

## Determination of Small Amounts of Tin in Alloys

### Isolation by Adsorption of Stannic Acid on Manganese Dioxide

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Isolation of small percentages of tin from alloys has been, and is still, something of a problem. When a bronze with a low tin content is dissolved in nitric acid, the stannic acid will be obtained in partly disperse and partly colloidal form, so that complete filtering-off is impossible. Furthermore iron and possibly also chromium shows a tendency to prevent the colloidal stannic acid from coagulating. The presence of phosphorus will also be troublesome. Certainly, there are chemical micro-methods for the isolation and determination of tin, but they are inadequate in cases, where the amounts of other elements present are disproportionately much larger than the amount of tin. Exemplifying methods are precipitation with phenylarsonic acid<sup>1</sup>, as also precipitation with cupferron<sup>2</sup>.

Blumenthal<sup>3</sup> has investigated a method for isolating very small amounts of antimony in copper. The copper is dissolved in nitric acid, after which the solution is made only slightly acid with nitric acid and diluted to a considerable volume. Through addition of manganous nitrate and potassium permanganate a precipitate consisting of manganese dioxide is formed, which will adsorb most (96—97 %) of the antimonious acid present. By repeating the precipitation in the filtrate, a practically complete isolation of antimony is obtained. Blumenthal states, that in all likelihood tin and bismuth will also be precipitated quantitatively.

In »Analyse der Metalle»<sup>4</sup> Blumenthal's method is referred to in respect to the determination of tin.

Park<sup>5</sup> estimates spectrographically traces of antimony, tin, bismuth and molybdenum in copper after co-precipitation with manganese dioxide. As in »Analyse der Metalle» the precipitate is dissolved in hydrochloric acid and

bromine by boiling, until the solution is reduced to a considerably smaller volume.

During experimentation in our laboratory in this way it proved difficult to avoid loss of tin, as also antimony (*cf.* Table 1, IV and V). The loss of tin and antimony depends on the concentration of hydrochloric acid. After the method in »Analyse der Metalle», as well as the method of Park, a subsequent precipitation with hydrogen sulphide is used with regard to further purification.

We have made a few experiments in order to compare the volatility of tin, antimony and arsenic in circumstances similar to those used in »Analyse der Metalle» when dissolving manganese dioxide plus stannic acid or antimonic acid. a) A solution of arsenic is made by dissolving 4.917 g arsenic trioxide in a solution of 15 g sodium hydroxide in water and diluting to 1000 ml. The arsenic content is determined by titration with 0.1 *N* potassium bromate. b) 6.111 g pure antimony is dissolved in 30 ml conc. sulphuric acid. The solution is diluted to 1000 ml with water and at the same time with 150 ml conc. hydrochloric acid. The antimony content is determined by titration (in hot solution) with 0.1 *N* potassium bromate. c) 11.3 g cryst. stannous chloride is dissolved in 100 ml conc. hydrochloric acid, diluted with water, oxidized with hydrogen peroxide and finally diluted with water to 1000 ml. The tin content is determined as usual by reduction with aluminium and titration with potassium iodate.

All the experiments given in Table 1 are carried out in a beaker. When carried out in an Erlenmeyer flask, the loss will be somewhat smaller. 25 ml (representing about 1.25 millimole of respectively arsenic, antimony and tin) of the stock solutions are used in each experiment. The results show, that the procedure in »Analyse der Metalle» might bring about a considerable loss of antimony, but no loss or only a small loss of tin. Nevertheless, when, for instance, dissolving lead with a small percentage of tin by boiling with nitric acid and treating as in »Analyse der Metalle», only a part of the tin will be found — in all likelihood due to formation of metastannic acid, which will not dissolve in hydrochloric acid plus bromine. Of course this metastannic acid could be filtered off and fused with sodium peroxide, but that is an unpleasant and time-wasting complication.

Fainberg and Troitzkaja<sup>6</sup> have described a procedure for the determination of tin in electrolytic copper using Blumenthals method and the titration method of Clarke<sup>7</sup>: To the slightly acid (with nitric acid) solution of the electrolytic copper is added manganous sulphate and potassium permanganate. The manganese dioxide precipitate, which has adsorbed all stannic acid present is boiled with nitric acid, so that all the tin will be at hand as

Table 1. Experiments showing the amounts lost of arsenic, antimony and tin by boiling — in a beaker — solutions acidified with hydrochloric acid as in »Analyse der Metalle».

		Percentage volatilized		
		As	Sb	Sn
I	25 ml solution is diluted to 100 ml (6 N as to hydrochloric acid) and boiled down to 40 ml. Titration .....	84.5	0	0
		91.6	0	0
I a	The same procedure as in I except that 10 ml conc. sulphuric acid is added before boiling .....	95.6	6.5	0
		98.0	6.5	0
II	25 ml solution is diluted to 60 ml (4 N as to hydrochloric acid). Boiling at constant volume (addition of water) for 1 hour. Titration .....	6.0	0	0
		14.3	0	0
II a	The same procedure as in II except that 10 ml conc. sulphuric acid is added before boiling .....	80.0	4.4	0
		79.1	3.0	0
III	25 ml solution is diluted to 125 ml (9 N as to hydrochloric acid) 2 g sodium sulphite is added, after which the solution is boiled down to 50 ml. Titration ..	99.0	1	0
		99.2	1	0
IV	25 ml solution is diluted to 150 ml (8 N as to hydrochloric acid), 10 ml bromine water added. Boiling down to 50 ml. After this 1 g sodium sulphite and 25 ml water is added. Boiling down to 50 ml. Titration .....	84.0	4.7	0.7
			4.0	1.4
V	25 ml solution is diluted to 100 ml (6 N as to hydrochloric acid), 20 ml bromine water added. Boiling down to 50 ml. After this 2 g sodium sulphite and 75 ml conc. hydrochloric acid is added. Boiling down to 50 ml. Titration ..	99.5	0.5	0
			0.5	

metastannic acid. After filtering and drying the precipitate is fused in a porcelain crucible with sodium peroxide. The melt is dissolved in water, and the tin is determined by reduction with lead foil in carbon dioxide atmosphere and titration with 0.01 *N* iodine solution with starch as indicator. The method yields good results, but it is tedious and particular.

We have, as will appear later, made a closer investigation of the adsorption of stannic acid on manganese dioxide and at the same time altered the determination of tin in this precipitate, so that a fairly speedy and convenient method is available.

### PROCEDURE

An appropriate solution with known tin-content is produced by dissolving about 50 mg Banca tin in hot conc. sulphuric acid; the sulphur hereby formed is removed by gently heating the sides of the flask. The solution is diluted with water to 100 ml in a volumetric flask. From this solution 10 ml is taken out with a pipette — for each experiment.

10 ml tin-solution (about 5 mg tin) is diluted to 600 ml in a beaker with redistilled water (in all experiments redistilled water, condensed in a silica condenser, is used). 10 ml conc. nitric acid and one drop of methyl red is added, after which neutralization with conc. ammonium hydroxide takes place. The final degree of acidity is imparted by addition of 2 ml conc. nitric acid. The precipitate of manganese dioxide is now generated by adding 5 ml 0.4 *M* manganous nitrate and 5 ml 0.04 *M* potassium permanganate solution. The permanganate is added while vigorously stirred, so that a homogeneous solution is obtained before formation of the precipitate. The beaker is now while stirring, heated, to boiling point, or at least until the manganese dioxide is aggregated in large flakes. The hot suspension is filtered on a soft analytical filter paper, and the precipitate is washed with hot water 6—8 times. Into the beaker used for the precipitation is poured 5 ml conc. nitric acid and a couple of drops of 30 % hydrogen peroxide. Hereby the small amount of manganese dioxide, covering the bottom and the sides of the beaker, is dissolved, and the possibly adsorbed stannic acid will become suspended in the solution \*, which — without further cleaning of the beaker — is transferred to a 300 ml Erlenmeyer flask. The filter paper with the manganese dioxide precipitate is pushed into the flask and 10 ml conc. sulphuric acid added. By heating until sulphur trioxide fumes are generated the paper gradually becomes oxidized. At the beginning of this destruction it is advisable to almost cover the mouth of the flask with a watch-glass to avoid splashes escaping. As a rule it is sufficient for complete destruction to add twice a few drops of fuming nitric acid, each time heating until fumes of sulphur trioxide are formed. The solution will now in addition to sulphuric acid, manganous sulphate and stannic sulphate contain some nitrosylsulphuric acid, which can be broken down by twice adding 10 ml dist. water, each time heating until all water is evaporated.

The tin titration is carried out in a test tube 230 × 40 mm fitted with a three-hole stopper carrying in one hole a gas inlet tube extending to the bottom of the test tube, in the second a vertical outlet tube, 70—80 cm in length, and in the third hole a small glass stopper, which can be removed when the tip of the burette is to be inserted. The solution

\* For the possible adhesion of SnO<sub>2</sub> to the bottom of the beaker see by »Results» exp. no 5.

of stannic and manganous sulphate in 10 ml conc. sulphuric acid is diluted with 25 ml of water, cooled, and poured into the titration test tube. The flask is washed with a cold mixture of 25 ml of water and 15 ml conc. hydrochloric acid. As a reducing agent a piece of aluminium sheet  $70 \times 7 \times 0.4$  mm (about 0.5 g) is used. This aluminium is spectrographically found to be tin free and furthermore, when a blank analysis is carried out as described, no tin is found. After addition of the aluminium the stopper is inserted and a slow current (2—3 bubbles per second) of carbon dioxide is started through the solution (carbon dioxide from a pressure cylinder is sufficiently pure).

In the course of about  $\frac{1}{2}$  hour all aluminium will be dissolved, and the stannic ions have been reduced to free tin, which again is brought into solution by heating the test tube in a steam bath of with a pilot flame (without boiling). Finally, the tube is cooled in cold water after increasing the current of carbon dioxide to prevent back pressure.

The solution — now containing stannous ions — is titrated with potassium iodate or potassium bromate solution with starch plus potassium iodide as an indicator. Hereby the stannous ions will be oxidized to stannic ions, while iodate and bromate are reduced to iodide and bromide. 1 ml standard solution is equal to about 2 mg tin.

When the solution is cold, the stopper in the third hole is removed, and 5 ml of a solution of starch and potassium iodide added from a pipette. The outlet capillary tip of the burette is now inserted — the tip extending to below the surface of the solution, and the solution is titrated to a faintly blue colour. The carbon dioxide current is used for stirring. The indicator liquid is made of 50 ml fresh 1 % starch solution and 4 g potassium iodide. Just before use 10 ml of this solution is mixed with 1 ml 4 n sulphuric acid and a small spatula of sodium bicarbonate, in order to remove most of the oxygen dissolved. A 5 ml burette with 1/100 ml divisions, the tip drawn down to a capillary, is used.

The titre of the iodate or bromate solution must be determined by direct reduction and titration of a known amount of the solution of tin in sulphuric acid, because the theoretical titre is a little too low due to oxygen dissolved in the standard solution.

We have obtained the procedure detailed above through several unsuccessful experiments not described.

## RESULTS

Experiments nos. 1, 2, 3 and 4 are carried out exactly as given in the procedure above. As Table 2 shows, all tin is found again.

In experiment no. 5 10 ml solution containing 6.61 mg tin, 9 ml water and 1 ml conc. sulphuric acid is boiled for 1  $\frac{1}{2}$  hour with nitric acid in the beaker later used for the manganese dioxide precipitation. The volume is kept at about 100 ml by adding, from time to time, conc. nitric acid. As a result of this treatment some of the colloidal stannic acid will become disperse; furthermore a thin, nearly invisible film of stannic acid, covering the bottom of the beaker, will be produced. After boiling the solution is diluted with water, neutralized with ammonium hydroxide and an excess of 2 ml conc. nitric acid added, after which the manganese dioxide precipitation takes place. The tin content in the manganese dioxide precipitate is found to be 2.80 mg. The bottom of the beaker is now covered with 10 ml conc. sulphuric acid, which

Table 2. Determination of tin under diverse conditions.

No.	Tin present	Tin found	
1	4.86 mg	4.81 mg	As above
2	4.86 »	4.84 »	
3	6.61 »	6.60 »	
4	6.61 »	6.61 »	
5	6.61 »	6.57 »	Prolonged boiling of the stannic acid solution
6	7.39 »	7.33 »	Ferric ions present
7	7.39 »	7.34 »	
8	7.39 »	7.40 »	Ferric ions present
9	7.15 »	7.04 »	Cupric ions present
10	7.15 »	7.07 »	
11	5.30 %	5.33 %	Bronze
12	5.30 »	5.36 »	
13	2.88 mg	2.85 mg	Lead ions present
14	2.89 »	2.89 »	
15	7.54 »	7.36 »	Nitric acid present
16	7.54 »	7.22 »	
17	6.71 »	6.63 »	Nitric acid present
18	6.71 »	6.60 »	

is kept at boiling point for about 15 minutes. The tin in this solution is determined and found to be 3.77 mg. The total amount of tin found will thus be 6.57 mg — only little less than the 6.61 mg added.

It appears from this experiment, that, when dissolving low tin content alloys in boiling nitric acid, a considerable amount of the tin can be lost by adsorption to the bottom of the beaker. That production of the stannic acid film only takes place on the bottom, through which the heat is conducted, can

be shown by mixing 10 ml solution containing about 5 mg tin and 0.5 ml conc. sulphuric acid with 100 ml conc. nitric acid and heating in a beaker for about 30 minutes with a pilot flame. Where the flame has touched the bottom of the beaker, a just visible spot will be found.

Experiments nos. 6 and 7 show, that it is possible to separate small amounts of tin from large amounts of ferric ions. 1 g of ferrous ammonium sulphate is oxidized with conc. nitric acid. 7.39 mg tin is added and manganese dioxide precipitation carried out as above. For sake of further purification the manganese dioxide precipitation is repeated. The precipitate is dissolved in nitric acid and hydrogen peroxide, after which the excess of the latter is removed by adding, in drops, permanganate solution. The second precipitation can now be carried out exactly as the first.

Experiment no. 8 is similar to nos. 6 and 7, except that 10 g ferrous ammonium sulphate is added instead of 1 g, and only one manganese dioxide precipitation has taken place. In this case also the result is excellent. Separation of stannic acid from ferric ions has a special interest, because the latter to a considerable degree hinders the precipitation of stannic acid<sup>8</sup> when carried out in the usual way.

Experiments nos. 9 and 10 show separation of stannic acid from cupric ions. 3 g of very pure electrolytic copper is dissolved in nitric acid, stannic sulphate solution is added, after which the procedure is as above. That the results are a little low may be explained by inclusion of free tin in copper. When the free tin in the titration tube is dissolved, a small lump of free copper will remain, and it seems likely that the tin not found is included in this lump.

In experiments nos. 11 and 12 a bronze with the tin content known in advance is analyzed. The tin content is determined as stannic oxide by treating with ammonium iodide<sup>9</sup>. About 1 g bronze is dissolved in nitric acid, 10 ml conc. sulphuric acid is added, and the solution is gently heated until fumes of sulphuric acid are given off. Some water is now added and — after cooling — the solution is transferred to a volumetric flask and diluted to 100 ml. With a pipette 10 ml is taken out and treated as above. As the results show, there is good accordance between the two methods. The low residue in the second column are probably due to a small iron contents in tin bronze, which hinders the total precipitation of  $\text{SnO}_2$  when carried out in the usual way by treating with nitric acid alone.

Experiments nos. 13 and 14 show separation of stannic acid from large amounts of lead ions. The tin is added as a zinc alloy containing 1.029 % tin, because adding of stannic sulphate solution would give rise to a precipitate of lead sulphate. The alloy is dissolved in diluted nitric acid, and lead nitrate derived from 25 g Tadanac lead is added, after which precipitation and deter-

mination is carried out as above. The tin contained in the lead is determined by running a blank analysis on 50 g of Tadanac lead. The tin content is found to be 0.00012 and 0.00015 %. Before the titration it is convenient to cool the solution to only 30—35° C to prevent precipitation of lead sulphate and lead iodide (some lead will always be adsorbed to the manganese dioxide). The higher temperature has not any noticeable influence on the results.

In experiments nos. 15 and 16 50 ml conc. nitric acid was added just before the manganese dioxide precipitation. The beaker was heated for  $\frac{1}{2}$  hour in a steambath because the high acidity hinders the precipitation. The results show, that not all stannic acid is adsorbed.

Experiments nos. 17 and 18 are similar to nos. 15 and 16, except that the manganese dioxide precipitation is carried out while stirring with a spatula. The results are better but not good.

From the experimental results here detailed, it is evident, that isolation of small amounts of tin as stannic acid by adsorption on and inclusion in, manganese dioxide is an excellent method, one single precipitation usually being sufficient. When titrating, potassium iodate as well as potassium bromate can be used.

If tin has to be isolated from a solution containing chloride, the latter must be expelled as chlorine by boiling with a large excess of conc. nitric acid. In this case the stannic acid possibly adhering to the bottom of the beaker must be dissolved in hot conc. sulphuric acid. This procedure is not quite reliable, when considerable amounts of chloride are present. A small percentage of the tin may be volatilized when boiling with conc. nitric acid.

As arsenic is partly and antimony is nearly completely precipitated together with tin by the mentioned procedure, and as these elements to a certain extent interfere with the titration of tin, they must be separated when present in considerable amounts.

#### SUMMARY

On the basis of the fact — observed by Blumenthal<sup>3</sup> — that colloidal and despersoid antimonious acid is readily adsorbed on and included in a manganese dioxide precipitate, a convenient and rapid method for the isolation and determination of small percentages of tin is worked out.

Separation of small amounts of tin from large amounts of ferric ions, cupric ions and lead ions is investigated (compare with Table 2). If dissolution of an alloy requires boiling with nitric acid, the bottom of the beaker must be treated with hot conc. sulphuric acid, because some of the stannic acid present may adhere as a film.



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