.m. or 2 mgs. PO_4 per liter was obtained. This is well below the concentration at which the phosphate ion interferes in the electrometric titration of boric acid.

Several investigators have pointed out the well-known principle that certain neutral salts cause boric acid to ionize to a greater extent than is indicated by the ionization constant of boric acid. Cikritova and Sandra[10] tried titrating boric acid in the presence of potassium iodide, barium chloride, calcium nitrate, calcium chloride and lithium chloride. They found with lithium and calcium chlorides, present in very high concentrations, that boric acid could be titrated as efficiently as in the presence of glycerin or mannitol. Mellan and Swim[28] tested the effect of lithium, sodium, and potassium chlorides, sodium and potassium sulphates, and sodium and potassium nitrates. Of these they found only lithium and calcium chlorides had a large effect on the ionization of boric acid. The sodium and potassium nitrates showed a more or less steady increase of potential, depending on concentration. Prideaux[35] also noticed that a dilute solution of boric acid saturated with sodium chloride required more sodium hydroxide for neutralization than a solution of boric acid without the salt.

In the solutions which are titrated electrometrically in this method probably barium chloride, sodium nitrate and sodium chloride are present to the greatest extent, the sodium nitrate being formed in the neutralization of the nitric acid with sodium hydroxide. Sodium chloride present in a concentration of 0.2 equivalent of chloride ion will not interfere in any degree. See work of Prideaux.[35] To see if the barium chloride or sodium nitrate would interfere several determinations on pure borax and boric acid solutions were made. The data are given on the following page. Numbers 1, 2, 5, and 6 were treated with 25 ml. of 2 N sodium chloride, and boron determined by the usual electrometric titration. Numbers 3, 4, 7, and 8 were treated with 12.5 ml. of 1 N barium chloride, 18.75 ml. of 2 N sodium chloride. Also the same amount of nitric acid as used to decompose the plant ash was added. Or in other words, samples 3, 4, 7, and 8 were run for boron just exactly as the boron would be determined in the plant itself.

Inspection of the results shows that almost exactly the same amount of sodium hydroxide was required by duplicate samples. This leads to the conclusion that salts, which had been added or formed by the neutralization in this devised method, do not interfere with the titration of the boric acid, in the concentration in which they are present.

NO.		SOURCE OF BORON	NaOH REQUIRED TO NEUTRALIZE BORIC ACID	AVERAGE
	ml.		ml.	ml.
1	5	Standard Borax Solution	4.16	4.15
2	5	Standard Borax Solution	4.14	....
3	5	Standard Borax Solution	4.18	4.14
4	5	Standard Borax Solution	4.10	....
5	5	Standard Boric Acid Sol.	3.40	3.39
6	5	Standard Boric Acid Sol.	3.37	....
7	5	Standard Boric Acid Sol.	3.40	3.39
8	5	Standard Boric Acid Sol.	3.37	....

D. Recovery of Added Boron

Determinations of boron in several varieties of plant tissue were carried out and at the same time recovery of boron added to the plant before ashing was tested.

For adding boron to plant tissue, it was decided to add it in the form of a solution of borax. The borax, $Na_2B_4O_7 \cdot 10H_2O$, was twice crystallized from water, dried and ignited in the muffle at 300°C, whereon it fused to a clear glassy substance having the formula, $Na_2B_4O_7$, according to Mellor.[29] One gram was dissolved in water and made up to a liter, this solution was then standardized against the standard sodium hydroxide. All plant samples were analyzed in sets of four. To two samples 5 ml. of the standard borax solution was added, to the other two, nothing was added. These samples were then ashed overnight at 350°-400°C and the boron content determined as outlined on page 14.

Double precipitations of the phosphates, and iron and aluminium hydroxide were carried out. In most cases the sodium hydroxide titre from the second precipitation was equal to or almost equal to the blank titration, showing that all the boron had been obtained after the first precipitation. The results of these analyses are given in table 1, page 31.

E. Discussion of Analyses

Results of the analyses made show that of the plants analyzed, the oat straw contained the least boron, 0.02 mg., while the sample of sugar beet leaves had the most boron, 0.31 mg. The sample of wheat contained 0.03 mg. This last is to be expected because most of the grains are known to require very little boron for normal growth. The analysis of the sugar beets and sugar beet leaves are interesting because they show respectively 0.07 and 0.31 mg. It is known that boron accumulates to a greater extent in the leaves of the plant. Samples 1 and 2, both apple leaves, were collected from the same orchard. Sample 2 came from a tree which had been treated with eight ounces of boric acid, while sample 1 came from a tree which received no application of boron. The boric acid application increased the boron content of the leaves.

The alfalfa samples 3 and 4 also afford some interesting results. Sample 3 was collected from a soil containing 4 p.p.m. of soluble boron. Sample 4 was collected from a soil whose analysis gave 0.6 p.p.m. of soluble boron. In this case the difference of the boron content of the alfalfa grown on a low and high boron soil is very striking.

The per cent recovery of boron as noted in the last column of table 1 is very good considering the small amount of boron added, and the small

Table I

Analysis of Plants Testing Recovery of Added Boron

Sample No.	Sample	TOTAL BORON PRESENT 5 g. Plant Material	 5 g. Plant + 1.06 mgs. Added Boron	Total Boron Recovered	Boron Recovered
		mgs.	mgs.	mgs.	Per Cent
No B - Gerer - 1	Apple Leaves	0.05	1.11	1.09	98.2
+ B → 2	Apple Leaves	0.06	1.12	1.10	98.2
3	Alfalfa	0.25	1.31	1.29	98.5
4	Alfalfa	0.09	1.15	1.10	95.7
5	Oat Straw	0.02	1.08	1.04	96.3
6	Sugar Beet Leaves	0.31	1.37	1.37	100.0
7	Dry Land Wild Hay	0.09	1.15	1.09	94.8
8	Wheat	0.03	1.09	1.02	93.6
9	Sugar Beets	0.07	1.13	1.14	100.9
	Average				97.4

amount originally present in the sample itself. The average recovery was 97 per cent. In the distillation method 95 per cent is a common recovery. In the samples of very low boron content as in 5 and 8, it was found that the gross titration was only a few hundreths of a ml. This is disturbing because an error of one drop of base in the titration would produce a very appreciable error in the determination of boron, especially in these low boron content samples. It has been found that this can be remedied very easily, either by increasing the size of the sample or by decreasing the strength of the standard base. Both will increase the accuracy of the method.

V. ANALYSIS OF SOIL EXTRACTS

A. Method

A number of determinations of boron in soils were made using essentially the boiling extraction method as given in the Methods of Analysis of the Rubidoux Laboratory.[31] This method consists essentially of the following: place 500 grams of air-dry soil in a Buchner funnel, so arranged in a water jacket so that it can be kept at the temperature of boiling water, and add hot 0.01 N calcium sulphate solution until there is a layer of solution on top. Allow to stand 20 minutes and then filter with suction, always maintaining a layer of the solution on top of the soil. When the volume of the filtrate reaches 250 ml., replace the filter flask with an empty one and determine boron in the filtrate, by electrometric titration. The extraction is continued until the gross titration approaches that of the blank titration, as determined by using distilled water.

Several modifications were made to increase the speed of the determination and also the accuracy. The sample was reduced to 100-200 grams, which was immersed in excess hot calcium sulphate solution in a liter Erlenmeyer flask. This was heated for 30 minutes on a hotplate and then filtered through a water-jacketed Buchner funnel kept hot by steam. It was found by following this procedure that almost all of the boron was extracted in the first filtrate, a factor which saves a great deal of time. Also the blank titration was determined using calcium sulphate solution instead of distilled water because this seems more appropriate to me.

B. Interfering Ions

Also since phosphates interfere in the electrometric titration of boric acid, several of the filtrates were tested for phosphate ions in the same manner as on page 27. The filtrates showed less than 1 p.p.m. of phosphate ion, well below the limit of interference.

C. Recovery

To check recovery of boron added to soils 100 ml. of a boric acid solution, which contained 0.01 gram of boric acid, was added to two 200-gram soil samples which had been previously run for boron. The following results were obtained:

SOIL FROM BIG HOLE AREA

NO.	B IN SAMPLE	B ADDED	TOTAL BORON RECOVERED	B RECOVERED FROM AMT. ADDED	RECOVERY
	mg.	mg.	mg.	mg.	Per Cent
1	0.43	1.75	2.17	1.74	99.4
2	0.18	1.75	1.90	1.72	98.3

D. Analysis of Montana Soils

The analysis of a number of soil samples all collected in Montana are given in table 2, page 35-36. The general location and legal description are both given where possible.

E. Discussion

Table 2, page 35-36, shows that of the soil analyzed, the amount of soluble boron ranged from a low of 0.3 p.p.m. to a high of 7.8 p.p.m. It would seem likely that there are indications of boron deficient areas in Montana. This depends, of course, entirely on the plants which are grown on the soil, some requiring more boron and some exhibiting a greater tolerance to boron.

Of special interest is the group of soils collected from the Bitterroot Valley in Western Montana. These samples were all taken from orchards in the valley. Samples 35 and 37 were collected from the same orchard, sample 37 having had an application of boric acid while sample 35 was untreated. The analysis shows that boric acid application increases soluble boron in the soil. Sample 33 and 36 were also collected from the same orchard. Apples grown on soil represented by sample 33 exhibited the phenomenon of "corky apple" which is believed to be due to a boron deficiency. Soil sample 36 was treated with one-half pound of boric acid per tree and the fruit on these trees was in a much healthier condition than those which had been untreated. The analysis of these samples also showed the effect of the application of boric acid.

This method is believed to give a fairly accurate picture of the amount of soluble boron in soil.

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Table II

Analysis of Soil Extracts for Soluble Boron

Sample No.	Area	Boron Soluble in Hot 0.01 N $CaSO_4$ Solution
		p.p.m.
1	Big Hole Valley--N½S34-T1S-R16W	0.9
2	Rife Ranch, Dillon	2.3
3	P and O Ranch, Dillon	1.4
4	Mont. Ag. Expt. Sta. Farm--East end	0.9
5	Mont. Ag. Expt. Sta. Farm--NW corner	1.4
6	Mont. Ag. Expt. Sta. Farm--NE corner	0.8
7	Mont. Ag. Expt. Sta. Farm--SW corner	0.9
8	Mont. Ag. Expt. Sta. Farm--SE corner	0.6
9	Mont. Ag. Expt. Sta. Farm--Middle Area	0.9
10	Forsyth, Montana	4.0
11	Forsyth, Montana	3.9
12	Plains, Montana--S35-T20N-R26W	0.6
13	Plains, Montana--S15-T20N-R26W	1.1
14	Ravalli County	0.5
15	Libby, Montana--S36-T30N-R31W	0.6
16	Libby, Montana--S36-T30N-R31W	0.3
17	Gallatin County	1.0
18	Missoula County--SE¼S4-T13N-R28W	2.2
19	Lake County--SE¼S21-T19N-R21W	2.9
20	Galen, A.C.M. Ranch--SW¼S31-T6N-R9W	1.4

Table II, continued

Analysis of Soil Extracts for Soluble Boron

Sample No.	Area	Boron Soluble in Hot 0.01 N $CaSO_4$ Solution
		p.p.m.
21	Broadwater County--S30-T8N-R2E	7.8
22	Broadwater County--S23-T4N-R1E	2.8
23	Jefferson County	4.5
24	Galen--S30-T6N-R9W	0.9
25	Powell County--S20-T7N-R9W	0.5
26	Powell County, Deer Lodge Farms	1.4
27	Missoula County	1.6
28	Ravalli County--S21-T7N-R20W	2.2
29	Lake County--S31-T21N-R19W	0.8
30	Lewis and Clark County--S10-T20N-R6W	1.9
31	Teton County--S22-T22N-R2W	2.3
32	Teton County--S36-T22N-R3W	1.8
S - B 33	Bitterroot Valley	1.0
S + B 34	Bitterroot Valley	1.4
G - B 35	Bitterroot Valley	0.3
S + water - B 36	Bitterroot Valley	6.0
S + B 37	Bitterroot Valley	3.9
Hwr Tom Parah 38	Bitterroot Valley	0.9
Hwr. 39	Bitterroot Valley	0.9

VI. SUMMARY

1. By means of electrometric titration, boron, after removal of certain interfering ions, can be determined accurately in plants and soil extracts.
2. The method devised has the advantage of being faster than the distillation method, and due to its being easily controlled, it is considered more accurate than the colorimeter method.
3. The better reproducibility of results is another advantage of this method.
4. The method is especially suited for routine analysis of boron in soil and plants because of its simplicity and rapidity.
5. The method is sensitive to 0.03-0.04 ml. of standard base, (1 ml.= 0.2584 mgs. B), which is equivalent to 0.007-0.008 mgs. of boron.
6. An average recovery of 97 per cent was obtained by this method on boron added to plant tissue.
7. Results have shown that it is unnecessary to add a base to the plant tissue before ashing to prevent loss of boron.
8. It has been proved that ordinary evaporating dishes are as satisfactory as platinum for ashing plant tissue.
9. Results of analysis obtained of soils fertilized with boron, and plants grown on soils fertilized with boron, are fairly consistent with the treatments given.

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