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A New Method for Determining Tin and Antimony in their Mixture

By

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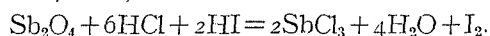
Since tin and antimony may, without much difficulty, be transformed into the oxide forms it occurred to the writer that this property might in some way be utilized for the quantitative determination of these metals existing as a mixture. Following up this idea, he transformed the two metals simultaneously into a mixture of their oxides by treating them with concentrated nitric acid, and the oxide mixture thus formed was ignited at 800° – 820° C. for half an hour, and weighed. The mixture, which was presumed to contain tin in the form of SnO_2 and antimony in that of Sb_2O_4 was now treated with potassium iodide in a tartaric-hydrochloric acid solution in order to reduce antimony to the antimonous state and the antimony thus reduced was determined iodometrically. As is shown in the experimental part, the results turned out fairly satisfactory, showing that the method above described is applicable to practical purposes. The experiments were further extended to the case in which tin and antimony form a mixture with another metal such as copper, and in this case too a tolerably good result was obtained.

Experimental Part

I. Analysis of a sample consisting only of tin and antimony

In the experiment tin and antimony obtained from Kahlbaum were used. The purity of the former was confirmed to be 99.95% and that of the latter 99.98%. About 0.2–0.25 grams of various mixtures containing the two metals in different proportions were weighed out, and left to stand with 10 c.c. of conc. HNO_3 and a few c.c. of water

till the fumes of nitric oxide ceased to be evolved, whereupon the excess of nitric acid was evaporated off and the residue was made slightly alkaline with ammonia and again evaporated to dryness. The mixture of oxides was then transferred to a crucible and heated gradually to 800° – 820° C. at which it was maintained for about half an hour. The heating was repeated till the weight became constant. To the oxide mixture were next added 5–10 c.c. of 10% potassium iodide solution, 3–5 grams of tartaric acid, 40 c.c. of 12N-HCl, 0.3 grams of potassium chloride and 10 c.c. of water, and the mixture was heated in a sand-bath. By this treatment the antimony in the Sb_2O_4 was reduced and dissolved as antimonous chloride, iodine being liberated at the same time, thus,.....



The heating having been continued till all the iodine was nearly evaporated off, the solution was treated with a few drops of dil. sodium thiosulphate solution in order to get rid off the last trace of iodine, and neutralized with a caustic soda or sodium carbonate solution. The solution was then diluted to 200 c.c. and a saturated solution of sodium bicarbonate, which must be taken in the proportion of 10 c.c. to every 0.1 gram of metallic antimony, was added to it. With the solution thus prepared, antimony was titrated iodometrically with 1/10N-iodine solution. From the weight of the antimony, the weight of the Sb_2O_4 was calculated by multiplying it by the factor 1.2663, and the amount of the SnO_2 and therefore that of the tin present in the mixture were calculated by subtracting the weight of the Sb_2O_4 from the total weight of the mixed oxide. The results are shown in Table I.

Table I

No.	Sn gms.	Sb gms.	Sn %	$SnO_2 + Sb_2O_4$ gms.		Diff. gms.	Sb gms. Found	Diff. gms.
				Calc.	Found			
1	0.0236	0.2123	10	0.2988	0.2986	-0.0002	0.2120	-0.0003
2	0.0400	0.1597	20	0.2530	0.2531	+0.0001	0.1600	+0.0003
3	0.0672	0.1575	30	0.2848	0.2850	+0.0002	0.1573	-0.0002
4	0.0875	0.1305	40	0.2764	0.2766	+0.0002	0.1304	-0.0001
5	0.1046	0.1043	50	0.2648	0.2654	+0.0006	0.1040	-0.0003
6	0.1163	0.0782	60	0.2467	0.2482	+0.0015	0.0779	-0.0004
7	0.1367	0.0589	70	0.2481	0.2498	+0.0017	0.0589	$\pm 0.0000?$
8	0.1743	0.0445	80	0.2776	0.2784	+0.0008	0.0450	+0.0005?

As is seen in the above table, the value of the two oxides is always too high when the content of tin in the mixture becomes greater than 60%. Probably this is due to the fact that the conversion of tin oxide into the form of SnO_2 is not complete at $800^\circ\text{--}820^\circ\text{C}$. The error thus produced is, however, insignificant, when the content of tin is less than 50%.

Several experiments were conducted to learn how the dehydration of tin oxide is governed by the temperature, and the results shown in Table II were obtained.

Table II

0.2037 gram of tin corresponding to 0.2586 gram of SnO_2 were employed.

Temperature	Time of ignition in minutes	SnO_2 Found	Diff.
780°	20	0.2639	+0.0053
820°	15	0.2600	+0.0014
"	30	0.2600	"
850°	20	0.2587	+0.0001
870°	20	0.2587	"

There are several reports on the temperature suitable for the conversion of Sb_2O_5 into Sb_2O_4 . According to H. Bilz,¹ Sb_2O_5 changes into Sb_2O_4 at 450° and the latter into Sb_2O_3 at 1060° . T. Carnelly and T. Walker² state that Sb_2O_4 is stable between $585^\circ\text{--}775^\circ$, while Baubigny³ regards the temperature between $750^\circ\text{--}850^\circ$ as the best for the quantitative conversion of Sb_2O_5 into Sb_2O_4 , which gradually changes into volatile Sb_2O_3 at temperatures higher than 950° . The results of the present author's experiments were found to agree with those of Baubigny comparatively well. The transformation of Sb_2O_5 into Sb_2O_4 was found to proceed very slowly at 750° and only at $800^\circ\text{--}820^\circ$ to become very significant. When, however, the temperature was raised higher than 840°C , loss due to the formation of Sb_2O_3 was unavoidable as is seen in Table III.

1. H. Bilz: *Z. f. phys. Chem.*, **19**, 385, 1896.
2. T. Carnelly & T. Walker: *J. Chem. Soc.*, **53**, 86, 1888.
3. Baubigny: *Compt. rend.*, **124**, 499, 1897.

Table III

Sb ₂ O ₄ gms.	Temperature	Time of ignition in minutes	Loss in weight gms.
0.3178	840°	30	0.0036
0.0250	850°	10	0.0095
0.2429	850°	30	0.1534

Though stannic tin is not reduced by hydrogen iodide, the end point in the titration of antimony becomes indistinct unless some tartaric acid is added to the solution. In the solution in which tin exists in a large excess, titration of antimony cannot be conducted accurately even in the presence of tartaric acid, as is shown in Table IV.

Table IV

Sb used : 0.1090 gm.

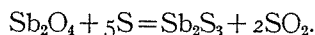
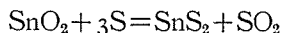
Sn gms.	Tartaric acid gms.	Sb gms. Found	Diff.	Remarks
0.05	3	0.1090	±0.0000	
0.1	0	0.1044—0.1055	—0.0046—35	End point somewhat indistinct.
„	3	0.1088	—0.0002	
0.2	5	0.1089	—0.0001	
0.3	5	0.1087	—0.0003	
0.4	0	—	—	End point indistinct.
„	5	0.1073?	—0.0017?	Somewhat indistinct.
„	7	0.1084?	—0.0006?	„

II. Analysis of a sample containing some other metals besides tin and antimony.

To see how the above method for determining tin and antimony can be applied to the analysis of a sample containing other metals also, an alloy consisting of tin, antimony and copper was analysed in the following way :—

0.3 gram of the alloy was dissolved in 40 c.c. of concentrated

hydrochloric acid containing some bromine, and the solution, after having been concentrated to 20 c.c. in a water-bath, was neutralized with caustic soda and diluted to 150 c.c. Now 50—100 c.c. of the sodium sulphide solution prepared by dissolving 60 gms. of $\text{Na}_2\text{S } 9\text{H}_2\text{O}$ and 40 gms. of NaOH in 1000 c.c., 3—5 gms. of tartaric acid and 5 c.c. of a saturated solution of sodium acetate were added to the solution and the whole heated in a sand bath till copper sulphide had completely subsided. It was then filtered and the precipitate was washed with water containing sodium acetate and sodium sulphide, and the filtrate together with the washings was acidified with HCl so as to precipitate the sulphides of tin and antimony. To make the precipitation of the sulphides complete, 10 c.c. of a saturated solution of ammonium nitrate was added to the solution in which the sulphides were suspended and a current of hydrogen sulphide was passed into it. The sulphides were then filtered and washed as usual and dried. The dried precipitate¹ was left to stand in a closed vessel containing some fuming nitric acid, in order to expose the precipitate to a nitric acid gas atmosphere. By this treatment the sulphides were gradually oxidized, sulphur being set free. After the nitric acid still adhering to the precipitate had been driven off, the precipitate was washed with alcohol and carbon bisulphide and then with alcohol and ether successively, and finally ignited in a crucible. It is here to be noted that the ignition must be conducted at first very gradually, otherwise the sulphur still remaining acts upon the oxides in the manner represented in the following equations, before it is completely oxidized to sulphur dioxide :—



When the evolution of sulphur dioxide had ceased the temperature was raised to 800° — 820° and the heating was continued till the weight became constant. Sometimes sulphuric acid formed by oxidation obstinately adheres to SnO_2 . In such a case a small quantity of ammonium carbonate should be added and ignited. The results were as shown in Table V.

1. Sulphides adhering to the filter-paper were removed by dissolving them in ammonium sulphide and recovered by evaporating the ammonium sulphide solution to dryness.

Table V

No.	Sn gms.	Sb gms.	Sn %	SnO ₂ +Sb ₂ O ₄ gms.		Diff. gms.	Sb gms. Found	Diff. gms.
				Calc.	Found			
1	0.0188	0.1692	10	0.2381	0.2378	-0.0003	0.1690	-0.0002
2	0.0475	0.1901	20	0.3010	0.3006	-0.0004	0.1899	-0.0002
3	0.1184	0.1185	50	0.3004	0.3002	-0.0002	0.1179	-0.0006
4	0.1820	0.0454	80	0.2886	0.2917	+0.0031	0.0454?	±0.0000?

The author takes this opportunity warmly to thank Professor Motooki Matsui, under whose guidance and encouragement this work was carried out.