In the bromide determinations of Table IV the silver bromide was not filtered off, and the iodide titration was performed in its presence. It will be seen that under these conditions an error of 1–2% must be allowed for, because of the reaction between HI and AgBr already discussed.

TABLE IV.—DETERMINATIONS ON KNOWN AMOUNTS OF BROMIDE. TITRATION PERFORMED IN PRESENCE OF AgBr PRECIPITATE.

Cc. KBr solution (1 cc. = 0.667 mg. Br).	Cc. $N/29.25$ $AgNO_3$.	Cc. $N/58.5$ KI.	Mg. Br found.	Mg. Br present.	Error. Mg. Br.	Error, Per cent.
4.00	2.00	2.08	2.620	2.668	—0.048	—1.8
4.00	2.00	2.10	2.593	2.668	—0.075	—2.8
5.00	2.00	1.58	3.305	3.335	—0.030	—0.9
5.00	2.00	1.58	3.305	3.335	—0.030	—0.9
10.00	4.00	3.18	6.580	6.670	—0.090	—1.35
10.00	4.00	3.20	6.555	6.670	—0.115	—1.70
25.00	7.00	2.10	16.250	16.690	—0.440	—2.6
25.00	7.00	1.92	16.500	16.690	—0.190	—1.1

From inspection of Tables I, II and III it will be seen that the titration error exceeds 0.05 cc. (1 drop) of the $M/58.5$ KI solution, equivalent to 0.03 mg. Cl or 0.07 mg. Br, only when the amounts titrated are so large that this error falls within or near the 1 pro mille limit. In most cases where small amounts were analyzed, the results indicate that the absolute error was within half a drop.

The percentage error ranges from a maximum of 3% in analyses of the smallest amounts, 0.7 mg. Cl and 2.6 mg. Br, down to 0.1% towards the other end of the scale, where amounts up to 70 mg. of Cl and 33 mg. of Br were determined.

Summary.

A method for titration of halides is described which permits utilization of the starch-iodine color for the end point. Because of the sensitiveness of the color change under the conditions ascertained, and the simplicity of the manipulation, amounts of halide no greater than 0.5 mg. molecule can be determined with an accuracy of one part per thousand.

THE OXIDATION OF SULFIDES WITH POTASSIUM IODATE.

BY REGINALD S. DEAN.

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L. W. Andrews[1] has shown that in solutions containing 50% by volume, or more, of concentrated hydrochloric acid at the end of the titration, potassium iodate may be used as an oxidizing agent, and that under such conditions the iodine, which is at first liberated by the reduction of iodate, is finally completely converted into iodine chloride, ICl, and the end of the titration can be shown by the disappearance of the iodine color in

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[1] THIS JOURNAL, 25, 756 (1903).

some chloroform which is mixed with the liquid to be titrated. This method has been applied to the determination of copper,[1] antimony,[2] mercury,[3] hydrazine[4] and lead peroxide.[5] Not the least striking of the advantages of the method is its applicability in the presence of solid material and organic matter such as filter paper. This made it seem not improbable that the method could be extended to the determination of sulfides, especially where the sulfide is easily washed without oxidation, as is the case with arsenic and antimony. We would expect the reaction to proceed according to one of the following equations:

$$2MS + KIO_3 + 6HCl = 2MCl_2 + 2S + KCl + ICl + 3H_2O \quad (1)$$

$$MS + 2KIO_3 + 6HCl = MCl_2 + H_2SO_4 + 2KCl + 2ICl + 2H_2O \quad (2)$$

we have found that the amount of iodate solution required for the oxidation of cadmium, zinc and lead sulfides does not correspond to either of these equations, but instead, $^1/_3$ of the sulfur is oxidized to sulfuric acid, while $^2/_3$ is liberated as free sulfur in accordance with the equation

$$3MS + 3KIO_3 + 12HCl = 3MCl_2 + 2S + H_2SO_4 + 3KCl + 3ICl + 5H_2O. \quad (3)$$

When a smaller proportion of hydrochloric acid is present, however, the amount of iodate corresponds more nearly to the first equation.

Experimental.

(*a*) **Cadmium.**—Cadmium sulfide was chosen to work with since it is comparatively easy to wash without oxidation and is easily soluble in hydrochloric acid. Ten cc. of 0.1 molar cadmium sulfate solution was precipitated with H_2S, the precipitated sulfide was filtered and washed free from H_2S and then the filter and contents were placed in a bottle containing nearly the required amount of iodate and hydrochloric acid. The liberated iodine was titrated with iodate, using chloroform or carbon tetrachloride as indicator. If an excess of iodate was used it was titrated back with standard iodide. The results were as follows:

Cadmium sulfide used was 0.144 g. = 1 millimol.

Concentration of HCl (% by vol.)	10	15	30	40	75	75	75	80
Cc. 0.05 *M* KIO_3	10	10.1	14.2	17.5	19.8	20.0	20.1	19.9
Concentration of HCl (% by vol.)	80	96						
Cc. 0.2 *M* KIO_3	4.95	5.00						

The acid concentrations are calculated on the volume after titration.

From the above results we see that, in solutions containing 10–15% concentrated acid, the reaction proceeds as represented in Equation 1; below this concentration difficulties are encountered in dissolving the sulfide

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[1] Jamieson, Levi and Wells, THIS JOURNAL, **30**, 760 (1908).

[2] Jamieson, *J. Ind. Eng. Chem.*, **3**, 250 (1911).

[3] Jamieson, *Am. J. Sci.*, **33**, 349 (1912).

[4] Jamieson, *Ibid.*, **33**, 349 (1912).

[5] R. S. Dean, *Chem. News*, **111**, 2 (1915).

and in the hydrolysis of the iodine chloride; with increasing concentration of acid, the consumption of iodate increases and reaches a maximum when the ratio of iodate to sulfide is 1 : 1, as represented by Equation 3, according to which only one-third of the sulfur is oxidized to sulfuric acid.

In order to test this last assumption, four solutions from the above titrations, two of 75% acid, and one each of 80% and 96% acid, were filtered from the filter paper, sulfur, etc., and, after boiling off the HCl and ICl, were precipitated with barium chloride, the barium sulfate being weighed and calculated to sulfur. The results were as follows:

Cadmium sulfide used = 0.1444 g. = 0.0321 g. sulfur.

Concentration of HCl (% by vol.).	75	75	80	96
Sulfur found as H_2SO_4	0.0106	0.0110	0.0103	0.0109

It will be noticed that the sulfur oxidized to H_2SO_4 is, within the experimental error, exactly one-third of the total sulfur.

(*b*) **Zinc.**—We would expect zinc sulfide to oxidize exactly as the cadmium and we find that such is the case; only two concentrations of acid were used. The zinc was precipitated from a formic acid solution and treated exactly as the cadmium. The zinc solution used was of such strength that, oxidizing according to Equation 1, 25 cc. of 0.05 molar iodate would be required, while oxidizing according to Equation 3, 50 cc. would be required. The results were:

Concentration of HCl (% by vol.).....	15	15	15	65	65	65	65
Cc. 0.05 *M* iodate..................	25.4	25.2	24.8	49.8	50.2	50.5	49.8

(*c*) **Lead.**—Lead sulfide was precipitated from a solution of known strength, filtered, washed, and titrated in the same manner as the zinc and cadmium. The concentration of acid used was about 75%. The sulfide was of such an amount that if oxidized according to Equation 3, 24.0 cc. of 0.05 *M* iodate would be required. The results were 23.9, 24.0, 24.0, 24.2, respectively.

(*d*) **Antimony.**—Antimony was chosen as a representative of the sulfides, in which the metal shows two states of oxidation. From our work on cadmium we would expect that antimony would be oxidized at low concentrations according to the equation

$$2Sb_2S_3 + 5KIO_3 + 30HCl = 4SbCl_5 + 6S + 5KCl + 5ICl + 15H_2O, \quad (4)$$

while with increasing concentration it would approach and finally reach the reaction represented by the following equation:

$$Sb_2S_3 + 4KIO_3 + 18HCl = 2SbCl_5 + 2S + H_2SO_4 + 4ICl + 4KCl + 8H_2O \quad (5)$$

That the above gives the correct ratio is shown by the following results:

The antimony was precipitated from 10 cc. of a 0.1 molar solution of potassium-antimonyl tartrate and treated exactly as was the cadmium; the reaction proceeding according to Equation 4 would require 25 cc.

0.05 molar iodate while according to (5) it would require 40 cc. The results were as follows:

Conc. of HCl (% by vol.)	26	31	36	40	60	65	70	90
Cc. 0.05 *M* KIO_3	26.2	28.2	29.6	32.2	40.4	39.9	40.2	40.0

The above results show, as with the cadmium, that with maximum oxidation only one-third of the sulfur is oxidized to sulfuric acid; they do not show the minimum found with cadmium, as the insolubility of antimony sulfide makes it inconvenient to work in the less concentrated solution.

(*e*) **Arsenic.**—As L. W. Andrews explicitly states, with higher concentrations of hydrochloric acid no oxidation of arsenic takes place. We would naturally predict then that only the sulfur from the arsenious sulfide would be oxidized, thus:

$$As_2S_3 + 3KIO_3 + 12HCl = 2AsCl_3 + 2S + H_2SO_4 + 3ICl + 3KCl + 5H_2O \quad (6)$$

The results with arsenious sulfide showed, however, only $^2/_3$ of the iodate called for by this equation; no satisfactory explanation has been found for this result.

10 cc. of an 0.08 *M* solution of arsenious chloride was precipitated as sulfide and titrated with 0.05 *M* iodate with about 80% concentrated acid. The iodate required according to Equation 6 would be 24.0 cc. The iodate consumed was 16.0, 16.0, 16.3, 16.0, respectively. Whether this apparently exact ratio of 2 iodate to 1 arsenic sulfide is accidental or not we have not determined, because the insolubility of the sulfide limits the applicable concentration to practically pure acid.

This work was done under the direction of Prof. U. H. Gottschalk.

Missouri School of Mines,
Rolla, Mo.

THE DETERMINATION OF BORON IN IRON.

By J. M. Lindgren.

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The present work has had to deal with the determination of small percentages of boron in iron. Two procedures have been tried. First, the well-known method of Gooch,[1] which consists in the formation of methyl borate and distillation of the ester in a properly arranged apparatus, with recovery of the boron in the form of calcium borate. The complications involved in this method are accentuated by reason of the large quantity of iron oxide and the fact that distillation must be repeated at least six times.

The other method made use of is that proposed by Wherry[2] which involves titration with alkali of the boric acid in the filtrate obtained

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[1] *Am. Chem. J.*, **9**, 23 (1887).

[2] This Journal, **30**, 1687 (1908).