106. $Hg_4N_7H_{20}.7C_7H_5O_3$. Balestra[1] prepared this compound by dissolving mercuric oxide in ammonium salicylate and evaporating the solution to crystallization. Balestra gave his product the formula, $2Hg_2N.C_7H_5O_3.NH_4.C_7H_5O_3$. More probably, however, it was a somewhat ammonolyzed specimen of the normal salt as indicated by the formula in Table VII. It is decomposed by the action of water.

107. $Hg_2NH_4O_2.C_2H_3O_2$. Hirzel[2] obtained a compound of this composition by heating the ammoniated mercuric acetate, (30). According to Gerresheim[3] the acetate of Millon's base is formed by the action of acetic acid on the base.

108. $Hg_2NH_2O.SCN$ This sulphocyanide of Millon's base[4] has been prepared by the action of ammonia on a solution of mercuric sulphocyanide, on a solution of the double potassium mercuric sulphocyanide, and by the action of water on the ammoniated mercuric sulphocyanide, (29). It forms a yellow amorphous powder.

The material contained in this paper was collected during the earlier part of the past year, for the purpose of determining whether or not the writer's theory concerning the constitution of the mercury nitrogen compounds is worthy of further consideration, and to serve as a basis for a thorough experimental review of the whole field. It was not the original intention to publish, until after a reasonable amount of experimental work had been done, which, it is expected, will eliminate as definite chemical compounds many of the products which have been described in the past. However, as a result of the demoralization of our laboratory by the great earthquake and the consequent impossibility of carrying on much research work in the immediate future, it seems advisable to print this summary at the present time. Experimental work will be continued as soon as possible.

STANFORD UNIVERSITY, CALIFORNIA, AUTUMN, 1906.

DETERMINATION OF ANTIMONY AND TIN IN BABBITT, TYPE METAL OR OTHER ALLOYS.

[APPLICABLE ALSO WHEREVER THE ANTIMONY AND TIN ARE OBTAINED AS SULPHIDES.]

BY WILSON H. LOW.

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The accurate determination of antimony and tin in alloys has always been a more or less troublesome operation, and almost all of the published

[1] Jsb. Chem. 1892, 816.
[2] Ibid. 1852, 421.
[3] Ann. 195, 378.
[4] Philipp: Ibid. 180, 341. Ehrenberg: J. pr. Chem. 138, 62.

schemes of analysis seem to be satisfied with approximate results. Some processes are excellent with alloys of certain composition, but are not applicable. Among these are all processes of volatilizing the antimony and tin as chlorides, and although the authors of the processes have apparently obtained splendid results for the alloy on which they worked, it will be found to fail in most cases. Launcelot Andrews published a process[1] some years ago in which he made use of a current of dry hydrochloric acid gas passed through nitric acid of 1.50 sp. gr. We have tried this process on many alloys, following directions as closely as possible and also trying many modifications, but failed to get the good results obtained by Andrews. Antimony and tin are very easily volatilized at a gentle heat, in a current of dry chlorine or in a mixture of dry chlorine and dry hydrochloric acid gas, and although the condensation or absorption of the volatilized chlorides presents some difficulties, the main trouble is due to other causes. Volatilizing antimony and tin as chlorides from solid alloys containing considerable other metals forming chlorides non-volatile at the temperature employed, is at best a slow operation. The heat of the reaction often melts the non-volatile chlorides and the melted chlorides covering the remaining metals prevents any action on them of the chlorine. Further than this, incandescence with the chlorine is always followed by volatilization or mechanical carrying-away of some of the copper and iron, from the boat to the sides of the tube. Copper always forms some cuprous chloride, requiring acid to dissolve the residue left in the boat. To overcome the carrying along of other metals as the antimony and tin are volatilized, A. G. Levy[2] makes use of a small flask instead of a combustion tube and fills the neck of this with glass wool. He volatilizes the last traces of the antimony and tin and carries them into the absorption tubes, by introducing a little strong hydrochloric acid and boiling this down to dryness. This modification has been tried, but the combustion tube was preferred. Turning then to the better established methods, it is seen that most schemes start out by decomposing the alloy with nitric acid. Nothing is said usually about the antimony and tin residue being contaminated with iron, copper and lead, if these metals were present in the alloy. Even were this residue pure there is nothing rapid about it, if a separation of the antimony and tin is contemplated. As a matter of fact this residue is rarely free from other metals. Decomposing the alloy by boiling with strong sulphuric acid offers some advantages, but the precipitation of the antimony and tin after dilution, by boiling, gives a precipitate more or less contaminated by copper and which contains practically all of the lead as sulphate.

[1] This Journal, 17, 869.
[2] Analyst, 1905, 361.

Walters and Affelder[1] offer some good suggestions, but they are satisfied apparently with the purity of the residue left on treatment with nitric acid, with their ability of igniting antimonic acid to the correct composition of Sb_2O_4 and with the purity of the metallic antimony left on boiling the alloy with hydrochloric and hydriodic acids, though the author of the process, Andrews, states that this residue contains water or occluded hydrogen that simple drying will not remove. H. Yockey[2] also accepts the purity of the nitric acid residue and also falls into the error of weighing the residue of antimony directly after drying. Subsequently he corrects his method[3] as to the antimony by dissolving the residual antimony as antimonic chloride and making use of the reaction of antimonic chloride in strong hydrochloric acid solution, upon hydriodic acid. This is much better and the process described below of taking the asbestos filter with the antimony on it and boiling the whole with sulphuric acid and titrating the antimony after proper dilution and acidification, is quicker and open to less objection. The titration of antimony by making use of the action of antimonic chloride in strong hydrochloric acid solution, upon hydriodic acid, is open to the objection that it is difficult to get potassium iodide and hydrochloric acid of such purity that a mixture of them will not give some free iodine. Furthermore, hydriodic acid in solution is quickly acted on by the oxygen of the air and some iodine set free. Still with care very good results are obtained by this method. The determination of antimony in an alloy by boiling with 1 : 1 hydrochloric acid and 1 gm. of potassium iodide, separates the other metals from the main lot of antimony, but some antimony is almost sure to go into solution for the reason that a little free iodine is present at some stage of the proceedings through impurities in the reagents or the action of the air. Repeated experiments have shown that some antimony goes into solution. An experiment with diluted acid made with boiled water, C.P. powdered antimony and C.P. potassium iodide containing not more than a trace of iodate, and the boiling conducted in an atmosphere of carbon dioxide, showed that some antimony still went into solution. This was not a perfectly satisfactory process, and so attention was directed to processes where the tin and antimony were separated by means of alkaline sulphides. The process of A. Rossing[4] appeared favorable, and experience with it has shown it to be a reliable method of separation. This method dissolves the alloy in a minimum of aqua regia, using a little potassium chlorate to insure complete oxidation. After some dilution a little tartaric acid is added, the solution almost exactly neutralized with sodium hydroxide solution and a

[1] This Journal, 25, 632.
[2] Ibid. 28, 646.
[3] Ibid. 28, 1435.
[4] J. Soc. Chem. Ind. 1902, 191.

sufficient quantity of colorless sodium hydrosulphide, NaSH, added to precipitate copper, lead, etc., and to retain all the antimony and tin in solution. By using a gentle heat and with enough sodium sulphide the antimony and tin will go into solution, but on washing the precipitate the wash water of hot dilute sodium sulphide must be acidified to make sure all the antimony and tin have been washed out of the insoluble residue left on the filter.

The following process found generally applicable to alloys and to the sulphides of antimony and tin, either in the solid state or in proper solution, claims nothing in particular as original, except the direct determination of the antimony and tin in one portion of the alloy without separating the other ingredients, and the titration of antimony and tin when both are present in solution. The direct titration in an alloy without separation of the other ingredients may not be applicable in all cases, but it is in most cases, and where it is not the sulphide separation mentioned above is made use of and the sulphides treated in almost the same way as the original alloy. If other metals, besides tin and antimony, are to be determined, Rossing's method given above gives a good, quick separation, but the antimony and tin are determined by direct titration, if possible, in another portion of the alloy.

Where only antimony and tin are sought, the alloy may be decomposed by nitric acid, by sulphuric acid, or by a mixture of sulphuric acid and potassium sulphate. Where possible, sulphuric acid alone is used. If nitric acid is first used, it must subsequently be expelled by boiling with sulphuric acid, and after the nitric acid is expelled, some tartaric acid and some potassium sulphate must be added, and the melt heated till all carbon has been oxidized. This leaves the antimony and tin in the proper state for the titrations.

The two standard solutions required are an N/10 potassium permanganate, and an N/10 iodine solution. For antimony determination, the permanganate solution should be standardized by C.P. antimony or tartar emetic (anhydrous) of the proper composition. If properly done, these standards will agree and both will agree with a standardization made with oxalic acid in the regular way, but always standardize with antimony or its compounds by heating with sulphuric acid, diluting and adding the same amount of hydrochloric acid, as is used with the alloy. In this way correct results are insured. The iodine solution is compared with a solution of sodium thiosulphate of known value.

From 0.5 gm. to 1 gm. of the finely divided alloy is taken, and as the method is generally the same, the standardization of the permanganate will be described together with the subsequent titration of the tin.

0.1202 gm. of finely powdered C.P. antimony (= 0.3234 gm. tartar emetic) and 0.1190 gm. of tin are placed in a 450 cc. Jena glass Erlen-

meyer flask and about 10 cc. of strong sulphuric acid (free from chlorine compounds) added; 3-4 gms. of potassium sulphate are sometimes used and can be added here. Heat till the metals are all in solution (or the alloy thoroughly decomposed) and all separated sulphur has been boiled out of the flask. All sulphurous acid will also be expelled by this time. Do not drive off all free sulphuric acid, but have enough left to keep the melt from getting hard on cooling. About 7-10 cc. left is enough. These operations take only a few minutes. Cool and add 50 cc. of water and 10 cc. of strong hydrochloric acid and heat to get all possible in solution. Large quantities of lead sulphate, even, will dissolve, and the solution will become clear. However, the object is to get the antimony and tin in solution, and this is all that is necessary. With the quantity of antimony taken no tartaric acid is necessary, but with larger quantities a few grams of tartaric acid must be added. Tartaric acid has no effect on either titration. Some stannic compound with sulphuric acid may go into solution with some difficulty, but no attention need be paid to it here, as it will dissolve when we get through with the antimony, if not before. Cool the solution and add about 110 cc. more of water and 25-30 cc. (with small amounts of Sb, such as is in solder, a total of 20 cc. strong HCl in total volume of 200 cc. appears enough) more of strong hydrochloric acid. Thoroughly cool this mixture and proceed to titrate with permanganate. Add the latter till the last drop colors the whole solution pink. The end point is sharp, but the color may not remain long, owing to the large quantity of hydrochloric acid present. If less hydrochloric acid were present, say 10 cc. in the total volume of 200 cc., the end point would be sharp, but would apparently occur at about 19.60-19.70 cc., instead of 20.00 cc., as it should. The true end point under these circumstances is troublesome to find. But even an incorrect end point may give good results, if the solution has been standardized in exactly the same way. The determination of the antimony or standardization of the permanganate is now finished and the tin is the next consideration. The titrated solution contains antimonic chloride and stannic chloride, besides other things of no particular moment. Pour this solution into a 500 cc. round-bottomed flask and rinse out the Erlenmeyer flask with about 50 cc. of strong hydrochloric acid and add washings to main solution. The main solution should be at least ⅓th by volume of strong hydrochloric acid (the regular strong C.P. acid). Add about 1 gm. of finely powdered C.P. antimony and place on the steam bath for about 15 minutes, shaking once in a while. Next remove from the bath and connect with an apparatus capable of giving a rapid current of carbon dioxide. The connection is made by means of a cork carrying two tubes. The first dips below the surface of the solution in the flask and the second or outlet tube is bent downward and the end

dips slightly below the surface of some water or mercury. This allows any tendency to back pressure to be instantly detected. While passing a rapid stream of gas, heat the contents of the flask to boiling, using a naked flame, but taking care to heat the sides of the flask and avoid directly heating the bottom. This is because the antimony lies on the bottom and the flask might be cracked by unequal heating in contact with solution. Boil 2-3 minutes after the liquid commences to boil. Cool quickly by surrounding the flask with cold water and take care that the current of carbon dioxide is strong enough to prevent back pressure due to sudden condensation. When cold loosen the cork somewhat and introduce 5 cc. of good starch solution, and then withdraw the flask gently so as not to allow air to enter by forming currents. Cork quickly and take to the burette. Introduce the spit of the burette far down into the neck of the flask and rotating the latter gently run in or drop in N/10 iodine solution. Towards the end the starch blue will appear and remain mostly in the middle portion of the solution, requiring stronger agitation to mix with the rest of the solution. This causes the metallic antimony in the bottom of the flask to become stirred up and slightly obscure any slight blue tint. For this reason the titration is continued till the last drop gives a strong blue to the whole solution, and then we deduct about 0.05 cc. from the burette reading. Do not fear that the end point will not be recognized within one drop or less. It is unmistakable with good starch solution, and no doubtful ending should be taken. With correct solutions, etc., the titration should have taken just 20.00 cc. Mixtures of C.P. antimony and C.P. tin (allowing for 0.10 per cent. impurities found to be present) give exact results. No trouble has been found in titrating tin correctly with iodine. Objections to this method may be founded on accepting C.P. tin as actually nothing but tin, while most of it contains impurity.

To test tin or antimony for impurity, a quick method of considerable accuracy is to take about 0.5 gm. in a porcelain boat, place in a combustion tube and pass a slow current of dry chlorine and dry hydrochloric acid gas. The tin or antimony is quickly volatilized and lead, copper, iron, etc. remain mostly in the boat. Displacing the chlorine with carbon dioxide and then heating in a current of hydrogen reduces the chlorides left in the boat to metal, and their weight can be deducted from the original metal, or the percentage determined. This is not strictly accurate, as on first heating in hydrogen there is a slight volatilization of some of the chlorides.

In the case of an alloy a good qualitative analysis should always be made, unless the approximate composition is known. If there are no interfering metals, the alloy is decomposed and the antimony and tin titrated, as shown above, without removing the lead sulphate, copper sulphate, etc. Lead in large amount does not interfere. Theoretically, any amount of

copper should not interfere, and practically small amounts are known to cause no trouble, while large amounts have not been present in the tests made. Should the alloy contain iron in any quantity, there might be some danger of ferrous sulphate being left after boiling with sulphuric acid. This difficulty is overcome by decomposing the alloy with nitric acid, as usual, boiling off most of the nitric acid, adding about 10 cc. of sulphuric acid and 3-4 gms. potassium sulphate, boiling to complete expulsion of the nitric acid, and then adding a little tartaric acid or other organic matter, and after the carbonization, continuing the boiling till all organic matter has been destroyed. This will always leave the antimony and tin in the "ous" and "ic" states, respectively. From this point, the determination is carried on in the manner described above. Where the antimony and tin have been separated from the other metals by means of alkaline sulphides, the details of operation depend on whether the decomposition of the alloy was made with aqua regia or with sulphuric or nitric acid. It will be assumed that the alloy has been dissolved in aqua regia and the tin and antimony are in solution combined with alkaline sulphides. Add slight excess of sulphuric acid and heat gently to precipitate the sulphides of antimony and tin. Filter, preferably through a 60 mm. Witt's plate and an S. & S. white ribbon filter No. 589, and wash the precipitate on the filter with dilute hydrogen sulphide water containing enough ammonium acetate to prevent stannic sulphide from giving a turbid or opalescent filtrate. After washing somewhat, test each succeeding 10-20 cc. of filtrate by boiling off the hydrogen sulphide, acidifying with nitric acid and adding three or four drops of silver nitrate solution. The last filtrate should be entirely free from chlorine, as shown by this test. With a Witt's plate of 60 mm. diam., this is quickly accomplished. The residue on the filter and filter itself may now be placed in a 450 cc. Jena glass Erlenmeyer flask, 3-4 gms. potassium sulphate added and 10-20 cc. strong sulphuric acid, and the whole mass boiled till all organic matter has been destroyed and the antimony and tin are present as sulphates, while there is not over 10 cc. of free sulphuric acid left in the flask. As organic matter is not really necessary in this operation, and it takes some time to oxidize the filter paper, the precipitate on the filter can be handled differently, if some alkaline sulphide, free from chlorine compounds, is available. This desideratum will probably be found best in ammonium sulphides or polysulphides, as the best C.P. by alcohol caustic soda contains enough chloride to cause some loss of tin. The precipitate is washed from the filter into the flask with as small a quantity of water as possible. What remains on the filter is dissolved off with alkaline sulphide free from chlorine and the solution added to the flask. Enough alkaline sulphide is now added to the flask to dissolve the sulphides of antimony and tin on warming. When this is accomplished, acidify with sulphuric acid and then add about 10-15

cc. in excess and 3-4 gms. potassium sulphate and boil down to sulphuric acid fumes and till all sulphur has been expelled and the antimony and tin remain only as sulphates. The final amount of free sulphuric acid left should not be over 10 cc. Tin tends to form a stannic sulphate, very insoluble in strong sulphuric acid, but subsequent heating and boiling in the presence of hydrochloric acid dissolves it. The boiling with strong sulphuric acid and destruction of organic matter is carried on easily and quickly over a naked flame of good heating power. The Jena glass Erlenmeyer flasks stand the operation very well, and none have cracked. The flask is generally held in the hand by means of a clamp (Chaddocks' clamp with rubber removed is very good) and rotated to insure even heating. In this way the sulphuric acid may be completely driven off, leaving a melt of acid potassium sulphate, and the flask will not break. If there is any doubt that the antimony does not exist in the "ous" condition, a little tartaric acid or other organic matter may be added and burned off by boiling. The antimony and tin now exist as sulphate and the procedure is the same as in the standardization of the permanganate.

This method for the sulphides of antimony and tin is in every way much more satisfactory than the gravimetric separation and determination, and takes little time.

Mixtures of C.P. antimony and tin (allowing for any impurities) give exact results. An alloy run through recently gave the following results. Qualitative analysis showed the metals indicated to be the only ones present, except in minute traces.

Lead,	74.19	Alloy dissolved in aqua regia, alkaline sulphide separation, lead separated from copper as sulphate in presence of alcohol. Two determinations checked.
Antimony,	15.44	Alloy boiled with sulphuric acid and antimony titrated direct, as in standardizing permanganate.
Tin,	9.88	Determined in same solution, after the antimony.
Copper,	0.44	Determined after the lead, driving off alcohol and determining by A. H. Low's iodide process. Check test.
Iron,	trace	
	99.95	

If arsenic were present, it would interfere with the antimony titration or be counted as antimony. It may easily be removed.

It is often stated that the titration of tin with iodine gives slightly low results. Experience with the above method has given confidence that the results for tin are exact, if the conditions are observed. Tin may be lost somewhere in the process, but all that remains is surely indicated by the titration.

Acknowledgments are due Mr. A. H. Low for suggestions in treating the sulphides with sulphuric acid and acid potassium sulphate, while Frederick Ibbotson and Harry Brearley gave the idea of reducing tin solution with powdered antimony, in an article appearing in the Analyst, 1902, 25.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE DETERMINATION OF THE SAPONIFICATION NUMBER OF LUBRICATING OILS CONTAINING SAPONIFIABLE FATS.

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In examining lubricating oils, which were mixtures of mineral oil with saponifiable fat, much difficulty was experienced in determining the saponification number.

Saponifications made with alcoholic potash require a long time and tend to give slightly high results due, in part at least, to the etching of the glass. The substitution of a silver flask for glass (as has been proposed) would undoubtedly be an advantage, but if one to three dozen samples are to be examined at one time, the process will be tedious unless a goodly supply of silver is available.

Several solvents of mineral oil were tried, together with alcoholic potash, and it was finally found that a mixture of benzene and alcoholic potash gave very satisfactory results.

About 5 grams of oil were treated with 25 to 50 cc. of approximately half-normal alcoholic potash and 25 cc. of benzene. In case of some heavy cylinder oils more benzene was used with equal success. However, it was not found necessary with any oil so far examined to use more than 50 cc. of benzene to obtain a clear solution when warmed. If one is obliged to use 50 cc. of benzene, it is sometimes necessary to add neutral alcohol to clear the solution.

The oil was weighed into a 200 cc. Erlenmeyer flask, the alcoholic potash and benzene run in, and a rubber stopper, fitted with a three-foot air condenser, tightly inserted in the neck of the flask. The flask was then set on the iron plate, which forms the top of the steam bath, so that the steam would not strike it directly, and the heat so regulated that the condensing liquid would not be forced out of the top of the condenser. In this way the content of the flask can be boiled without apparently losing any of the solvent. One-half hour was found long enough to saponify any oil examined. The benzene does not interfere with the titration in any way. It separates out, leaving the alkali in the lower layer. In making the alcoholic potash 95 per cent., alcohol was used.

In determining the value of the method, the following results were obtained: