X.—*On Meta-stannic Acid, and the Detection and Estimation of Tin.*

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RECENT experiments led me to examine the characters of meta-stannic acid, when I obtained some results which were greatly at variance with the properties hitherto ascribed to it.

I prepared a quantity of meta-stannic acid by acting on granulated tin with nitric acid, evaporating nearly to dryness, diluting, and washing well by decantation and on the filter. Portions of the product were boiled with concentrated hydrochloric acid (sp. gr. 1.11) in moderate quantity for a few minutes, the residue allowed to settle, and

the clear liquid was decanted and tested with hydrosulphuric acid. The liquid in every case contained abundance of tin; and when much hydrochloric acid was employed the solution was sometimes nearly perfect. The residue possessed the properties attributed to it by Miller and Fresenius, but its aqueous solution showed far less liability to precipitation by excess of acid than I had expected. Any method of analysis depending on the insolubility of meta-stannic acid in hydrochloric acid is utterly worthless.* The presence of stannic phosphate or arseniate in no way alters the solubility of meta-stannic acid, but renders the solution liable to precipitate on addition of water, especially when heated.

The residue left when antimony has been oxidised by nitric acid is perfectly soluble in hydrochloric acid.

When meta-stannic acid is heated to boiling with strong sulphuric acid, it dissolves completely, becoming converted into ordinary stannic sulphate. If the liquid be poured into cold water, a solution of stannic sulphate is at first obtained, but this quickly deposits some of the tin as *ortho*-stannic hydrate, the precipitate giving no yellow stannous meta-stannate when moistened with stannous chloride. On boiling the solution of stannic sulphate, the whole of the tin is precipitated as *meta*-stannic acid.

There is thus a close analogy in the behaviour of stannic and titanitic sulphates, when treated with water, though the latter compound does not seem to be decomposed by mere dilution, but is completely decomposed by long-continued boiling.

Commercial stannic oxide (freed from lead by nitric acid) when heated with concentrated sulphuric acid is partially converted into stannic sulphate, but I have not succeeded in obtaining complete solution.

When meta-stannic acid is fused with hydro-potassic or hydro-sodic sulphate, a product is obtained which dissolves partially in cold water, the solution containing a small quantity of tin, as stannic sulphate; meta-stannic acid is precipitated from it by boiling.

The portion insoluble in cold water also contains stannic hydrate, which, by treatment with boiling water, forms meta-stannic hydrate. It is completely and readily soluble in hydrochloric acid.

Ignited stannic oxide is also acted on by hydro-potassic sulphate, and the product contains stannic hydrate, which is entirely precipitated by boiling. In this respect, therefore, tin shows its usual resemblance to titanium. The fused product is readily soluble in hot hydrochloric acid, but a second fusion is sometimes necessary to effect perfect solution.

* Fresenius makes use of the supposed insolubility of meta-stannic acid in hot concentrated hydrochloric acid in his method of qualitative analysis. (7th edition, page 110.)

Native stannic oxide (crystallised cassiterite) when finely powdered, is largely converted into a soluble modification by fusion with hydropotassic sulphate, but I did not succeed in effecting complete decomposition, even by a second fusion. For the estimation of the tin I prefer to fuse with potassium cyanide.

On adding about twice the bulk of strong hydrochloric acid to the stannic sulphate, a solution is formed which will bear copious dilution without suffering precipitation. This solution gives *no* yellow colour with stannous chloride, as would be the case were *meta*-stannic chloride present. On addition of tartaric acid and excess of ammonia, a perfectly clear solution is obtained, from which any phosphate or arseniate can be directly precipitated as the ammonio-magnesium salt. (Meta-stannic acid is not dissolved by addition of tartaric acid and excess of ammonia.) If ammonia be added to the solution, the precipitate produced is readily soluble in nitric acid, and the solution so obtained can even be boiled without precipitation. Of course, were meta-stannic acid present, no solution could be effected by nitric acid.

These results all prove that hot concentrated sulphuric acid converts meta-stannic acid into ortho-stannic sulphate, a change similar to that produced by prolonged treatment with hot hydrochloric acid, which is stated by Watts to convert it into normal stannic chloride.

The residue left by the oxidation of *antimony* by nitric acid is readily acted on by strong sulphuric acid, but the solution produced by subsequent treatment with hydrochloric acid, is very readily precipitated by water. Of course this can be avoided by addition of tartaric acid. Ignited Sb_2O_4 is not dissolved by sulphuric acid.

The above method of effecting the solution of meta-stannic acid is especially serviceable for analysing the residue left on acting on alloys by nitric acid. The residue is washed and heated with concentrated sulphuric acid in moderate quantity, till copious fumes are evolved. The solution (which should be quite clear) is allowed to cool, and is then treated with two or three times its bulk of concentrated hydrochloric acid, and boiled, if not still perfectly clear. In this solution the metals may be estimated by the usual methods. For their qualitative detection, I recommend dilution with about an equal bulk of water, and division into several portions.

1. The tin is detected by boiling (without further dilution) with metallic iron, and testing with mercuric chloride. The reduction to the stannous state is often perfect; antimony and copper are precipitated as metals; mere traces of tin may be detected.

2. After dilution, the presence of iron or copper is readily detected by potassium ferrocyanide.

3. The liquid is diluted, treated with tartaric acid, excess of ammo-

nia added, and phosphate or arseniate detected by magnesium. Streaks of arseniate are readily distinguished from phosphate by the method described by me in the *Chemical News* (vol. xxiv, page 120). Small quantities of arseniate are difficult of detection. Direct application of the molybdic acid test to the acid liquid usually indicates phosphate or arseniate when present, but the reaction seems uncertain.

4. The detection of antimony presents no difficulty.

The action of nitric acid on alloys of tin and gold produces a beautiful purple residue, which owes its colour to Purple of Cassius. This residue, when heated with concentrated sulphuric acid, is changed to a purplish liquid, which on further heating becomes colourless, the whole of the tin being dissolved, and the gold remaining as a heavy brown metallic residue. This curious reaction, I believe to be due to the formation of an unstable sulphate of gold, which is decomposed at a higher temperature, or by reaction with an equivalent amount of stannous sulphate. The residue was always washed quite free from nitric acid.

If hydrochloric acid be added before the purple solution decomposed, a small quantity of gold remains in permanent solution, probably as chloride. As a precaution against this source of error, if the solution has any yellow tint after addition of hydrochloric acid and an equal bulk of water, it is well to boil with a fragment of ferrous sulphate.

I had hoped from these results to obtain some insight into the obscure constitution of Purple of Cassius. The fact that it is formed by the action of nitric acid on an alloy of gold and tin, would seem to indicate the formula $\text{Au}_2 + 3\text{SnO}_2 + 4\text{H}_2\text{O}$, but its solubility in ammonia negatives this view, which is also at variance with the fact that mercury removes no gold from the colouring matter.

If we suppose the purple to contain $\text{Au}_2\text{O}_3 \cdot 3\text{SnO} \cdot 4\text{H}_2\text{O}$, the fact of a purple liquid being formed with sulphuric acid is difficult to understand, if the oxides are merely converted into sulphates, as neither auric nor stannous sulphate has a deep colour, and they could scarcely co-exist in a liquid.

If the purple be regarded as containing aurous and stannous stannate ($\text{Au}_2'\text{SnO}_3, \text{Sn}''\text{SnO}_3 + 4\text{aq.}$), the action of sulphuric acid would probably result in the formation of aurous, stannous, and stannic sulphates ($\text{Au}_2'\text{SO}_4 + \text{Sn}''\text{SO}_4 + 2\text{Sn}^{\text{iv}}(\text{SO}_4)_2$), and at a higher temperature the aurous and stannous sulphates might easily react to form metallic gold and stannic sulphate, which are undoubtedly the ultimate products.

I have recently shown that auric sulphate is more stable than had been supposed,* and although aurous sulphate has never been obtained, it may possibly exist and possess a purple colour like the aurous stan-

* See page 285.

nate supposed to be present in the Purple of Cassius. Aurous oxide is stated by Figuier to have a violet colour, and to combine with acids. On diluting the sulphuric solution with water, the purple is gradually deposited in an apparently unchanged state.

I do not believe the purple solution can owe its colour to suspended gold.

I have found the sulphuric acid method especially serviceable for the qualitative and quantitative analysis of dentists' alloys containing gold, silver, and tin. After obtaining the nitric acid residue, and thus separating the silver, the gold and tin are acted on with sulphuric and hydrochloric acids as before described, the gold being weighed direct, and the usual methods applied to the estimation of the tin in the solution. For this purpose I prefer to neutralise the free acid, add a moderate excess of sulphuric acid, dilute largely and boil, when the whole of the tin is thrown down as a white precipitate of meta-stannic hydrate, which can be readily filtered and washed.

The purity of the gold was ascertained by dissolving it in bromine water, which in every case effected complete solution.

By the above method all residues left by the action of nitric acid on alloys can be rapidly and accurately analysed in the wet way, thus avoiding all processes of fusion or ignition.