the combined filtrate and washings concentrated to 2 cc. and transferred to a test tube. The test was then carried out in the manner already described in the determination of the sensitiveness of the test. The preceding results were obtained.

The preceding results show that the silver arsenate test is capable of detecting as little as 0.5 mg. of arsenic in systematic analysis.

Summary.

1. With pure solutions of arsenate the test with silver nitrate is sensitive to 0.02 mg. of arsenic.

2. Ammonium nitrate, which is generally formed in carrying out this test, exercises no influence on the detection of 0.2 mg. of arsenic as sodium arsenate.

3. A procedure is given by which, in systematic analysis, the test is capable of detecting 0.5 mg. of arsenic with certainty.

NEW YORK, N. Y.

THE DETERMINATION OF ALUMINIUM AS OXIDE.

BY WILLIAM BLUM.[1]

Received May 10, 1916.

I. Introduction.

Although a considerable number of precipitants have been proposed for the determination of aluminium, direct precipitation of aluminium hydroxide by means of ammonium hydroxide, followed by ignition to oxide, is most commonly used, especially if no separation from iron is desired, in which case special methods must be employed. While the general principles involved in this determination are extremely simple, it has long been recognized that certain precautions in the precipitation, washing, and ignition, are necessary if accurate results are to be obtained. While, however, most of these details have been studied and discussed by numerous authors, it is noteworthy that few publications or text books have taken account of all the factors. In the present paper it seems

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[1] Published by permission of the Director of the Bureau of Standards. This paper will appear in somewhat more detailed form as Scientific Paper No. 286, copies of which can be obtained upon request addressed to the Bureau of Standards, Washington, D. C.

desirable, therefore, to assemble the various recommendations, and to consider their basis and their accuracy. No attempt has been made, however, to include a complete bibliography. The experiments described in this paper were conducted in 1912, in connection with a study of the determination of alumina in phosphate rock. As the latter research was interrupted, this paper is confined to the direct determination of aluminium as oxide.

II. General Principles.

In precipitations of metallic hydroxides by means of ammonia or other bases, the process may be considered as a progressive hydrolysis, brought about by the neutralization of the acid continuously set free. In the case of such hydroxides as ferric hydroxide, which are practically insoluble in bases, it may be readily shown that the solubility is decreased and precipitation rendered more complete by the addition of an excess of the precipitant, thereby increasing the hydroxyl ion concentration. In the case of amphoteric hydroxides, however, such as aluminium hydroxide, it is obvious that an excess of the base is to be avoided, and it therefore becomes desirable to select that degree of alkalinity which will ensure most nearly complete precipitation, and at the same time avoid resolution of the precipitate. As will be shown later, the study of the progress of the precipitation, and the selection of the proper "end point" of precipitation can readily be accomplished by means of the hydrogen electrode, the conditions selected being subsequently defined by means of suitable indicators.

III. Historical.

Early recognition of the fact that, when considerable excess of ammonia is used in the precipitation of aluminium hydroxide, appreciable amounts of aluminium pass into the filtrate, led to the time honored procedure of boiling out most of the free ammonia. The latter method, however, has its defects, owing to the attack of glass vessels by the hot ammoniacal solution (leading to contamination of the precipitate with lime, silica, etc.); and to the possible resolution of alumina, when through excessive boiling the solution becomes slightly acid. Various authors have therefore urged the use of a very slight excess of ammonia with only a short period of boiling,[1] especially when a considerable amount of ammonium chloride is present in the solution.[2] While the beneficial effect of ammonium chloride in reducing the solubility of aluminium hydroxide in ammonia, has been pointed out by numerous authors, and has formed a basis

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[1] S. L. Penfield and D. N. Harper, *Am. J. Sci.*, **32**, 107 (1886); *Chem. News*, **54**, 90, 102 (1886); W. H. Daudt, *J. Ind. Eng. Chem.*, **7**, 847 (1915).

[2] Malaguti and Durocher, *Ann. chim. phys.*, [3] **17**, 421 (1846); J. Hanamann, *Z. anal. Chem.*, **3**, 367 (1864); C. F. Cross, *Chem. News*, **39**, 161 (1879); L. Blum, *Z. anal. Chem.*, **27**, 19 (1888); G. Lunge, *Z. angew. Chem.*, 1889, 634.

for the procedures recommended in most text books, few attempts have been made to explain this effect, which in some cases has been attributed to the coagulation of the colloidal aluminium hydroxide by the salt.[1] While undoubtedly this is an important function of the ammonium chloride, it will be shown later that the reduction of the alkalinity (hydroxyl ion concentration) of ammonia by the presence of ammonium chloride also exerts a marked influence upon the completeness of precipitation.

While many authors recommend the customary method of using an indicator such as litmus paper to detect roughly the presence of an excess of ammonia, few have suggested the accurate definition of the desired alkalinity by means of suitable indicators. Hinrichsen[2] used rosolic acid in a study of the effect of fluorine upon the precipitation of aluminium by ammonia, but gives no experimental or theoretical basis for its selection. Numerous authors, in efforts to develop methods for the volumetric determination of aluminium or for testing the neutrality of aluminium salts, have used various indicators for determining the beginning and completion of the precipitation of aluminium hydroxide; but few, if any, have shown that complete precipitation actually occurs at the color change selected.

IV. Precipitation of Aluminium Hydroxide.

1. Hydrogen Electrode Studies.

(*a*) **The Method.**—The application of the hydrogen electrode to a study of the changes taking place in solution during precipitations was suggested in a paper on the determination of magnesia in limestone,[3] and was elaborated in an article by J. H. Hildebrand,[4] in which are given numerous curves for such precipitations, including the action of sodium hydroxide upon aluminium sulfate. The principle of the method is very simple, involving the measurement of the electromotive force of a cell consisting of a hydrogen electrode and a calomel half cell, immersed in the solution to be investigated. The hydrogen ion concentration of the solution may then be calculated from the formula

$$\log \frac{1}{[H^+]} = \frac{\pi - 0.338}{0.058}$$

where π is the observed e. m. f. in volts (at 25°). The apparatus and method of measurement were essentially those used by Hildebrand and Harned, precautions being taken to exclude carbon dioxide during the titrations.

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[1] A. Classen, "Quantitative Analysis," p. 145, 6th Ger. Ed. (1912).

[2] *Z. anorg. Chem.*, 58, 88 (1908). Hinrichsen showed that fluorine may hinder or entirely prevent the precipitation of aluminium hydroxide by ammonia.

[3] J. H. Hildebrand and H. S. Harned, *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 1, 217 (1912).

[4] THIS JOURNAL, 35 864 (1913).

(*b*) **Results of Experiments.**—The data obtained by measurement of the changes in hydrogen ion concentration occurring upon addition of alkaline hydroxides to solutions of aluminium chloride are shown graphically in Fig. 1. The abscissas represent cubic centimeters of alkaline hydroxide added, and the ordinates on the left side are the observed e. m. fs. expressed in millivolts. On the right side the value of the ordinates is expressed in terms of hydrogen ion concentration, calculated as previously stated. Curves A, B, and C, are the same as were

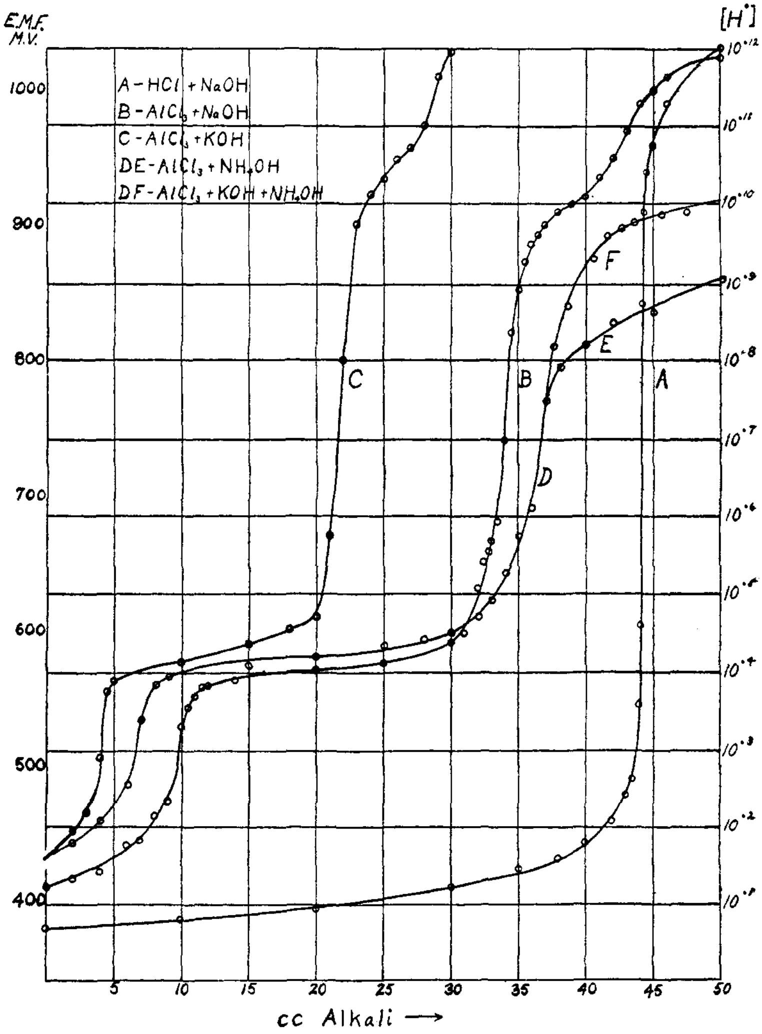

Fig. 1.—Precipitation of aluminium hydroxide.

published in a preceding article by the author[1] on the constitution of aluminates. The curve A for the neutralization of hydrochloric acid with sodium hydroxide is shown simply to indicate the normal course of such a reaction in the absence of any metals precipitable as hydroxides. While Curves B and C are chiefly of interest in relation to the formation of aluminates, they are included here in order to show the similarity in the course of the precipitations with fixed alkalies and with ammonia.

The Curve DE shows the progress of the reaction when ammonium hydroxide is added to a solution of aluminium chloride containing a small amount of free acid. In order to eliminate the influence of ammonium chloride (to which reference will be made later) the Curve DF was plotted, in which the portion F was obtained by the addition of ammonium hydroxide to a solution, in which the aluminium hydroxide had been exactly precipitated by the addition of a calculated amount of potassium hydroxide. While the Curve F should strictly, therefore, be attached to Curve C, it has been placed in its present position in order to emphasize the comparison between the effect of ammonium hydroxide with and without the presence of ammonium chloride.

(*c*) **Conclusions from Hydrogen Electrode Experiments.**—From the curves shown in Fig. 1, it is evident that the changes taking place during the precipitation of aluminium chloride are practically independent of the alkali used. In general, it may be seen that precipitation[2] begins when $[H^+]$ is about 10^{-3} and is complete before $[H^+]$ is 10^{-7}. In the case of the fixed alkalies it was pointed out in a former paper that appreciable resolution of the precipitate, probably with the formation of aluminates, occurs soon after the neutral point is passed, *e. g.*, when $[H^+]$ is less than 10^{-9}. When ammonium hydroxide is used as the precipitant, it may be seen from the Curve DE, that it is difficult to obtain a solution in which $[H^+]$ is less than 10^{-9}, even when appreciable excess of ammonia is present. While, therefore, as is to be expected, it is not possible by this method to obtain complete solution in ammonia of any considerable quantity of aluminium hydroxide,[3] an appreciable amount was always

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[1] W. Blum, THIS JOURNAL, **35**, 1499 (1913).

[2] By "precipitation" in this sense is meant the chemical formation of $Al(OH)_3$, which (especially in the absence of salts) may not actually coagulate or form a visible precipitate, until from one-third to half of the alkali required for complete precipitation has been added. The point at which a visible precipitate occurred in the different experiments, was found to be very variable. The formation of such regular curves as are shown, however, indicates the improbability of the existence in solution of any definite basic salts such as have been supposed to be formed by solution of freshly precipitated aluminium hydroxide in neutral aluminium chloride or sulfate solutions. Consult H. W. Fischer, Habilitationsschrift, Breslau, 1908, C. B., **1909**, I, 260; R. Kremann and K. Hüttinger, *Jahrb. K. K. Geol., Reichsan.*, **58**, 637 (1909); C. B., **1909**, II, 1200.

[3] *Existence of Ammonium Aluminate.* In a previous communication the evidence

found dissolved in any solutions in which $[H^+]$ is less than 10^{-9}. The effect of even small amounts of ammonium chloride in reducing the alkalinity of ammonium hydroxide is clearly shown by comparison of Curves E and F, there being present no ammonium chloride in F, and in E only the amount equivalent to about 37 cc. of 0.2 *N* NH_4OH, *i. e.*, the solution at the end was about 0.08 *N* in NH_4Cl. This effect of ammonium chloride is also illustrated in Fig. 2, in which the hydrogen ion concentration of various ammonia-ammonium chloride solutions has been calculated from the ionization constant of ammonia at 25°.[1]

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}$$

and that of water $K_{w25°} = 1.1 \times 10^{-14}$, upon the assumption that the mass law holds for such solutions. For the sake of simplicity the ionization of ammonium chloride, which in solutions from *N* to 0.1 *N* varies from 75 to 85%,[2] has been taken as 80%. For convenience the results have been expressed in cc. of *N* ammonium hydroxide present in a volume of 100 cc. of ammonium chloride solutions of various concentration.

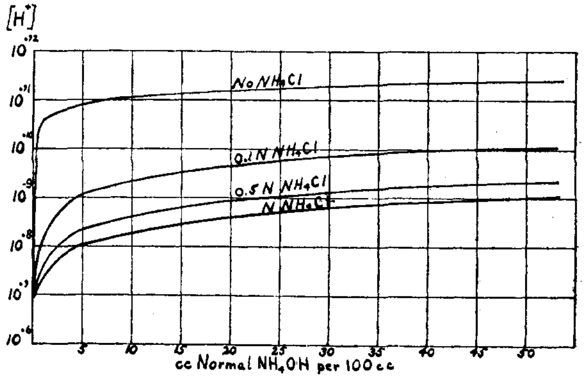

Fig. 2.—Effect of ammonium chloride upon the alkalinity of ammonia.

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in favor of the formation in solution of definite aluminates of sodium and potassium was presented. While no such definite evidence of the existence of ammonium aluminate is available, owing to the above mentioned impossibility of securing ammonia solutions of high alkalinity, there seems to be no reason to doubt the analogy of the solutions in ammonia and the fixed alkalies. In this connection, it is interesting to consider the evidence presented by C. Renz (*Ber.*, 36, III, 2751 (1903)). This author dismisses the possibility of the existence of an ammonium aluminate, even though by an indirect method (*viz.*, solution of $Al(OH)_3$ in $Ba(OH)_2$ and subsequent addition of $(NH_4)_2SO_4$) he was able to obtain a clear solution free from Ba^{++} and $SO_4^{=}$, 50 cc. of which contained 0.1 g. Al_2O_3. The fact, observed by Renz, that freshly precipitated $Al(OH)_3$ is readily soluble in organic amines, far from being an argument against the existence in solution of ammonium aluminate, would appear to indicate that by the solution of aluminium hydroxide in any base, aluminates are formed, the maximum concentration being dependent upon the alkalinity of the resultant solution and its consequent ability to repress the hydrolysis of the aluminate.

[1] A. A. Noyes and R. B. Sosman, "Electrical Conductivity of Aqueous Solutions," *Carnegie Inst. Pub.*, 63, 228 (1908).

[2] F. W. G. Kohlrausch and L. Holborn, "Leitvermögen der Elektrolyte," p. 159 (1898).

From Fig. 2, it is evident (1) that even small additions of ammonium chloride cause a marked decrease in the alkalinity of ammonium hydroxide solutions, (2) that above 0.5 *N* an increase in the concentration of ammonium chloride has little effect, and (3) that with any reasonable concentration of ammonium chloride, it is impracticable to so limit the alkalinity that a solution in which $[\mathrm{H}^+]$ is less than 10^{-9} (*i. e.*, one which dissolves appreciable $\mathrm{Al(OH)_3}$) is not formed when any large excess of concentrated ammonia is added. (It should be noted that 50 cc. *N* $\mathrm{NH_4OH}$ is about equal to 3.3 cc. conc. $\mathrm{NH_4OH}$, sp. gr. 0.90.)

2. *Selection of an Indicator for Defining the Conditions of Precipitation.*

In Table I are shown the results of experiments conducted to determine which of the common indicators is most satisfactory for defining the completion of the precipitation. In each case the solution of the aluminium chloride and indicator was heated just to boiling in a platinum dish, and dilute ammonium hydroxide (about 2 *N*) was added till the first definite color change occurred. The solution was boiled for about two minutes, filtered and evaporated to dryness, and the total residue weighed after expulsion of the ammonium salts. Corrections were made for the small amounts of impurities in the distilled water and the ammonium chloride.

TABLE I.

Precipitation of $\mathrm{Al(OH)_3}$ by $\mathrm{NH_4OH}$. Using Various Indicators.

(The $\mathrm{AlCl_3}$ solution, equivalent to 0.10 g. $\mathrm{Al_2O_3}$ was precipitated in a volume of 200 cc.)

Expt.	Indicator.	Color change $[\mathrm{H}^+]$ = approx.[1]	$\mathrm{NH_4Cl}$ added, g.	$\mathrm{Al_2O_3}$ in filtrate.	Remarks.
1........	*p*-Nitrophenol	10^{-6}	5	0.0010	
2........	*p*-Nitrophenol	10^{-6}	5	0.0012	
3........	Methyl red	$10^{-6.5}$	0	appreciable	Coagulated poorly
4........	Methyl red	$10^{-6.5}$	5	0.0001	
5........	Methyl red	$10^{-6.5}$	5	0.0000	
6........	Rosolic acid	$10^{-7.5}$	0	0.0000	
7........	Rosolic acid	$10^{-7.5}$	5	0.0000	
8........	Rosolic acid	$10^{-7.5}$	5	0.0002	Macerated paper used
9........	Phenolphthalein	10^{-9}	0	0.0004	
10........	Phenolphthalein	10^{-9}	5	0.0004	

From Table I it is evident that considerable aluminium hydroxide remains unprecipitated when the solution is just alkaline to *p*-nitrophenol, while a smaller amount, but still appreciable, is redissolved when the solution is just alkaline to phenolphthalein. So far as accuracy is concerned, there is no choice between the use of methyl red and of rosolic acid. Practically, however, methyl red has been found preferable, because of its sharper color change, and because the end point is reached while approaching neutrality, *i. e.*, a slight excess of ammonia is less

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[1] The approximate points of color change selected were measured with the hydrogen electrode at room temperature.

likely to cause resolution. Moreover, solutions just alkaline to methyl red are less likely to attack Jena or similar glassware, than are solutions slightly alkaline to rosolic acid. In using methyl red, however, it is essential to have appreciable ammonium chloride present to facilitate coagulation. The fact that coagulation occurs more readily, even in the presence of only small amounts of ammonium chloride, when the solution is just alkaline to rosolic acid, *i. e.*, when $[H^+]$ is less than 10^{-7}, would appear to indicate that the OH^- ion itself exerts a coagulating effect upon the colloid.

3. Factors Affecting the Form of the Precipitate.

It is difficult to obtain a precipitated colloid, such as aluminium hydroxide, in a form that is readily filtered and washed. In general, it has been recognized that while short boiling is desirable to effect coagulation, longer boiling renders the precipitate slimy and difficult to filter. As previously noted, the use of ammonium chloride is advantageous in producing the well-known salt effect in the coagulation of such a precipitate, as well as in reducing the actual solubility. These two factors were the only ones found to have a favorable influence upon the method of precipitation. The conclusion of W. E. Taylor,[1] that if the solution be heated to just 66° before the addition of ammonia, and subsequently boiled, the precipitate is "granular," could not be confirmed by R. Sudgen[2] nor by the author. The recommendation of A. Guyard[3] to add glycerol to the solution before precipitating with ammonia, was tried, and no improvement in the character of the precipitate was noted, while about 5 mg. of Al_2O_3 was found in the filtrate. Similarly, the procedure of R. E. Divine,[4] *viz.*, precipitation in the presence of tannic acid, while it produced an appreciable improvement in the character of the precipitate, yielded a filtrate containing from 1 to 5 mg. of Al_2O_3, depending upon whether the solution was boiled for some time, or was filtered after a couple minutes' boiling.

While, therefore, it seems impossible to specify satisfactory conditions for the rapid filtration of considerable amounts of aluminium hydroxide, it is believed that for amounts of alumina up to 0.10 g. Al_2O_3, the following conditions will yield fairly satisfactory results; *viz.:* (1) the presence of at least 5 g. of ammonium chloride in a volume of 200 cc., (2) addition of dilute ammonia to the nearly boiling solution until it is just alkaline to methyl red (or rosolic acid), (3) boiling for not more than 2 minutes, and (4) filtration without waiting long for the precipitate to subside. (In some cases the precipitate was found to settle quite readily; while

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[1] *Chem. News*, 103, 169 (1911).

[2] *Ibid.*, 104, 35 (1911).

[3] *Z. anal. Chem.*, 22, 426 (1883).

[4] *J. Soc. Chem. Ind.*, 24, 11 (1905).

in others it showed a tendency to rise to the surface, and would not settle, even on long standing.) The addition of macerated filter paper before precipitation has been found advantageous in aiding filtration (and also ignition), especially of large amounts of the precipitate.

4. Precipitation in the Presence of Iron.

As previously noted, it is often necessary to precipitate ferric and aluminium hydroxides together. This can readily be accomplished by the procedure above recommended, since it was found that ferric hydroxide is completely precipitated by ammonia before the solution is alkaline to methyl red or to rosolic acid. In case sufficient iron is present to obscure the color of the indicator, it may be precipitated first by the careful addition of ammonia, and caused to settle by short boiling, after which the color of the indicator can readily be recognized in the supernatant liquid and more ammonia added if necessary, or any decided excess of ammonia may be neutralized with dilute acid, and the solution again boiled.

V. Washing the Precipitate.

Upon washing precipitates equivalent to 0.10 g. Al_2O_3, with only 75 cc. of hot water, from 0.5 to 2 mg. of Al_2O_3 was found in the washings. The obvious remedy, *viz.*, washing with a solution of a volatile ammonium salt such as ammonium chloride or nitrate, has been suggested by numerous authors.[1] From the standpoint of the "salt" action there appears to be no preference between ammonium nitrate and chloride. The former has been used most frequently partly because of its slight advantage in assisting combustion of the filter paper, and partly because of the opinion, still prevalent, though frequently disproven, that the presence of ammonium chloride during ignition would cause loss of alumina by volatilization of the chloride.[2] As pointed out by W. F. Hillebrand,[3] when the original solution contains chlorides and it is desired to evaporate the filtrate and washings in platinum, and expel ammonium salts, it is impractical to use ammonium nitrate in the wash water, owing to attack of the platinum vessels. In the present research, therefore, a hot 2% solution of ammonium chloride was used. It was found that there was no appreciable difference in the amount of alumina dissolved by the neutral ammonium chloride solution, and that rendered slightly alkaline with ammonia, the residues obtained from 100 cc. of the washings in each case being less than 0.3 mg. The use of solutions of the pure salts, with no addition of ammo-

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[1] W. H. Daudt, *J. Ind. Eng. Chem.*, 7, 847 (1915); Penfield and Harper, *Am. J. Sci.*, 32, 107 (1886); W. Trautmann, *Z. angew. Chem.*, 26 (Aufsatz), 702 (1913).

[2] It has been shown by Daudt (*Loc. cit.*) that 1% ammonium chloride solution may be used for washing precipitates containing ferric hydroxide with no loss of iron by volatilization.

[3] U. S. Geol. Survey, *Bull.* 422, 99 (1910).

nia, is therefore recommended, especially as solutions rendered alkaline are more likely to act upon the glass of the wash bottle and become contaminated.

VI. Separation from Other Elements.

Owing to the relatively gelatinous condition of the precipitated aluminium hydroxide, the only practical method of eliminating elements such as the alkalies, which are likely to be present in considerable amount in the solution, is to dissolve and reprecipitate. That such a procedure is quite efficient, may be judged by the fact that from a solution containing 0.1000 g. Al_2O_3, and 10 g. of sodium chloride in a volume of 200 cc., the precipitate obtained after a single precipitation, and washing ten times with 2% ammonium chloride, weighed 0.1071 g., and contained much NaCl, while a similar precipitate which was washed only five times, dissolved in hydrochloric acid, reprecipitated and again washed five times, weighed 0.1008 g., and contained only a trace of NaCl.

It is well recognized[1] that the separation of aluminium from such elements as zinc, manganese, nickel, and cobalt by means of ammonia is unsatisfactory, since the alkalinity required for the resolution of their hydroxides is such as to cause appreciable solution of the aluminium hydroxide also. Moreover, it was found that even in solutions just alkaline to methyl red, oxidation and precipitation of manganese occurred so rapidly as to preclude a quantitative separation. For such separations, therefore, other procedures, *e. g.*, the basic acetate method, must be employed.

The precipitation conditions above recommended have been found especially favorable in the separation from those elements such as barium, calcium, and strontium, and to a less extent, magnesium, whose carbonates are likely to be formed by absorption of carbon dioxide, and carried down by the precipitated alumina. It has been found experimentally that in solutions containing barium and calcium, which are neutral, or even slightly alkaline to rosolic acid (*i. e.*, $[H^+] = 10^{-7}$ to $10^{-7.5}$) it is impossible to form a precipitate of the carbonates by exposure to the atmosphere.[2] Aluminium hydroxide precipitates obtained from solutions

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[1] A. A. Noyes, W. C. Bray and E. B. Spear, *J. Am. Chem. Soc.*, 30, 482 and 532 (1908).

[2] This observation is approximately in accordance with the result obtained by calculating the alkalinity of barium chloride or calcium chloride solutions (*e. g.*, 0.1 *N*), saturated with respect to the neutral carbonates, in equilibrium with the normal atmosphere (see J. Johnston, THIS JOURNAL, 37, 2001–20 (1915)). Thus, the ionization of 0.1 *N* barium chloride solution may be assumed as 70%, *i. e.*, $[Ba^{++}]$ is 0.07. Since at 16° the solubility product $[Ba^{++}]\ [CO_3^{=}]$ is 7×10^{-9}, $[CO_3^{=}]$ is equal to 10^{-7}. In any solutions at 16° in equilibrium with an atmosphere containing CO_2 with a partial pressure P, $\frac{[OH^-]^2}{[CO_3^{=}]} = \frac{3.4 \times 10^{-11}}{P}$. While the ordinary atmosphere

containing 0.1000 g. Al_2O_3 and calcium and barium chlorides equivalent to 0.2 g. CaO and BaO respectively (*i. e.*, twice the amount of Al_2O_3), and washed five times with 2% ammonium chloride solution, weighed 0.0998 and 0.0999 g., and were found to be free from calcium and barium.

The beneficial effect of ammonium chloride in the separation of aluminium from magnesium has long been recognized. Formerly it was explained by the formation of a double salt, though more recently it has been attributed to the repression by the ammonium chloride, of the alkalinity of the ammonium hydroxide, to a point insufficient to precipitate the magnesium hydroxide.[1] The latter view is confirmed by the results of Hildebrand and Harned,[2] who found that $Mg(OH)_2$ is not precipitated until $[H^+]$ is less than 10^{-9}; and by the curves shown in Fig. 2 of this paper, in which the above effect of ammonium chloride is clearly shown. That the procedure recommended is effective in the separation of aluminium and magnesium, is shown by experiments in which aluminium hydroxide (equivalent to 0.10 g. Al_2O_3) precipitated in the presence of magnesium chloride equivalent to 0.2 g. MgO, contained less than 0.0010 g. MgO.

VII. Ignition and Weighing of the Precipitate.

1. Hygroscopicity of Aluminium Oxide.

The fact that ignited Al_2O_3 readily absorbs water has been recognized and pointed out by many authors.[3] This property has in fact been made the basis for the recommendation of the use of Al_2O_3 as a dehydrating agent.[4] It should be noted, however, that for the latter use the Al_2O_3 should not be strongly ignited. Many of the experiments that have been conducted to determine the hygroscopicity of such substances as Al_2O_3 have little bearing upon analytical procedures, since no distinction was made between the amount of water absorbed, and the rate of absorption, especially during the first few minutes' exposure. Tests at this Bureau

contains about 3 parts of CO_2 in 10,000 the air in a laboratory may often contain 5 parts, or more, in 10,000. In such a case $P = 5 \times 10^{-4}$, and therefore $[OH^-]$ is 0.84×10^{-7}. If $K_{w16°} = 0.5 \times 10^{-14}$, then $[H^+]$ is about 0.6×10^{-7}, or $10^{-7.2}$, *i. e.*, the solution must be slightly alkaline before any $BaCO_3$ can be precipitated by exposure to air containing the normal amount of CO_2.

From similar calculations for 0.1 *N* $CaCl_2$, assuming that $[Ca^{++}][CO_3^{=}] = 0.98 \times 10^{-8}$, it may be shown that $[OH^-] = 1.0 \times 10^{-7}$; or $[H^+] = 0.5 \times 10^{-7}$ or $10^{-7.3}$ before any $CaCO_3$ will be precipitated upon exposure to the atmosphere. (Since such carbonates are prone to form supersaturated solutions, precipitation may not occur even at the points designated.)

[1] J. M. Loven, *Z. anorg. Chem.*, 11, 404 (1896); F. P. Treadwell, *Ibid.*, 37, 326 (1903); W. Herz and G. Muhs, *Ibid.*, 38, 138 (1904).

[2] *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 1, 217 (1912).

[3] E. T. Allen and V. H. Gottschalk, *Am. Chem. J.*, 24, 292–304 (1900); Hess and Campbell, THIS JOURNAL, 21, 776 (1899); C. F. Cross, *Chem. News*, 39, 161 (1879).

[4] F. M. G. Johnson, THIS JOURNAL, 34, 911 (1912).

have shown that in common with most substances capable of absorbing moisture (even those not intrinsically hygroscopic) recently ignited Al_2O_3 absorbs within the first ten minutes' exposure to the atmosphere a large proportion of the water which it will absorb in twenty-four hours. Since, as frequently pointed out, the atmosphere in an ordinary desiccator which has recently been opened, is not greatly different from the atmosphere prevailing in the room, it is obvious that the all too common practice of placing in a desiccator ignited precipitates such as Al_2O_3, in uncovered crucibles, is likely to lead to even greater errors than are involved during the period required for rapid weighing. That a well fitting cover on a platinum crucible is efficient in preventing rapid absorption of moisture in the desiccator or on the balance, has been frequently demonstrated. Thus a crucible containing 0.10 g. ignited Al_2O_3, which when allowed to stand covered upon the balance, showed no appreciable change in weight in five minutes; gained as much as 0.0010 g. when uncovered for five minutes. For any accurate work in the determination of alumina, therefore, and especially in any experiments designed to test the temperature and period required for the ignition of such substances, it is absolutely essential that the crucible be well covered both in the desiccator and upon the balance.

2. *Temperature and Time of Ignition.*

Directions for the ignition of alumina[1] have usually prescribed blasting for periods varying from ten to thirty minutes, followed by successive short periods till constant weight is secured. While it is evident that in order to expel the last traces of moisture from such a precipitate, originally in a gelatinous condition, the use of a high temperature is desirable, it may be readily shown that long blasting is not necessary, at least for precipitates up to 0.2 g. Al_2O_3. In numerous experiments with 0.1 g. Al_2O_3 the total loss in weight produced by various periods of blasting following the first five minutes' blasting, was less than 0.0002 g. In order to show conclusively that dehydration is complete after five or ten minutes' blasting (at a temperature from 1100° to 1150°), a covered crucible (of especially pure platinum) containing 0.7 g. Al_2O_3, derived from three precipitates each of which had been blasted for five minutes, was again blasted for five minutes, and placed in a vacuum sulfuric acid desiccator, which was quickly exhausted. After cooling, the crucible was quickly weighed (against a tared crucible) and was then heated for three periods of ten minutes each to a temperature of 1440° to 1460° in an electric furnace.[2]

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[1] H. Moissan, *Compt. rend.*, **121**, 851 (1895); W. H. Daudt, *J. Ind. Eng. Chem.*, **7**, 847 (1915); P. H. Walker and J. B. Wilson, *Chem. Eng.*, **16**, 159 (1912), and numerous text books.

[2] Thanks are due to Messrs. R. B. Sosman and J. C. Hostetter of the Geophysical Laboratory for assisting in these high temperature experiments (in 1912).

The results of the experiment were as follows:

TABLE II.

Ignition of Al_2O_3.

	Weight against tare. Grams.	
Empty crucible	3.1665 g.	
Including Al_2O_3 (previously blasted but exposed in transfer)	3.8953	
After five minutes' blasting	3.8943	
Weight of Al_2O_3	....	0.7278
After 10 minutes at 1440–1460°	3.8943	
Additional 10 minutes at 1440–1460°	3.8941	
Additional 10 minutes at 1440–1460°	3.8940	
Weight of empty crucible after brushing out precipitate	3.1662	
Weight of Al_2O_3 after heating	....	0.7278

From these results it is evident that, making allowance for the loss in weight of the platinum crucible (0.0003 g.), exposure to a temperature of over 1400°, produced no appreciable change in weight of Al_2O_3 previously blasted for not over fifteen minutes.

From these results it is apparent that the continued losses in weight noted by some authors upon successive blastings of Al_2O_3 were probably due, not to further dehydration of the precipitate, but to losses in weight of the crucibles (which in commercial platinum may be quite appreciable); or, in case the crucibles were not covered while in the desiccator and on the balance, to a decrease in the hygroscopicity of the precipitate. In other words, at no time was the true anhydrous weight obtained, but always a weight including some amount of absorbed moisture, which amount decreases (and may become almost negligible) after the precipitate has been heated to high temperatures for a considerable period. Owing to the frequent failure to mention whether the crucibles were covered during the ignition and weighing, it is impossible to determine in which cases the above criticism applies. Such omissions indicate, however, a lack of appreciation of the importance of covering the crucibles.

3. *Effect of Ammonium Chloride upon the Ignition.*

The still prevalent misconception that when aluminium hydroxide containing ammonium chloride is ignited, there is loss of aluminium, dates back at least to 1875.[1] It has been disproven so frequently[2] that it would be superfluous to dwell upon it were it not for the fact that it is still referred to in recent text books. The following experiments, while probably not essential to disprove this conception, are perhaps of interest in still further demonstrating the absence of such an effect. Measured portions of a pure $AlCl_3$ solution were evaporated to small volumes in

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[1] C. R. Fresenius, "Quantitative Analysis," 6 Ger. edition (1875).

[2] W. F. Hillebrand, U. S. Geol. Survey, *Bull.* 422, 99 (1910); Allen and Gottschalk, *Am. Chem. J.*, 24, 292–304 (1900); W. H. Daudt, *J. Ind. Eng. Chem.*, 7, 847 (1915).

weighed platinum crucibles, after which pure ammonia in slight excess was added. Evaporation was continued to dryness and the residues were heated till expulsion of all ammonium salts, and finally blasted and weighed. The results, together with those obtained by the method of precipitation, etc., recommended below (which had been found to give accurate results with metallic aluminium) are shown in Table III.

TABLE III.

Effect of Ammonium Chloride upon Ignition.

Method.	Direct evaporation.		Precipitation.			
Al_2O_3 from 50 cc. $AlCl_3$......	0.0998	0.0997	0.1002	0.1001	0.1000	0.0999

From Table III it may be seen that in Expts. 1 and 2, where the aluminium hydroxide was certainly in very intimate contact with an excess of ammonium chloride, any loss of aluminium by volatilization was so small as to be negligible. Moreover, the weights in the last four experiments include corrections for the filter ash, and for known small impurities in the reagents and water, and therefore are probably somewhat less accurate than those obtained by direct evaporation.

VIII. Procedure Recommended.

From the foregoing considerations the following conditions are recommended for the determination of aluminium hydroxide: To the solution containing at least 5 g. of ammonium chloride per 200 cc. of solution (or an equivalent amount of hydrochloric acid) add a few drops of methyl red (0.2% alcoholic solution) and heat just to boiling. Carefully add dilute ammonium hydroxide dropwise until the color of the solution changes to a distinct yellow. Boil the solution for one to two minutes, and filter at once. Wash the precipitate thoroughly with hot 2% ammonium chloride (or nitrate) solution. Ignite in a platinum crucible, and after the carbon is all burned off blast for five minutes, cover the crucible and place it in a desiccator till cool. Weigh (covered) as rapidly as possible. A second blasting of five minutes is desirable, especially as it permits a more rapid weighing, and consequently probably more accurate results.

IX. Confirmatory Experiments.

A weakness of many of the published researches upon the determination of aluminium is the lack of suitable standards by which to test the proposed methods. The use for this purpose of hydrated salts of possibly uncertain hydration, such as the alums, is not to be recommended for accurate work, and in the few cases where metallic aluminium has been used, no detailed evidence of the purity has been presented. The following few experiments, though by no means exhaustive, show that the method just described will yield results accurate to at least one part in three hundred and probably better.

Two samples of the purest aluminium that could be obtained in 1912 from the Aluminum Company of American were analyzed by the methods described by J. O. Handy,[1] yielding the following results for the only elements that could be detected:

TABLE IV.

Analysis of Aluminium.

Sample.	A.	B.
Silicon	0.13%	0.16%
Copper	0.01	0.01
Iron	0.25	0.17
Aluminium (diff.)	99.61	99.66

Weighed portions (about 1.3 g.) of these samples were dissolved in hydrochloric acid and the solutions were oxidized with a small amount of nitric acid, and filtered to remove silicon. The filtrates were diluted to measured volumes and aliquots used for the determination of aluminium as above described, about 0.25 g. of Al_2O_3 being weighed in each determination. The ammonia was redistilled and all reagents carefully tested and found free from appreciable contamination. The weights of precipitates were corrected for the filter ash, and for the amount of Fe_2O_3 corresponding to the iron found by the previous analysis. The results are shown in Table V.[2]

TABLE V.

Aluminium Determination in Metallic Aluminium.

			Found.		Al %.	
Expt.	Sample.	Weight of Sample. Gram.	Al_2O_3. Gram.	Al. Gram.	Found.	By diff.
1	A	0.12980	0.2445	0.12967	99.90	99.61
2	A	0.12980	0.2443	0.12956	99.82	...
3	B	0.12884	0.2428	0.12877	99.95	99.66

X. Conclusions.

From the above experiments the following conclusions may be drawn, many of which simply confirm those of previous investigators:

(1) From observations made with a hydrogen electrode and with suitable indicators, it was found that the precipitation of aluminium

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[1] THIS JOURNAL, 18, 768 (1896).

[2] In calculating the weight of aluminium present in the Al_2O_3 the 1916 atomic weight of Al = 27.1, has been used. It is at least interesting, though probably not significant with so few experiments, to note that if the round atomic weight 27 be used for Al, the values for % Al found, become, respectively, 99.73 and 99.67 for A, and 99.78 for B, *i. e.*, approaching the amount found by difference, well within the experiment limit. No probable source of error in the determinations in Table V is likely to account for the existing discrepancies, amounting to from 0.0006 to 0.0008 g. Al_2O_3. More experiments are required to throw light upon these discrepancies. The point is merely mentioned as of interest in connection with the statement of F. W. Clarke ("Recalculation of the Atomic Weights," p. 268, 3rd edition (1910)) that "the atomic weight of aluminium needs reinvestigation."

hydroxide by ammonium hydroxide is complete when $[H^+] = 10^{-6.5}$ to $10^{-7.5}$, points approximately defined by the color change of methyl red and of rosolic acid.

(2) The presence of ammonium chloride during precipitation is advantageous in limiting the alkalinity, and in coagulating the precipitate.

(3) Solutions of ammonium nitrate and chloride are equally satisfactory for washing the precipitate.

(4) The conditions of precipitation recommended are favorable for the simultaneous precipitation of aluminium and ferric hydroxides; and for their separation from calcium, strontium, barium, and magnesium.

(5) Crucibles containing ignited alumina should be kept covered in the desiccator and on the balance.

(6) For precipitates of from 0.1 to 0.2 g. Al_2O_3, five or ten minutes' blasting is sufficient.

(7) The presence of ammonium chloride during ignition causes no appreciable loss of alumina.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF VIRGINIA.]

THE ESTIMATION OF VANADIC ACID, AFTER REDUCTION BY METALLIC SILVER.

BY GRAHAM EDGAR.

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Among the many reactions of vanadic acid to be found in the literature, that with metallic silver seems to have been almost overlooked by the numerous investigators who have studied the element vanadium. The only reference which the writer has been able to find bearing at all on this subject is the statement in a paper by Campbell and Griffin[1] that "silver, lead, copper and other elements were tried (as reducing agents on mixed uranyl and vanadyl solutions) but * * * offered no advantages for this purpose." It is true that Perkins[2] reduced vanadic acid to the tetroxide by the action of hydriodic acid and metallic silver, but he considered that the function of the silver was merely that of absorbing the iodine set free in the reaction, and the possibility of any direct action between the silver and vanadic acid seems not to have been thought of.

That silver should be capable of reducing pentavalent vanadium to tetravalent could be predicted with a considerable degree of certainty by consideration of the values obtained by Rutter[3] for the oxidizing potentials of solutions of vanadic acid, and also from the fact that silver is

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[1] *J. Ind. Eng. Chem.*, **1**, 661 (1909).

[2] *Am. J. Sci.*, [4] **29**, 540.

[3] *Z. anorg. Chem.*, **52**, 368 (1907).