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THESIS ON

" THE VOLUMETRIC DETERMINATION

OF FREE ACID and BASIC

ALUMINA IN ALUMINIUM SULPHATES. "

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By.- Thomas John Ireland Craig B.Sc.

May 9th.1910.

PART I.INTRODUCTION.
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This paper is chiefly concerned with the volumetric determination of free acid and basic alumina in aluminium sulphates and I shall first of all give an account of my experiments and describe the method arrived at therefrom in connection with aluminium sulphates.

The above method, however, is applicable to other soluble salts of alumina as for example the chloride and the acetate and I therefore propose to refer to these other salts in a subsequent part of this paper.

I propose also to touch upon the question of the volumetric determination of the "neutralisable" acid in aluminium sulphates and later of the same determination in other soluble salts of alumina, as, by a combination of the two analyses viz.- (1) the free acid or basic alumina and (2) the total "neutralisable" acid" one may arrive at the total amount of alumina present, due reckoning of course being made of other bases when such are present.

The method I hereinafter describe for determination of free acid or basic alumina in aluminium sulphates is applicable for determining the free acid or excess of base in a considerable number of salts of other bases such as ferric or ferrous oxides, chromic oxide, manganese oxide, zinc oxide etc. and I intend afterwards to go into the method as applied to other bases than alumina.

HISTORICAL.

The following methods have been proposed for the detection and determination of free acid and (in two cases) of basic Al_2O_3 in aluminium sulphates.

Erlenmeyer & Levinstein (1), treated with ammonium magnesium phosphate and titrated the free acid in the filtrate.

W.Stein (2) used ultramarine papers for the detection of free acid in sulphate of alumina.

C.Giseke (3) suggested two methods [1] the free acid is extracted with alcohol and titrated with normal soda and litmus, [2] is based on the behaviour of alums and free acid in presence of logwood, neutral salts give a characteristic deep violet color which changes to brown when free acid is present. The free acid is determined by comparison with solutions containing known amounts of alum and free acid.

G.Merz (4) also used logwood and very weak soda to determine free acid in alums.

O.Miller (5) recommended that the alcoholic extract of aluminium sulphates should be evaporated before titrating with alkali and methyl orange.

B.S.Proctor (6) studied the behaviour of free acid, in presence of various salts, towards methylorange and stated that after adding alkali and then acid to alum solution, the red color produced by the acid disappears in a short time through a part of the alumina precipitate dissolving and a permanent color is only obtained when all the Al_2O_3 is in solution.

H.Hagar (7) detected free acid in aluminium sulphates by adding about .25 gram of the finely powdered salt to a previously warmed mixture of 2 drops of gurjun balsam and 3 cc of acetic acid: on warming, a bright blue with traces of acid or a dark blue coloration in case of larger quantities, results.

E.Egger (8) applied Pettenkofer's reaction for bile to the detection of free acid in aluminium sulphate, alum etc.

- (1) J.B.1860,638. J.f.Prak.Chem.LXXXI,254,DRJ.158,126
- (2) Zeit.Anal.Chem.1866,V,35
- (3) Dingl.Poly.Jour.183,43
- (4) Dingl.Poly.Jour.220,229, J.B.1876,997.
- (5) Zeit.Anal.Chem (1884) XXIV,258.
- (6) New Remedies XI,338,Zeit.Anal.Chem(1885)XXIV,237.
- (7) Pham.C.H.1886,XXVII,440, J.S.C.I.1886,617.
- (8) Zeit.Anal.Chem.XXVII,725,J.S.C.I.1889,479.

R. Williams (1) stated that the substance should be digested at least 12 hours with alcohol, filtered and washed with the same agent and titrated at once with $\frac{7}{10}$ alkali and phenolphthalein. Evaporation of the alcohol is to be avoided as it causes loss of H_2SO_4 .

In Sutton's "Volumetric Analysis" 7th Edition 1896, p.50 is given a method for determining free acids and bases in earthy and metallic solutions by means of normal ammonio-cupric solution prepared by dissolving cupric sulphate or nitrate in warm water and adding ammonia to the clear solution until the bluish-green precipitate which first appears is nearly dissolved. The solution is then filtered and titrated by running it from a burette into normal acid. When the acid is in excess the blue-green precipitate which occurs when the drop falls into the acid solution disappears, but as soon as the exact **point** of saturation is reached the previously clear solution becomes turbid. The process is useful for determining free acid in zinc, copper, and magnesia salts and also in protoxides of iron, cobalt and nickel.

F. Beilstein & T. Grosset (2) gave a review of various methods of determining free acid in presence of neutral or acid salts. Erlenmeyer & Levinstein's method (see p.2) is only accurate when the double phosphate is freshly prepared. B & G. consider that the methods depending on the insolubility of the sulphates in alcohol, and on the direct titration with alkali employing one of the tropeolin colors as indicator are inaccurate. They give the following as the most reliable they know.-

Dissolve 1-2 grams of the substance, according to its richness in free SO_3 , in 5cc H_2O and add 5cc of a cold saturated neutral solution of sulphate of ammonia, allow to stand for quarter of an hour with repeated shaking and precipitate with 50cc of 95% alcohol. Filter wash with 50cc of 95% alcohol, evaporate the filtrate on the waterbath, dissolve the residue in water and titrate with decinormal KOH using litmus as indicator. The mean error of 6 tests was .15%. The samples varied in free acid from 1.27 to 5.89% of SO_3 .

H. de Keler & G. Lunge (3) Monit. Scient. 1896, 40 declare that the method for determination of free acid in aluminium sulphates consisting in the direct titration of the substance with tropeolin **D.D.** methyl orange &c. is inaccurate.

(1) Chem. News, 1889, LVI, 194.

(2) Zeit. Anal. Chem. XXIX, 73. J.S.C.I. 1890, 416.

(3) H. de Keler & G. Lunge Monit. Scient. 1896, 40.

L.Geschwind (1) states that free acid can be detected in aluminium sulphate by campeachy wood extract (1 part wood, 3 parts water, 1 part alcohol) the violet tinge of which becomes brown if free acid is present.

C.R.Gysander (2) suggested the following method for the determination of free acid in aluminium sulphates. It is based on the behaviour of sulphate of alumina to ultramarine. 2 grams of the sulphate in question are dissolved in 20 cc of distilled water and ultramarine is added. Then by comparing the time required for decolourisation after gently warming with the time required for standard tests, one is able to arrive at the free acid. To determine basic Al_2O_3 , .5 gram is taken, methyl orange and phenol phthaline are added then a measured amount of standard acid is run in and standard alkali is added until the color changes from pink to orange (not yellow). The difference between the acid and alkali used corresponds to the basic Al_2O_3 .

S.E.Moody (3) determined the free acid and basic Al_2O_3 in aluminium salts by treating them with KIO_3 & KI solution and ~~titrating~~ distilling and absorbing the liberated iodine in KI solution and titrating it with thiosulphate. $Al_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2Al(OH)_3 + 3K_2SO_4 + 6I$. The individual bases (if others are present) are determined separately and the SO_3 for each is calculated. The SO_3 found by the titration of the liberated Iodine is distributed among the bases according to their requirements and any left over is reckoned as free acid. Any less than that required to combine with all the bases is calculated to basic alumina.

A method which has been in use for some time among chemists who examine aluminium compounds is to use congo red as an indicator. It gives a blue color with acids and a red with bases. With a neutral sulphate of alumina it gives an intermediate color which however, the same person may at one time reckon as one tint and at another a different degree of color and for separate individuals to regularly hit off the exact time of neutrality is practically impossible. So many circumstances, such as the light, the presence of ferric sulphate, the amount used to spot with, and the small change of color for a relatively large addition of standard acid or alkali, interfere with the test and make it unreliable as an accurate method. It is however decidedly useful for technical purposes as one can easily distinguish with it between acid and basic sulphate of alumina and can to a certain

(1) "The Manufacture of Alum" 1901, 367.

(2) Chem. News (1901) LXXXIV, 298.

(3) Amer. J. Sci. 1906 [4] XXII, 483.

extent ascertain what the degree of acidity or basicity is.

Up to the present date no really satisfactory simple and rapid method of determining the free acid or basic alumina in aluminium sulphates appears to have been published. Aluminium sulphates of various kinds are now made and used to a very large extent. These sulphates are either basic, neutral, or acid, and vary in quality according to the amounts of Al_2O_3 , Fe_2O_3 or FeO , free SO_3 &c. which they may contain. Rapid, accurate and easy methods for determining the free SO_3 , Al_2O_3 , combined SO_3 and the basic alumina in commercial aluminium sulphates are greatly to be desired, and would prove decidedly useful both to the manufacturer and the consumer. Moreover a really good method for determining the free SO_3 in aluminium sulphates, rapidly and accurately on volumetric lines could be employed by both seller and buyer as a standard method and would save disputing and much laborious gravimetric analysis.

For years I have been on the lookout for such a method and recently it occurred to me that if the aluminium sulphate could be removed from the sphere of action or rendered inactive by a neutral reagent, which would not combine with the free acid, the determination of the latter by simple titration with standard alkali and a suitable indicator might easily be accomplished. Having commenced investigations on the lines hereinafter described I meanwhile studied the already published literature on the subject and found that BAUD (Ann.Chim.Phys.[8]I,1904,60) states that aluminium fluoride (AlF_3) in water solution reacts acid towards litmus and neutral to helianthin and therefore by means of the latter indicator any free hydrofluoric acid may be determined in presence of aluminium fluoride (AlF_3).

So far, however, as I can ascertain no one appears to have published the fact that double fluoride of aluminium and potassium is neutral to phenolphthalein; and no one hitherto appears to have based a volumetric process for determining free acid or basic alumina, as the case may be, in aluminium sulphates, on this property of aluminium potassium fluoride.

The method hereinafter described for the determination of free acid in sulphates of alumina and also of basic alumina in the same, is based upon the remarkable fact that precipitated double fluoride of aluminium and potassium in presence of a moderate excess of

potassium fluoride is not attacked by dilute acid or dilute caustic alkali (even at the boil). When therefore aluminium sulphate (or other soluble salt of aluminium) is treated with potassium fluoride in excess (twice the theoretical amount is ample) all the alumina is carried out of solution as a double aluminium potassium fluoride according to the following equation.- $\text{Al}_2(\text{SO}_4)_3 + 12 \text{KF} = 2(\text{AlF}_3 \cdot 3\text{KF}) + 3\text{K}_2\text{SO}_4$. The precipitate of insoluble $\text{AlF}_3 \cdot 3\text{KF}$ is colourless and transparent and does not interfere with the subsequent titration.

Berzelius (Lehrbuch 3 Aufl. 4, 324. Pogg 1.43) in 1822 noted that a solution of alum gives a precipitate with potassium fluoride only when an excess of the latter is used. This fact I am able to confirm as if one takes a solution of alum or sulphate of alumina and adds to it gradually a solution of potassium fluoride, a precipitate is at first locally formed and dissolves in the solution. Later a slight permanent precipitate forms and this increases with further addition of potassium fluoride and finally all the alumina is precipitated. If a little phenolphthalein be added to some of the pure precipitated aluminium potassium fluoride suspended in cold distilled water and dilute alkali added, I find that one drop of alkali instantly produces a strong permanent red color, thus showing that the above double fluoride is neutral to phenolphthalein. It is of course well known that aluminium sulphate reacts acid towards phenolphthalein. This fact has been noted by Thompson (C.N. XLVII, 135) and has been utilized by Bayer (Zeit. Anal. Chem. XXV, 180) E.B. (Zeit. Anal. Chem. XXV, 183) Lunge (Zeit. Angew. Chem 1890 293) and Gysander (CN. LXXXIV 296) to form the basis of a volumetric method for determining the total "neutralisable" acid in soluble aluminium salts by titrating them with standard alkali.

I have also carefully and exhaustively studied this method and I shall hereinafter describe my experimental investigations thereupon and explain in detail what I find to be the most accurate and reliable manner of carrying out this volumetric determination of the "neutralisable" acid.

By finding the total "neutralisable" acid in a sulphate of alumina and then the free acid or basic alumina (according to which is present) one is able to arrive at the total alumina in the material in question. It is understood of course that if any other base is present combined with "neutralisable" acid it must be separately determined and allowed for as regards its equivalent of SO_3 .

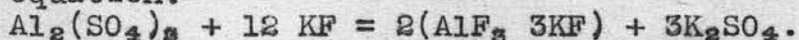
Exactly neutral sulphates of alumina are exceptional. The manufactured articles found in commerce are as a rule either more or less acid or else somewhat basic and therefore the method of determining the Al_2O_3 in them by titration with standard alkali and phenolphthalein is of little service without a reliable method of also determining the free acid or basic alumina as the case may be, and also of proving that the salt is neutral when it is neither acid nor basic.

Other bases combined with "neutralisable" acid which are often present in appreciable amount in the sulphates of alumina of commerce are Fe_2O_3 , FeO , TiO_2 , and (in American products) sometimes ZnO through metallic zinc having been used to reduce the Fe_2O_3 to FeO in order to improve the colour of the manufactured article. I therefore deemed it necessary to study the behaviour of salts of these bases when they are treated in the same way as aluminium sulphate is treated for the determination of the neutralisable acid, and also for the determination of free acid or excess of base, and I shall deal with these other bases in due course after I have first described the investigations carried out in regard to pure sulphate of alumina.

Experimental investigations on the
determination of free acid and basic
alumina in sulphates of alumina.

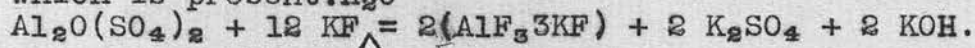
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On pages 5 and 6 I have already described the principles on which this new method is based. I may here however briefly repeat that it depends on the aluminium sulphate (and other such like salts when they are present, e.g. sulphates of Fe_2O_3 , FeO , ZnO) being decomposed by the addition of a sufficient excess of pure neutral potassium fluoride, according to this equation.-



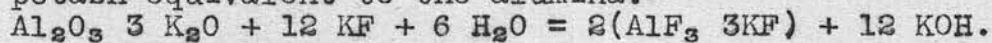
In sulphates containing free acid the latter remains in solution and is determined by means of standard alkali and phenolphthalein. When a neutral sulphate of alumina is treated in the same way, a solution results which is instantly turned a permanent red by one drop of $\frac{1}{2}$ alkali. When on the other hand

a soluble basic Sulphate of alumina is treated with excess of pure neutral potassium fluoride, caustic alkali is liberated equivalent to the basic Al_2O_3 which is present. H_2O



The caustic alkali thus generated is easily determined by titrating with standard acid and phenolphthalein as indicator. The standard acid and alkali should contain no alumina or other substance acting similarly towards potassium fluoride. Acid and alkali which have been standardised using phenolphthalein as indicator in the cold can be made to agree with each other whether alumina is present or not, but if the standard acid or alkali contain alumina then, when they are tested against one another in presence of pure neutral KF they will be found to differ in proportion to the Al_2O_3 present. Thus when aluminium sulphate is in the acid the KF carries down the Al_2O_3 and neutralises its equivalent of SO_3 . $\text{Al}_2\text{O}_3 \cdot 3 \text{SO}_3 + 12 \text{KF} = 2(\text{AlF}_3 \cdot 3 \text{KF}) + 3 \text{K}_2\text{SO}_4$.

In the second place when the alkali contains aluminate the potassium fluoride generates caustic potash equivalent to the alumina.-



Potassium Fluoride.

The purest obtainable salt should be used. The potassium fluoride employed in my experiments was a "chemically pure" quality obtained from de Haën, Seelze, near Hanover, at 1/4 per lb. Its solution was prepared by dissolving 1000 grams in distilled water to form a solution of 1.450 in the cold, neutralising with a little pure KOH so that 10 cc. in 50 cc. water showed a faint pink with phenolphthalein, filtering and diluting to 1.350 at 18°C.

The solution is best preserved in a wax-lined glass bottle or other vessel which it will not corrode. Its action on glass is very slow but in time the glass appears to be slightly dissolved and the solution becomes alkaline.

De Haën also supplies a "pure" quality of KF at 8d. per lb. which answers quite well.

Standard acid and alkali.

The acid is prepared in the usual way from pure sulphuric acid and distilled water and standardized against pure anhydrous sodium carbonate using methyl orange as indicator.

The alkali is prepared from caustic potash which has been purified by boiling with slaked lime, settling

and decanting the clear liquor and diluting to strength required. Or it may be made by dissolving pure caustic potash in distilled water in the usual way. The alkali must be standardised against the acid in presence of pure potassium fluoride since all the determinations of free acid and basic alumina by the method herein described are carried out with an excess of potassium fluoride in the solutions.

The standardisation is carried out as follows, in a platinum basin or other vessel which will not be attacked by hydrofluoric acid. A porcelain basin coated with paraffin or white bees wax answers very well as all the titrations are performed in the cold. 10 cc of the KF solution (1.350 sp.gr) are taken and diluted with 60 cc distilled water and .5 cc of the phenolphthalein solution (.2%) is added and the liquid brought to a faint pink color, should it not already be in that condition. A measured quantity of the standard acid is now run in from the burette and then the soda solution, until a faint permanent pink color is obtained. The titre of the alkali is thus ascertained. If desired the alkali may be made equal to the acid in the ordinary manner adopted with standard solutions provided the titrations are carried out as above described.

Having standardised the acid and alkali by titrating say 40 cc of acid with the alkali, it is advisable to test 1 cc acid against the alkali; if the solutions are free from objectionable impurity then their relationship will proportionately correspond to what it was for the larger amount.

If there is any discrepancy the impurity (probably alumina) must be identified and fresh solutions prepared free from it.

As a check on the correctness of the ascertained strength of the standard alkali the titration may be carried out in the reverse way by taking 10 cc of the KF solution in 60 cc distilled water adding .5 cc phenolphthalein and making pink if necessary. 40 cc of the alkali are now added and then standard acid is run in to the neutral point. This titration should agree with the other above mentioned.

In regard to the amount of liquid present during titration a considerable amount of latitude is allowable as the following tests show.

Half normal sulphuric acid was used and the standard potash solution was exactly equal to the half normal sulphuric acid when using methyl orange as indicator, 20 cc $H_2SO_4 = 20$ cc KOH. With phenolphthalein however 20 cc $H_2SO_4 = 20.2$ cc of the KOH.

A series of tests were made in each of which 10 cc of the pure neutral potassium fluoride solution (1.350 sp.gr) were present. The amount of water used varied from 20 cc up to 120 cc and both porcelain and platinum vessels were employed.

1.20cc	H ₂ SO ₄ +20cc H ₂ O	=	20.15 cc	KOH in porcelain &
			20.15 cc	, in platinum.
2.20cc	KOH + 20cc H ₂ O	=	19.8 cc	H ₂ SO ₄ in porcelain &
			19.8 cc	,, in platinum
3.20cc	H ₂ SO ₄ + 60cc H ₂ O	=	20.15 cc	KOH in porcelain &
			20.2 cc	, in platinum.
4.20cc	KOH + 60cc H ₂ O	=	19.8 cc	Acidin porcelain &
			19.8 cc	,, in platinum.
5.20 cc	H ₂ SO ₄ +120ccH ₂ O	=	20.2 cc	KOH in porcelain &
			20.25 cc	, in platinum.
6.20cc	KOH + 120cc H ₂ O	=	19.75 cc	H ₂ SO ₄ porcelain &
			19.75	in platinum.

Taking 1,3,& 5 in platinum and comparing them No.3 is the mean and the total volume is 100cc so, in my titrations I aim to have approximately this volume present.

I may here state that I used a set of burettes, pipettes and flasks graduated and stamped at the Reichanstalt Charlottenberg and their accuracy confirmed by myself.

Phenolphthalein solution.

2 grams are dissolved in 1000 cc of 50% alcohol and rendered faintly pink with a little potash. .5 cc is used for each titration for free acid or basic alumina.

Having now described the reagents required for the free acid determination and the principle on which it is founded, I shall next proceed to give an account of the investigations made to ascertain the correct conditions regarding temperature, dilution, amount of KF required and quantity of material being tested and later to ascertain the influence, if any, of other bases on the test. I may here state that I adopted for these volumetric determinations the method of adding the standard solution from the burette in a rapid succession of drops with constant stirring until near the end point and then slowly drop by drop to the finish. First of all I carefully prepared a number of pure salts containing alumina and SO₃, viz.-

1. Pure potash alum by mixing 164.2 grams pure potassium sulphate with 730 grams of the pure sulphate

of alumina of commerce (containing 14% Al_2O_3) in distilled water, boiling at 1.3 sp.gr. filtering, concentrating to 1.36 at the boil and allowing to crystallise over night. The crystals were drained from the mother liquor and well washed with cold distilled water. They were again dissolved in distilled water to 1.36 at the boil and again the liquor was crystallised. The crystallising was carried out a third time after which the well-washed crystals were broken down small and air dried at a temperature of from 18° - 20°C over night and bottled for use. On determining the alumina gravimetrically it was found to be 10.77%. Theory requires 10.78%.

2. Crystallised sulphate of alumina.- Made by dissolving pure sulphate of alumina in distilled water, bringing to 1.350 sp.gr. at 60°C and cooling with agitation to ordinary temperature then further cooling to 0°C when the soft crystals became transformed into hard crystals of $\text{Al}_2(\text{SO}_4)_3 \cdot 27\text{H}_2\text{O}$ (Mettzer Z.ges.Naturw. 7 24, J.B.1856, 876). These crystals were rapidly filtered on the suction pump, washed with ice cold water sucked very dry and spread out to air-dry-over night at 20°C ground fine and bottled.

1. 2.5 grams by gravimetric determination gave .4024 gram Al_2O_3 .
2. 2.0 grams ignited on the blowpipe until no further loss gave .3225 grams of Al_2O_3 .
3. 2.5 grams gave 2.7535 grams BaSO_4 .
4. 2.5 grams gave 2.7530 grams BaSO_4 .

1.	makes the Al_2O_3 to be	16.096%) mean 16.11
2.	,, ,, ,, ,,	16.12 %	
3.	,, ,, SO_3 ,,	37.813%) mean 37.81.
4.	,, ,, ,, ,,	37.806%	

Theoretically 16.11 Al_2O_3 (Al= 27.1) require 37.83 SO_3 . This product as above prepared approximates to $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 16 \text{H}_2\text{O}$.

		<u>Calculated.</u>	<u>By analysis.</u>	
Al_2O_3	1022	16.22	16.10	16.12
3SO_3	240.	38.08	37.81	37.81
$16\text{H}_2\text{O}$	288.	45.70	46.09	46.07 (by difference)
<hr/>				
$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	630.2	100.00	100.00	100.00.
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3. Crystallised basic sulphate of alumina soluble in water. This was prepared by dissolving metallic aluminium in pure sulphuric acid keeping the strength at about 1.3 sp.gr. at 100°C . When $\frac{30}{33}$ of the alumina were basic as $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3$, the aluminium was removed and the liquor filtered. The perfectly clear solution

containing basic sulphate of alumina was brought to 1.45 sp.gr. at the boil, cooled to 44°C and agitated at this temperature for a few hours until a "brei" was obtained containing crystallised soluble basic sulphate of alumina. The crystals and mother liquor were separated by the suction pump and after washing with cold water the crystalline mass was drained dry, redissolved, crystallised again, filtered, drained and air dried at 18°-20°C for 2 days.

It was analysed and found to contain.-

(a) 1 gram ignited till no further loss, left a residue weighing .2285 grams (=Al₂O₃).

(b) 1 gram dissolved in 500cc distilled water precipitated by NH₃, filtered, washed, redissolved in HCl, reprecipitated by NH₃ filtered and washed free from Cl then dried, ignited and weighed gave .2288 gram Al₂O₃.

(c) 1 gram treated as in (b) gave .2283 gram Al₂O₃.

(d) .5 gram precipitated by BaCl₂ gave .483 gram BaSO₄.

(e) the concentrated filtrate of (b) precipitated by BaCl₂ gave .9668 gram BaSO₄.

(f) 5 gram precipitated by BaCl₂ gave .4826 gram

Addendum to p.12 to be read after the fourth line from the bottom.

These pure salts viz.- potash alum, normal aluminium sulphate and soluble basic aluminium sulphate (Al₂O₃·2SO₃) were used as standards and by adding known amounts of sulphuric acid to weighed quantities of them, various aluminium sulphates were accurately prepared of known free acid and basicity and were employed to test the method herein described for determining free acid or basic alumina in aluminium sulphates.

Experiments to ascertain the amount of KF required to completely precipitate the Al₂O₃ from aluminium sulphate solutions.

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(f) .5 gram precipitated by BaCl₂ gave .4826 gram BaSO₄.

Mean of (a) (b) & (c) = 22.85% Al₂O₃.

,, ,, (d) (e) & (f) = 33.16% SO₃

By difference we have 43.99% H₂O.

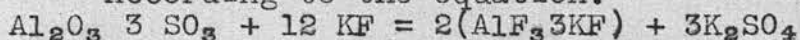
This analysis approximates to Al₂O₃·2SO₃ + 11 H₂O. which contains 22.21% Al₂O₃, 34.76% SO₃, 43.03% H₂O

Taking the figure found for the sulphuric acid viz.- 33.16% and calculating its equivalent of Al₂O₃ to form Al₂O₃·3SO₃ we obtain 14.12 for the Al₂O₃ ~~330~~ equivalent to 3SO₃ on 33.16%

Now deducting 14.12 from the total of 22.85% Al₂O₃ we have 8.73% Al₂O₃ in the basic form i.e. excess over what is required to form normal aluminium sulphate. This basic aluminium sulphate preparation is therefore somewhat more basic than the compound Al₂O₃·2SO₃.

Experiments to ascertain the amount of KF required to completely precipitate the Al₂O₃ from aluminium sulphate solutions.

According to the equation.-



102.2 parts of Al_2O_3 require 697.2 parts KF.

Potash alum contains 10.78% Al_2O_3 , therefore 1 gram (.1078 Al_2O_3) should require .7354 gram KF.

1 gram of potash alum will neutralise 12.7 cc $\frac{1}{2}$ KOH using phenolphthalein as indicator.

I now tested portions of 1 gram of alum in 80 cc. H_2O with varying amounts of neutral KF sol. (1.405 sp. gr. & containing .5628 gram KF per cc), to arrive at the quantity of KF which will exactly make the solution neutral to phenolphthalein according to the above equation.

- A. 1. with 1cc KF sol. (.5628 gram KF) 3.5cc $\frac{1}{2}$ KOH were required.
 2. ,, 2cc ,, (1.126 ,, ,,) 1 drop ,, gave a red color.
 3. ,, 1.5cc ,, (.8442 ,, ,,) 1 ,, ,, ,, ,,
 4. ,, 1.4cc ,, (.788 ,, ,,) 1 ,, ,, ,, ,,
 5. ,, 1.3cc ,, (.73 ,, ,,) 1 ,, ,, ,, ,,

In this last test the end point was not so sharp.

6. with 1.2cc KF sol. (.675 gram KF) .1cc $\frac{1}{2}$ KOH were required.

In this case also there was an uncertainty and paleness about the red color.

Another series of tests with 2 grams alum were as follows.-

- B. 1. with 4cc KF (2.25 grams KF) 1 drop $\frac{1}{2}$ KOH gave a red color.
 2. ,, 3 ,, (1.688 ,,) 1 ,, ,, ,, ,,
 3. ,, 2.5 ,, (1.407 ,,) 1 ,, ,, ,, ,,
 4. ,, 2 ,, (1.126 ,,) 4.7 cc. ,, ,, ,,
 5. ,, 2.1 ,, (1.182 ,,) 1.4 cc. ,, ,, ,,
 6. ,, 2.2 ,, (1.238 ,,) .5 cc. ,, ,, ,,
 7. ,, 2.3 ,, (1.294 ,,) 1 drop ,, ,, ,,

C. Again with 3 grams of alum (theoretically requiring 2.2062 KF)

1. with 4.5cc KF (2.53 grams KF) 1 drop $\frac{1}{2}$ KOH gave a red color.
 2. ,, 4.2 ,, (2.364 ,,) 1 ,, ,, ,, ,,
 3. ,, 4.0 ,, (2.252 ,,) 1 ,, ,, ,, ,,
 4. ,, 3.5 ,, (1.97 ,,) 1 ,, ,, just ,, ,,
 5. ,, 3.4 ,, (1.914 ,,) 1 ,, ,, gave a very uncertain red.

With pure neutral aluminium sulphate containing 16.11% Al_2O_3 portions of 2 grams each were used in 80cc H_2O . 2 grams contain .3222 gram Al_2O_3 requiring 2.2078 grams KF.

1. with 4cc KF sol (2.25 grams KF) 1 drop $\frac{1}{2}$ KOH gave a red color.
 2. ,, 2.5 ,, ,, (1.407 ,,) 9cc ,, were required.
 3. ,, 3 ,, ,, (1.688 ,,) 4cc ,, ,,
 4. ,, 3.3 ,, ,, (1.857 ,,) 1 drop ,, gave a red color.
 5. ,, 3.4 ,, ,, (1.914 ,,) 1 drop ,, ,, ,,

No. 4 was somewhat uncertain but No. 5 was sharp enough.

Nos. 2 & 5 were repeated with the addition of pure

K_2SO_4 (5.492 grams) equivalent to the $Al_2O_3 \cdot 3SO_3$ to ascertain if K_2SO_4 has any influence.

In the case of No.2 the result was identical.

In the case of No.5 the result was also identical.

Selecting the KF in each of the 3 alum experiments which became neutral to phenolphthalein viz.-

In A.No.5 = .73 KF for 1 gram alum

B.No.7 = 1.294 ,, 2 ,,

C.No.4 = 1.97 ,, 3 ,,

and taking the average for 1 gram alum (.1078 gram Al_2O_3)

$.73 + 1.294 + 1.297 = 3.994$ grams KF.

$3.994 \div 6 = .666 =$ KF for .1078 Al_2O_3 (1 gram alum)

$.666 \div 58.1 = .01146 = 10.9$ molecules KF. (KF = 58.1)

$1.1078 \div 102.2 = .01055 = 1$ molecule Al_2O_3 . ($Al_2O_3 = 102.2$)

Again in the case of the pure aluminium sulphate

No.5 = 1.914 gram KF for 2 grams (.3222 gram Al_2O_3)

$1.914 \div 58.1 = .033 = 10.5$ molecules KF.

$.3222 \div 102.2 = .00315 = 1$ molecule Al_2O_3 .

From these experiments one may conclude that the compound $AlF_3 \cdot 2KF$ is first formed thus:-

$Al_2O_3 \cdot 3SO_3 + 10 KF = 2(AlF_3 \cdot 2KF) + 3K_2SO_4$.
(According to Berzelius $AlF_3 \cdot 2KF$ is formed when water solution of AlF_3 is precipitated by a limited amount of KF solution, and the compound $AlF_3 \cdot 3KF$ is produced when solution of AlF_3 is added to KF solution, keeping the latter in excess). Doubtless also the compound $AlF_3 \cdot 2KF$ which is first formed passes into $AlF_3 \cdot 3KF$ in the experiments I carried out where an excess of KF was present.

At the commencement of my investigations the standard alkali I used was half normal soda but I soon abandoned it for half normal potash, as under certain conditions the presence of sulphate of soda leads to erroneous results. For example 3 portions of 2 grams of pure neutral sulphate of alumina in 30cc H_2O were taken and to them were added respectively (1) 4.4cc $\frac{N}{2}$ NaOH, (2) 6.2cc $\frac{N}{2}$ NaOH and (3) 9cc $\frac{N}{2}$ NaOH. On gently warming, three solutions were thus obtained of basic sulphate of alumina with different degrees of basicity and in each there was Na_2SO_4 equivalent to the $\frac{N}{2}$ NaOH taken. After cooling, phenolphthalein and 10 cc. neutral KF solution (1.36 sp.gr) were added to each and they were separately titrated with H_2SO_4 .-

(1) required only 4.1 cc $\frac{N}{2}$ H_2SO_4 to neutralise it.

(2) ,, 4.8 ,, ,,

(3) ,, 6.4 ,, ,,

This result surprised me, as, theoretically the amount of $\frac{N}{2}$ Acid required should have exactly corresponded to the Soda taken in each case.

A repetition of these experiments under varying

Al.

8 H₂O

Al OH (SO₄) 4H₂O

27.1

17

96

72

21 2 1) 72 (

conditions regarding amount of KF present and dilution invariably gave misleading results - always low in regard to the amount of acid required to neutralise, even when carried out in platinum instead of porcelain.

Alkali has evidently disappeared from the solution and gone into the precipitate to form a basic compound neutral to phenolphthalein. As it is quite likely that one might have to test a basic aluminium sulphate which contained sodium sulphate e.g. a basic solution prepared by adding caustic soda or carbonate of soda to aluminium sulphate solution, it is therefore important that means be taken to obviate this discrepancy and I carried out a series of investigations with this end in view. A solution of pure neutral aluminium sulphate was prepared by dissolving 50 grams of the salt in 100 cc hot distilled water and then 125 cc. of a nearly $\frac{1}{2}$ Caustic soda solution were added and the mixture warmed till it cleared. It was then cooled and made up to 250 cc. Thus, each 10 cc. contain 2 grams aluminium sulphate with a basicity equal to 5 cc of the nearly $\frac{1}{2}$ NaOH which exactly neutralised 4.95 cc $\frac{1}{2}$ H_2SO_4 . For a time the best result I could obtain was to take 10 cc KF solution dilute it with 60 cc H_2O in a platinum basin add 10 cc $\frac{1}{2}$ H_2SO_4 (to have free acid present and prevent tendency to form basic fluoride) and then run in slowly 10cc of the above basic solution. Phenolphthalein was now added and standard KOH run in to the neutral point (until a permanent pink was obtained). 4.9cc standard KOH were used instead of the theoretically required amount of 5.1cc standard potash -

(5cc $\frac{1}{2}$ H_2SO_4 = 5.05cc of the NaOH solution and)
 (5cc $\frac{1}{2}$ H_2SO_4 = 5.05cc of the KOH solution.)

An error of .2cc on 2 grams aluminium sulphate equal to .08% in reckoning the basic alumina (1cc of the KOH solution = .00843 Al_2O_3).

I next tried 2 grams of pure potash alum made basic by addition of 5cc of the same soda solution and on dealing with this solution in the same way, viz.- by adding ~~to~~ it to 10 cc. KF solution, 60cc H_2O and 10cc H_2SO_4 , then adding phenolphthalein and standard KOH till neutral I found that 5.05 cc of the latter were required. This brings the error down to .02%.

It struck me that the K_2SO_4 present in the alum must have had an influence in preventing the sodium sulphate from coming into play so I now returned to the basic aluminium sulphate solution and repeated the test, first of all adding pure potassium sulphate (neut. to phenolphthalein) and the result was quite successful. Results of a few tests.-

1. 10cc of the basic aluminium sulphate solution with 5cc of a saturated solution of pure K_2SO_4 were slowly added to 10cc KF solution + 10cc $\frac{N}{2}$ H_2SO_4 in 60cc H_2O and the whole well stirred. Phenolphthalein was now added and standard KOH to the neutral point. 5.02cc of the latter were used.
2. A similar test with 10cc saturated solution of K_2SO_4 required 5.05 standard KOH.
3. Another with 20cc K_2SO_4 solution required 5.05cc.
4. In this test I used only 5cc KF solution with 10cc $\frac{N}{2}$ H_2SO_4 and 10cc K_2SO_4 solution and the standard KOH required was 5.1cc. Exactly theory.

With basic sulphates of alumina made basic by caustic potash the same method of adding the basic sulphate of alumina to the KF acidified with $\frac{N}{2}$ H_2SO_4 and titrating back with standard alkali gives satisfactory results, e.g.

2 grams neutral aluminium sulphate in 10cc H_2O were basicised with 4.5 cc nearly $\frac{N}{2}$ KOH solution and were then slowly added to 10cc KF (1.5 sp.gr) + 10cc $\frac{N}{2}$ H_2SO_4 + 60cc H_2O and titrated with standard KOH (10cc $\frac{N}{2}$ acid = 10.1 of the KOH). The amount of KOH required to neutralise was 5.55cc. The theoretical amount is 5.6cc. This error makes the basic Al_2O_3 only .02% too high.

I find also that aluminium sulphate made basic by KOH can be satisfactorily tested if carried out as follows.- 2 grams pure neutral aluminium sulphate made basic by the addition of 5 cc of standard KOH (=4.95cc $\frac{N}{2}$ H_2SO_4) then, after warming till dissolved, and cooling, 10cc KF solution (1.35 sp.gr) were slowly added drop by drop with continual vigorous stirring and the mixture titrated with $\frac{N}{2}$ H_2SO_4 and phenolphthalein, required 5cc of acid to decolorise. The reaction was slow and the red color kept vanishing and returning until 5cc acid had been run in, at which point no further change occurred. Returning to the question of NaOH again for a moment I may here state that I obtained satisfactory results with it when determining free acid in aluminium sulphates. For example 3 portions of pure potash alum of 2 grams each were taken and each acidified with a known amount of SO_3 and then titrated with standard NaOH after adding 10cc KF solution (1.35 sp.gr). Results.-

	Amount of SO_3 taken.	Amount of free SO_3 found.
1.	.178 gram.	.180 gram
2.	.07 ,,	.072 ,,
3.	.288 ,,	.288 ,,

I also found standard NaOH to answer quite well in determining the excess of acid in the test for a basic aluminium sulphate made basic by NaOH as described on pp.15&16. The basic aluminium sulphate solution with K_2SO_4 added is run into the KF acidified with a known excess of standard acid and titrated with standard alkali. NaOH answers for this purpose quite as well as KOH, e.g.-

1. 2 grams pure neutral aluminium sulphate in 10cc H_2O made basic by addition of 5cc. standard NaOH (= 4.95cc $\frac{1}{2}$ acid) were mixed with 20cc. saturated solution of K_2SO_4 and added to 10cc KF (1.35 sp.gr) + 60cc. H_2O + 10cc $\frac{1}{2}$ H_2SO_4 and titrated back with standard NaOH. 5cc of the latter were required. The theoretical amount is 5.1.

2. A similar test but with 5cc. KF used 5.05cc. standard NaOH.

It was only when testing aluminium sulphate which had been made basic with NaOH that I found the aforementioned disturbing influence, and in order to avoid the presence of soda and the possible chance of error caused thereby I employed caustic potash for the standard alkali.

I may observe at this point that in testing basic aluminium sulphates which have been made basic by alkali or alkali carbonate or which contain alkaline salts, it is necessary to modify the titration.

I shall refer to this again when summing up.

I next proceeded to investigate the behaviour of pure basic aluminium sulphates which contain no alkali salts, e.g. those which have been made basic by dissolving alumina in them or by adding lime and removing the calcium sulphate or by some other similar means.

For this research I used the pure basic aluminium sulphate described on p.11 .

Experimental investigations regarding the determination of basic alumina by means of KF in basic aluminium sulphates.-



For these experiments the soluble basic aluminium sulphate described on pp 11 & 12 was employed. A solution of it was made up to contain 1 gram in each 5cc.- the amount of $\frac{1}{2} \text{H}_2\text{SO}_4$ required to theoretically convert 1 gram into normal $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3$ is 10.25cc.

1. 5cc above solution were added to 10cc. neutral KF solution (5.3 gram KF) diluted with 60cc H_2O , phenolphthalein was added and the mixture which was strongly red in color required only 9.5cc of $\frac{1}{2} \text{H}_2\text{SO}_4$ to bring to the neutral point - an error of .55% basic alumina too low.

2. 5cc above solution were added to 10cc KF + 60cc H_2O , acidified with 12cc $\frac{1}{2} \text{H}_2\text{SO}_4$ and the excess of acid ascertained by titration with standard KOH and phenolphthalein. 2.45cc $\frac{1}{2} \text{KOH}$ were required. $12 - 2.45 = 9.55\text{cc} \frac{1}{2} \text{H}_2\text{SO}_4$ neutralised by the 1 gram basic aluminium sulphate. Theory requires 10.25 as stated above.

There is here a disappearance of a certain amount of base - an action resembling that already remarked upon on p.15. Even in experiment 2 where excess acid was added to the KF before running in the basic aluminium sulphate solution there is a certain amount of base carried out of solution by the double fluoride.

I next tried adding excess of acid to the basic sulphate before mixing it with the KF solution. The following 3 trials were made with 1 gram of the basic aluminium sulphate in each and without warming after adding the acid.

3. With addition ^{of} 12cc $\frac{1}{2} \text{H}_2\text{SO}_4$ to the basic aluminium sulphate and then adding this acid solution to 10cc KF solution + 60cc H_2O . On titrating with $\frac{1}{2} \text{KOH}$ 2.2cc were required. $12 - 2.2 = 9.8\text{cc} \frac{1}{2} \text{H}_2\text{SO}_4$ taken up by the basic aluminium sulphate. (Theory requires 10.25).

4. A similar experiment to (3) but with 15 cc. $\frac{1}{2} \text{H}_2\text{SO}_4$ required 6cc $\frac{1}{2} \text{KOH}$. $15 - 6 = 9.0\text{cc} \frac{1}{2} \text{H}_2\text{SO}_4$ neutralised.

5. Similar to (3) but with 20cc $\frac{1}{2} \text{H}_2\text{SO}_4$ required 9.95cc $\frac{1}{2} \text{KOH}$. $20 - 9.95 = 10.05\text{cc} \frac{1}{2} \text{H}_2\text{SO}_4$ neutralised.

These experiments show that even with an excess of acid in the basic aluminium sulphate solution a certain amount of base is still carried down.

In the next trials the 1 gram portions of basic aluminium sulphate were acidified with excess of H_2SO_4

and heated to the boil to ensure combination, then cooled and added to 10cc KF + 60cc H₂O and titrated with $\frac{N}{2}$ KOH to ascertain the excess of H₂SO₄.

6. 1 gram basic aluminium sulphate in 10cc. H₂O + 12cc $\frac{N}{2}$ H₂SO₄ heated and then cooled and added to 10cc KF + 60cc. H₂O required 1.9cc $\frac{N}{2}$ KOH to neutralise the free acid. Therefore 12 - 1.9 = 10.1 cc = amount of acid taken up by the basic aluminium sulphate.

7. A similar experiment to (6) but with 16cc $\frac{N}{2}$ H₂SO₄. 5.75cc $\frac{N}{2}$ KOH were required to neutralise the free acid, therefore 16 - 5.75 = 10.25cc = $\frac{N}{2}$ H₂SO₄ taken up by the basic aluminium sulphate. This is the theoretical amount required.

8. Using 20cc $\frac{N}{2}$ H₂SO₄ and requiring 9.75cc. $\frac{N}{2}$ KOH. 20 - 9.75 = 10.25 cc. H₂SO₄.

It is now conclusively proved from these experiments and from previous experiments recorded on p. 14 that in testing basic aluminium sulphates inaccurate results will be obtained if the sample in question is simply added to potassium fluoride and the basicity ascertained by titrating the liberated alkali by means of standard acid.

A modification has to be adopted on the lines indicated viz.- the basic aluminium sulphate solution must be acidified by a known considerable excess of standard acid then added to the KF solution and titrated back with standard alkali. I shall return to this later and state the method fully when summing up.

Application of the potassium fluoride test to determine the free acid and basic alumina in a few samples of aluminium sulphates.-

1. Pure crystallised aluminium sulphate.
On analysis, 2.5 grams gave 2.6657 grams BaSO₄.
Another 2.5 grams gave 2.6654 grams BaSO₄.
The mean of these two = 36.61% SO₃ = 15.59 Al₂O₃.
Three separate grams gave respectively .1578, .1574 and .1580 grams Al₂O₃.
The mean of these three = 15.77% Al₂O₃.
15.77 - 15.59 = .18 = amount of Al₂O₃% in basic form.

2. grams in 10cc of water were acidified with 5cc $\frac{N}{2}$ H₂SO₄ heated, cooled and then added to 10cc KF solution + 60cc H₂O and titrated with standard KOH and phenolphthalein as indicator. 4.65cc $\frac{N}{2}$ KOH were required to neutralise the excess of acid, therefore 5 - 4.65 = .35 = cc. representing the basic alumina.
.35 x .008517 = .00298 gram Al₂O₃ basic = .15% = an

error of only .03% too low.

2. Soluble basic aluminium sulphate.-

From a solution of soluble basic aluminium sulphate which had been standing in a bottle for some months, a salt crystallised out. This was separated from the liquid and air dried, then analysed. It proved to be mainly $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 12\text{H}_2\text{O}$ and was used as a material upon which to try the determination of basic alumina by means of potassium fluoride and titration with standard acid and alkali.

- (1) .5 gram gave .1072 gram Al_2O_3)
 (2) 1 ,, ,, .2145 ,, Al_2O_3) = 21.44% Al_2O_3 .
 (3) 1 ,, ,, 1.014 ,, BaSO_4)
 (4) .5 ,, ,, .5063 ,, BaSO_4) = 34.79% SO_3 .

(5) 2 grams titrated with standard alkali in the manner hereinafter described in part II required 17.55cc (1cc = .039617 gram SO_3 and .0169 gram Al_2O_3)
 $17.55 \times .039617 = .6952$ grams $\text{SO}_3 = 34.76\%$ SO_3 .

Also $17.55 \text{ cc} \times .0169 = .2966$ grams Al_2O_3 combined as neutral $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 = 14.83\%$.

The total $\text{Al}_2\text{O}_3 = 21.44\%$ therefore $21.44 - 14.83$ equals the basic Al_2O_3 , viz. 6.61%.

Taking (3) and (4) the 34.79% SO_3 require 14.815 Al_2O_3 to form $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3$. Therefore $21.44 - 14.815 = 6.625\%$ basic Al_2O_3 .

A series of tests were now made to determine the basic Al_2O_3 by means of potassium fluoride.

(a) 1 gram dissolved in 10cc H_2O was added to 10cc neutral KF solution (5.3 grams KF) + 60cc H_2O . This mixture went red on adding phenolphthalein and required 7.55cc H_2SO_4 to neutralise it. $7.55 \times .008516 = .0643$ gram Al_2O_3 in basic form, = 6.43%.

(b) 1 gram in 10cc H_2O + 20cc $\frac{1}{2}$ acid and the whole heated to ensure combination between the basic Al_2O_3 and the additional SO_3 , cooled and added to 10cc KF solution + 40cc H_2O , required 12.3cc $\frac{1}{2}$ KOH to neutralise. $20 - 12.3 = 7.7$ cc $\frac{1}{2}$ acid neutralised by the basic aluminium sulphate. $7.7 \times .0085166 = .0656$ gram basic $\text{Al}_2\text{O}_3 = 6.56\%$.

(c). Another test similar to (b) gave the same figure, viz. - .0656 gram basic $\text{Al}_2\text{O}_3 = 6.56\%$. Gravimetric analysis made the basic Al_2O_3 6.62% so that in (b) and (c) the error is only .06% too low. 6

These tests also show the reliability of the method (hereinafter described) of determining the neutralisable acid in aluminium sulphate by means of standard alkali and phenolphthalein. (p.45)

Compare Nos. 3, 4, & 5 above.

3. A sample of commercial sewage precipitant (basic).
20 grams were dissolved in water and filtered and washed into a 200cc flask. The solution was deep red showing the presence of basic ferric sulphate.

(1) 20cc were acidified with 5cc $\frac{2}{1}$ H₂SO₄ and heated then cooled and added to 20cc KF solution. Phenolphthalein was added and then $\frac{2}{1}$ KOH to the neutral point. 3.9cc were required. 5 - 3.9 = 1.1cc $\frac{2}{1}$ H₂SO₄ taken up by the basic compound. 1.1 x .0085167 x 50 = .47% Al₂O₃ basic.

(2) Another similar test showed 1.05 H₂SO₄ utilised = .45% basic Al₂O₃. 4

(3) 10cc were oxidised with a little HNO₃ and precipitated by NH₃. The precipitate washed, dried and ignited weighed .1795 grams = Al₂O₃ + Fe₂O₃ + TiO₂.

(4) 10cc reduced with excess of pure zinc in acid solution required .65cc $\frac{7}{10}$ KMnO₄ to oxidise the TiO₂ to TiO₃, spotting with sulphocyanide as indicator. Then a further 9.5cc were required to oxidise the FeO to Fe₂O₃.
.65 x .008 x 100 = .52% TiO₂.
9.5 x .008 x 100 = 7.6% Fe₂O₃ (Total) 2

(5). 10cc. titrated direct with KMnO₄ required .75cc.
.75 x .0072 x 100 = .52% FeO (equivalent to .58 Fe₂O₃ which must be deducted from the Fe₂O₃ in (4).

(6). The concentrated filtrate of (3) precipitated by BaCl₂ gave .999 gram BaSO₄ = 34.30% SO₃.

From (3) & (4) the Al₂O₃ = 17.95 - 8.12 = 9.83%.

The analysis now reads.-

Al ₂ O ₃	9.83	=	23.08	SO ₃ .
Fe ₂ O ₃	7.02	=	10.53	,,
FeO	.52	=	.58	,,
TiO ₂	.52	=	1.04	,,
			35.23	= total SO ₃ if

all the bases were exactly satisfied.

35.23 - 34.3 [the SO₃ by (6)] = .93 and this converted to Al₂O₃ amounts to .39% basic Al₂O₃. By the KF test the basic alumina was .46%. .46 - .39 = .07% error too high.

4. A sample of commercial "high strength" pure aluminium sulphate (slightly basic).

A solution containing 1 gram per 10cc was made up and filtered.

- (1) 20cc were acidified with 5cc $\frac{N}{2}$ H_2SO_4 heated then cooled and added to 10cc KF solution + 40cc H_2O . Phenolphthalein was added and then $\frac{N}{2}$ KOH to the neutral point. 3.7cc were required.
 $5 - 3.7 = 1.3 = \text{cc } \frac{N}{2} H_2SO_4 \text{ taken up by the basic } Al_2O_3.$
 $1.3 \times .0085167 \times 50 = .55\% \text{ basic } Al_2O_3.$
- (2). A similar test gave 1.35cc $\frac{N}{2}$ H_2SO_4 taken up.
 $1.35 \times .0085167 \times 50 = .57\% \text{ basic } Al_2O_3.$
- (3). 100cc acidified with H_2SO_4 and treated with potassium sulphocyanide developed a color equal to standard containing .0008 gram Fe_2O_3 .
 $\therefore \% Fe_2O_3 = .008.$
- (4). 10cc. precipitated by ammonia and precipitate washed, dried, ignited and weighed = .1660 gram.
 $16.6 - .008 = 16.59 = \% Al_2O_3.$
- (5). The filtrate of (4) concentrated and precipitated by $BaCl_2$ gave 1.0954 gram $BaSO_4 = 37.61\% SO_3$.
 Deducting .01 for SO_3 equivalent to .008 Fe_2O_3 there remains 37.60 SO_3 .

37.60 SO_3 are equivalent to 16.01 Al_2O_3 .

$$\begin{array}{r} Al_2O_3 \text{ by (4)} = 16.59 \\ Al_2O_3 \text{ by (5)} = 16.01 \\ \hline .58 = \text{basic } Al_2O_3. \end{array}$$

By KF (1) and (2) the basic Al_2O_3 was .56% an error of .02% too low.

Determination of free acid and basic alumina in aluminium chlorides.

For the following experiments I employed two preparations of aluminium chloride (A) dry powder of $\text{Al}_2\text{Cl}_6 \cdot 12 \text{H}_2\text{O}$ and (B) solution containing 41.88 gram Al_2Cl_6 in 100cc.

(A) was prepared by passing dry HCl gas into a solution of aluminium chloride (1.3 sp.gr) whereby $\text{Al}_2\text{Cl}_6 \cdot 12 \text{H}_2\text{O}$ crystallised out in a very pure form. This was filtered off and washed with HCl, sucked dry on the pump and dried in an open porcelain basin at about 110°C until it became pure white powder. It was then bottled and analysed.

(1) 1 gram gave .2178 gram Al_2O_3
 (2) 1 gram ,, .2176 ,, ,,) = 11.54% Al.

(3) .5 ,, ,, .8755 gram AgCl)
 (4) .5 ,, ,, .8765 ,, ,,) = 43.32% Cl.

		Calculated.	By analysis
Al_2	54.20	11.24	11.54
Cl_6	212.22	43.99	43.32
$12\text{H}_2\text{O}$	216.00	44.77	(45.14)
	<u>482.42</u>	<u>100.00</u>	<u>100.00</u>
	=====	=====	=====

This preparation is slightly basic due to loss of HCl in the drying. It was completely soluble in water.

The basicity expressed in terms of Al_2O_3 is equal to .91% Al_2O_3 , since $11.54 \text{ Al} = 21.77 \text{ Al}_2\text{O}_3$ and $43.32 \text{ Cl} = 20.86 \text{ Al}_2\text{O}_3$. Therefore $21.77 - 20.86 = .91 =$ basicity % as Al_2O_3 .

Experiments with this aluminium chloride and potassium fluoride.

According to the following equation for a normal salt, $\text{Al}_2\text{Cl}_6 + 12 \text{KF} = 2(\text{AlF}_3 \cdot 3\text{KF}) + 6\text{KCl}$.

54.2 grams Al are equivalent to 697.2 grams KF.

In each of the following trials I used 1 gram of aluminium chloride, containing .1154 gram Al and theoretically requiring 1.4843 gram KF.

1. 1 gram aluminium chloride in 10cc H_2O were added to 10cc neutral KF solution (5.3 grams KF) + 60cc distilled water. .5cc phenolphthalein solution was added and at once went red, showing that the aluminium chloride was basic. $\frac{1}{2} \text{H}_2\text{SO}_4$ was now added till the red color just disappeared. .8cc were required. $.8 \times .008517 \times 100 = .68136\%$ Al_2O_3 in the basic form. This is an error of .23% too low and points to alkali or Al_2O_3 having gone down with the fluoride precipitate as it did in the case of basic aluminium sulphate.

2. 10cc acid were added to 1 gram aluminium chloride in 10cc H₂O and the mixture warmed then cooled and added to 10cc KF + 60cc H₂O and titrated with standard KOH and phenolphthalein, required 8.8cc KOH to neutralise.

3. A test similar to (2) but without warming the aluminium chloride and acid before adding it to the KF, required 8.8 cc KOH.

4. A repetition of (2) required 8.85 cc KOH.

5. A repetition of (3) required also 8.85cc KOH.

The mean of these 4 tests is 8.825cc KOH. $10 - 8.825 = 1.175$. $1.175 \times .008517 = 1.00\%$ Al₂O₃ in basic form. This is an error of only .09% too high on the gravimetric analysis so that in regard to aluminium chloride the method gives good results.

For confirmation two additional tests were made with the basicity increased as follows.-

1. 1 gram of the aluminium chloride dissolved in 10cc H₂O were taken and made further basic by adding 3.8cc KOH and warming till a clear solution was obtained. The basicity already in the aluminium chloride was equivalent to 1.2cc KOH so that now after adding the 3.8cc its basicity is equal to 5cc KOH. The strongly basic solution was now acidified by adding 10cc H₂SO₄ and then added to 10cc. KF solution and 60cc water and titrated back with KOH and phenolphthalein. Exactly 5cc KOH were required, being the theoretical amount.

(2). A similar experiment to the last was made, except that after acidifying the basic solution it was warmed and cooled before adding to the KF solution. The result was the same, viz.- 5cc KOH were required to neutralise.

(B). This was a solution of aluminium chloride prepared by digesting hydrate of alumina Al₂(OH)₆ in ordinary pure HCl solution at 100°C until the acid was neutralised. The solution was then cooled, filtered and analysed.

1.	3.33cc	gave	.5418	gram	Al ₂ O ₃)	
2.	3.33cc	,,	.5420	,,	,,)	= .2874 gram Al.
3.	.667cc	,,	.8968	,,	@gCl)	
4.	.667cc	,,	.8960	,,	,,)	= .2217 gram Cl.

From these figures 100cc of the aluminium chloride solution contain Al equal to 16.24 grams Al₂O₃ and

33.24 grams of Cl equal to 16.01 grams Al_2O_3 .
Therefore $16.24 - 16.01 = .23 =$ grams Al_2O_3 in basic form in each 100cc.

Experiments with KF.

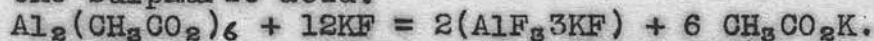
1. 1.667cc acidified with 5cc $\frac{1}{2}H_2SO_4$ and then added to 10cc KF solution (5.3 grams KF) + 60cc H_2O and titrated with standard KOH and phenolphthalein required 4.5cc $\frac{1}{2}KOH$ to neutralise.

2. A similar test but the mixture of aluminium chloride and acid was warmed and cooled before titrating. This required also 4.5 cc $\frac{1}{2}KOH$.

$5 - 4.5 = .5$; and $.5 \times .008517 = .0042585$; & $\frac{.0042585 \times 100}{1.667}$
= .25 grams basic alumina per 100cc - an error of .02 grams too high per 100cc

Determination of free acid and basic alumina in aluminium acetate by means of potassium fluoride.-

The same reactions take place here as in the case of aluminium sulphate except that acetic acid replaces the sulphuric acid.



For these investigations I used aluminium acetate solution prepared by adding pure barium acetate solution to pure aluminium sulphate solution until the clear liquid when filtered off gave no precipitate either with barium acetate or aluminium sulphate.

The solution thus prepared was slightly basic possibly due to loss of acetic acid during the manipulation.

Analysis of the solution.-

- (a) 25cc yielded .724 grams Al_2O_3
- (b) 25 " " .723
- (c) 10cc distilled with H_2SO_4 into $\frac{1}{7}$ alkali, neutralised 16.55cc $\frac{1}{7}NaOH$
- (d) 10cc titrated with $\frac{1}{7}$ alkali and phenolphthalein as hereinafter described in part II required 16.54 NaOH to neutralise the acid in them.

The average of (a) and (b) makes the Al_2O_3 .2894 gram in 10cc.

The average of (c) and (d) multiplied by .051 (the $C_2H_5C_2O_3$ per each cc. $\frac{1}{7}$ alkali) = .8437 grams $C_2H_5C_2O_3$ in each 10cc.

.8437 grams $C_2H_3C_2O_3$ are equivalent to .2816 gram Al_2O_3 .
Therefore $.2894 - .2816 = .0078$ gram = the amount of
basic Al_2O_3 in each 10cc.

Experiments with addition of potassium fluoride.--

(1) 10cc of the above basic aluminium acetate solution were added to 10cc KF solution (5.3 gram KF) + 60cc H_2O and on adding phenolphthalein a strong red color was produced. Half normal H_2SO_4 was now added to the neutral point and .8cc were required.

(2) 10cc were this time acidified with 5cc half normal H_2SO_4 and then added to 10cc KF solution, + 60cc H_2O and titrated as before. 4.05cc $\frac{N}{2}$ alkali were required to ~~bring~~ neutralise the excess of acid. Therefore $5 - 4.05 = .95$ cc = the $\frac{N}{2}$ acid which has gone into combination with the basic alumina.

(3) Another test similar to (2) but the 10cc acetate + 5cc acid were gently warmed and then cooled before adding to the KF. In this case 4.1cc $\frac{N}{2}$ KOH were required to neutralise.

Therefore $5 - 4.1 = .9$ cc = the amount of $\frac{N}{2}$ acid taken up by the basic alumina.

The average of (2) & (3) = .925cc $\frac{N}{2}$ acid.
.925 multiplied by .0085167 (Al_2O_3 equivalent to each cc $\frac{N}{2}$ acid) = .0079 gram basic Al_2O_3 .
By the analyses (a), (b), (c) & (d) on p.23 the basic alumina came to .0078 gram so that satisfactory results can be arrived at in determining the basic alumina in aluminium acetate by the help of potassium fluoride.

It will be observed that (1) gave a somewhat low figure showing the advisability of acidifying basic solutions before adding them to the KF.

Series of experiments with aluminium acetates containing free acid.

In these tests .92cc half normal acetic acid was first added to each of three 10cc portions of the above slightly basic acetate solution and then each was acidified with a further amount of $\frac{N}{2}$ acetic acid and then added to 10cc KF solution + 60cc water and titrated with half normal KOH and phenolphthalein.

1.	with	1cc $\frac{N}{2}$	acetic acid required	1cc $\frac{N}{2}$	KOH
2.	"	5	"	5	"
3.	"	10	"	10	"

Free acetic acid therefore in aluminium acetate may be accurately determined also by this potassium fluoride method.

Behaviour of potassium fluoride towards ferric and ferrous salts.

Since aluminium sulphates nearly always contain ferric or ferrous sulphate or both, it is important that the behaviour of potassium fluoride towards them and the reaction of the resulting compounds towards phenolphthalein be studied.

For this purpose I used a pure ferric sulphate solution prepared by oxidising pure ferrous sulphate with nitric acid, with addition of a certain amount of sulphuric acid to leave the resulting ferric sulphate slightly basic. After heating to expel all nitrous gases then washing with acetone and ether, the dry powder was dissolved in water, the solution carefully analysed and then the required amount of H_2SO_4 added in the form of normal sulphuric acid to form a "neutral" salt. The solution thus prepared contained.-

6.82 grams Fe_2O_3 and 10.23 grams SO_3 per 100cc.

For ferrous sulphate I employed a freshly crystallised preparation of the pure salt, washed, drained, dried between filter paper, ground fine and further dried between filter paper. It contained 25.92% Fe_2O_3 (1 gram = 7.2cc $\frac{2}{3}$ $KMnO_4$) Theory requires 25.90.

I. Experiments with ferric sulphate.

According to the equation.-

$Fe_2O_3 + 3 SO_3 + 12 KF = 2(FeF_3 \cdot 3KF) + 3K_2SO_4$ 160 grams of Fe_2O_3 (as ferric sulphate) require 697.2 grams KF.

A solution was made containing .1 gram Fe_2O_3 per 100cc by diluting 73.5cc of the above ferric sulphate solution up to 500cc with distilled water. .1 gram Fe_2O_3 is equivalent to .436 KF. I found that a comparatively large excess of KF must be present when titrating ferric sulphate for free acid by means of standard alkali. If too little KF is used the alkali attacks the fluoride precipitate and turns it brown; whereas with a sufficient excess the precipitate is quite unattacked and remains unchanged in color, viz.- nearly white.

I may here mention by the way that Knobloch (Pharm. Zeitschrift XXXIX 558) has based a process for determining fluorine in soluble fluorides on the fact that when a solution of ferric chloride is mixed with its equivalent of KF, the decomposition is complete and the resulting ferric fluoride solution is colorless. In this state the iron is not detectable by thiocyanate, salicylic acid etc. and does not liberate iodine from KI.

1. 10cc of the dilute ferric sulphate solution (containing .1 gram Fe_2O_3 per 10cc) were added to 5cc KF solution (2.65 grams KF) + 40cc H_2O . A white precipitate resulted and the solution was colorless. Upon adding phenolphthalein and standard KOH a brown color like that of ferric hydrate was developed, showing decomposition of the fluoride precipitate.

2. A repetition of (1) but using 10cc KF solution. In this case one drop of $\frac{1}{2}$ KOH produced a red colour while the precipitate remained white.

3. 10cc ferric sulphate solution were acidified with 1cc of $\frac{1}{2}$ H_2SO_4 and added to 15cc KF solution + 40cc. H_2O and then titrated with standard KOH and phenolphthalein. 1cc of $\frac{1}{2}$ KOH was required to bring to the neutral point.

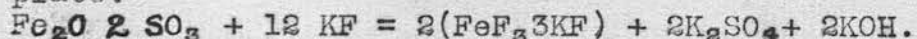
4. The following experiments set down in tabular form show that the test works perfectly as regards free acid in ferric sulphate. 10cc = .1 gram Fe_2O_3 used in each case.-

H_2SO_4	Amount H_2O	KF sol.	KOH.
5cc.	40cc	15cc	5cc.
10 "	40 "	15 "	10 "
10 "	40 "	20 "	10 "
1 "	40 "	20 "	1 "
5 "	40 "	20 "	5 "
5 "	40 "	30 "	5 "
5 "	40 "	10 "	5 "

Experiments with soluble basic ferric sulphates and KF.

1. 10cc of the solution of normal ferric sulphate containing .1 gram Fe_2O_3 were taken and made basic by the addition of 1.5cc $\frac{1}{2}$ KOH. On warming a clear, very red, basic solution was thus obtained of known basicity (which amounted to 2.31% of the Fe_2O_3).

This basic solution was added to 20cc KF solution (10.6 grams KF) + 60cc H_2O and upon adding phenolphthalein it turned strongly red showing the presence of free alkali - the following reaction having taken place.-



Standard acid was now added until the red color disappeared and only 1cc $\frac{1}{2}$ H_2SO_4 was required.

Theoretically 1.5cc should have been required but here again there is evidently formed a basic fluoride precipitate carrying down alkali with it or else a certain amount of Fe_2O_3 . This is confirmed by the color of the precipitate which is brown instead of being nearly white.

2. Another similar experiment using 1cc $\frac{N}{2}$ KOH to basicise required only .6cc $\frac{N}{2}$ H₂SO₄ instead of 1cc.

3. The determination has therefore to be modified as in the case of basic aluminium sulphate by adding a known amount of standard acid to the basic sulphate before the latter is added to the KF.

10cc ferric sulphate solution as formerly were made basic by the addition of 1.5cc $\frac{N}{2}$ KOH and applying gentle heat till the precipitate redissolved forming a deep red solution. This was cooled and 5cc $\frac{N}{2}$ H₂SO₄ were added to it when the color lightened considerably showing that normal sulphate has been reformed and of course an excess of acid was present.

This acidified ferric sulphate solution was now added to 15cc KF solution (7.95 grams KF) + 60cc H₂O. A whitish precipitate was formed and on adding phenolphthalein and titrating with standard KOH, 3.5cc $\frac{N}{2}$ KOH were required to neutralise. This is the theoretical amount.

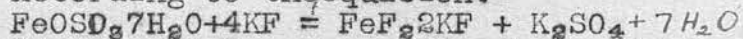
4. A similar experiment to (3) but after adding the 5cc H₂SO₄ to the ferric sulphate heat was applied to ensure combination and then after cooling and titrating with $\frac{N}{2}$ KOH 3.5cc of the latter were again required.

5. Another experiment similar to (3) but using NaOH instead of KOH for basicising gave a similar result.

The test is therefore quite satisfactory when carried out as described in (3), (4) & (5).

Experiments with ferrous sulphate and KF.

According to the equation.-



72 grams FeO are equivalent to 232.4 grams KF.

For these investigations a solution was made up containing .1295 gram FeO in each 25cc. .1295FeO requires .4105 gram KF.

1. 25cc ferrous sulphate solution were added to 5cc KF (2.65 grams KF) + 40cc water and phenolphthalein added and then standard $\frac{N}{2}$ KOH. .2cc produced a very indistinct red color.

2. With 10cc KF solution .1cc $\frac{N}{2}$ KOH produced a red color also indistinct.

3. With 15cc KF solution one drop $\frac{N}{2}$ KOH produced a red color with decided sharpness.

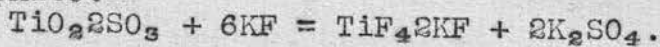
4. Table showing further results, 25cc ferrous sulphate solution used in each case.

Acid.	KF sol.	Water.	Alkali.
1cc	15cc	40cc	1cc
5cc	15 "	40 "	5 "
10cc	15 "	40 "	10."

Here also the test answers perfectly provided sufficient excess of KF is present.

Ferrous sulphate does not form a soluble basic compound, so no further experiments were made with it.

Behaviour of potassium fluoride towards titanate sulphate.-



The titanate sulphate was prepared by dissolving pure insoluble basic titanate sulphate $(\text{TiO}_2)_3\text{SO}_3$ in sulphuric acid so that the resulting solution was still somewhat basic. This solution was analysed for TiO_2 and SO_3 and contained in 1cc .1034 gram TiO_2 and .1854 gram SO_3 .

In these experiments I experienced a considerable amount of trouble in arriving at the correct manner of procedure when testing titanate salts. Titanate salts have a great tendency to decompose and form basic salts, and also to precipitate TiO_2 and liberate free acid. The TiO_2 in the ortho form also readily passes into the meta condition. From these three causes the troubles doubtless arose.

After making many experiments I invariably obtained results indicating that free acid in greater or smaller amount was present. These results of course were contrary to expectation seeing a pure specially prepared TiO_2SO_3 was being used.

The conclusion I came to was that on adding the titanate sulphate to the KF solution the precipitate formed is acted on by alkali or else a basic fluoride is formed carrying down basic TiO_2 and consequently liberating free acid, and on taking steps to prevent this happening the test was found to work quite correctly. The compound K_2TiF_6 is slightly soluble in water and therefore one must keep the liquid under test as strong as conveniently possible. I found also that it is necessary to heat the mixture of titanate sulphate and potassium fluoride to ensure proper combination, and before titration the heated liquid containing the double fluoride must be cooled to ordinary temperature. Since heating is here required a platinum or other non-corrodable vessel which will also stand heating to 100°C must be used.

A few of the tests giving discordant results were as follows.-

1. 3cc titanitic sulphate solution (containing .3102 gram TiO_2 and theoretically requiring 1.36 gram KF) were treated with 3.2cc $\frac{1}{2}$ H_2SO_4 to make the somewhat basic titanium sulphate into $TiO_2 \cdot 2SO_3$ and added to 30cc KF solution (15.9 grams KF) diluted with 100cc. H_2O and titrated with KOH required 9.5cc⁽²⁾. Theoretically one drop $\frac{1}{2}$ KOH should have produced the red color of the phenolphthalein.
2. A similar trial with 10cc KF used 5.2 $\frac{1}{2}$ alkali.
3. Same as (1) but the mixture of $TiO_2 \cdot 2SO_3$ + KF was heated and cooled before titration. 2.7cc $\frac{1}{2}$ KOH were required.
4. Same as (2) but heated and cooled, required 2.55cc alkali.

The procedure was successfully adopted of adding a measured amount of standard acid to the titanium sulphate and then adding it to the KF solution and warming on the water bath till a clear solution was produced, cooling to ordinary temperature and titrating with standard alkali and phenolphthalein.

The basic titanium sulphate solution was diluted to contain .1034 grams TiO_2 in 10cc. The SO_3 present was .1854 grams. .1854 grams SO_3 require .0927 grams TiO_2 to form $TiO_2 \cdot 2SO_3$.
 $.1034 - .0927 = .0107 =$ the amount of TiO_2 present in the basic form.

Experiments.-

1. 10cc of the basic titanium sulphate solution (.1034 gram TiO_2) were acidified with 10cc $\frac{1}{2}$ H_2SO_4 and added to 10cc KF solution (5.3 grams KF) + 50cc water. The whole was then warmed for a few minutes on the water bath in a platinum basin until a clear solution resulted. This was then cooled (quite cold) and titrated with standard alkali and phenolphthalein 8.9cc $\frac{1}{2}$ KOH were required to produce a red color.
 The K_2TiF_6 crystallised out in transparent crystals rendering the liquid easy to titrate.
2. A similar experiment but with 5cc KF solution required 8.85cc $\frac{1}{2}$ KOH.
3. Another trial with 10cc KF and 5cc $\frac{1}{2}$ H_2SO_4 required 3.9cc $\frac{1}{2}$ alkali.
4. A fourth experiment using 5cc KF and 5cc $\frac{1}{2}$ H_2SO_4 required 3.95cc $\frac{1}{2}$ alkali.

Taking the mean of the acid absorbed in these 4 tests viz.-

$$\frac{1.1 + 1.15 + 1.1 + 1.05}{4} = \frac{4.4}{4} = 1.1 \text{ cc } \text{H}_2\text{SO}_4.$$

$\frac{2}{3}$ Alkali corresponds to .01 gram TiO_2 per cc.
 $1.1 \times .01 = .011$ gram TiO_2 in basic form.
 The gravimetric analysis indicated .0107 gram.

There is thus a difference of .0003 gram TiO_2 amounting to .09% on $\text{TiO}_2 \cdot 2\text{SO}_3$.

These experiments with a somewhat basic soluble titanium sulphate serve the double purpose of demonstrating the feasibility of determining both free acid and free base. For by the addition of a known amount of standard acid the salt is converted into an acid one and by determining the free acid by the help of KF the amount of acid gone into combination to form a normal salt is easily found and is a measure of the basicity. These last remarks apply equally well to the cases of aluminium and ferric salts and the method is really simplified down to one process, viz.- the determination of free acid in these salts. It has been clearly shown that in order to obtain accurate results when analysing basic salts ~~before~~ they must first be converted into acid salts before adding to potassium fluoride.

For technical work this might be unnecessary but it is a simple expedient and since it leads to accurate results I would recommend it to be always adopted.

Behaviour of potassium fluoride towards zinc sulphate.-



A solution of pure $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was made up to contain 10 grams per 100 cc.

1. 10cc of this solution (containing .2822 gram ZnO equivalent to .3072 gram KF) added to 10cc. KF solution (5.3 gram KF) + 60cc water produced a whitish precipitate: on adding phenolphthalein and then standard KOH .1cc of the latter was required to produce a pink color which was somewhat indistinct.

2. A repetition on similar lines but with 15cc KF solution required only 1 drop of standard KOH to produce the pink color.

3. 10cc $ZnSO_4$ solution + 5cc $\frac{7}{2}H_2SO_4$ were added to 15cc KF solution and 60cc water and the titrated with standard KOH and phenolphthalein as indicator. 5.05cc (the theoretical amount) of standard KOH were required.

4. On attempting to make a basic zinc sulphate by adding a little potash to the above solution a precipitate was formed which would not redissolve so nothing further was done as regards a basic solution.

It is evident that neutral zinc sulphate can be rendered inactive to phenolphthalein by means of KF and if free acid is present it may then be determined by titration with standard alkali.

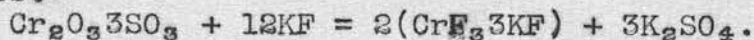
Having studied the behaviour of potassium fluoride towards aluminium salts, ferric and ferrous sulphates, titanitic sulphate, zinc sulphate, I next made investigations in regard to the determination of free acid by means of KF in salts of other bases, e.g. chromium salts, cupric salts, cobalt, nickel, manganese and lead salts and the results are hereinafter recorded.

For these latter investigations I used specimens of the various salts which happened to be to hand. There were all "pure" but were not specially prepared by myself. Further complete and systematic research will have to be made to establish this method in regard to these other metallic salts and will form the subjects for other papers.

Meanwhile as interesting and promising results were obtained in these preliminary experiments I have thought it worth while to record them here.

All these salts react acid to phenolphthalein until their combined acid has been neutralised.

Behaviour of potassium fluoride towards chromium salts.-



For this investigation I used chrome alum, 10 grams dissolved in water and made up to 100 cc.

1. 10 cc of this solution (containing .1533 gram Cr_2O_3 equivalent to .703 gram KF) were taken, diluted with 60cc H_2O and added to 10cc KF solution (5.3 gram KF). No precipitation occurred and on adding standard KOH 10.6cc were required to neutralise to phenolphthalein.

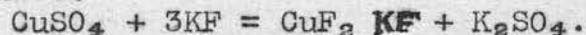
2. With 20cc KF solution 8.8cc standard KOH were required. On adding more alkali, the precipitate which had formed redissolved. (Here suggests itself a method of separating chromium from other metals, e.g.

from aluminium by adding potassium fluoride to the solution containing them in the cold. The aluminium goes down as $AlF_3 \cdot 3KF$ while the chromium remains in solution).

3. with 50cc KF solution. 7.85 cc standard $KOH(\frac{m}{2})$ were required to neutralise.
4. With 10cc KF solution but the mixture was brought to the boil. At $60^\circ C$ the green color of the liquid began to fade and at $75^\circ C$ a pale green precipitate began to form. After bringing to the boiling point .5cc standard KOH were required to neutralise.
5. Similar to (4) but the liquid was cooled before titration. .55cc standard KOH were required.

Possibly the chrome alum used contained a little free acid.

Behaviour of potassium fluoride towards copper sulphate.

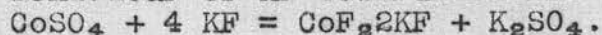


10 grams of the pure salt were dissolved in water and made up to 100cc.

1. 10cc of this solution (containing .319 grams CuO equivalent to .7005 grams KF) were added to 10cc. KF solution (5.3 grams KF) in 60cc H_2O and titrated with standard KOH and phenolphthalein, required 10.6cc $\frac{m}{2}$ alkali.
2. Using 20cc KF solution and 20cc H_2O 12.6cc $KOH(\frac{m}{2})$ were required.
3. 10cc. $CuSO_4$ solution added to 30cc KF solution and brought to the boil was blackened on addition of KOH to the hot mixture.
4. 10cc of the $CuSO_4$ solution were added to 30cc KF solution (1.35 sp.gr) without the addition of any water. The mixture was brought to the boil, then cooled, made up to 50cc. and filtered and an aliquot part titrated. The filtrate was acid to the extent that 1.7cc standard KOH were required to neutralise it. The filtrate contained copper, as ammonium sulphide produced a black precipitate. On washing the precipitate it partially dissolved and went through the filter paper. The precipitate formed by adding KF to cupric sulphate is evidently soluble in water to a considerable extent but less soluble in KF solution. Possibly some modification of the method of determining the free acid by the help of potassium fluoride

may be found which will give satisfactory results with cupric salts, and further experimenting will have to be carried out to arrive at the required conditions.

Behaviour of KF towards Cobalt salts.



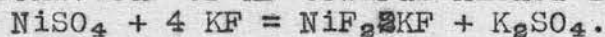
Cobalt sulphate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) was used for this investigation in the form of a solution containing 10 grams $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in 100cc.

1. 10cc. of the cobalt sulphate solution (containing .267 gram CoO equivalent to .828 gram KF) were diluted with 60cc H_2O and added to 30cc KF solution (15.9 gram KF). A beautiful pink precipitate at once formed which resembled the color of alkaline phenolphthalein, so the mixture was made up to 100cc and filtered through a dry funnel and paper. 50cc. of the colorless filtrate titrated with standard KOH required .05cc to neutralise.

2. 10cc cobalt sulphate with 5cc $\frac{7}{2}$ H_2SO_4 and 60cc H_2O added to 30cc KF solution made up to 100cc. and filtered, 50cc. titrated with standard KOH required 2.5cc $\frac{7}{2}$ KOH = 5cc for the 100cc. Theory = 5.00cc.

Here also there is promise of the free acid determination in cobalt salts being made to answer satisfactorily

Behaviour of KF towards nickel salts.



For this test I used pure nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) 10 grams dissolved in water and made up to 100cc.

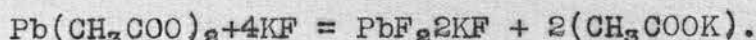
1. 10cc (containing .266 gram NiO equivalent to .828 gram KF) were diluted with 60cc H_2O and added to 10cc KF solution (5.3 gram KF). No precipitation occurred. On heating to the boil a precipitate of pale greenish white color was produced. On adding standard alkali to the hot solution 9.5cc were required to neutralise it to phenolphthalein.

2. With 20cc KF solution bringing to the boil as before, then cooling and titrating with standard KOH, .3cc was required to neutralise.

The method will doubtless apply to nickel salts also.

Here a method is suggested of separating nickel from other metals, e.g. from cobalt by adding KF to the solution containing Ni and Co in the cold, whereby the Ni remains in solution and the Co is carried down (see p. 33).

Behaviour of KF towards lead salts.

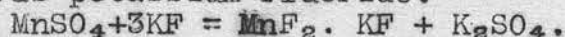


For this test I employed lead acetate and made up a solution of 10 grams in 100 cc.

1. 10cc (containing .6855 gram PbO equivalent to .712 gram KF) were diluted with 60cc H₂O and added to 10cc KF solution (1.06 gram KF). On adding phenolphthalein and titrating with standard KOH .1cc was required to produce a pink color.
2. 10cc of the Pb(CH₃COO)₂ solution with 5cc $\frac{7}{2}$ H₂SO₄ and 60cc H₂O were added to 10cc KF solution and then the mixture titrated as before. 5.25cc standard alkali were required to neutralise instead of the theoretical amount of 5.05cc. (5cc $\frac{7}{2}$ acid = 5.05cc of the standard KOH).
3. A similar test to (2) but using 2.5 cc $\frac{7}{2}$ HCl instead of 5cc $\frac{7}{2}$ H₂SO₄, gave the same result viz.- 5.25 cc standard KOH were required.

Further investigation will doubtless arrive at a satisfactory method in the case of lead salts.

Behaviour of Manganese sulphate (MnSO₄·4H₂O) towards potassium fluoride.



A solution of the pure salt 10 grams in 100cc. was prepared.

1. 10cc. of this solution (containing .3184 gram MnO equivalent to .782 gram KF) added to 10cc KF in 60cc H₂O and then titrated with standard alkali and phenolphthalein required only 1 drop of alkali to produce a pink color.
2. 10cc of the solution of MnSO₄ + 5cc $\frac{7}{2}$ H₂SO₄ were added to 10cc KF in 60cc H₂O and titrated as before. 5.05 cc standard KOH were required. This is the theoretical amount.

3. On attempting to make the $MnSO_4$ solution basic by addition of alkali it precipitated and went brown even with .2cc standard alkali.

Free acid in manganese sulphate can also be determined by means of KF solution.

Note.- in regard to determining the excess of base in insoluble basic salts this might be done by dissolving the substance in a known amount of suitable standard acid and then proceeding as usual with addition of KF etc.

Influence of the presence of insoluble matter.-

Insoluble matter must in all cases be filtered off, as hydrofluoric acid being formed (or else is potentially present) by $2KF + H_2SO_4 = K_2SO_4 + 2HF$, it is apt to attack the insoluble matter and become neutralised.

Examples.-

A. A sample of commercial precipitant for sewage (crude ferruginous aluminium sulphate) containing 12.4% insoluble matter was experimented with. 2 grams dissolved in water and added unfiltered to 10cc KF solution required only .25cc $\frac{N}{2}$ alkali to neutralise, = .25% Free SO_3 .

Another 2 grams filtered required 3.55cc $\frac{N}{2}$ alkali = 3.55% free SO_3 .

B. A sample of commercial aluminium sulphate used for purifying water supplies was next tried. It contained .34% insoluble matter.

1. 2 gram unfiltered required 1.5cc $\frac{N}{2}$ alk. = 1.5% free SO_3 .

2. 2 ,, filtered ,, 1.85 ,, = 1.85% ,,

The necessity of filtering is here apparent. This may be rapidly accomplished by taking a known weight and dissolving up to a known volume with water. Then after a thorough mixing, the solution is filtered through a dry funnel and paper, and an aliquot portion taken for the test.

Influence of ammonium salts e.g. when testing an ammonium alum liquor for free acid.

(1) 2 grams pure recrystallised ammonium alum dissolved in 20cc distilled water were acidified with 5cc. $\frac{N}{2}$ H_2SO_4 and added to 10cc KF solution + 40cc water. On adding phenolphthalein and titrating with $\frac{N}{2}$ KOH a very indistinct indication of neutrality was obtained when 5.3cc $\frac{N}{2}$ KOH had been added.

(2) 2 grams ammonium alum in 20cc H₂O were acidified with 2.5cc $\frac{7}{1}$ H₂SO₄; then 25cc $\frac{7}{1}$ alkali were added and the NH₃ entirely driven out by heating. 35cc $\frac{7}{1}$ H₂SO₄ were now added and heat applied until a clear solution was obtained. This was cooled and added to 10cc KF solution and titrated with $\frac{7}{1}$ alkali. 12.45cc were required to neutralise.

Total acid = 37.5cc.

Total alkali = 37.45cc.

Ammonium salts are well known to affect phenolphthalein, therefore NH₃, if present, must first be eliminated by heating with a known excess of standard alkali.

S U M M A R Y.

Method for determining the free acid and basic alumina in aluminium sulphates based upon the researches described in the preceding pages.-

The solutions required and the preparation thereof are fully described on pp. 8, 9 & 10.

A portion of the material to be tested is taken and dissolved in water so that each 10cc or 20cc contains from .1 to about .3 gram Al₂O₃ and the solution must be filtered if there is any insoluble matter. This should never be omitted.

A portion of this solution is now taken containing from about .1 gram to about .3 gram Al₂O₃ and is added to 10cc (or more) of the neutral KF solution which has been diluted with about 60cc of distilled water in a platinum basin or other vessel not attackable by HF.

Phenolphthalein (about .5cc) is now added and if a red color shows up, then the material being tested is basic and a fresh portion must be taken in a small beaker and rendered acid by means of a measured amount of standard acid and heated (preferably in platinum) for a few minutes to ensure combination. It is then cooled and added to the KF as before and after adding phenolphthalein it is titrated with standard alkali. The cc. acid minus the cc. alkali = the cc. standard acid gone into combination and represents the basicity of the material. An idea of how much standard acid to add to make the second portion acid may be arrived at by ascertaining the cc. standard acid required to discharge the red color produced by the first portion.

(An alternative method is to add the basic solution to the KF solution after the latter has been strongly acidified with a measured amount of standard acid.)

If on the other hand the first portion of the material produced no red color then it is either neutral or acid and standard KOH is now used to determine the degree of acidity by titrating in the usual way. Each cc $\frac{24}{2}$ H₂SO₄ = .02 gram SO₃ and .0085167 gram Al₂O₃.

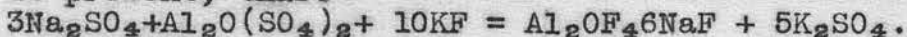
If much iron is present the KF solution must be increased sufficiently to prevent the alkali attacking the double iron fluoride, which should not become changed in color during addition of standard alkali.

If any salt of ammonium is present the NH₃ must be got rid of by boiling with a measured amount of standard alkali in excess and then, when the NH₃ is all off, standard H₂SO₄ is added and heat applied to render the whole soluble and acid. After thoroughly cooling the process is carried out as already described above.

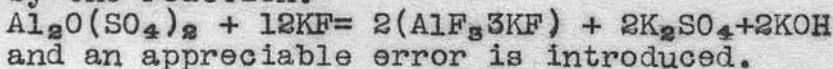
It is of course well known that ammonia and its salts render titration in presence of phenolphthalein useless.

When analysing basic aluminium sulphates which contain sodium salts, e.g. Na₂SO₄ through sodium carbonate having been used for basicising, it is necessary to add from 10-20cc of a saturated solution of neutral K₂SO₄ to the portion of the basic solution taken for analysis. The mixture is then slowly added to the KF solution after the latter has been strongly acidified with a known amount of standard H₂SO₄.

This is to prevent the formation of any basic sodium-aluminium double fluoride which appears to be formed in small yet appreciable amount when Na₂SO₄ is present, this.-



This basic double fluoride appears to be neutral to phenolphthalein and if any is formed there is of course an equivalent deficiency in the alkali formed by the reaction.-



In the experiments herein described it was noticeable that whenever incorrect results were obtained through a basic compound being formed, it gave a whiter and more opaque appearance to the precipitate. The normal double fluoride precipitate is of a more or less transparent nature and its appearance is an indication whether the reaction has taken place properly or not.

PART II.I N T R O D U C T I O N .

This section refers to the volumetric determination of combined acid along with free acid if it is present in aluminium sulphates and other aluminium salts.

Since both free acid and combined acid are simultaneously determined I shall use the term "neutralisable" for the acid which is determined by the method which consists in titrating the substance with standard alkali using phenolphthalein as indicator.

As it might prove useful I have collected all the volumetric methods of determining alumina that I could find. With regard however to the above special method it has already been studied by several investigators whose names are given on p. 5 (part I) and abstracts of their papers (with reference) will be found in the historical account following this introduction.

I have also examined the method in regard to determining the neutralisable acid in ferric, ferrous, titanium, and zinc sulphates since a small percentage of some or all of these bodies may occur in the aluminium sulphates of commerce.

In regard to the determination of neutralisable acid in aluminium, ferric, ferrous, zinc and titanium sulphate I have already referred to the previous work done by other investigators in the case of aluminium and here I make further reference to previous work in regard to other salts in general.-

Langer and Wanikiewicz (Ann.Chem.u.Pharm.1861,239) went very fully into the determination of combined acid in metallic salts. The investigations I carried out were done to familiarise myself with the method in regard to the salts mentioned above as these come under my daily notice.

The results obtained are herein recorded, as this test and the determination of free acid or free base are invariably both carried out when aluminium sulphates are being analysed.

H I S T O R I C A L .

Erlenmeyer & Levinstein Zeit.Chem.Pharm.1860,572
 J.pr.Chim LXXXI,254,D.P.J.CLVIII,126,Arch.Pharm.[2]
 CIV.275,Chem.Centr.1860,942,Rép.Chim.pure III,231.
 Recommended that aluminium sulphates should be converted into chlorides by means of $BaCl_2$ before titration so that formation of basic salts may be obviated. When free acids are present ammonium magnesium phosphate is added and the free acid titrated in the filtrate.

G.Merz Dingl.Poet.Jour.220 (1876)229,J.B.1876,997, titrated alums with alkali using corallin as indicator. In this way $\frac{23}{24}$ of the acid are neutralised and a precipitate formed which contains 8 molecules Al_2O_3 and 1 molecule SO_3 . Should the salts contain free acid this is first of all determined by the application of very weak soda solution with logwood solution as indicator.

G.Willgerodt, D.P.J.220,49, J.B.1876,997, has devised a similar method for the determination of alumina but makes no mention of free acid.

Reis, Ber.14,1172,J.B.1881,1154, in determining alumina volumetrically adds to the neutral solution a little $CaCl_2$ then titrates with $(NH_4)_2C_2O_4$ until a permanent precipitate remains, then the alumina is exactly combined with 3 molecules of oxalic acid.

R.T.Thomson, Chem.News 47,(1883) 135. On the use of litmus, methyl orange, phenacetin, and phenolphthalein as indicators. XII. Effect of alumina in alkaline solutions. On titrating aluminate using litmus as indicator the results are a little high and the end point indistinct. With methyl orange the results give "nearly the whole of the alumina along with the soda". With phenacetin and phenolphthalein the real amount of the soda present is obtained. The alumina obscures the end reaction slightly.

O.Miller, Z.Anal.Chem(1884) 24,258, recommends evaporating the alcoholic extract of sulphate of alumina to expel the alcohol and then titrating with alkali and methyl orange.

Dr.K.J.Bayer, Z.Anal.Chem.24 (1884) 542 titrates a 10% solution of the substance in water with $\frac{2}{7}$ soda and tropeolin ~~DD~~ or methyl orange.

The acid alumina solution is mixed with sufficient soda to redissolve the precipitated Al_2O_3 . It is then

divided into equal portions and titrated with H_2SO_4 using litmus in one case and tropeolin OO in the other.

With litmus the red coloration commences as soon as the excess soda and that as aluminate are neutralised. With tropeolin an additional quantity of acid being that required to convert the Al_2O_3 into $Al_2(SO_4)_3$ is required before the change from yellow to orange begins. The titration with tropeolin is best performed in a porcelain basin using not more than 50cc. liquid and a comparative color is prepared in a second basin. Warming should be avoided and the acid should finally be in excess and titrated back with normal alkali. Metals whose oxides are soluble in soda must first be removed. Bases precipitated by soda can be filtered off before titrating. Alkaline silicates are without influence.

Dr. K. J. Bayer, Chem. News 52 (1885) 277, Z. Anal. Chem. 25, 180. On a volumetric method for the determination of alumina. He determined the Al_2O_3 in aluminate of soda by means of the two indicators litmus and tropeoline.

In presence of litmus an aluminate titrated with standard acid to incipient reddening shows that only the three molecules of Na_2O combined with the Al_2O_3 and the free Na_2O are neutralised - the precipitated alumina being inactive.

If tropeoline be employed and the standard acid be added till the alumina just redissolves (when the pure lemon yellow of the tropeoline begins to pass into orange) the amount of acid added is equivalent to the total neutralisable alkali and the alumina. From the two determinations the alumina is found. Bayer recommends titrating with tropeoline in porcelain capsules using 40-50cc of liquid for $\frac{1}{2}$ cc of tropeoline (1-1000) and for "inexperienced persons" a blank may be made for comparison of colour. Excess of acid must be added and titrated back with soda. The application of heat must be avoided. Bayer in his experiments used .9154 gram alum (made alkaline with a measured amount of soda) in each trial.

E. B. Zeit. Anal. Chem. 1885, 25, 183. The author has used but not published a process, identical with Bayer's (Zeit. Anal. Chem. 24, 542) 3 years earlier. Tropeolin OO is to be used. The titration of excess of alkali is so troublesome and uncertain that it is easier to determine it by distilling with ammonium chloride and collecting the ammonia in standard acid and titrating it with Na_2CO_3 and methyl orange. A little rosolic acid is added to the distillation flask showing by becoming yellow the moment when all the NH_3 is expelled.

B.S.Proctor (New Remedies II,338) Zeit.Anal.Chem. (1885)24,237, studied the behaviour of free acid in presence of various salts, towards methyl orange and states that after adding alkali to alum solution and then acid the red color produced by the acid disappears in a short time through a part of the alumina precipitate dissolving and a permanent color is only obtained when all the Al_2O_3 is in solution.

R.W.Atkinson, Chem.News 52,(1885) 311 "On a volumetric method for the determination of alumina" states that Bayer's method (G.N.52,277) was fore-shadowed by R.T.Thomson (G.N.47,135) so that the principle of Bayer's method is not new.

Atkinson moreover asserts that the end points are too ill-defined to make the process reliable and suggests the use of phenolphthalein. He gives a comparison which shows in the case of ammonia alum that litmus gives a markedly low result (10.95% Al_2O_3 , 10.78 and 10.79 instead of 11.2 required by theory) whereas phenolphthalein gave 11.28. Quantitative gravimetric analysis showed 11.24. No account is given as to how the determination should be carried out.

Dr.K.J.Bayer, Chem News 53 (1886) 40 having read Atkinson's paper (G.N.52.311) points out he was unacquainted with Thomson's paper (G.N.47,135) and further states that a comparative test is indispensable.

H,Prunier, J.Pharm[5] X97, Volumetric determination of alumina in lime and cement. A known weight of cement is dissolved in HNO_3 and neutralised with ammonia using tropeolin as indicator. A known amount of $\frac{2}{2}$ ammonia is added and the whole made up to a given bulk, filtered and the excess NH_3 formed by titration with $\frac{2}{10}$ HNO_3 and litmus as indicator.

R.Gatenby, Chem News 55 (1888) 289 "On a volumetric determination of alumina". G. determines first the total neutralisable alkali by phenolphthalein and normal HCl. As soon as the red color disappears methyl orange is added and normal HCl until a pink color is obtained (in the cold) which does not vanish in a few seconds. This titration indicates the alumina and alkaline soda salts (e.g. Na_2CO_3). Then add litmus and titrate back with normal alkali till a distinct blue colour is obtained. The method is stated to be rapid, and accurate enough for technical use.

G.Lunge, Z.Angew.Chem, 1890,293. Monit.Scient. 1891,285,J.B.1890,2431 gives the following method for analysis of aluminate of soda.- A portion of clear

aluminate solution is treated with phenolphthalein and titrated in the warm with normal HCl until decolorisation occurs. This gives the soda combined with Al_2O_3 and SiO_2 and any free soda if present. A drop of methyl orange is added and titration continued at $30^\circ-37^\circ C$ until the red tinge becomes permanently yellow, this change marking the end point of the alumina determination.

K.J.Bayer (Chem.Zeit.1890,736) J.B.1890,II,2433 refers to Lunge's process (Z.Angew.Chem1890,227) and states that some years previously he described a process (J.B.f.1885,1928) which is practically the same method as Lunge's.

H.Heidenham, Chem.Centr.1890b,607,J.B.1890,2434 gives a direct method for the determination of total acid in aluminium salts. Using phenolphthalein as indicator he found that alumina in presence of a little tartrate acts like a weak alkali but in presence of a proportionately large amount of acetates it is indifferent. Also that the alkaline character of Al_2O_3 is more prevalent in hot than in cold solution. In water solution he advises 1 part Al_2O_3 per 100 to 200 of neutral potassium acetate, then add standard alkali until a part of the acid is still uncombined, now heat to drive out CO_2 , cool and titrate to the end.

Kritzschar, Chem.Ztg.1890,1223, J.B.1890,2431 determines alumina volumetrically by precipitating it from acetic acid solution by a measured quantity of disodium hydrogen phosphate and titrates the H_3PO_4 with uranium solution.

Cross & Bevan, J.S.C.I. X (1891)202,J.B.1891,2470 describing the determination of alumina by titration with standard alkali and methyl orange as indicator, assert that the neutral point is reached when the $Al(OH)_3$ is to the SO_3 in the molecular ratio of 2:2.5.

Lunge, J.S.C.I. X (1891) 314,J.B.1891,2471, maintains that the neutral end point, in titrating aluminium sulphate with $\frac{2}{3}$ soda using methyl orange as indicator, is reached when the $Al(OH)_3$ is to the SO_3 in the molecular ratio of 2:3.

H.Lescoeur, Bu 11.Soc.Chim,17/18,25-56,119-114 706-712,J.B.1897,721. On the alkalimetric determination of metals. With regard to aluminium he recommends phenolphthalein as being superior to litmus. In weak solution good results are obtained using alkali or baryta solution. The latter effects the separation of other metallic oxides (except Beryllium) which are insoluble therein.

C.R.Gysander, Chem. News 84, (1901)296, 306. "On volumetric determination of alumina for technical purposes". Gysander claims to easily obtain practically correct results by a process based on the following reactions.-



The reagents used are.-

Standard caustic soda solution free from aluminate and carbonate. Standard acid (sulphuric).

Distilled water free from carbon dioxide and ammonia.

Methyl orange solution (1 gram - 1000cc).

Phenolphthalein solution (2 grams - 1000cc).

Pure potash alum was used as the experimental material.

To carry out the process with regard to "pure" sulphate of alumina, 10 grams of the salt are dissolved in 1000 cc. H₂O and 50 cc. = .5 gram taken for the test.

2 drops of methyl orange solution and 4 drops of phenolphthalein are added along with 2cc. standard acid. Standard soda is now run in drop by drop with constant stirring until the color changes from pink to orange (not yellow) and if the material being tested was normal, exactly 2cc of the standard soda will be used. If the material was basic then the excess of alumina will form sulphate with the acid added and thus less than 2cc. of the standard soda will be required to neutralise the solution. The difference corresponds to the basic alumina present. The addition of soda is continued until the phenolphthalein shows a distinct pink, and the cc. used between the orange color of the methyl orange and the pink of the phenolphthalein indicate the per cent of total alumina.

The standard soda solution contains in 100 cc soda equivalent to 1.137 grams acid sodium oxalate.

PRECAUTIONS. (1). End point. It is well to make a solution of pure potash alum of a strength corresponding to that of the material being tested and add to it 2 drops methyl orange. This gives a color for comparison. The phenolphthalein end point is sharpest at about 30°C, above this temperature the results are incorrect and in excess of the theoretical amount "as alumina at high temperatures is acid to phenolphthalein". Below 20°C the reaction is very tardy and the end point obscure. At 50°C no pink color was obtained when even a slight excess of alkali was added over that equivalent to the SO₃ present. As the solution cooled the pink color began to appear and at 35°C the color was intensely red, "which shows that alumina is acid to phenolphthalein at high temperatures."

If basic sulphates of alumina are being tested they must be first neutralised with a measured amount of standard acid or else a serious error will be caused

by the formation of basic sulphate, in an insoluble form.

In sulphates of alumina containing small quantities of free acid the end point is very uncertain and the free acid must be determined by another method, (see p.4). When applied to commercial sulphates containing ferrous or ferric sulphate or both together the same procedure is adopted provided the amount of iron salt or salts present does not obscure the end point. The iron present must be determined separately and a corresponding correction made.

Addendum to be read after line 11 on page 44.-

A.H.White, 1902, J.Amer.Chem.Soc. 24[5] 457.
Volumetric determination of aluminium and free and combined sulphuric acid in alums.

On titrating a solution of alum containing neutral potassium sodium citrate with barium hydroxide solution only the free sulphuric acid and that combined with the aluminium are determined, whilst that in combination with sodium or potassium is not shown (phenolphthalein is the indicator used).

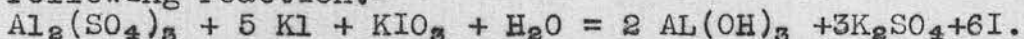
Again by evaporating a duplicate portion of the alum solution to dryness, dissolving the residue in neutral sodium citrate solution, and titrating with barium hydroxide, the difference between the result and that obtained in the former titration is equivalent to a third of the aluminium and from these results the amounts of sulphuric acid and aluminium can be calculated, and it can be determined whether the alum was basic or acid.

O.Schmatoela Ber.1905,38,985. J.S.C.I.XXIV, 349. The author recommends as the most reliable method for the determination of acids combined with aluminium, the titration of the boiling solution of the aluminium salt with alkali carbonate till phenolphthalein turns distinctly red, subsequently titrating back with acid if necessary. To compensate for the ~~the~~ incomplete decomposition of aluminium sulphate, the number of cc. of alkali solution used should be increased by .75%. For acetates, chlorides and nitrates the addition of an excess of alkali and back titration is always advisable on account of the volatility of the respective acids. The author recommends alkali carbonates for use in the titration as the amount of aluminium sulphate which they leave undecomposed is a constant = $\frac{1}{140}$ of the total amount.

by the formation of basic sulphate, in an insoluble form.

In sulphates of alumina containing small quantities of free acid the end point is very uncertain and the free acid must be determined by another method, (see p.4). When applied to commercial sulphates containing ferrous or ferric sulphate or both together the same procedure is adopted provided the amount of iron salt or salts present does not obscure the end point. The iron present must be determined separately and a corresponding correction made.

S.E.Moody, Amer.J.Sci.1905 [4] XX 181 finds a volumetric method for determining the alumina in aluminium chloride and aluminium sulphate on the following reaction.-



A convenient portion of aluminium salt is measured into a Voit flask. The KI and KIO₃ required are added and the whole distilled in a current of H.for 15-20 minutes and the I caught in KI solution and titrated with sodium thiosulphate.

S.E.Moody, Amer.J.Sci 1906 [4] XXII, 483 gives an extension of his former paper to include cases where free acid or basic alumina are present.

The individual bases are determined separately and the SO₃ for each is calculated. The SO₃ formed by the titration of the liberated I is distributed amongst the bases according to their requirements and any left over is reckoned as free acid. Any less than that required to combine with all the bases is calculated to basic alumina.

Fleischer. Maasanalyse. has given the following as a volumetric method of determining alumina.-

The aluminic solution is treated with sodium acetate and poured into a burette - having previously, if alkaline, been saturated with HCl - and is then run, drop by drop, into a standardised phosphate solution. To ascertain whether the end point of the reaction has been attained, it is necessary to filter a few drops of the phosphate liquid at intervals and see whether it still gives a turbidity with the aluminium solution. An alcoholic solution of "brasiline", which gives a violet-blue coloration with a slight excess of aluminium acetate in the warm may also be used as indicator.

Method for determining the total neutralisable acid in alums and sulphates of alumina.

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The water taken for the test is boiled for a few minutes in a suitable vessel. A porcelain basin on a good going burner answers quite well. The amount of water required varies from about 500cc for .2 gram Al_2O_3 in the portion taken for the test, to about 700cc for .5 gram Al_2O_3 .

After the water has boiled a few minutes 2cc. of phenolphthalein solution are added and then a little alkali to produce the pink color fixed for the end point.

Note.— One must boil the water before making it pink with alkali as even with distilled water an appreciably greater amount of alkali is required to produce the pink color at the boil if the alkali is added while the water is being heated up. This extra alk. would be subsequently active towards the sulphate of alumina and would introduce an appreciable error.

Having obtained the desired pink color the portion of the material being tested is now introduced into the boiling solution, which is kept briskly boiling right to the end of the test. Standard alkali is now added from a burette until a strong red color is produced. This excess (about 2-3cc) of alkali is to break up and neutralise any basic sulphate which may be formed. A measured amount of standard acid is now added in quantity just sufficient to discharge the red color completely and leave about .5cc in excess, and then standard alkali is slowly and carefully added until the agreed upon pink color appears. The total alkali added, minus the acid gives the alkali equivalent to the "neutralisable" acid.

When testing basic aluminium sulphate the portion taken for analysis must first be made acid by adding a measured quantity of standard acid until a drop shows a blue color when spotted with congo red and then heating to the boil to ensure combination between the basic sulphate and the acid. The point is that basic aluminium sulphates must preferably first be made into sulphates containing a little free acid before they are analysed otherwise results which are incorrect are liable to be obtained owing to precipitation of basic salt during the titration. The standard acid used for this purpose being known, it is of course reckoned in when calculating out the percentage of SO_3 .

A familiarity with the end point is easily attained by making a few tests with pure potash alum. The end of the neutralisation is indicated by the first appearance of a light permanent pink. Daylight

answers best for the test but equally good results are also obtainable in a suitable artificial light (e.g. electric or incandescent gas). The light pink color obtained in the boiling liquid becomes intensified as the latter cools and this may be used as an indicator that at least sufficient alkali has been added. An operator might imagine he had reached the end point when testing a ferruginous sulphate of alumina as the red color of the ferric hydrate might deceive him. If the right amount of alkali has been added the pink color will gradually deepen as the liquid cools. If this deepening does not occur then the liquid should be reboiled and a little more alkali added until the pink appears.

Gysander (Chem. News LXXXIV 296) considers that Al_2O_3 is acid to phenolphthalein at high temperatures because when he added to a solution of pure potash alum a slight excess of alkali over what is required to neutralise the SO_3 no pink color was obtained at $50^\circ C$. As the solution cooled the pink color began to appear and at $35^\circ C$ it was intensely red.

My experiments do not support this theory that Al_2O_3 is acid to phenolphthalein at high temperatures as if one takes a known amount of pure potash alum in boiling solution and neutralises it with alkali to produce a pink color to phenolphthalein and at once filters off the alumina it will be found that the clear solution containing the phenolphthalein (but no alumina) will develop a deeper red color as it cools. This I take it is a property of the phenolphthalein itself and is not due to any action of the alumina.

The tendency of basic salts to form, when dilute solutions are heated is well known, and in Gysander's case a basic salt of alumina and alkali is probably formed at $50^\circ C$ thus liberating a certain amount of free acid which decolorised the phenolphthalein; on cooling again the basic salt and the free acid re-united and the red color reappeared owing to the disappearance of the free acid.

STANDARD SODA SOLUTION. The soda solution employed was exactly equal to normal acid when titrated with methyl orange as indicator. This was standardised against exactly normal sulphuric acid adopting the same procedure as is observed when determining the total neutralisable acid.- 500 cc. distilled water were boiled for a few minutes in a 1000cc Berlin porcelain basin, 2cc of the phenolphthalein solution were

added and a little alkali to produce the pink color of the end point. 29cc normal acid were now added and then while keeping the solution boiling briskly the soda was added until a strong red color was produced. 1cc of acid was now added to decolorise the red and then soda was carefully and slowly added until the permanent pink of the end point was formed. For the 30cc normal acid I used 30.3cc of the soda solution.

Another trial with 32cc normal acid required 32.3cc of the soda solution.

62cc normal acid neutralise exactly 62.6cc of the soda solution.

Therefore each cc. of the soda solution will neutralise .039617 gram sulphuric acid (SO₃) equivalent to .01687 gram Al₂O₃ when titrating with phenolphthalein for indicator as above described. Exactly the same figures were obtained using tap water (Manchester supply) and carrying out in the same manner.

Investigations regarding the determination of total "neutralisable" acid in aluminium salts by titration with standard alkali and phenolphthalein as indicator.-

For these investigations I used pure recrystallised potash alum (p. 10).

Regarding the dilution - in each of the following tests (carried out as described on p. 5 grams of alum (.539 grams Al₂O₃) were used and 2cc phenolphthalein solution. 5 grams of alum theoretically should neutralise 31.95 cc of the standard NaOH solution each cc of which corresponded to .01687 gram Al₂O₃. In each case also the water taken was first boiled and then the phenolphthalein made pink by adding a drop of standard alkali. Porcelain basins were used for the tests.

1.	500cc distilled H ₂ O	required	31.70cc stand.alk.
2.	500 ,, ,	,,	31.75 ,, ,,
3.	500cc tap H ₂ O	,,	31.75 ,, ,,
4.	500 ,, ,,	,,	31.75 ,, ,,

The mean of these 4 tests is 31.74cc standard alkali 31.74 x .01687 = .53545 grams Al₂O₃ = 10.709% Al₂O₃ (Potash alum contains 10.78)

(5)	750cc	distilled H ₂ O	- required	31.9cc	stand.alkali.
(6)	750	,,	,,	31.95	,,
(7)	750	tap	,,	31.95	,,
(8)	750	,	,,	31.95	,,

The mean of these 4 trials is 31.91cc standard alkali. $31.91 \times .01687 = .538$ grams Al₂O₃ = 10.76%. (Theory = 10.78).

With 750cc water the end point is rather more difficult to determine probably due to the dilution, not of the alum, but of the alkali mixing in the large volume of water.

(9)	250cc	distilled H ₂ O	required	31.65cc	stand.alkali.
(10)	250	,,	,,	31.65	,,
(11)	250	tap	,,	31.55	,,
(12)	250	,	,,	31.60	,,

The mean of these 4 trials is 31.61cc standard alkali. $31.61 \times .01687 = .53325$ grams Al₂O₃ = 10.66% Al₂O₃. (Theory = 10.78).

In nos. 9, 10, 11 & 12 the precipitate was not so transparent as in the more dilute experiments. It was whitish and opaque probably owing to the presence of some basic sulphate which persisted as such and caused less alkali to be required to reach the neutral point.

Care should also be taken to avoid using too much phenolphthalein as it precipitates in the liquid rendering it opaque and disguising the end point.

Series of similar tests using 2 grams Alum (.2156 gram Al₂O₃).

In this series of tests the end point produced by addition of standard alkali (1cc = .085 gram Al₂O₃) was noted then $\frac{1}{2}$ acid was run in to discharge the pink color and then standard alkali added to bring it back - quite a noticeable difference is observed in the amounts of standard alkali required for the two end points.

				For 1st. end point.	For 2nd. end point.
(1)	250cc	distilled H ₂ O	required	25.4cc.	25.0cc
(2)	250	,,	,,	25.35	24.95
(3)	250	tap	,,	25.4	24.95
(4)	250	,	,,	25.45	25.05

The average of the 1st set is 25.4cc standard alkali. $25.4 \times .085 = .2159$ grams Al₂O₃ = 10.79%. The average of the 2nd. set is 25.0cc standard alkali $25.0 \times .085 = .2125$ gram Al₂O₃ = 10.62%

		for 1st. end point.	for 2nd. end point.
(5)	500cc. distilled water required	25.5	25.2
(6)	500 " " "	25.5	25.2
(7)	500 tap " "	25.6	25.35
(8)	500 " " "	25.55	25.4

The mean of the 1st set is 25.54cc standard alkali. $25.54 \times .085 = .2171$ gram $Al_2O_3 = 10.85\%$.

The mean of the 2nd. set is 25.29cc. standard alkali. $25.29 \times .085 = .2155$ gram $Al_2O_3 = 10.77\%$ Al_2O_3 .

		1 st e.p.	2 nd e.p.
(9)	750cc distilled water required	26.0	25.4
(10)	750 " " "	26.1	25.55
(11)	750 tap " "	25.75	25.52
(12)	750 " " "	25.80	25.55

The mean of the 1st. set is 25.91cc standard alkali. $25.91 \times .085 = .2202$ gram $Al_2O_3 = 11.01\%$.

The mean of the 2nd. set is 25.50cc standard alkali. $25.5 \times .085 = .2167$ gram $Al_2O_3 = 10.83\%$.

The best results were obtained by using 750cc. water when using a portion containing .539 grams Al_2O_3 and 500cc H_2O when using .2156 gram Al_2O_3 and I have indicated this in the description of the method given on p.45.

Application of the titration by standard alkali to ascertain the "neutralisable acid" in aluminium sulphate.

The preparation described on p.11 was used.

(1) 2.5 grams were taken (containing by gravimetric analysis 37.81 gram SO_3) and added to 500cc. tap water which had been boiled and made pink with 2cc. phenolphthalein solution and a drop of standard alkali (1cc. = .0199 gram SO_3) was added till a strong red color was produced 2cc $\frac{2}{2}$ acid were now added and a pink color developed by slowly adding standard alkali. 49.4cc in all of alkali had been used and deducting 2cc for the $\frac{2}{2}$ acid, 47.4cc of the alkali were required to neutralise the 2.5 gram aluminium sulphate to phenolphthalein.

$47.4 \times .0199 = .94326$ gram $SO_3 = 37.73\%$
an error of .08% too low.

(2) A repetition of this test using 500cc distilled water and alkali, 1cc of which = .03962 gram SO_3 required 23.75cc standard alkali.

$23.75 \times .03962 = .941$ gram $SO_3 = 37.64\%$, an error of .15% too low.

Further application of the determination of neutralisable acid to a few samples of aluminium salts. -

1. This was a specimen of aluminium sulphate crystallised in the usual manner from pure aluminium sulphate

solution.

It contained by gravimetric analysis 37.02% SO_3 (1.25 gram gave 1.348 BaSO_4 and 1 gram gave 1.0785 gram BaSO_4).

2 grams taken and added to 500cc boiled distilled water and titrated with standard alkali (1cc. = .03982 gram SO_3) as described on p.45, required 18.65cc standard alkali. $18.65 \times .03912 = .7389$ grams $\text{SO}_3 = 36.94\%$. Too low a result by .08%.

A similar test using 750cc boiling distilled water required 18.8cc. standard alkali: $18.8 \times .03912 = .7448$ gram $\text{SO}_3 = 37.24\%$. Too high a result by .22%.

This confirms previous results - the proportion of water was too large for the amount of Al_2O_3 present.

2. Basic aluminium sulphate p.11. This contained 33.16% SO_3 (.5 gram gave .483 gram BaSO_4).

1 gram was taken and acidified with 10cc. $\frac{n}{7}$ H_2SO_4 brought to the boil to ensure combination, then added to 500cc boiling distilled water and titrated with standard alkali (1cc = .03962 grams SO_3) and phenolphthalein as indicator, required 8.35cc.

$8.35 \times .03962 = .3318$ grams $\text{SO}_3 = 33.18\%$. Error of .02% too high.

3. Aluminium chloride.-

The preparation described on page 21 was employed.

It contains by gravimetric analysis 43.32 grams Cl.

1 gram titrated in 600cc boiling distilled water with standard NaOH (1cc = .0345 gram Cl) and phenolphthalein, required 12.6cc NaOH to neutralise it.

Another trial using 1 gram required 12.55cc NaOH.

The mean of these two is 12.575cc.

$12.575 \times .0345 = .4338$ grams Cl = 43.38% - an error of .06% too high.

4. Aluminium acetate solution.

This solution is described on p. 23 and contains .844 grams $C_2H_6C_2O_3$ per 10cc, determined by distilling 10cc with H_2SO_4 into normal soda.

(1). 10cc. were taken and added to 700cc boiling distilled water and .5cc phenolphthalein solution first made pink by a drop of alkali solution, then rendered strongly alkaline with 20cc $\frac{N}{1}$ NaOH to absorb the acetic acid in the boiling liquid. 4cc $\frac{N}{1}$ H_2SO_4 were now added and the red color disappeared. An addition of .54cc $\frac{N}{1}$ NaOH brought it back. Therefore $20.54 - 4 = 16.5cc = \frac{N}{1}$ alkali required to neutralise the $C_2H_6C_2O_3$. 16.54 multiplied by .051 = .8435 gram $C_2H_6C_2O_3$.

(2). Another experiment required 16.5 cc $\frac{N}{1}$ NaOH.

$16.5 \times .051 = .8415$ gram $C_2H_6C_2O_3$.

Average = .8425 gram $C_2H_6C_2O_3$ per 10cc.

Found by distillation .844. Error .0015 gram on

.844 too low = .18% on the $C_2H_6C_2O_3$.

This amounts to .12% on the aluminium acetate

(anhydrous), $Al_2O_3(C_2H_6C_2O_3)_3$.

Determination of neutralisable acid in Ferric Sulphate.

For this investigation I used the preparation described on p. 25.

It contained 1.023 grams SO_3 per 10cc by gravimetric analysis.

1. 10cc added to 500cc boiling distilled water and titrated with standard alkali (1cc = .03962 gram SO_3) and phenolphthalein as indicator required 25.95cc alkali to neutralise.

$25.95\text{cc} \times .03962 = 1.027$ gram SO_3 - an error of only + .004.

2. A similar test with tap water gave an identical result, viz., 25.95cc alkali were required.

3. With 750cc tap water also required 25.95cc of alkali.

In carrying out this test a good excess of standard alkali must be used to ensure decomposition of the basic sulphate of iron which forms in the boiling dilute solution. In the above tests 5cc excess of alkali were used after the red colour appeared. Then a measured quantity of $\frac{n}{1}$ acid added to discharge the red colour, and then standard alkali was carefully added until the red reappeared in the clear liquid.

This is observed after the ferric hydrate is allowed to settle by removing the flame for a minute or so. The pink colour is by the practised eye easily detected round the edge against the white of the basin.

In actual practice when testing samples of aluminium sulphates containing iron the latter is almost invariably in relatively small proportion compared to the alumina which, being colourless, dilutes the red colour of the ferric sulphate and thus the end point is easily observed.

The highest proportion of iron to alumina generally found in commercial aluminium sulphates ranges from 2.5 to 1% Fe_2O_3 on 14% Al_2O_3 .

Determination of "neutralisable" acid in ferrous sulphate.-

Pure recrystallised ferrous sulphate containing 28.78 grams SO_3 was used for this investigation.

A solution was made up containing .5 gram in each 25cc. (1) 50cc (1 gram $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were added to 600cc boiling distilled water, phenolphthalein was added and then $\frac{m}{1}$ NaOH was run in until a red color could be observed round the edge against the white of the basin 8.8cc alkali were added before a red color was apparent. Each cc. $\frac{m}{1}$ alkali = .04 gram SO_3 therefore $8.8 \times .04 = .352$ grams $\text{SO}_3 = 35.2\%$ SO_3 . Theory

requires 28.78%. This is an unsatisfactory test and great difficulty is experienced in determining when sufficient alkali has been added owing to the color of the precipitate. A modification has therefore to be adopted in the manner of the next two tests.-

(2) 25cc ferrous sulphate solution were introduced into a 200cc flask and 15cc $\frac{7}{1}$ NaOH added, then the volume made up to the mark and the contents of the flask well shaken and filtered through a dry paper and funnel into a dry 100cc measure. This 100cc of clear liquid was then titrated with acid and phenolphthalein to determine the excess alkali present. 3.9cc $\frac{7}{1}$ acid were required for the 100cc. Multiplying this by 2 and subtracting it from 15 we have $15 - 7.8 = 7.2 =$ cc $\frac{7}{1}$ NaOH taken up by the ferrous sulphate. $7.2 \times .04 = .288$ grams $\text{SO}_3 = 28.8\%$. Theory requires 28.78% SO_3 .

(3) A similar experiment showed 7.17cc $\frac{7}{1}$ NaOH neutralised by 1 gram $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. 4

$$7.17 \times .04 = .2868 \text{ gram } \text{SO}_3 = 28.68\%.$$

The mean of these two tests is 28.74% SO_3 - an error of .04% too low.

Determination of neutralisable acid in titanium sulphate.-

For investigations on this point a solution was employed of pure titanium sulphate. This was prepared by dissolving pure basic titanium sulphate in hot strong sulphuric acid to form an ultimate solution which proved to be slightly basic as the following analysis shows.-

(1) 10cc of the titanium sulphate solution precipitated by excess of ammonia, redissolved in excess of hydrochloric acid and again precipitated by ammonia, filtered, washed, dried, ignited and weighed yielded .1157 gram TiO_2 .

(2) Another 10cc after the same treatment gave .1148 gram TiO_2 .

(3) The filtrate from (1) concentrated and precipitated by barium chloride gave .6159 gram BaSO_4 .

(4) The ~~ms~~ filtrate from (2) gave .6156 gram BaSO_4 .

The mean of (1) and (2) = .1152 gram TiO_2 per 10cc.

The mean of (3) and (4) = .61575 ,, $\text{BaSO}_4 =$
.2114 gram SO_3 per 10cc.

.1152 TiO_2 requires .2304 SO_3 to form $\text{TiO}_2 \cdot 2\text{SO}_3$ therefore the SO_3 is somewhat deficient to the extent of .019 gram per 10cc.

The following titration tests were made to volumetrically determine the neutralisable acid.

Since no free acid was present, the neutralisable acid represents the combined acid.

(1) 750cc water were boiled, phenolphthalein was added and then a drop of $\frac{N}{7}$ alkali to make the liquid pink. 10cc of the titanium sulphate solution were now added and then standard alkali to produce a strong red colour, in all 10cc NaOH (1cc = .04 SO_3) were run in. 6.1cc $\frac{N}{7}$ H_2SO_4 were now added and the color disappeared. 1.4cc were required to bring it back.

Total alkali 11.4. Acid=6.1cc, therefore $11.4 - 6.1 = 5.3\text{cc}$ $\frac{N}{7}$ NaOH = amount of alkali to neutralise the total SO_3 .

(2) Another similar trial required 5.25cc $\frac{N}{7}$ NaOH.

(3) In this test only 350cc H_2O were used and the alkali required was 5.4cc .

(4) Similar to (3) and required 5.5cc $\frac{N}{7}$ alkali.

The mean of (1) & (2) is 5.275cc $\frac{N}{7}$ alkali.
 $5.275 \times .04 = .211$ gram SO_3 .

By gravimetric analysis the SO_3 in 10cc = .2114 so that the error is only .0004 on .2114 gram SO_3 = .19% on the acid or .12% on the $\text{TiO}_2 \cdot 2\text{SO}_3$.

The mean of (3) & (4) is 5.45cc which give a result which is .0066 gram SO_3 too high = 3.12% on the SO_3 .

The neutralisable acid in titanium sulphate can therefore be accurately determined volumetrically in the same way as aluminium sulphate considerable dilution being necessary to obtain accurate results.

Titanium sulphate occurs only in relatively small quantities in aluminium sulphates so that in analysing the latter for neutralisable acid, the dilution required for the aluminium sulphate will be ample for the small amount of titanium sulphate which may be present.

Determination of neutralisable acid in zinc sulphate.

1. 2 grams pure $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (containing 27.87% SO_3) were dissolved in 500cc boiling distilled water, phenolphthalein added and standard alkali added until the neutral point was reached. 13.90cc NaOH (1cc = .04 gram SO_3) were required.

2. Another trial on the same lines required 13.95cc NaOH.

The mean of these two tests is 13.925.

$13.925 \times .04 = .557$ gram SO_3 = 27.85% - an error of only .02% too low.

% Peter Stewart Esq
Alum Works

Manchester

11th May 1910

In accordance with the
regulations I herewith
declare that the Thesis
on "The determination of free
acid and basic Alumina
in Aluminium sulphate"
which I have forwarded to
Professor Speckie this day
is entirely my own work
and has been composed
by myself.

Thomas J. Corang