

LIV.—*On the Separation of Tin from Antimony, and on the Analysis of Alloys containing Lead, Tin, Antimony, and Copper.*

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THE separation of tin from antimony, with a view to their direct quantitative estimation, has hitherto been regarded as an analytical process involving considerable difficulty, on account of the similarity which exists in the behaviour of the compounds of those metals with reagents.

The method proposed by Gay Lussac consists in precipitating the tin and antimony together by means of a strip of zinc; the weight of the precipitated metals having been ascertained, they are then redissolved in nitro-hydrochloric acid, and the antimony

separated from the diluted solution by a strip of tin, the amount of this metal originally associated with the antimony, being estimated by difference. The more recent method, by Rose, provides for the direct estimation of each metal, the separation being effected by fusing the oxides with hydrate of soda, and digesting the antimonate and stannate of soda produced, with diluted alcohol, the insoluble antimonate of soda being afterwards washed on a filter with alcohol of increased strength as the operation of washing approaches completion.

Having had occasion to examine some alloys containing lead, tin, and antimony, with small quantities of copper, and having failed to obtain sufficiently accurate results in the separation of tin from antimony by either of the processes mentioned, I made several attempts to effect the object in view, but without success, when the reaction between the sulphides of tin and antimony and hydrochloric acid (gas) occurred to me as likely to afford a method free from objection.

When tersulphide of antimony is exposed to the action of hydrochloric acid (gas), decomposition is effected at the ordinary temperature, with production of sulphide of hydrogen and terchloride of antimony, which, when gently heated, is easily volatilized in a current of the gas. Protosulphide of tin, when treated in a similar manner, is also decomposed, the products of decomposition being sulphide of hydrogen and protochloride of tin, which may be heated to incipient fusion in an atmosphere of hydrochloric acid, without undergoing any further change. A necessary condition, therefore, to the success of a separation by means of the reactions just stated, would be that the tin should exist in solution in the state of protoxide. By the method of analysis to be further described, the tin was obtained in the state of bichloride, and in endeavouring to effect the reduction of the bichloride to the state of protochloride, an experiment was made to ascertain the action of metallic iron upon the mixed chlorides of tin and antimony, in presence of an excess of hydrochloric acid, the result of which was, that while the bichloride of tin was reduced to protochloride, the whole of the antimony appeared to be separated in the metallic state.

Gmelin states, on the authority of Fischer, that iron does not precipitate tin from the protochloride at the boiling heat. To see how nearly separation could be effected by iron in the presence of

hydrochloric acid, 6.03 grs. of pure antimony and 4.16 grs. of tin were dissolved in hydrochloric acid, with addition of a few drops of nitric acid; the solution was diluted with water, and, after adding more hydrochloric acid, digested at a gentle heat with 15 grs. of thin sheet iron, until the whole of the iron was dissolved; a considerable quantity of cold water was then added, and the antimony collected on a weighed filter, after being washed with water and dried, the antimony weighed 6.02 grs. In a second experiment, 9.145 grs. of pure antimony and 1.065 grs. of pure tin were dissolved as before; the antimony in this case after drying weighed 9.18 grs., the tin was precipitated from the filtrate by sulphuretted hydrogen, the protosulphide of tin dried, and converted into binoxide by careful ignition, the amount of binoxide obtained was 1.36 grs., containing 1.069 grs. of metallic tin.

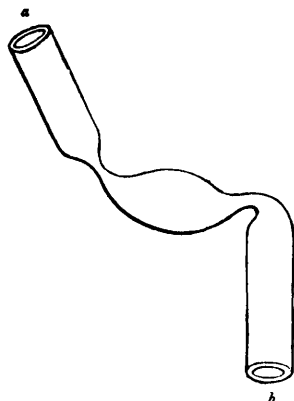
In the analyses of the alloys containing lead, tin, and antimony, with small quantities of copper, the ordinary method for separating tin and antimony from other metals was used, viz., oxidation with nitric acid, the action being promoted by heat, and the excess of acid expelled by evaporation, the nitrates of lead and copper were removed by washing on a filter with hot water. By proceeding in this manner it was found, in two analyses of the same alloy, that the amounts of lead, and also the collective weights of the oxides of tin and antimony differed to a considerable extent. The same discrepancy was observed, whether the acid used for oxidation was in the concentrated state, or previously diluted with water. In order to ascertain the source of error, the oxides of tin and antimony were examined, and found to contain oxide of lead in a state of combination, in which it could not be separated by washing with water, and to see whether the application of heat affected the result, two equal weights (10 grs.) of the same alloy were taken, one was treated in the usual manner, heat being applied to promote the oxidation by nitric acid, the excess of acid being expelled by evaporation; boiling water was then added, and after perfect washing, the mixed oxides weighed, on ignition, 8.92 grs. The other was oxidized by nitric acid, without the application of heat, and the resulting oxides weighed 7.31 grs. The application of heat causes therefore a large proportion of the lead to remain with the oxides of tin and antimony. When an alloy of lead and antimony is heated with nitric acid, the

latter metal is converted into antimonious acid, which combines with the oxide of lead, the resulting compound being insoluble in water.

That the whole of the lead might be separated from the other metals, the following process was employed. The alloy was oxidized by nitric acid, but little more acid being used than was necessary for oxidation; after removing the excess of acid by evaporation at a low temperature, the residue was digested with hot water, the oxides of tin and antimony being collected on a weighed filter, and after perfect washing, dried at  $110\text{--}120^{\circ}\text{C}$ . After ceasing to lose weight, they were carefully transferred to a glass boat; the filter with the small portion of oxides still adhering to it was again dried and weighed, the difference between the two weights giving the amount of oxides operated upon. The boat was then placed in a condensing apparatus, through which a slow current of hydrochloric acid was transmitted, and when the contents of the boat had become liquid from the absorption of gas, a gentle heat was applied in order to distil over the chlorides of tin and antimony. When the distillation was nearly finished, a greater heat was used to expel the last traces of bichloride of tin, and, the tube having cooled, the boat was withdrawn, and its contents (chloride of lead) dissolved out, and added to the solution containing the nitrates of lead and copper. These two metals were determined as usual, the solution being evaporated nearly to dryness, with a slight excess of sulphuric acid, the sulphate of lead washed with water acidified with sulphuric acid, and the oxide of copper precipitated from the filtrate by a solution of potash. The chlorides of tin and antimony were poured into a small beaker; the apparatus rinsed out with dilute hydrochloric acid, and, after adding more hydrochloric acid, the solution was heated gently and digested with metallic iron (as pure as possible) until the whole of the iron had dissolved, cold water was then added, the antimony collected on a weighed filter, and after washing with cold water, dried at  $110^{\circ}\text{C}$ . The filtrate from the antimony, if not sufficiently dilute, was mixed with water, and then saturated with sulphuretted hydrogen. The sulphide of tin being afterwards converted into binocide by ignition.

In order to simplify the process as much as possible, the following plan was eventually adopted. Ten grains or more

of the alloy to be analysed were introduced into a small piece of apparatus, having the following form, sufficient nitric acid to complete the oxidation was poured upon the alloy by means of a funnel-tube; the end *a* was corked, and the oxidation effected at a moderate temperature. When the alloy had been converted into a perfectly white mass, the excess of acid was expelled by attaching a tube and cork to *a*, and causing a gentle current of air to traverse the apparatus, either by means of an aspirator, or a pair of bellows; during



this operation the apparatus should be heated sufficiently to cause the evaporation of the excess of nitric acid. The end *a* was now connected with an apparatus for generating dry hydrochloric acid (which should be made from fused chloride of sodium and sulphuric acid), while the end *b* was immersed in a small quantity of water contained in a beaker; the remaining part of the operation may be conducted as in the former process, care being taken not to distil the volatile chlorides too rapidly, and to avoid the fusion of the chloride of lead until all the bichloride of tin has been expelled.

The iron employed to precipitate the antimony should be in the form of thin sheet, about three times the weight of the antimony present, being usually sufficient for complete precipitation. It is necessary that the flask for generating the hydrochloric acid be provided with a funnel-tube, dipping just below the surface of the fluid, in order to prevent the too rapid absorption of the gas by the water which is used to condense the chlorides of tin and antimony.

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