

Precipitation of Aluminium with Hydrogen Ammonium Carbonate

By

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In the previous communications¹⁾ it was reported that aluminium hydroxide is obtained in a form very suitable for analysis when it 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 become a very useful precipitant of aluminium, perhaps surpassing all others. It was with the hope of accomplishing this that the present work was undertaken.

Commercial ammonium carbonate mostly consists of hydrogen ammonium carbonate and ammonium carbamate, and the pH value of a solution of it, 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 in the bottom of the vessel, the pH 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 the pH value of 7.5 at 20°, which changed to 7.8 after three weeks. To prepare the reagent so as to make it suitable for aluminium analysis, it is not necessary to isolate hydrogen ammonium carbonate in the 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 m.m..

1. Now in press.

Results of Analysis

The analysis of aluminium in potassium alum was conducted with the above-stated hydrogen ammonium carbonate solution, and the results were compared with those obtained when commercial ammonium carbonate solution and also normal ammonium carbonate solution, prepared by dissolving 50 gms. of commercial carbonate in 200 c. c. of 6 normal ammonia water, were used. Hydrogen ammonium carbonate gave the best results in every respect and normal salt the worst. For analysis 15 c. c. of an alum solution (0.1446 gm. as Al_2O_3) was taken, and after diluting it with 15 c. c. of water and adding two drops of brom-thymol blue solution to it, aluminium was then precipitated by the above-mentioned precipitants. The point, at which brom-thymol blue begins to acquire a blue colour was taken as the end point of the precipitation reaction.

Table 1

Reagent	Description of precipitate	Al_2O_3	Error
Normal carbonate	Colloidal; white, then transparent; unsuitable for treatment	0.1441	-0.0005
		0.1444	-0.0002
Commercial salt	Fine powder form, fairly suitable for treatment	0.1440	-0.0006
		0.1449	+0.0003
Hydrogen Ammonium Carbonate	Powder form, very suitable for various treatment	0.1445	-0.0001
		0.1450	+0.0004

Not only is the precipitate formed by hydrogen ammonium carbonate in all respects very similar to that obtained with hydrazine carbonate, but the curves showing the results of electrometric titration of aluminium with the two precipitants well resemble each other, as will be seen below.

Electrometric Titration

By the aid of Wendt's apparatus 60 c. c. of an alum solution containing 0.1446 gm. of Al_2O_3 were titrated with the hydrogen ammonium carbonate solution at $20^\circ-21^\circ$. The pH value was determined two minutes after the addition of every 0.2 c. c. of the precipitant.

Table II

Precipitant: 1.5 M-NH₄HCO₃, pH: 7.6, Temperature: 20.5°-21°

Precipitant c. c.	pH	Precipitant c. c.	pH
0.0	3.40	4.8	6.30
0.2	3.70	5.0	6.50
0.4	3.85	5.2	6.55
0.6	3.90	5.4	6.90
0.8	3.95	5.6	7.00
1.0	4.00	5.8	7.10
1.2	4.02	6.0	7.15
1.4	4.05	6.2	7.30
1.6	4.10	6.4	7.40
1.8	4.10	6.6	7.45
2.0	4.15	6.8	7.50
2.2	4.20	7.0	7.50
2.4	4.25	7.2	7.50
2.6	4.30	7.4	7.55
2.8	4.35	7.6	7.60
3.0	4.40	7.8	7.60
3.2	4.45	8.0	7.65
3.4	4.55	8.2	7.65
3.6	4.80	8.4	7.65
3.8	5.00	8.6	7.65
4.0	5.30	8.8	7.65
4.2	5.50	9.0	7.65
4.4	5.75	10.0	7.65
4.6	6.05	11.0	7.65

For the sake of comparison similar titration experiments were also carried out with commercial ammonium carbonate and hydrazine carbonate as the precipitant. The results are shown in Tables III and IV.

Table III

Precipitant: About 1 M-Commercial Ammonium Carbonate, pH: 8.7, Temperature: 21°

Precipitant c. c.	pH	Precipitant c. c.	pH
0.0	3.40	4.6	8.25
0.2	3.80	4.8	8.35
0.4	3.95	5.0	8.40
0.6	4.00	5.2	8.40
0.8	4.05	5.4	8.40
1.0	4.10	5.6	8.45
1.2	4.20	5.8	8.50
1.4	4.30	6.0	8.55
1.6	4.30	6.2	8.55
1.8	4.35	6.4	8.55
2.0	4.45	6.6	8.55
2.2	4.70	6.8	8.60
2.4	5.10	7.0	8.60
2.6	5.60	7.2	8.60
2.8	5.95	7.4	8.60
3.0	6.50	7.6	8.60
3.2	7.10	7.8	8.60
3.4	7.55	8.0	8.60
3.6	7.70	8.5	8.60
3.8	7.95	9.0	8.60
4.0	8.10	9.5	8.60
4.2	8.15	10.0	8.65
4.4	8.20	11.0	8.65

Table IV

Precipitant: About 2M-Solution of $\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$, saturated with CO_2 , pH: 7.4, Temperature: 20°—20.5°

Precipitant c. c.	pH	Precipitant c. c.	pH
0.0	3.40	4.0	6.35
0.2	3.80	4.2	6.55
0.4	3.90	4.4	6.65
0.6	4.00	4.6	6.80
0.8	4.00	4.8	6.90
1.0	4.05	5.0	7.00
1.2	4.05	5.2	7.00
1.4	4.10	5.4	7.00
1.6	4.15	5.6	7.05
1.8	4.20	5.8	7.05
2.0	4.23	6.0	7.15
2.2	4.25	6.2	7.20
2.4	4.30	6.4	7.25
2.6	4.35	6.6	7.25
2.8	4.45	6.8	7.25
3.0	4.60	7.0	7.25
3.2	4.95	7.5	7.25
3.4	5.30	8.0	7.30
3.6	5.72	9.0	7.30
3.8	6.10	10.0	7.30

The precipitates formed with hydrogen ammonium carbonate and hydrazine carbonate behaved similarly, viewed from the analytical

standpoint, while those produced with commercial carbonate settled down with difficulty, making their filtering and washing very tedious. The titration curve (Fig. 1) representing the above results will clearly show the close similarity existing between hydrogen ammonium carbonate and hydrazine carbonate.

Fig. 1

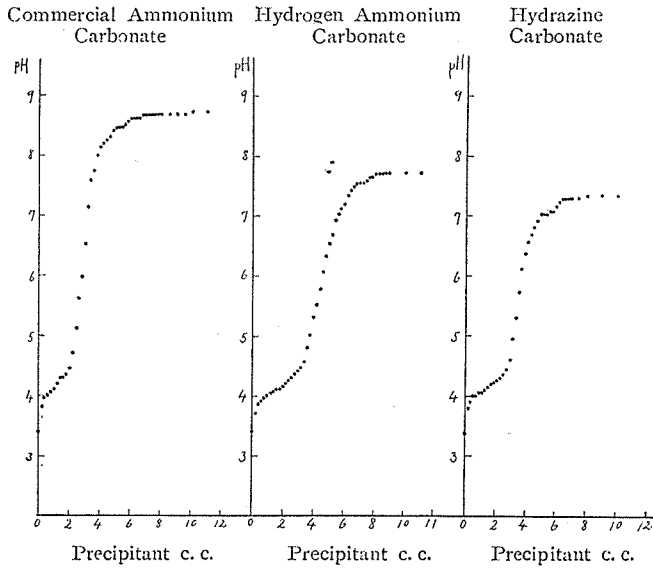
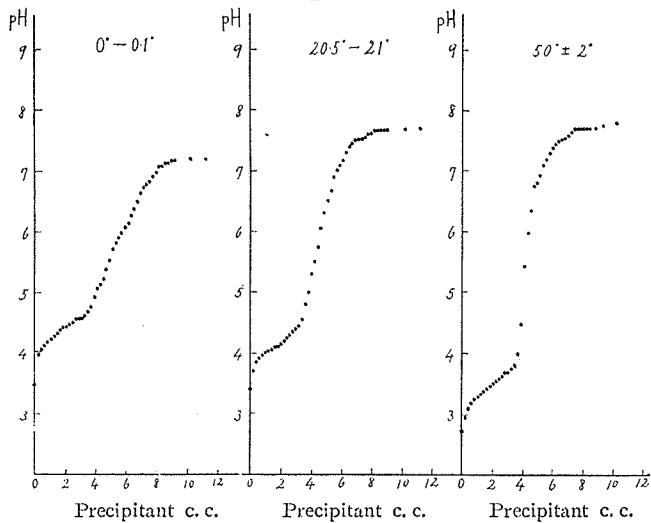


Fig. 2



It will be observed that there always is a small jump in the curve near the end point of the precipitation reaction. This jump may be regarded as showing the transformation of basic carbonate of aluminium from an unstable form to a stable. In the case of hydrogen ammonium carbonate the pH value corresponding to the middle point of this jump is 7.58. Therefore, if we wish to know the exact end point of the reaction by means of an indicator, brom-thymol blue may be selected as one of the most suitable ones.

In order to find the influence of temperature on the titration, the experiments were repeated at $0^{\circ}-0.1^{\circ}$ and also at $50^{\circ}\pm 2^{\circ}$. The results are shown in Tables V and VI, and Fig. 2.

Table V

Temperature: $0^{\circ}-0.1^{\circ}$

Hydrogen Ammonium Carbonate c. c.	pH	Hydrogen Ammonium Carbonate c. c.	pH
0.0	3.45	4.8	5.50
0.2	3.95	5.0	5.70
0.4	4.02	5.2	5.80
0.6	4.10	5.4	5.90
0.8	4.15	5.6	5.95
1.0	4.20	5.8	6.05
1.2	4.25	6.0	6.10
1.4	4.30	6.2	6.25
1.6	4.35	6.4	6.35
1.8	4.40	6.6	6.45
2.0	4.40	6.8	6.60
2.2	4.45	7.0	6.70
2.4	4.50	7.2	6.75
2.6	4.55	7.4	6.80
2.8	4.55	7.6	6.90
3.0	4.55	7.8	6.95
3.2	4.60	8.0	7.05
3.4	4.65	8.2	7.10
3.6	4.75	8.4	7.10
3.8	4.90	8.6	7.15
4.0	5.05	8.8	7.15
4.2	5.10	9.0	7.15
4.4	5.20	10.0	7.15
4.6	5.35	11.0	7.15

Table VI

Temperature : $50^{\circ} \pm 2^{\circ}$

Hydrogen Ammonium Carbonate c. c.	pH	Hydrogen Ammonium Carbonate c. c.	pH
0.0	2.75	4.6	6.70
0.2	2.95	4.8	6.80
0.4	3.10	5.0	6.95
0.6	3.20	5.2	7.10
0.8	3.25	5.4	7.20
1.0	3.30	5.6	7.30
1.2	3.35	5.8	7.40
1.4	3.40	6.0	7.45
1.6	3.42	6.2	7.50
1.8	3.47	6.4	7.52
2.0	3.50	6.6	7.55
2.2	3.55	6.8	7.60
2.4	3.60	7.0	7.65
2.6	3.65	7.2	7.70
2.8	3.70	7.4	7.70
3.0	3.70	7.6	7.70
3.2	3.75	7.8	7.70
3.4	3.80	8.0	7.70
3.6	4.00	8.5	7.70
3.8	4.50	9.0	7.75
4.0	5.45	10.0	7.80
4.2	6.00	11.0	7.83
4.4	6.35		

In the low temperature titration the pH value becomes constant at about 7.15 giving no second jump in the curve. When, however, the solution is agitated at room temperature without further addition of the precipitant, the pH value gradually increases and reaches 7.65 after 35 minutes. In the titration curve obtained at 50° the second jump is present though not so marked as in the case at room temperature. The precipitate formed at high temperature is found to be fit for analytical treatment.

Gravimetric Analysis

To determine aluminium gravimetrically, about 30 c.c. of potassium alum (containing 0.1446 gm. Al_2O_3) with two drops of brom-thymol blue were slowly treated with hydrogen ammonium carbonate under

constant agitation, till the indicator exhibited a 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 pH 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 $\text{SO}_4^{''}$. It was first dried at 100° and then ignited at 1100°. The results of analysis were as follows :

Table VII

Al₂O₃ (taken) : 0.1446 gm.

Al ₂ O ₃ (found) (gm.)	Error	Al ₂ O ₃ (found) (gm.)	Error
0.1445	–0.0001	0.1451	+0.0005
0.1448	+0.0002	0.1444	–0.0002
0.1442	–0.0004	0.1444	–0.0002
0.1443	–0.0003	0.1448	+0.0002
0.1447	+0.0001	0.1446	±0.0000
0.1446	±0.0000	0.1442	–0.0004
0.1442	–0.0004		

Not even a trace of aluminium was ever found in the filtrate.

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 and filtered with a glass filter and well washed with water. After water had been removed by suction as completely as possible, the precipitate was placed in a vacuum desiccator containing calcium chloride. The precipitate, which had a powdery amorphous form, gave the following results on analysis :

- 0.14100 gm. of precipitate gave 0.02437 gm. CO₂ and 0.04937 gm. H₂O
- 0.21810 gm. ,, ,, ,, 0.03793 gm. ,, ,, 0.07848 gm. ,,
- 0.34459 gm. ,, ,, ,, 0.16442 gm. Al₂O₃
- 0.28007 gm. ,, ,, ,, 0.12942 gm. ,,

	Found		Calc. from $4\text{Al}(\text{OH})\text{CO}_3 \cdot 6\text{Al}(\text{OH})_3 \cdot 9\text{H}_2\text{O}$
Al ₂ O ₃	(3) 47.71	(4) 46.20	48.72
H ₂ O	(1) 35.01	(2) 35.98	34.44
CO ₂	(1) 17.28	(2) 17.39	16.82

The formulas hitherto given by several authors for basic aluminium carbonate differ from each other and also from that of the present author, perhaps owing to divergence in the conditions under which the precipitate was probably 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 the 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 gm. of potassium alum in 30 c. c.—70 c. c..

The basic aluminium carbonate begins to change into the hydroxide at temperatures near 30°. Hence, if the precipitate is warmed with the mother liquor before filtration, the temperature at which the precipitate is prepared does not much effect the results of analysis, as is seen in Table VIII.

Table VIII

Precipitation temperature	Al ₂ O ₃ (0.1446) (gm.)	Error (gm.)
20.5°	0.1450	+0.0004
0°	0.1442	−0.0004
0°	0.1445	−0.0001
0°	0.1442	−0.0004
11°–12°	0.1444	−0.0002
10°–11.5°	0.1441	−0.0005
32°–34°	0.1449	+0.0003
54°–60°	0.1443	−0.0003
60°–80° ?	0.1446	±0.0000
60°–80° ?	0.1447	+0.0001

If basic carbonate is to be precipitated at room temperature or below it and directly filtered without heating it beforehand, the precipitate must be washed with cold water, otherwise no small loss is produced. Long standing of the precipitate was found superfluous as the consistency of it is not much improved by that treatment.

Procedure.—From what has been given so far 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 gm. 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 brom-thymol blue, previously added, 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 to be weighed, it must be enclosed tightly in a well-stoppered weighing tube.

Summary

1. Hydrogen ammonium carbonate prepared by saturating a commercial ammonium carbonate solution with carbon dioxide may conveniently be used for quantitatively precipitating aluminium, as exactly and suitably as hydrazine carbonate.

2. The precipitate formed by hydrogen ammonium carbonate at ordinary temperatures is fairly stable in a solution having the pH value of 7.6, and its composition is represented by $4\text{Al}(\text{OH})\text{CO}_3 \cdot 6\text{Al}(\text{OH})_3 \cdot 9\text{H}_2\text{O}$.

3. The solubility of the basic carbonate in water is found to be 0.00242 gm. per 1000 c. c. at 20°—21°.

4. The analytical procedure for gravimetrically determining 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.