PRECIPITATION OF ALUMINIUM WITH HYDROGEN AMMONIUM CARBONATE.⑴

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In the previous communication⑵ it was reported that aluminium is precipitated with a hydrazine solution saturated with carbon dioxide. If, by a similar treatment, ammonia might be made equally suitable for aluminium analysis it would be a very useful precipitant of aluminium, perhaps surpas-

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(1) An abstract from the original, *Mem. Coll. Sci., Kyoto Imp. Univ.*, A, 1934, 17.

(2) *J. Chem. Soc. Japan*, **54** (1933), 682.

sing all others. It was for the hope of accomplishing this purpose that the present work was undertaken.

The *p*H value of a solution of commercial ammonium carbonate having the concentration of about one molar, is 8.70 at 21°. When this solution is cooled with ice and saturated with carbon dioxide, hydrogen ammonium carbonate begins to crystallize out on the bottom of the vessel, the *p*H value of the solution at this instant being lowered to 7.6. The molar solution of hydrogen ammonium carbonate thus separated was found to have *p*H 7.5 at 20°, which changed to 7.8 after three weeks. To prepare a reagent suitable for aluminium analysis, it is not necessary to isolate hydrogen ammonium carbonate in solid form ; we have only to saturate a molar solution of commercial ammonium carbonate with carbon dioxide till hydrogen ammonium carbonate begins to separate out, and then to expel the excess of carbon dioxide dissolved in it by exposing the solution to a reduced pressure of about 15 mm.

Gravimetric Analysis. To determine aluminium gravimetrically, a potassium alum solution containing 0.1446 g. Al_2O_3 in about 30 c.c. with two drops of bromo-thymol blue was slowly treated with hydrogen ammonium carbonate under constant agitation, till the indicator exhibited blue colour. The precipitation of aluminium was always accompanied by the evolution of carbon dioxide. After standing for 20 minutes the vessel containing the precipitate was warmed on a water bath for 40–60 minutes with occasional shaking. The heating should be continued till ammonia gas, recognizable by its odour, ceases to evolve. The *p*H value of the mother liquor at this instant was observed to be 7.45 at 21°. The precipitate was then filtered and washed with water warmed to 50–60°, till the filtrate no longer showed the reaction of SO_4''. It was first dried at 100°and then ignited at 1100°. The results of analysis are shown in Table 1. Even a trace of aluminium was never found in the filtrate.

Table 1. Al_2O_3(taken) : 0.1446 g.

Al_2O_3 found (g.)	Error (g.)	Al_2O_3 found (g.)	Error (g.)
0.1445	−0.0001	0.1446	−0.0000
0.1448	+0.0002	0.1442	−0.0004
0.1442	−0.0004	0.1444	−0.0002
0.1443	−0.0003	0.1451	+0.0005
0.1447	+0.0001	0.1444	−0.0002

To determine the composition of the aluminium compound precipitated by hydrogen ammonium carbonate the precipitate formed at room temperature was left to stand for a night, filtered with a glass filter, and well washed with water. After water was removed by suction as completely as possible, the precipitate was placed over calcium chloride in a vacuum desiccator. The precipitate, which had a powdery amorphous form, gave the following results on analysis: Al_2O_3, 47.71; H_2O, 35.01; CO_2, 17.28. Calc. for $4Al(OH)CO_3 \cdot 6Al(OH)_3 \cdot 9H_2O$: Al_2O_3, 48.72; H_2O, 34.44; CO_2, 16.82%.

The formulas hitherto given by several authors for basic aluminium carbonate differ from one another and also from that of the present author, perhaps owing to divergence in the conditions under which the precipitate was prepared.

The solubility of the basic aluminium carbonate in water was found to be 0.00242 at 20.5°, and 0.00307 at 21.5° per 1000 c.c.

When precipitated from a very dilute solution, basic aluminium carbonate takes the form of very fine particles which when warmed with mother liquor, become unsuitable for analytical treatment, being changed thereby into a colloidal form.

The most suitable concentration was found to be 47.4–23.7 millimol solution of potassium alum, that is, the solution containing 1.3459 g. of potassium alum in 30–70 c.c.

Procedure. The procedure of the new method for analysing aluminium as its oxide may be stated as follows: To a solution containing 0.05–0.1 g of aluminium in the form of potassium alum in 30 c.c.–40 c.c. about one molar hydrogen ammonium carbonate solution is slowly added with stirring, till bromo-thymol blue, added beforehand, turns blue. As the evolution of carbon dioxide ceases at this stage the end point of the reaction is easily recognized without the use of an indicator. After standing for 20–30 minutes the precipitate is warmed on a water bath, whereupon carbon dioxide accompanied by some ammonia is again evolved. Heating is continued for 40–60 minutes till the odour of ammonia becomes unrecognizable. Add some water, if necessary, taking care to keep the total volume of the mother liquor always less than 50 c.c. The precipitate is then filtered and washed with warm water of about 60° till the filtrate shows no reaction of SO_4''. After drying at about 100° the precipitate together with the filter paper is placed in a crucible and ignited at about 1100°. When the crucible is weighed, it must be enclosed tightly in a well-stoppered weighing tube.

Summary.

(1) Hydrogen ammonium carbonate prepared by saturating the solution of commercial ammonium carbonate with carbon dioxide may conveniently be used for quantitative precipitation of aluminium.

(2) The precipitate formed with hydrogen ammonium carbonate at ordinary temperature is fairly stable in a solution having the pH value of 7.6, and its composition is represented by $4Al(OH)CO_3 \cdot 6Al(OH)_3 \cdot 9H_2O$.

(3) The solubility of the basic carbonate in water is found to be 0.00242 g. per 1000 c.c. at 20–21°.

(4) The analytical procedure for gravimetric determination of aluminium with hydrogen ammonium carbonate is given.

(5) Several precautions which are to be taken in the analytical treatment of basic aluminium carbonate are fully described.

In conclusion the author wishes to express his warm thanks to Prof. Motooki Matsui for his kind guidance and valuable suggestions.

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