A New Method of Reduction of Tin and Antimony Prior to Titration.*

By B. S. EVANS, M.C., Ph.D., F.I.C.

UP to the present the agents in use for the reduction of tin to the stannous condition appear to be exclusively metals, no soluble reducing agent apparently being known, or, at any rate, used. A large number of metallic reducing agents have been tried with varying success, of which, perhaps, the best is lead (A. R. Powell, *J. Soc. Chem. Ind.*, 1918, **37**, 287T.). They, one and all, however, suffer from certain drawbacks which are inherent in their metallic condition, and of which the principal one is due to the fact that any metal which will reduce tin will also reduce certain other metals, notably antimony, to the metallic condition; this reduced antimony, if present in any amount, will not only completely obscure the end-point, but will also withdraw a certain proportion, too large to be neglected, of tin from solution (K. Järvinen, *Z. anal. Chem.*, 1923, **62**, 184; S. G. Clarke, ANALYST, **1931**, 82). Some metals in use, *e.g.* zinc, reduce the tin itself to the metallic condition, necessitating re-solution, and the tin deposited on the reducing metal may hinder further reduction (Oesterheld and Honegger, *Helv. Chim. Acta*, 1919, **2**, 398; ANALYST, 1919, **44**, 359). Iron, which is very commonly used, has certain disadvantages, pointed out by K. Sandved (ANALYST, 1927, **52**, 2), and is, in addition, very liable to contain disturbing impurities; nickel has been stated to give very incomplete reduction (A. Jilek, *Chem. Listy*, 1923, **17**, 223, 268, 295).

HYPOPHOSPHOROUS ACID AS REDUCING AGENT.—In the course of an investigation into the reduction of antimony by hypophosphorous acid it was noted that whereas, alone, antimony gave correct figures on titration, in the presence of tin, the results were very much too high, pointing obviously to the partial reduction of the tin. More careful titrations, carried out in an atmosphere of carbon dioxide, however, failed to give the full figure for the tin, 0·05 grm. of tin giving a titration of 5·75 c.c. of $N/10$ iodine, instead of the theoretical 8·42 c.c. Various catalysts were tried, and successful reduction was accomplished by the addition of a trace of mercury to the reducing solution. The peculiar reducing properties of hypophosphorous acid make it unique as an analytical reducing agent; whereas in strongly acid (say, 1:1 conc. HCl) boiling solution it is capable, as has been seen, of reducing tin to the stannous condition, yet, in cold solution of one-fifth of this acid strength, its reducing power is so low that an iodine titration of, say, reduced tin can be carried out in it without any interference from the hypophosphorous acid, beyond a tendency towards slow fading

---

* Communication from the Research Department, Woolwich.

of the end-point. This being the case, a method was worked out on the following broad lines:

(*a*) The tin was reduced by boiling in a carbon dioxide atmosphere with a solution of sodium hypophosphite in hydrochloric acid (1:1) and a little mercuric chloride.

(*b*) The solution, after cooling, was diluted with 2½ times its volume of cooled boiled-out water containing citric acid, starch and potassium iodide.

(*c*) The resulting mixture was titrated with standard iodine solutions.

The tin solution from start to finish was kept in an atmosphere of carbon dioxide.

APPARATUS.—It should not be necessary at this time to insist on the desirability of conducting titrations of tin entirely in an inert atmosphere; this point has been stressed many times (*e.g.* by A. Boller, Diss. Zurich, 1915; K. Sandved, *loc. cit.*; S. G. Clarke, *loc. cit.*); and if, as is the case, the operation can be carried out as quickly and with very little more trouble than the direct titration in air, it seems obviously preferable to use a method which can be performed at one's leisure, which involves no "personal factor," and which employs the theoretical factor for calculation, rather than one which relies on standardisation against metallic tin as a method of correction for a host of errors, which are necessarily always varying with the conditions. The apparatus used in this work was that which I described in a former paper (ANALYST, 1927, **52**, 570), and, for convenience of reference, the description and figure are repeated here. The apparatus consists of a 750 c.c. Erlenmeyer flask, the mouth of which is closed by a three-holed rubber stopper carrying the following attachments:

(*a*) A leading tube, connected by about 2 feet of rubber tubing with a Kipp's apparatus delivering carbon dioxide, and passing down to within about ½ inch above the liquid in the flask.

(*b*) A small tapped funnel with its stem bent twice, so that the bulb of the funnel clears the burette, which is subsequently inserted in the third hole.

(*c*) A removable glass plug.

The reduction is carried out in the flask, the air being displaced by a stream of carbon dioxide, which passes in through the leading tube and out through the funnel, the tap of which is left open; the glass plug is left in position. When reduction is complete, the tap of the funnel is closed, that of the Kipp's apparatus fully opened, and the flask is cooled under pressure of the carbon dioxide in the Kipp's apparatus. When cool, the glass plug is removed, the tap of the Kipp's apparatus being simultaneously regulated to deliver a steady stream, and any desired reagent admitted through the tapped funnel, care being taken not to admit any air. Finally, a burette with a jet sufficiently long to pass completely through the stopper is inserted in the hole which carried the glass plug, and the titration is carried out. In the process described below the time of reduction (¼ hour) is so short that it is very improbable that the air would be adequately removed from the apparatus; consequently, the following procedure was adopted:

The stopper is removed from the flask, which is then completely filled with water; the glass plug is removed from the stopper, which is allowed to fall by its own weight into the neck of the flask, and when the water overflows through the empty hole the glass plug is re-inserted. On then pressing the stopper home the water is forced up the leading tube, which it should completely fill; if it does not it is made to do so by gently blowing into the funnel, the tap being open; the tap of the Kipp's apparatus is partly opened to allow a rapid stream of carbon dioxide to pass through the rubber connecting tube, which is then attached to the water-filled leading tube, so that air is completely excluded from the system. The apparatus is next inverted over a sink, the tap of the funnel being left open and the water allowed to run out, its place being taken by carbon dioxide. When all the water has been expelled the tap of the funnel is turned off, and the apparatus is ready for use.

DESCRIPTION OF PROCESS.—It must be emphasised that the acid strength of the solution during the reduction must not be much below 1:1 hydrochloric acid. The solution of the tin in about 30 c.c. of dilute (1:1) hydrochloric acid is run into the funnel of the apparatus, 1 c.c. of saturated mercuric chloride solution is added, and the liquid run into the flask by withdrawing the glass plug and opening the tap, care being taken not to let the surface of the liquid fall below the tap. About 5 grms. of sodium hypophosphite are placed in the beaker which contained the tin solution and rinsed into the apparatus with successive quantities of hydrochloric acid (1:1) until the total volume in the flask is about 100 c.c., the last addition being allowed to run through the tap and to within about an inch from the end of the funnel stem; the plug is now re-inserted and the tap opened, when the remaining few drops of acid are blown up into the funnel and a stream of carbon dioxide passes through the apparatus. The flask is next placed on the hot plate and the liquid allowed to boil for 15 minutes; meanwhile, 250 c.c. of water, 20 c.c. of citric acid solution (100 grms. of citric acid dissolved in 200 c.c. of water), 10 c.c. of potassium iodide solution (4 per cent.), and a few c.c. of fresh starch solution are boiled for 10 minutes in a separate flask and then cooled. At the end of the 15 minutes' reduction the tap of the funnel of the apparatus is closed, the flask removed from the plate, and the tap of the Kipp's apparatus fully opened; the flask is now cooled, the place of the contracting vapour being taken by carbon dioxide from the Kipp's apparatus. The tap of the Kipp's apparatus having been partially closed, so that only a steady stream of bubbles will pass, the plug is withdrawn and the boiled-out water, containing citric acid, potassium iodide and starch, is run into the flask, the burette containing standard iodine is inserted into the hole formerly occupied by the plug, and the solution is titrated.

For calculating the amount of tin present the theoretical factor, 1 c.c. of $N/10$ iodine=0·005935 grm. of tin, is used. When $N/100$ iodine solution is employed, a small blank, found experimentally, and representing the amount of iodine required to colour the starch, is deducted; for the present work the blank was found to be 0·2 c.c.

TEST RESULTS.—The following results were obtained with known amounts of tin in the form of stannic chloride:

Tin taken. Grm.	Titration. c.c.	Tin found. Grm.
0·0500	8·46 of $N/10$	0·0502
0·0400	6·72 ,,	0·0399
0·0300	5·02 ,,	0·0298
0·0200	3·48 ,,	0·0207
0·0100	1·74 ,,	0·0103
0·0050	8·6—0·2=8·4 of $N/100$	0·0050
0·0040	6·8—0·2=6·6 ,,	0·0039
0·0030	5·3—0·2=5·1 ,,	0·0030
0·0020	3·5—0·2=3·3 ,,	0·0020
0·0010	1·9—0·2=1·7 ,,	0·0010
Blank	0·2 ,,	

It was found that iron and copper must be separated and that nitric acid must be absent. These separations offer no great difficulty, and it is hoped shortly to publish a new method of effecting them. With regard to antimony, it was found that by increasing the amount of potassium iodide, accurate titrations of tin could be obtained in presence of a relatively large excess of antimony. The amount of potassium iodide used in the following experiments was 20 c.c. of 4 per cent. solution; larger amounts of antimony would probably require more:

Tin taken. Grm.	Antimony taken. Grm.	Titration. c.c. of $N/100$.	Tin found. Grm.
0·0050	0·0500	8·5—0·2=8·3	0·0049
0·0040	0·0500	7·0—0·2=6·8	0·0040
0·0030	0·0500	5·2—0·2=5·0	0·0030
0·0020	0·0500	3·6—0·2=3·4	0·0020
0·0010	0·0500	1·9—0·2=1·7	0·0010

ANTIMONY.—As might be expected the reduction of antimonic salts takes place much more readily than that of stannic salts, no mercury catalyst is required, and only five minutes' boiling in an open flask are needed. The antimony, dissolved in 60 to 70 c.c. of hydrochloric acid (1:1), is boiled gently for five minutes, after the addition of 5 grms. of hypophosphite, and is then cooled, after which 20 c.c. of citric acid solution (100 grms. in 200 c.c. of water) and a fragment of litmus paper are added. It is diluted with 100 c.c. of water, made alkaline with ammonia, and then slightly acid with hydrochloric acid, and again completely cooled; sodium bicarbonate is now added in decided excess (the litmus paper should be blue, and further addition of bicarbonate should not cause liberation of any more gas), followed by starch solution, and the liquid titrated with standard iodine solution (addition of potassium iodide is undesirable),

1 c.c. of $N/10$ iodine = 0·00609 grm. of antimony.

Experiments carried out with known amounts of antimony gave the following results:

Antimony added. Grm.	Titration. c.c.	Antimony found. Grm.
0·1000	16·50—0·05=16·45 of *N*/10	0·1002
0·0900	14·80—0·05=14·75 ,,	0·0898
0·0800	13·20—0·05=13·15 ,,	0·0801
0·0700	11·60—0·05=11·55 ,,	0·0703
0·0600	9·95—0·05= 9·90 ,,	0·0603
0·0500	8·20—0·05= 8·15 ,,	0·0496
0·0400	6·60—0·05= 6·55 ,,	0·0399
0·0300	5·00—0·05= 4·95 ,,	0·0301
0·0200	3·30—0·05= 3·25 ,,	0·0198
0·0100	1·70—0·05= 1·65 ,,	0·0100
0·0060	10·15—0·40= 9·75 of *N*/100	0·0059
0·0040	7·00—0·40= 6·60 ,,	0·0040
0·0020	3·60—0·40= 3·20 ,,	0·0019
0·0010	2·00—0·40= 1·60 ,,	0·0010
0·0100	17·00—0·40=16·60 ,,	0·0100
0·0080	13·60—0·40=13·20 ,,	0·0079

As in the case of tin, the blank deducted from titrations was found by experiment.

Trials were made of the titration carried out in the presence of various other metals:

LEAD.—The only alteration made in the process was that 10 c.c. of dilute (1:3) sulphuric acid were added before reduction.

Antimony added. Grm.	Lead added. Grm.	Titration. c.c.	Antimony found. Grm.
0·0020	0·22	3·7 —0·4 = 3·3 of *N*/100	0·0020
0·0040	0·22	7·1 —0·4 = 6·7 ,,	0·0041
0·0200	0·22	3·38—0·05= 3·33 of *N*/10	0·0203
0·0400	0·22	6·66—0·05= 6·61 ,,	0·0403
0·1000	0·22	16·42—0·05=16·37 ,,	0·0997

TIN, CADMIUM, AND BISMUTH.—The only alteration made was, that after dilution and addition of starch, and prior to the addition of citric acid and neutralisation, *N*/10 iodine was added in amount required to produce a blue colour lasting for a few seconds.* If this blue colour had not completely faded after the lapse of 3 or 4 minutes, the liquid was gently warmed until colourless. The citric acid was then added, followed by neutralisation, and the process finished as usual.

Antimony added. Grm.	Other metal added. Grm.	Titration. c.c.	Antimony found. Grm.
0·0010	0·20 Tin	2·2 —0·4 = 1·8 of *N*/100	0·0011
0·0020	0·20 ,,	3·7 —0·4 = 3·3 ,,	0·0020
0·0040	0·20 ,,	7·0 —0·4 = 6·6 ,,	0·0040
0·0200	0·20 ,,	3·33—0·05= 3·28 of *N*/10	0·0200
0·0400	0·20 ,,	6·66—0·05= 6·61 ,,	0·0403
0·1000	0·20 ,,	16·47—0·05=16·42 ,,	0·1000
0·0020	0·10 Cadmium	3·7 —0·4 = 3·3 of *N*/100	0·0020
0·0040	0·10 ,,	6·9 —0·4 = 6·5 ,,	0·0040
0·0200	0·10 ,,	3·28—0·05= 3·23 of *N*/10	0·0197
0·0400	0·10 ,,	6·56—0·05= 6·51 ,,	0·0396
0·1000	0·10 ,,	16·57—0·05=16·52 ,,	0·1006
0·0020	0·13 Bismuth	3·7 —0·4 = 3·3 of *N*/100	0·0020
0·0040	0·13 ,,	6·9 —0·4 = 6·5 ,,	0·0040
0·0400	0·13 ,,	6·66—0·05= 6·61 of *N*/10	0·0403

*It is desirable always to do this when tin is present as an impurity.

ARSENIC.—In this case the arsenic is precipitated in the form of element by the hypophosphorous acid; the following procedure was adopted:

The reduction was carried out in 30 c.c. of dilute (1:1) hydrochloric acid; the arsenic was filtered off and washed, first with 30 c.c. of dilute (1:1) hydrochloric acid, then once or twice with 5 per cent. ammonium chloride solution. The filtrate was neutralised, after addition of citric acid, as in the usual procedure, and titrated.

Antimony added. Grm.	Arsenic added. Grm.	Titration. c.c.	Antimony found. Grm.
0·0020	0·019	3·65—0·40 = 3·25 of *N*/100	0·0020
0·0040	0·019	6·80—0·40 = 6·40 ,,	0·0040
0·0200	0·019	3·30—0·05 = 3·25 of *N*/10	0·0198
0·0400	0·019	6·60—0·05 = 6·55 ,,	0·0399
0·1000	0·019	16·40—0·05 = 16·35 ,,	0·0996

If, as is usually the case, the antimony, prior to titration, has to be brought into solution from a precipitate containing sulphur (this applies to the antimony precipitated by hydrosulphite as well as to the sulphide, since the liquid used for washing the former contains hydrosulphite, B. S. Evans, ANALYST, 1929, **54**, 396), it is unsafe to effect this by treatment with bromine and hydrochloric acid, owing to the likelihood of formation of sulphur bromide, which causes bad end-points and very high results in the final titration. In such cases the precipitate can be dissolved by treatment of the filter in a beaker with 10 c.c. of 20 per cent. sodium hydroxide solution and 10 c.c. of hydrogen peroxide, warming slightly and stirring thoroughly and then making strongly acid with citric acid; in the presence of some other sulphides a little dilute sulphuric acid may also be required. When the precipitate has completely dissolved, the pulp is filtered off on a small pulp filter and washed with hot water. The filtrate is boiled down to about 30 c.c., an equal volume of hydrochloric acid added, and the solution transferred to a flask and rinsed in with sufficient dilute (1:1) hydrochloric acid to bring the total bulk up to 80 to 90 c.c. The reduction and titration are then carried out as usual, omitting the final addition of citric acid.

The following table shows results obtained from lead-antimony or lead-cadmium-antimony alloys, both by the Györy titration and by the present method, following precipitation of the antimony by hydrosulphite (B. S. Evans, *loc. cit.*):

Bromate* titration. (Antimony.) Per Cent.	Hypophosphite reduction followed by iodine titration. (Antimony.) Per Cent.
2·06 2·08	2·09
0·54	0·53
0·20	0·20
3·06 3·08	3·07
6·55	6·57
0·514	0·516
7·10	7·12
7·04	6·90

---

* S. G. Clarke's modification, to be published shortly.

The advantages of the method here described, as compared with the bromate titration, are three in number:

(*a*) Since $N/100$ iodine can be employed, considerably smaller amounts of antimony can be titrated.

(*b*) Since the reducing agent need not be removed, the boiling necessary to expel sulphur dioxide can be eliminated.

(*c*) Arsenic is automatically precipitated and can be simply filtered off.

With regard to (*c*), work to be published shortly by S. G. Clarke shows that it is practically impossible to eliminate arsenic by boiling down the hydrochloric acid solution, as directed in Rowell's modification of the Györy process, without at the same time losing an appreciable amount of antimony; if the drop adhering to the cover glass during solution of the metal in bromine hydrochloric acid is tested, antimony is always to be found in it. In this respect, therefore, the present method seems to be an advance.