hydrolysis: ethyl nonylate, 10 parts; ethyl alcohol, 40 parts; solid sodium hydroxide, 6 parts; water, 20 parts. This mixture was heated on an electric heater for two hours with a reflux condenser. The two separate layers disappeared after 20 minutes. The yellow solution was evaporated to dryness, and the residue extracted repeatedly with absolute alcohol. Both of the above methods yielded pure white products that gave practically identical results.

Experimental Methods

The determinations of surface tension were made by the drop-weight method, and the precautions and corrections of Harkins and Brown[3] were employed.

Summary

It is found that a 0.1 M solution of sodium nonylate has the lowest surface tension thus far found for a dilute aqueous solution (20.2). The addition of 0.008 M sodium hydroxide more than doubles this value, increasing it to 48.8 dynes per cm. Further addition causes a linear decrease of the surface tension.

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DETERMINATION OF SMALL AMOUNTS OF BORON IN TUNGSTEN

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Received March 5, 1925 Published July 3, 1925

Some time ago we had occasion to determine boron in tungsten alloys and lamp filaments. In the literature, one method has been described for the analysis of boron in borotungstates[1] wherein the authors precipitate the tungsten with an excess of barium hydroxide, neutralize the solution with hydrochloric acid using methyl orange as an indicator, then titrate the boric acid in a glycerol-alcohol mixture using phenolphthalein as an indicator. The method could not be used as it stands because our samples were alloys of tungsten and boron, and not soluble in water or hydrochloric acid. Some provision had to be made for dissolving the alloys and this, as will be shown later, introduced additional complications in the titration.

Barium hydroxide in neutral solution precipitates tungsten quantitatively. Barium borate also is precipitated, but is soluble in an excess of the hydroxide. The authors in the original method do not provide for the removal of the barium tungstate, or any barium carbonate which is sure to form, but adjust the acidity prior to the addition of glycerol-alcohol mixture and titrate the boron in the presence of the tungsten precipitate.

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[3] Harkins and Brown, This Journal, **41**, 499 (1919).

[1] Copaux and Boiteau, *Bull. soc. chim.*, [IV] **5**, 217 (1909).

Some experiments were made following the procedure as given. The results were not only high, but inconsistent. Such results are to be expected because some barium carbonate is sure to form and if this is not removed it will liberate carbonic acid when the preliminary neutralization is made. This carbonic acid will react with the standard alkali, giving high and inconsistent results. In addition to these errors, which are the most serious, there is the error due to the end-point, which is partly masked by a heavy precipitate of barium tungstate.

One-half g. of sodium tungstate was dissolved in 50 cc. of water and 2 g. of barium hydroxide was added to the solution. This was then neutralized with hydrochloric acid, using methyl orange as an indicator, glycerol was added and the titration carried out as though boron were present. The error amounted to as much as 1.43 mg. of boron. The next experiment tried was to add known amounts of boric oxide to sodium tungstate, precipitate with barium hydroxide and then carry out the procedure as described by Copaux and Boiteau. In the first case, 6.3 mg. of boron was added and 7.3 mg. was found. In the second case, 3.4 mg. of boron was added and 4.4 mg. of boron was found.

The error is mainly due to carbonate, so it was found necessary to filter the barium precipitate and exclude carbon dioxide from the filtrate containing the boron.

Before giving a description of the revised method some preliminary experiments will be described. Boric oxide was prepared by recrystallizing boric acid several times and fusing the dried crystals in a platinum dish until the bubbles evolved were no longer those of water vapor. The fused mass was removed by heating to melting and quickly cooling by placing the dish in ice water. Under such treatment the boric oxide shrinks and easily breaks off.

The standard alkali used was 0.05 *N* barium hydroxide solution, which was standardized against 0.05 *N* hydrochloric acid made up according to Hulett and Bonner,[2] and against Bureau of Standards benzoic acid.

The purity of the boric oxide was next determined by using it to standardize the alkali, carrying out the titration in a solution containing 20% by volume of glycerol. The results of the analysis are listed in Table I.

Table I

Purity of Boric Oxide

Boron added, mg.	8.79	3.51	9.07
Found, mg.	8.59	3.47	8.97

The average purity was taken as 98.6%.

Boric oxide was dissolved in water and treated with 1 g. of barium hydroxide. The barium borate dissolved, the barium carbonate was filtered and the solution neutralized preparatory to a boron titration, carrying out the procedure exactly as though tungsten were present; 5.24 mg. of boron was added and 5.15 mg. of boron was found.

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[2] Hulett and Bonner, This Journal, 31, 390 (1909).

To test the retention of boron by barium tungstate, mixtures of sodium tungstate and boric oxide were treated with barium hydroxide. The barium tungstate and carbonate were filtered off and the analysis was continued as usual. The results are given in Table II and show that practically no boron is retained.

Table II

Retention of Boron by Barium Tungstate

Boron added, mg.	4.48	4.04	5.21	5.12	11.14	3.53
Found, mg.	4.30	3.90	5.00	5.10	11.20	3.58
Na_2WO_4 present, g.	0.7	0.7	0.7	0.5	0.5	0.5

The procedure for analysis is very simple as long as we deal with soluble borotungstate, but the alloys we had were extremely insoluble. An acid solution could not be used for fear of losing boron, so an alkaline or neutral fusion was finally adopted. One method is a fusion with sodium nitrate and sodium chloride; the other, fusion with sodium peroxide and sodium hydroxide.

For testing the nitrate fusion method, 0.3 to 0.5 g. of tungsten metal in the form of powder or wire and weighed amounts of boric oxide were transferred to a platinum crucible. The procedure is as follows. Add 0.2 g. more of sodium nitrate than the weight of the tungsten, then add an amount of sodium chloride equal to two or three times the amount of materials already in the crucible. Cover the crucible and heat very slowly. There will be a slight flash showing that the reaction has begun. Remove the flame at this time until the action has ceased, indicated by the lessening of the crackling noise; then heat the crucible to redness until the contents are molten. The fusion takes about ten minutes.

Dissolve the cooled mass in 30 cc. of water in a porcelain, silica or platinum dish. Add 2 g. of solid barium hydroxide and heat just to boiling. (It is well to mention here that the solubility of Pyrex glass in the boiling barium hydroxide solution was tested and it was found that by boiling 1 g. of barium hydroxide in 30 cc. of water for one minute, 0.15 mg. of boron was extracted.) When the boiling was continued for 15 minutes, 0.35 mg. of boron was extracted.

If the volume has not exceeded 30 cc., filter directly into a 200cc. Erlenmeyer flask, using a fairly coarse paper. This filtration removes barium tungstate, carbonate and silicate, and should be carried out in such a manner as to exclude carbon dioxide. Add one drop of methyl orange and several crystals of potassium iodide. The iodide is added to reduce the nitrite formed during the fusion of the alloys. Acidify the solution with 1:1 hydrochloric acid and allow to stand for one or two minutes to complete the reduction. Sodium thiosulfate is then added until all the iodine has been reduced, as indicated by the change in color from brown to pink. Iodide must be added before the acid to take care of the nitrites as soon as set free, otherwise the indicator will be destroyed.

Pass a current of air free from carbon dioxide through the solution for 5 to 10 minutes to insure complete removal of oxides of nitrogen. Neutralize the solution with barium hydroxide free from carbonate. This may be easily done by filtering a saturated solution of barium hydroxide directly into the flask. Just restore the pink color with 0.05 *N* hydrochloric acid. A precipitate usually forms when barium hydroxide is added (perhaps barium sulfite or sulfate) and the slightly acid solution must be filtered, using a fairly fine paper.

Just discharge the pink color with 0.05 *N* barium hydroxide solution and add several drops of phenolphthalein and 20 cc. of glycerol. Mannitol may be used instead of glycerol. The volume should be about 100 cc. Titrate with 0.05 *N* barium hydroxide solution until a pink color just appears. The number of cubic centimeters of standard barium hydroxide solution needed after the addition of glycerol is the amount required to react with the boric acid. Run a blank after each determination and make the necessary correction.

To test the method completely, some preliminary experiments were made. Pure boric oxide was fused with sodium nitrate and sodium chloride in the absence of tungsten and the analysis carried out as indicated above. The results are given in Table III.

TABLE III

BORON DETERMINED IN ABSENCE OF TUNGSTEN

Boron added, mg.	5.44	2.95	2.10	1.89
Found, mg.	5.60	3.05	2.23	2.00

The only troublesome part of the method is the removal of the nitrites; when the amount of sodium nitrate is kept as low as possible the error here will be inconsiderable. To test the effect of an excess of sodium nitrate, more was added than would be required theoretically to oxidize all of the tungsten. One half g. of tungsten and 0.85 g. of sodium nitrate were used. The results were high; when 0.78, 2.18 and 2.86 mg. were added 0.80, 2.70 and 3.20 mg., respectively, were found. Using 0.5 g. of tungsten and 0.7 g. of sodium nitrate good results were obtained, 19.2 mg.

TABLE IV

RETENTION OF BORON DURING FUSION

Tungsten G.	Sodium nitrate G.	Boron added Mg.	Boron found Mg.
0.1	0.2	1.15	1.21
.1	.2	0.76	0.77
.3	.5	1.18	1.5
.3	.5	1.02	1.08
.5	.7	1.08	1.3

of boron having been added and 19.2 mg. having been found. For 0.3 g. of tungsten, only 0.5 g. of sodium nitrate was required, 6.0 mg. of boron was added and 5.8 mg. was found.

To test the retention of boron by tungsten during a fusion the amount of boron was kept approximately constant and the amount of tungsten was varied. Results are given in Table IV.

The amounts of boric oxide were varied, and the amounts of tungsten and nitrate kept constant; for example, 0.3 g. of tungsten and 0.5 g. of sodium nitrate.

Boron added, mg.	12.50	28.70	3.10	5.70	4.49	5.23	3.10	5.60
Found, mg.	12.2	29.5	3.5	6.0	4.47	5	3.16	5.53

From the results of these experiments the method was considered sufficiently satisfactory to proceed with the alloys. The wires were cut in lengths of about 5 mm. and if enough samples were available 0.5 g. was used. When properly prepared the samples were transferred to platinum crucibles and the analysis was carried out as usual. Some results are given in Table V.

TABLE V

ANALYSIS OF ALLOYS

	1			3		
Sample, g.	0.6997	0.4992	0.5542	0.5505	0.4400	0.4840
Boron found, mg.	.99	.68	.83	.76	.68	.76
%	.14	.14	.15	.137	.155	.157

	4		5			7	
Sample, g.	0.4080	0.5380	0.5845	0.5100	0.5313	0.5543	0.5500
Boron found, mg.	.83	.91	1.14	.98	.98	.75	.75
%	.20	.17	1.94	1.93	1.85	1.35	1.36

The second method for rendering the alloys soluble was peroxide-hydroxide fusion. This eliminates the nitrite trouble, but the manipulation is not as easy. The method can be made more general since chromates and molybdates are precipitated with the tungstate as barium salts. Either nickel or iron crucibles may be used. For testing the method the following procedure was adopted. Tungsten wire cut in lengths of about 5 mm. and weighed only roughly was placed with exact amounts of boric oxide in a nickel or iron crucible and covered with small pieces of sodium hydroxide,—about 1 g. The amounts of hydroxide used depended on the size of the crucible. The bottom of the crucible must be covered with a layer of sodium hydroxide, so that all of the sample is in contact with alkali, thus avoiding any loss due to volatilization.

When this was cooled, a considerable excess of sodium peroxide was sprinkled over the top of the melt, using perhaps 2 g. of peroxide. This excess must be used since there is no way of mixing the peroxide with the sample, and a considerable amount of peroxide is decomposed. The crucible was heated very slowly at first, then the temperature was gradually increased until a red heat had been reached, and held until all the wire had been attacked. The unattacked wire shows very plainly in the hot melt. It was found in many cases that the amount of peroxide added was insufficient to take care of the oxidation of all the tungsten, so it was necessary to cool the mass and add more peroxide, repeating the fusion until no more black particles could be seen.

When this had cooled, the crucible was placed in a covered platinum dish and the melt was dissolved out with water. The crucible was badly attacked and a precipitate of oxides of nickel and iron is formed. The water solution also contains much carbonate. As there is an excess of peroxide no indicator can be used here. The solution was acidified or made just neutral with hydrochloric acid, using litmus paper to test the end-point. Then an excess of solid barium hydroxide was added. Barium chloride may be used here instead of barium hydroxide. More barium hydroxide is needed here in the presence of the nickel and iron than in any nitrate fusion. In most of the experiments 4 g. of hydroxide was used.

Because of the ease of decomposing the peroxide the tungsten was precipitated in the presence of the nickel and iron. In every case the peroxide was decomposed and the results indicate plus and minus errors.

TABLE VI

RESULTS USING PEROXIDE FUSION

Boron added, g.	1.95	3.65	4.02	5.90	7.27	3.80	8.20	7.65	2.88
Found, g.	2.10	4.00	3.82	5.95	7.34	3.82	8.35	7.65	2.80

Aside from the error due to peroxide the only other trouble might arise from insufficient barium hydroxide. It is, of course, necessary to have a sufficient excess of barium hydroxide to precipitate all of the carbon dioxide present. For an average sample of 0.3 g. of tungsten and 1 to 10 mg. of boron, using the necessary amount of peroxide and hydroxide to put the alloy in a soluble form, 4 g. of barium hydroxide was found sufficient.

A few of the alloys were analyzed using both methods and the percentages are recorded in Table VII.

TABLE VII

ANALYSIS OF ALLOYS

Sample	Na_2O_2 + NaOH % boron	NaCl + $NaNO_3$ % boron
3	0.134	0.137
4	.24	.20
5	.183	.185

Summary

The Copaux and Boiteau method has been modified to give more accurate results for the determination of small amounts of boron.

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