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A New Volumetric Method for Determination of Tin Beside Antimony

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A volumetric method is described for the determination of tin in the presence of antimony. The antimony is at first titrated with bromate according to Györy and afterwards precipitated with thioacetamide and filtered off, while keeping tin in solution as oxalate complexes. After oxidizing the oxalate, tin is reduced to the stannous state and titrated with bromate in an inert atmosphere (CO_2). The complete time required for an analysis was 2—2½ h and the accuracy was 0.2 %.

The well-known determination of tin [7-9] based upon its reduction to the stannous state by means of some metal, *e.g.* lead, iron or aluminium, and subsequent titration with bromate in an inert atmosphere has for a long time been used in this laboratory, where the procedure, described by Kühnel Hagen *et al.*[12] has been followed. In connection with the Györy [10] titration of antimony it has been our standard method in the analysis for tin and antimony in "white metal" alloys. The method has the advantage of being a rapid one and is accurate as long as the ratio antimony/tin is low.

When, however, this ratio increases above 1 : 3, the method involves increasing difficulties for the accurate determination of the tin content due to interference from the large amount of solid antimony then suspended in the solution. The present work has been carried out in order to improve the accuracy while trying to maintain the rapidity of the previous procedure.

The suggestion by Barber and Grezekowiak [6] of using thioacetamide instead of hydrogen sulphide in quantitative analysis has been developed by Musil, Flaschka and their coworkers to valuable gravimetric methods for most of the heavy metals, including also tin and antimony [3,5]. The antimony is for example precipitated and weighed as Sb_2S_3, giving excellent results [2,5]. The quantitative precipitation of tin by means of thioacetamide is more difficult, but Flaschka [1] gives details of a procedure where the results are only slightly low, the weighing form being SnO_2. Flaschka, Musil and coworkers [1] point out, however, that no difficulties are encountered in the quantitative precipitation of tin when thioformamide is used instead of thioacetamide. Musil and co-

workers [4] describe a procedure for determination of arsenic, antimony and tin, in which arsenic and antimony are titrated with bromate and thereupon separated by precipitation with thioformamide in 6 N hydrochloric acid for arsenic and in weak acid solution for antimony. The tin is kept in solution as oxalate complexes and determined by electrolysis or gravimetrically as SnO_2. The method we propose below combines the advantages of the method of Musil and coworkers for the separation of antimony from tin (arsenic is not considered in the present paper) with that of the volumetric determination of tin.

PROCEDURE

The solution, which should contain the metals as Sn^{4+} and Sb^{3+} or Sb^{5+}, respectively, the latter being the case if the alloy is dissolved in hot sulfuric acid and subsequently titrated with bromate according to Györy to determine the antimony content. Aliquots containing approx. 0.15 g Sn are pipetted off from the titrated solution, and 7.5 g oxalic acid and 20 ml conc. hydrochloric acid added whereafter the aliquot is diluted to 100 ml with water. The solution is heated to boiling and 0.3 g of thioacetamide dissolved in 3 ml water is added for each 0.1 g antimony present. During the addition of the thioacetamide the solution is well stirred, and the stirring is continued while 100 ml hot water is added. After cooling to 50°C the crystalline red precipitate of Sb_2S_5 is filtered off on a G 4 glass-filter, which is washed beforehand with a 1 % solution of oxalic acid to avoid separation of SnS_2 in the collector flask. The precipitate is washed with warm 0.1 % oxalic acid. The filtrate is transferred to a 1 liter beaker or a 500 ml Erlenmeyer flask and sufficient ammonium persulfate (17 g) is added to oxidize all oxalic acid. The flask is warmed on a gas burner or an electric heater for 15–20 min in order to destroy all persulfate. After cooling 50 ml conc. hydrochloric acid, 10 ml conc. sulfuric acid and 200 ml of water are added. The tin can now be determined according to one of the well-known procedures. We usually add a sheet of high purity aluminium to reduce the tin to metallic state. After the aluminium (*ca.* 3 g) has been added, the flask is fitted with a stopper with 3 holes, one of which is fitted with a glass tube to the bottom and is used to pass a stream of carbon dioxide into the solution. The second is fitted with a long glass tube as a refluxer and the third is available for the burette tip but is initially closed by a glass rod. With the concentration of acid used the aluminium is slowly dissolved while the tin separates as a spongy mass. After 20 min the flask is heated without boiling and the tin and a possible rest of aluminium is dissolved. When all is dissolved the flask is cooled, while the flow of carbon dioxide is temporarily increased.

In a test tube 0.5 g KI and 5 ml of a 0.5 % starch solution are mixed with 0.5 ml diluted sulfuric acid, a little $NaHCO_3$ is added to expel dissolved oxygen. This mixture is added with a pipette to the analysis and the burette tip is introduced through the third hole. Bromate solution is added until one drop gives a pertaining blue colour.

Chemicals

Tin solutions were made by dissolving pure tin in hot sulfuric acid and diluting to known volumes. Tin was either "AnalaR" or in some cases "Banka Tin" of unknown manufacture.

Antimony solutions were made from "AnalaR" $SbCl_3$ and were analyzed by titration with potassium bromate according to Györy.

Potassium bromate solutions were made from Merck potassium bromate *p.a.* dried at 150°C. Weighed amounts were dissolved in water to known volumes. The solutions were also standardized on tin, and the usual corrections of the titer found by weighing off the potassium bromate were +0.4 % and 0.2 % compared to "AnalaR" tin and "Banka" tin, respectively. The titers used for calculation of "mg tin found" are the ones based on "AnalaR" tin.

Thioacetamide and ammonium persulfate were "Merck" products.

Table 1. Analysis of tin solution without antimony. Standard procedure, no oxalate or persulfate added.

Expt. No.	mg Sn taken	mg Sn found	Deviation mg	Deviation %
1	150.1	150.3	0.2	0.1
2	150.1	150.1	0	0
3	150.1	150.2	0.1	0.1
4	150.1	150.5	0.4	0.3
5	150.1	150.1	0	0
6	150.1	150.1	0	0
7	150.1	150.1	0	0

Table 2. Analysis of samples containing tin and antimony.

Expt. No.	mg Sb taken	mg Sn taken	mg Sn found	Deviation mg	Deviation %
8	38.71	104.8	104.9	0.1	0.1
9	79.41	104.8	104.9	0.1	0.1
10	79.41	104.8	104.6	−0.2	−0.2
11	119.2	104.8	104.1	−0.7	−0.7
12	119.2	104.8	104.0	−0.8	−0.8
13	238.4	104.8	104.8	0	0
14	238.4	104.8	104.9	0.1	0.1
15	101.1	147.1	147.1	0	0
16	101.1	147.1	146.9	−0.2	−0.2
17	101.1	147.1	147.0	−0.1	−0.1

Table 3. Analysis of samples containing only tin, but treated as the filtrate from Sb_2S_3. The destruction of excess persulfate is carried out in a 1 liter beaker.

Expt. No.	mg Sn taken	mg Sn found	Deviation mg	Deviation %
18	150.1	149.5	−0.6	−0.4
19	150.1	149.4	−0.7	−0.5
20	150.1	149.4	−0.7	−0.5
21	150.1	149.3	−0.8	−0.6
22	150.1	149.4	−0.7	−0.5
23	150.1	149.5	−0.6	−0.4
24	150.1	149.5	−0.6	−0.5
25	150.1	149.6	−0.5	−0.3
26	150.1	149.1	−1.0	−0.7
27	147.1	147.3	0.2	0.1
28	147.1	147.2	0.1	0.1
29	147.1	147.2	0.1	0.1

The aluminium sheet used for reduction was known to be 99.9 % pure.

Carbon dioxide was taken from cylinders which had been used for some time, so that the small amount of oxygen present in freshly filled cylinders had escaped.

Sulfuric and hydrochloric acids were chemically pure products.

All volumetric glasswares were calibrated before use.

The oxalic acid ($H_2Ox,2H_2O$) was a high grade "Merck".

RESULTS

The results given in Table 1 are obtained by pipetting off 20 ml samples from the stock solution of pure tin and analyzing the aliquots according to the nor-

mal procedure, *e.g.* reducing with aluminium and titration with potassium bromate. An average error of less than 0.1 % is found. When these results are compared with those in Tables 2 and 3, it is seen that the last two show a tendency to lower values. The samples in Tables 2 and 3 were both analyzed according to the procedure described above. In Table 3 no antimony was present, but the procedure was followed except that no thioacetamide was added. The somewhat higher error found when the sample was treated for antimony can evidently not be due to co-precipitation of tin when antimony sulfide is precipitated.

In order to see whether some tin escaped as $SnCl_4$ during the oxidation of oxalate with persulfate, we have carried out the experiments in Table 4. The procedure was changed such that the heating for destruction of oxalate and persulfate was carried out in the Erlenmeyer flask later to be used for the titration of tin. This flask was fitted with a stopper with a long glass tube acting as a refluxer. The results seem rather to indicate an increase than a decrease in the error.

That no tin seems to disappear during the heating to nearly 100°C for 20 min is in accordance with qualitative tests made in the following way: the tube otherwise used as a refluxer was bent downwards just above the stopper and the vapour now distilled was collected in dilute sodium hydroxide solution. After heating for 25 min, when approx. 10 % of the volume had distilled, the basic solution was neutralized and tested for tin with dithiol and mercaptoacetic acid, according to Charlot and Gauguin [11]. In four experiments no tin at all could be found with this very sensitive reaction. Experiments with prolonged heating (120 min) showed the same results.

It is important that all persulfate is destroyed during the heating, since the experiments show that persulfate remaining in the solution after the heating was not reduced completely by the aluminium and therefore invalidated the tin titration. We therefore made some experiments to find the time of heating necessary for the complete destruction of the excess of persulfate when different kinds of glassware were used: 1) a 1 liter beaker, 2) the 500 ml Erlenmeyer flask used as in Table 4. To the analysis containing 7.5 g oxalic acid and 15 g ammonium persulfate were added a few drops of a 0.1 N titanium chloride. The presence of peroxide is indicated by the formation of the yellow peroxytitanate ion when the solution is heated. With electrical heating of the solutions in the beaker the destruction temperature of the persulfate excess was measured to 80°C and somewhat higher (85—90°) in the Erlenmeyer flask owing to the higher partial pressure above the latter solution. Complete destruction, indicated by the sudden disappearance of the yellow colour, was obtained after 8 min in 1) and after 13 min in 2). The importance of a relatively long time of heating, when no catalyst is present, is emphasized by the results given in Table 5, where larger excess of persulfate has been combined with shorter time of heating with remarkable results.

That heating on a steam bath requires more time than heating by a free flame or electrical heating was realized from results obtained when 24 g (10.4 g excess) ammonium persulfate was used to oxidize 7.5 g oxalic acid and heating on a steam bath for 15 min. The average of 5 tin determinations was 4 % lower than calculated.

Table 4. As in Table 3 but using 500 ml Erlenmeyer flask and refluxer when destroying persulfate.

Expt. No.	mg Sn taken	mg Sn found	Deviation mg	Deviation %
30	150.1	148.8	−1.3	−0.9
31	150.1	148.9	−1.2	−0.8
32	150.1	148.8	−1.3	−0.9
33	150.1	148.8	−1.3	−0.9
34	150.1	148.8	−1.3	−0.9
35	150.1	148.7	−1.4	−0.9
36	150.1	148.6	−1.5	−1.0
37	150.1	148.5	−1.6	−1.1
38	150.1	148.5	−1.6	−1.1

The deviations are seen to be somewhat larger compared to the results of Table 3 when the Erlenmeyer flask is used.

Table 5. The influence of time of heating on excess of persulfate.

Expt. No.	mg Sn taken	mg Sn found	Deviation mg	gram per-sulfate used	Time of heating, min	°C
39	150.1	81.9	−68.2	24	5	
40	150.1	149.5	− 0.6	24	30	90−95
41	150.1	147.4	− 2.7	17	5	
42	150.1	144.4	− 5.6	17	5	

The experiments show that the treatment of the tin solution with persulfate will cause some lowering of the tin content found. The small — constant — deviation can easily be determined in the individual case (for other chemicals used). No tin seems to escape from the containers and excess persulfate is evidently completely removed by 20 min heating. It is likely then that the tin is to some extent transformed to a state not easily reduced. Experiments, where small glass pellets were introduced in order to increase the surface, showed no increase in error, which excludes the possible adhering of some tin to the walls of the containers. The error is, however, almost negligible when traces of antimony as in Table 2 are present, probably owing to catalytic effects.

We have finally made a few experiments using $KMnO_4$ as oxidizing agent instead of $(NH_4)_2S_2O_8$. When due care is taken to the vigorous evolution of CO_2 when adding $KMnO_4$ to the hot solution, this method has some advantages over the method described above, *i.e.* the destruction of excess oxidizing agent is avoided as the end point is easily visible and dissolving of the tin is very quickly accomplished due to catalytic effects ($Mn^{+2} \rightleftharpoons Mn^{+1}$). The theoretical amount of $KMnO_4$ for 7.5 g $H_2Ox,2H_2O$ is 3.76 g. Deviations with $KMnO_4$ as destructing agent for the oxalic acid were 0.1—0.3 %, and the complete analysis is accomplished in 2 h.

The dissolution of the spongy tin may be a rather tedious process when no traces of other metals are present (Table 1). The time for dissolution can be

reduced to less than 1 h by adding a few drops of a very diluted Pd solution. Owing to the same kind of catalytic effects as obtained by using a Pd (or Au) catalyst we have obtained considerably lower dissolution times in the experiments with both Sn and Sb where minute traces of Sb are still present at this stage. The time of dissolution should, however, not be shortened by adding more acid as the reaction will tend to be too vigorous with foaming and even splashing (thus invalidating the determination).

The method gives results with an average deviation of ± 0.2 % when the titer of the potassium bromate is increased by 0.3 %. The time required for a complete analysis was 2—2 ½ h.

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