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T 307

"The Determination of Aluminium."

THESIS

**Presented to the Faculty of the Mo. School of Mines for the Degree of Master of Science in
Chemistry,**

BY

V. H. Gottschalk.

JUNE, 1900.

**A NEW METHOD FOR THE QUANTITATIVE
DETERMINATION OF ALUMINIUM.**

The methods available for the determination of aluminium have all some inherent difficulties, which render the ^{nti} qualitative estimation of that metal, ~~is~~ even ⁱⁿ rather simple cases, a tedious operation. This applies particularly to the method in which ammonium hydrate is used as a precipitant. The result^{ing} hydrate of aluminium is bulky and gelatinous, having in a marked degree the property of clogging filters, thus impeding still further, the slow process of washing by decantation. Still other objectionable features of this precipitate are:- length of time required for its settling, and its partial solubility in slight excess of the precipitant.

Ammonium carbonate is recommended by some as giving a precipitate somewhat denser than that obtained by ammonium hydrate; Our experience with the precipitate obtained in this manner, hardly confirms this statement. If the precipitate thus obtained possesses any advantages, they are but slight, and not of sufficient importance to mention.

A third method, ~~for~~ which, it has been claimed, ~~that it~~ leads to a dense, rapidly settling precipitate, which filters easily, is the precipitation as aluminium hydroxide ^{form} ~~out of~~ a sodium or potassium alminate solution by boiling with ammonium chloride. This method, also, have we tested, and found to be no improvement on the ordinary one. Besides yielding a precipitate, equally ill-adapted to the mechanical operations of gravimetric analysis, it introduces additional difficulties; namely, the danger of incomplete precipitation and ~~the~~ contamination ^{with} the products of the prolonged action of a boiling alkaline solution on glass.

Still other methods have been proposed. The "Basic acetate" method, although adapted to the analogous determination of iron, is out of the question here because of the well known fact that it precipitates an aluminium solution incompletely. It may be stated here, *en passant*, that in qualitative analysis, also, it is not as well adapted as ammonium hydroxide, even with solution of pure aluminium, as it gives a much less manageable product.

The determination of aluminium as phosphate has also been tried. *We* find ~~one~~ this precipitate equally as gelatinous and difficult to handle as ^{the} others; besides, there seems to be some doubt as to the composition of the precipitate to be weighed #

For a determination of aluminium then it would seem that one would best choose the ammonium method. For the best manner of carrying out this determination we draw attention to the following ~~remarks~~

The first point to be observed is to obtain complete precipitation; this requires the avoidance of an excess of ammonia, and necessitates boiling in ^{the} presence of small amounts of ammonium chloride, ~~points that are~~ ^{as is} well known. After washing once by decantation it should be thrown on a filter and washed there several times with gentle suction and finally sucked as dry as possible. It is best to allow to remain thus some time:—It is then transferred by washing through the broken filter with hot water ^{into} with the first beaker; one or two boilings and decantation, now follow, — after which the precipitate is again transferred to ^{the} filter # Drown (Jr. Am. I.M.E. 20 p. 242) Also recent works by Veitch (Jr. Am. Ch. 3. 22 p. 246) where conditions are specified under which a constant composition (that of the normal phosphate) may be obtained for the final precipitate.

washed several times with hot water, ignited, etc. This treatment consumes much less time than if the decantations follow one another without the intermediate transference to the filter paper; furthermore it seems to wash much more effectively: others have already specified this mode of treatment;—none have however referred to the fact, that it invariably leads to a precipitate that is apparently more compact, and which settles much faster, and filters comparatively readily. However there is still one danger to apprehend;—namely, the tendency of the aluminium hydroxide to go into colloidal solution. As is well known, this is liable to occur, when all other salts have been washed out of the hydrated alumina. We have found further, that the addition of large amounts of boiling water favors this solution:—in fact, we have the extraordinary experience of almost complete solution of a precipitate of about one hundred milligrams, while adding one hundred and fifty cc. boiling water for the fourth washing (where the precipitate had not been thrown onto the filter first). The amounts thus dissolved may vary from traces to almost all of the precipitate, according to conditions not readily controlled. After having tried various means for its prevention, we have concluded that gentle boiling with a few drops of ammonium chloride solution, produces the desired effect: further, several especially designed experiments gave evidence that small amounts of ammonium chloride in the precipitate to be ignited had but slight effect on the results: of course the presence of large amounts of ammonium chloride in the precipitate to be ignited should be avoided.

0.243 grms. pure alumina (after 15 minutes ignition in blast); added 5 cc ammonium chloride solution (1 cc approximately 10 milligrams ammonium chloride): evaporated to dryness in this crucible, ignited and weighed again; weight of aluminium 0.2430 grms. loss 0.0008 grms. Repeated this experiment with following results:

Alum. taken	0.3599
after	0.3595
Less	.0004

Handy (J. Am. Chem. Soc. 18. p.766) draws attention to another property of pure alumina, which has, hitherto, not received sufficient emphasis: we refer to its extreme hydro^{sc}opicity, exceeding as Handy says, that of lime. We found that 0.1874 grams Al_2O_3 , after having stood in the balance case several days, gained eight milligrams H_2O , that is, there was 4.37 % H_2O taken up. A second portion of 0.1874 grams. Al_2O_3 gained 9.3 milligrams H_2O 5.07 percent. H_2O taken up. Al_2O_3 after having been heated in a ^{gasoline} gas muffle furnace to 1150⁰ ~~degrees~~ C. (as measured by a platinum-rhodium couple) was just as hydroscopic as before.

Handy has also mentioned the necessity of heating the alumina precipitate in the hottest blast-lamp flame for several (five to fifteen) minutes: we wish to lay stress on this observation as one of importance. The method we adopted for obtaining uniform, and correct weights of the precipitate is as follows: The crucible is heated for five to ten minutes in the blast, placed in a sulphuric acid desiccator with air-tight cover:- cooled fifteen minutes, and weighed as accurately as possible: the heating and cooling repeated, the weights as found before placed on the balance pan less 0.3 to 0.6 milligrams; the crucible placed on the the other pan without delay, the beam allowed to swing, and from the first complete vibration of the pointer (with a knowledge of the sensibility of the balance), it is estimated whether or not the counter-balancing weights are correct to 0.1 milligram, if not, the heating, cooling, etc., repeated until ^{the} ~~its~~ weight ^{the} on first swing is obtained. The crucible containing the precipitate is now heated, cooled, and weighed in exactly the same manner. In this way, any error due to possible change in the weight of the crucible or in the

precipitate due to water absorbed is avoided. All figures quoted in this paper, were obtained in this way, using a set of corrected weights.

With care and patience, a fairly good and reliable determination of aluminium can be made in this way. The gelatinous nature of the precipitate, however, requires a long time for washing and filtering, even after the precipitate has been thrown on the filter, and thus rendered of a better form for the operations to follow.

Precipitation by Means of Carbon Dioxide.

It has often been observed, ^{that} by passing carbon dioxide through an aluminate solution, there is obtained a compact, crystalline precipitate. We have succeeded in making this precipitate the basis of a quantitative estimation of aluminium. By this method of precipitation, a dense, white, crystalline product is produced, which settles rapidly and filters with great ease. There is always a slight amount of the precipitate which adheres more or less tenaciously (according to the conditions of precipitation) to the sides of the containing vessel and tube conducting the carbon dioxide, at the level of the liquid. One of the most noteworthy properties of the precipitate is its insolubility in water, being less soluble than barium sulphate.

We found, that between 17 degrees and 21 degrees.C.

1 part dissolves in 625000 parts water.

1 " " "66 2251 parts water.

Average 1 part in 643625.

These solubility determinations were made as follows:- several hundred milligrams of the air dried precipitate were put in a litre flask filled with distilled water and allowed to stand for a week or ten days, temperature being noted. A blank (litre of distilled

water) was placed beside the other to stand for the same length of time. The contents of first flask were then filtered through a dry filter into a clean dry litre flask. When ^{just} ~~first~~ one litre of the liquid had filtered through, it and the check were separately evaporated to dryness in large platinum dishes, transferred to large platinum crucibles, ~~gently dried,~~ ignited and weighed. ^{the} residue in check (representing the solubility of glass) ^{was then} subtracted. The same portion of the precipitate was used several times in this way, until two successive determinations gave approximately the same result; that is, until all traces of adhering soluble matter had been removed.

Chemically the precipitate seems to be a basic carbonate of aluminium, retaining some alkali. Day (Am. Ch. J. 19, p 700) has worked with compounds obtained under somewhat different conditions. We have ~~however~~ confirmed many of his statements regarding the nature and behavior of the supposed basic carbonate. We noticed further that the concentration, up to a certain limit, and the excess of alkali present ^{influenced} ~~effected~~ the amount of carbon dioxide and potassium oxide in the compound. For our purpose, a concentration ^{is} equivalent to one gram Al_2O_3 in 1500 c.c. gave the best results..

Greater dilution, up to one gram Al_2O_3 in 3000 c.c. seemed to have no effect on the composition of the precipitate, although the precipitate became finer and consequently more difficult of filtration as the concentration ^{diminished,} ~~increased~~.

Several preparations were made as follows: recrystallized ammonium alum was dissolved in water freshly distilled out of a tin lined vessel. The necessary amount of potassium hydroxide was then added, avoiding any excess, after which the whole was properly diluted

and a moderately fast stream of carbon dioxide passed for about one hour: (it had previously been found, that, except to insure complete precipitation, the time of passing the gas had no effect on the physical or chemical properties of the precipitate). After settling and washing by decantation with cold water several times, the precipitate was thrown on a filter and washed with cold water, then air-dried. Following ^{is} the analysis (washed twenty times).

Preparation I. 0.2144 grams gave 0.1092 gms. Al_2O_3 and .0027 gm K_2SO_4 : 0.3813 gms. lost 0.1825 gms. on ignition.

Preparation II 0.7440 gms. ^{gave} 0.3144 gms. H_2O , and 0.0430 gms.

CO_2

Analysis.

	I	II
Al_2O_3	50.94%	- - -
K_2O	.68	- - -
$H_2O + CO_2$	<u>47.87</u>	42.26 H_2O 5.78 CO_2
	99.49	

The Al_2O_3 and K_2SO_4 were determined in one portion by precipitation with ammonia, washing and evaporating the filtrate almost to dryness. The small amount of Al_2O_3 which usually separates now, is removed and added to the main Al_2O_3 precipitate. The filtrate ^{was} evaporated to dryness in a large crucible, ~~then~~ evaporated once or twice with several drops of sulphuric acid, finally ignited gently, with ammonium carbonate, heated to dull redness and weighed as K_2SO_4 . A blank is made at the same time, treated with the same amounts of the same reagents and water throughout, and correction made. H_2O and CO_2 ^{were} determined in ^{a separate} one portion by heating in ^{a hard-glass tube} stream of air passed through ~~drying and soda-lime tower~~ and absorbing ^{the} H_2O and CO_2 evolved in ~~an ordinary~~ ^{at 0.5, and H_2SO_4 respectively.}

(8)

As Day observed, the "basic carbonate" undergoes a change by the action of hot water. We noticed that when the precipitate is treated with water, at or near its boiling point, it becomes more voluminous and less opaque, in fact, seemed to revert to the ordinary $\text{Al}(\text{OH})_3$. Several degrees below the boiling temperature, this change is not so complete. Wishing to avoid any encounter with a slowly filtering precipitate, we at first carried out all our washings with water from sixty-five to eighty-five degrees C., or with cold water, or with both. With this method of washing we obtained a series of results on C.P. ammonium alum, purified by recrystallization; we append all results.

(9)

Grams Alum Taken	Theoretical Grams Al_2O_3	Found Grams Al_2O_3	Difference in Milligrams.
1.2144	0.13686	0.13737	+0.51
1.0289	.11596	.11737	+1.41
1.1111	.12521	.12550	+0.29
0.9314	.10495	.10530	+0.35
1.4191	.15993	.15921	-0.72
1.1545	.13010	.12911	-0.99
1.1632	.13100	.12966	-1.44
1.3483	.15200	.15230	+0.30
1.2818	.14450	.14460	+0.10
1.6831	.18969	.18796	-1.73
1.1086	.12496	.12648	+1.54
1.0359	.11675	.11881	+2.00
1.1651	.13130	.13229	+0.99
1.0164	.11455	.11548	+0.93
1.1964	.13483	.13482	-0.01
1.1256	.12690	.12272	-4.18

We have given all our figures, though many were obtained under conditions that proved later not to be the best, in fact the series may be taken to represent a series of trials as to the best method of washing. All figures are corrected for impurities in the potassium hydrate used #, and for ash. This correction is

All samples of KOH and NaOH analyzed by us contained varying amounts of impurities (made up of insoluble residue, iron and aluminium oxide). This was ^{the} ~~ture~~ also of ~~some~~ "NaOH by Sodium". "KOH by Alcohol" and other "C.P." samples.

necessary, as it was found that the precipitate carries these ^{impurities} matters down with it out of solution #.

Looking over the results on alum, the average seems to be a fair one (rejecting two determinations in which loss was known to have occurred), being 0.4 milligrams high. The method certainly was very rapid as compared to the best that could be done with ammonia. In general the treatment consisted of adding a known amount of KOH solution (roughly from a burette), precipitating with CO_2 , allowing to settle; decanting, washing several times (three to eight times) by decantation with cold water, throwing on the filter, washing there (four to six times) with cold water, breaking the filter and washing through into the same beaker with warm water, then washing three to five times by decantation with hot water, and finally washing three to six times with hot water on the filter. The small amount adhering to the beaker and gas conducting tubes was dissolved in one to two c.c. hot concentrated HCl, precipitated with ammonia, filtered and washed on a separate filter. The three filters and contents ^{washed} then ignited and weighed (in the manner indicated previously) and the necessary corrections made.

The attempting to apply the above method to the analysis of Aluminium metal, gave high results. Even after long and protracted washing the ignited precipitates were regularly found two to fifteen milligrams too high

Where great exactness is sought, care must be taken to choose pure water. In the present work we have used water distilled out of tin-lined vessels and condensed in a tin worm. Even then, we found appreciable amounts of residue on ignition. Water that has been distilled out of glass vessels or that has been stored for any time will give results that are too high. See Fresenius Quant. Anal. 6th German Edition p. Vol. II p. 798

After trying various schemes to overcome this, we decided to try boiling the precipitate with the water ~~for washing~~. As before observed, the precipitate underwent a change in appearance, it lost its crystalline structure and became more voluminous, however it settled rapidly and well, and filtered better than expected. In fact, although in some respects like the ammonia precipitate in appearance and behaviour, there is no comparison between the latter and the former as regards ease with which they filter, this having been determined, we examined the boiled precipitate.

Several preparations were made as before, except that instead of washing with cold water, the beaker and contents after addition of from one hundred and fifty to three hundred c.c. water, were boiled, allowed to settle and decanted several times. As the water began to boil, the precipitate rose to the surface of the water and there was ^vnoticeable evolution of CO_2 : When boiled too long the further management became more difficult. Following are the analyses of two such preparations.

Preparation I. (Boiled sixt times, air dried).

0.3353 lost 0.1146 grams on ignition.

.3461 grams gave 0.2284 gms. Al_2O_3 and .0023 gms K_2SO_4

Analysis I		calculated for $\text{Al}(\text{OH})_3$
Al_2O_3	65.70	65.43
H_2O	34.18	34.57
K_2O	<u>.36</u>	<u>0.00</u>
	100.24	100.00

Preparation II (Boiled eight times, air-dried)

0.2393 grams gave 0.1573 Al_2O_3 and no K_2SO_4

Al_2O_3 65.65%; Calculated for $\text{Al}(\text{OH})_3$ 65.43 %.

So that boiling transforms the basic carbonate to the ordinary normal hydroxide.

We now began another series of determinations of ^{aluminium} the metal, this time with boiling. Here however the boiling water caused the aluminium hydrate to go into solution to some extent so that the results were too low, while ^{several} from five to thirty milligrams $\text{Al}(\text{OH})_3$ could be recovered from the filtrate. By applying the remedy suggested in our direction for the determination by ammonia, -viz. addition of NH_4Cl , we have obviated this difficulty also.

We analysed two entirely different samples of sheet aluminium with following results:

No. 1. 1.0403 grams metal gave 0.0083 gms SiO_2 (total).
 1.0037 " " " 0.0374 milli grams Fe.

The first determination (total Si) was made according to directions given by Handy (J.A.M. Ch. Soc. 18 p. 768).

The determination of iron was made colorimetrically. As standard solution, we used a solution of $\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$ acidified with HCl, each c.c. of this solution corresponding to .0312 mgs. Fe.

The solution of the metal was measured from a burette, oxidized with pure chlorine water, diluted to 50 c.c. and the number of c.c. of standard, (oxidized also by pure chlorine water) and diluted to 50 cc. was determined that gave the same shade of color, after 2 cc. of a 10% KCNS solution was added to both. In the above case, 1.2 cc. of standard matched 10 cc. of a solution of 1.0037 grams sheet metal diluted to two hundred and fifty c.c.

Number II.

1.1878 grams metal gave 14.2 mgs. SiO_2 (total)
 1.0009 grams metal in 500 c/c. were taken for iron estimation.

Treated as directed before and against same standard solution.
 5 c.c. of this solution matched 1.4 cc. of standard
 \therefore 1.0009 grams metal contain 0.03136 milligrams Fe.

No other constituent could be discovered in the two samples of metal taken; therefore analyses are

	No. I	No. II
Total Si	0.37%	0.56%
Fe	0.094	0.44
Al (by difference)	99.536	99.00

Two solutions were now made.

Sol. I contained 1.0023 grams of metal #1 in 500 c.c.

" II " 1.0009 " " " #2 in 500 c.c.

The course of the analysis and preparation of the compounds showed that at each successive boiling, the amount of K_2O still retained, diminished. The last traces were difficult to remove. Boiling twice with NH_4Cl however accomplished the removal completely, as well as prevented colloidal solution. This is doubtless due to reaction between the ammonium salt and potassium carbonate as follows

$$K_2CO_3 + 2NH_4Cl = 2KCl + 2NH_3 + H_2O + CO_2$$

	Grams KOH# used	Grams impurity in KOH & ash of 3 filters.	Grams of Pp and impurities	Grams Al ₂ O ₃ Fe ₂ O ₃	Theor etical in gms.	Differ- in milli grams
50 c.c. #Sol. #1	1.560	0.00104	0.18939	0.18835	0.18825	+ 0.10
50 C.C. " 1	1.796	0.00111	0.18953	0.18843	0.18825	, +0.17
50 C.C. " #2	1.653	0.00109	0.18753	0.18744	0.18746	-0.02
50 C C. " #2	1.630	0.00107	0.18808	0.18701	0.18746	-0.45
50 cc. " #2	1.630	0.00107	0.18853	0.18746	0.18746	0.00
50/ cc " #2	1.503	.00101	0.18780	0.18679	0.18746	-0.67

KOH contained 0.95% Impurities (Insoluble $Fe_2O_3 + Al_2O_3$)

Above are analyses on the two solutions of the metal.

We can safely assert then that we have here a very accurate method for the determination of aluminium, which takes much less time than is required by the older methods. It remains still to state that several experiments were made to determine the effect of this method of procedure on iron. It was found that an excess of KOH and carbonation would give results for iron, on the metal alone and on iron and aluminium together, which showed no difference from the figure as obtained by the ordinary methods.

The following are the directions in detail:

To the solution containing the aluminium add just enough KOH, freshly dissolved, to redissolve the precipitate first formed (the solution may remain very slightly turbid). Dilute to the approximate concentration of 200 milligrams Al(OH)₃ to ~~150~~ 200 c.c. Pass a rapid stream of CO₂ for 20- to 30 minutes, allow to settle, decant through a filter, finally transfer the main precipitate on the filter (the small amount adhering to the beaker may be disregarded now, as the precipitate is to be washed back into this same beaker). Wash on the filter, ^{several times; break the filter} and wash the contents back into the beaker. Add 100 to 150 c.c. water and a little ammonium chloride

Boil gently two or three minutes, allow to settle, decant. This boiling is then repeated. Now transfer to filter as completely as possible, and wash there several times more with hot water. The small amount still adhering to the glass, is dissolved in hot concentrated HCl, precipitated with ammonia, filtered and washed on a separate filter. The three filters and contents are ignited and weighed as before indicated. Correct for impurities in potash and for ash.

For ordinary determinations, where great accuracy is not required it is evident that the correction for potash, and the solution of the portion adhering to the glass may be omitted.

Of course the method is not applicable in presence of metals of the alkaline earth group and lithium.