The Determination of Aluminium in Metals and Alloys by means of the Mercury Cathode*

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THE method here described is intended chiefly for the determination of aluminium in amounts ranging from about 10 to 0.5 per cent., but some reference is also made to amounts below 0.5 per cent. Of the two principal methods of determining aluminium, viz. as Al_2O_3 and by oxine precipitation, the former is limited to about 0.05 g. of aluminium and the latter to about 0.03 g., owing to the nature of the respective precipitates. The best way of obtaining a solution containing about these amounts, but free from interfering elements is to remove the latter by electrolytic deposition in mercury from a sulphate solution containing a very small amount of sulphuric acid.¹ The "heavy" metals (copper, bismuth, cadmium, etc.) are thus deposited; also iron, nickel, cobalt, zinc, chromium and molybdenum. Manganese is partly deposited, but is mainly left in solution. It is also deposited (as MnO_2) on the anode, but this deposit can be dissolved by means of a reducing agent, such as hydrazine sulphate, which is usually added. Metals not deposited are aluminium, magnesium, beryllium, titanium, vanadium,² cerium and rare earth metals, and alkaline earth and alkali metals. Also any phosphate, arsenate and borate present will be left in solution.

The great advantage of this process is the facility with which large amounts (up to 2 g.) of metal can be removed; this is not usually possible by ordinary methods, such as precipitation with hydrogen sulphide, which is limited to about 0.1 or 0.2 g. There are a few exceptions, however, notably copper, which can be deposited in large amounts (e.g. 5 g.) by electrolysis from acid solution, and lead, which can be removed as sulphate.

Of the elements left in solution with aluminium after electrolysis, manganese, magnesium and alkali metals are not precipitated by ammonia at the methyl red indicator change point, which controls the correct conditions for precipitating aluminium, but double precipitation may be necessary with large amounts, owing to the difficulty of washing the precipitate. Oxine cannot be used for the final precipitation of aluminium in presence of manganese, which it also precipitates from acetic acid solution, but the oxine method is suitable for separating aluminium from magnesium. Titanium is precipitated by ammonia, but, as it is unlikely to be present in large amounts, it can be conveniently removed with "cupferron." Aluminium is precipitated with ammonia, after destruction of excess of "cupferron," or (without destruction) with oxine. According to Taylor-Austin,¹ titanium is not precipitated with oxine under the conditions for the precipitation of aluminium. Most of the titanium in alloys rich therein is deposited as dioxide in the acid attack (unless sulphuric acid is used). It is generally assumed that this titanium dioxide is free from aluminium, but it is advisable to test it by igniting the filter-paper at a low temperature, fusing the residue with sodium carbonate and extracting with water, which yields insoluble sodium metatitanate and soluble sodium aluminate. The solution is filtered, and the filtrate and washings are acidified with hydrochloric acid, boiled to remove carbon dioxide, and treated with a few drops of methyl red indicator and then with ammonia until the colour of the indicator just changes. The liquid is then boiled for a few minutes and set aside for any precipitate of aluminium hydroxide to form. Vanadium is separated with "cupferron" in the same way (rather less acid must be used) and any aluminium in the precipitate is determined as in the titanium precipitate. Oxine precipitates vanadium from acetic acid solution, and thus cannot be used for separating it from aluminium. Alternatively, aluminium is precipitated with ammonia in the usual way and the coprecipitated vanadium is determined and deducted. For this purpose the weighed precipitate is fused with potassium pyrosulphate, the melt is extracted with 5 per cent. sulphuric acid, and the extract is reduced with sulphur dioxide and titrated in the usual way. Phosphorus is converted into phosphate, which is co-precipitated with aluminium by Taylor-Austin³ has shown that it is not satisfactory to precipitate and weigh ammonia. the aluminium phosphate, and I have confirmed this. It is best to determine the phosphorus pentoxide in the precipitate (Etheridge4). However, since phosphorus does not interfere, the oxine precipitation of aluminium is recommended. Arsenic is removed with hydrogen sulphide either in the early stages of the analysis or before the precipitation of aluminium. Beryllium is co-precipitated with aluminium by ammonia, but is not precipitated by oxine from acetic acid solution. Boron behaves like phosphorus, being coprecipitated as aluminium borate. It can be determined (with some difficulty) in the weighed precipitate, but the oxine method for aluminium is preferable in presence of boron.

PROCEDURE FOR ELECTROLYSIS.—One (or at most 2) g. of the metal or alloy is dissolved in 40 to 60 ml. of sulphuric acid (1:6), or in hydrochloric or nitric acid, or both, and converted into sulphate with 10 to 15 ml. of sulphuric acid (1:1). The solution is adjusted with ammonia (1:1) and sulphuric acid (1:3) so as to leave an excess of 15 to 20 drops of the acid (cf. Etheridge³) and electrolysed. The electrolyte is siphoned off from the mercury, treated with about 10 ml. of sulphuric acid (1:3) and evaporated to 200 to 250 ml., traces of mercury are removed with hydrogen sulphide, and the aluminium is precipitated, with due regard to the elements mentioned above. This method is applicable to copper and copper alloys, zinc, nickel, cobalt, iron and chromium alloys. Although copper can be separated in large amount by electrolysis with platinum electrodes from acid solution, the procedure offers no advantage because it yields an impure aluminium oxide.

Bronze and Special Brasses.—Alloys containing tin (e.g. bronzes and certain brasses) require special consideration. The permissible acidity of 15 to 20 drops of sulphuric acid (1:3) is insufficient to hold the tin in solution; also, it is difficult to deal with more than 0.05 g. of tin in sulphuric acid, owing to its tendency to be hydrolysed and precipitated as hydroxide. It is necessary to remove copper by electrolysis from acid solution, and precipitate tin from the electrolyte with hydrogen sulphide. The filtrate from the tin can be prepared for electrolysis over mercury, if desired. If, however, only traces of iron are known to be present it is satisfactory to precipitate the aluminium as usual and make the small correction for traces of iron, if worth while. If zinc or nickel is also present, it is necessary to carry out the mercury electrolysis (e.g. with gun metal); this is best effected after a preliminary ammonia precipitation (vide infra). Another useful method of dealing with alloys containing tin, especially in amounts greater than 0.05 g., is to eliminate it as volatile bromide at the beginning. The alloy is dissolved in hydrochloric and/or nitric acid, and the latter acid is removed by two or three evaporations with hydrochloric acid, after which hydrobromic acid is added and evaporation is repeated two or three times; finally, 10 to 15 ml. of sulphuric acid (1:1) are added and the mixture is evaporated until fumes of sulphur trioxide appear. The sulphates, now free from tin, are dissolved, and the solution is adjusted to the required small acidity and electrolysed over mercury. These remarks on tin apply equally to antimony, which is hydrolysed readily in weak acid solutions. It is also volatilised as bromide, but less easily than tin.

Chromium Alloys.—Of the metals deposited in mercury by electrolysis, chromium is the most troublesome. The deposition is so slow that a weight of 0.5 g. requires 4 or 5 hours at 4 amps. current. This appears to be due to the presence of ammonium sulphate resulting from the neutralisation of the sulphuric acid required for "sulphating." At any rate, trials with slightly acidified chromium sulphate showed that chromium can be deposited as readily as other metals. The obvious remedy is to remove the excess of sulphuric acid, leaving only the required 10 to 15 drops of acid (1 : 3). Elimination by evaporation is not permissible, as it would produce an insoluble form of chromium sulphate. The presence of ammonium sulphate does not seem to affect the deposition of other metals. With chromium, therefore, the method is limited to about 0.5 g.

Preliminary Ammonia Separation.—This is a convenient procedure when the solution contains large amounts of acid or salts. It is also advantageous for small amounts of aluminium (less than 0.5 per cent.), where it is necessary to use more than 2 g. of alloy. For instance, with copper-tin alloys (bronzes) referred to above, after copper has been removed by electrolysis in acid solution and tin with hydrogen sulphide, the neutralising of the sulphuric acid results in the formation of excessive amounts of ammonium sulphate, which makes the solution unsuitable for subsequent operations. A preliminary separation of aluminium from this solution with ammonia gives an impure product, which is dissolved in 20 ml. of sulphuric acid (1 : 3) and 20 ml. of water. As it is difficult to dissolve aluminium hydroxide by treatment with acid on the filter, it is best to digest paper and precipitate in the original beaker, filter the solution through a small pulp filter into an electrolytic beaker, and proceed as usual.

BY MEANS OF THE MERCURY CATHODE

Procedure in presence of Copper, Nickel and Cobalt.-The method fails when large amounts of copper, nickel or cobalt are present. The hydroxides of these metals are almost quantitatively precipitated at the methyl red change point, in spite of the presence of large quantities of ammonium salts. Excess of ammonia dissolves them, but this is prohibited for aluminium, since its hydroxide is appreciably soluble in ammonia. The method can be used with small amounts of these metals, such as might occur in certain alloys, provided that the precipitate can be filtered off and washed. With large amounts of zinc the method is successful, since zinc hydroxide is held in solution, even at the neutral point, by sufficient ammonium salt. In presence of aluminium, however, a certain amount of zinc is co-precipitated, and this cannot be separated completely by re-precipitation. Nevertheless, this method is often recommended, and the error is not very serious for small amounts of aluminium, after a second precipitation. An accurate determination can be made by means of the mercury cathode, in which zinc is completely removed from solution. It is advantageous to convert chromium into chromate. Although a small amount of aluminium chromate is precipitated, the chromium is easily removed from this on the mercury cathode. It is not practicable to convert large amounts of chromium into chromate by the sodium peroxide process, which is limited to a few decigrams; the same remark applies to the permanganate process. The oxidation can be effected with perchloric acid, however, which is added after dissolving the alloy with hydrochloric and/or nitric acid, and evaporating the solution until fumes appear.

A more recent procedure consists in the complete (or nearly complete) removal of chromium as volatile chromium oxychloride—also by the use of perchloric acid.⁶ As chromium is a troublesome element in analysis, this is an attractive procedure, but in practice its use appears to be limited to about 0.5 g. of chromium. Chromium, as chromate, is not precipitated from acetic acid solution by oxine. This, therefore, is an alternative method for dealing with the impure ammonia precipitate, provided that other interfering metals are absent. In this procedure iron is the usual difficulty, as it is nearly always present in amounts that would impair the accuracy of the determination and it is difficult to make a correction for it in the oxine method.

If there is any objection to the conversion of chromium into chromate, the only method of separation available appears to be the old one in which sodium hydroxide is This is not an attractive method, although it may be fairly accurate for small used. amounts of chromium. For large amounts, it would be necessary to take an aliquot part of the filtrate, as it is impossible to filter off and wash a large precipitate of chromium The technique is similar to that used for determining molybdenum in steel. hydroxide. *viz.* the slightly acid solution is "spotted" into excess of sodium hydroxide solution. The aluminium hydroxide obtained from an aliquot part of the filtrate is contaminated with silica from the glass vessels, and a correction is found by means of hydrofluoric acid in the usual way. Under such conditions it is better to precipitate aluminium with oxine, for this avoids the silica trouble. In general, the treatment in presence of chromium depends upon what other substances are present, but conversion into chromate, followed by procedures previously described, is recommended.

References

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