DETERMINATION OF FREE ACIDITY IN ALUMINIUM SULPHATE AND ALUMS USING HEXAMINE AND POTASSIUM FLUORIDE AS COMPLEXING AGENT

by

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ABSTRACT

The paper describes a modification effected in respect of the conventional fluoride method for determination of free acidity in aluminium sulphate and alums, by using hexamine as an acid binder in addition to potassium fluroide as complexing agent.

Introduction

Determination of free acidity in aluminium salts and alums is required in the evaluation of these materials. Direct alkali-metric method using suitable indicators were first recommended by Simmons[1], Birstein[2], and others [3-6] but were not found accurate. Recent methods for the determination of free acidity are, therefore, based on the fixation of aluminium as a stable complex with oxalate [7], [8] and fluoride [9-14] ions, prior to titration with alkali. The conventional fluoride method proposed by Craig[9], has come in wide use and is recommended among others by Scott[10], Rosin[11] and Thorpe[12]. It has however, recently been shown by Graham [13], that even this method gives low results. He has, therefore, suggested further improvement which, in practice demands several titrations for the completion of one single estimation. In a recent publication, Verma, Bhuchar, Therattil and Rai[14] while advocating the conventional fluoride method, point out that a mixture of phenol red and methylene blue gives sharp end point as compared to phenolphthalein used by the previous authors.

The method described in this paper is a modification of the conventional fluoride method, wherein hexamine has been used as an acid binder in addition to potassium fluoride as complexing agent. Satisfactory results can be obtained by a single titration.

Experimental

In this investigation carbon dioxide, free distilled water and analytical/pure grade reagents were used.

Methods

A. *Hexamine Fluoride Method*:—40 ml of 5% aluminium sulphate or 60 ml of 5% alum solution were taken in a 250 ml wax lined Erlenmeyer flask or polythene beaker. To this, 2 ml of standard 0·1 N. sulphuric acid solution, 18 ml of 20% hexamine solution (neutral), 35 ml of 25% potassium fluoride solution (neutral) and 3 ml of indicator (mixture of equal volumes of B.D.H.

9011, phenolphthalein 0·1% and thy-molphthalein 0·1%) were added. The mixed solution was titrated with standard 0·1 N sodium hydroxide solution to a distinct orange end point.

A blank determination with the reagents used above, but without aluminium sulphate/alum solution was also carried out simultaneously.

B. *Formaldehyde Hexamine Fluoride Method*—Same as method 'A' except that 5 ml of formaldehyde (40% neutral) solution was added prior to the addition of hexamine.

C. *Deferred Titration Method*—This method requires two titrations, an 'Initial' and a 'Deferred' titration.

(*i*) *Initial titration*—Same as method 'A' above.

(*ii*) *Deferred titration*—Same as method 'A' above except that volume of alkali solution equivalent to 90% of the 'Initial titration' value was added to the solution prior to the addition of hexamine and potassium fluoride assay value.

D. *Conventional Potassium Fluoride Method*—Same as method 'A' except that addition of hexamine was omitted.

Calculation

Per-cent free acidity expressed as H_2S0_4=

$$\frac{(a-b) \times N \times 0{\cdot}04904 \times 100}{W}$$

where a=volume in ml of sodium hydroxide solution required for the assay.
b=volume in ml of sodium hydroxide solution required for the blank.
N=strength in normality of sodium hydroxide solution, and
W=weight in gram of aluminium sulphate/alum taken for the assay.

N.B.—When 'b' is found to be greater than 'a' aluminium sulphate/alum contains basicity and not acidity.

Results

Results on free acidity determinations by the methods A, B and D are given in Table I. Table II contains comparative results on free acidity as obtained by the method developed by Verma et al [14] and the methods described in this paper. The results presented in Table III show the effect of mode of addition of complexing agent on the % recovery of free acidity, and Table IV gives the critical concentrations of hexamine and potassium fluoride required for complete recovery of acid. Table V summarises the results of indicators studied. The potentiometric titration curves obtained by different methods are given in Fig. 1.

Discussion of the Results

Source of error in the conventional fluoride method :—Graham[13], as early as 1946 during his investigation on the determination of free acidity of acidic aluminium salts solutions, noticed that the method is not accurate. This was attributed to the occlusion of a part of the acid in cryolite formed in situ.

If, therefore, this finding of Graham [13] is accepted, then one would expect the low recovery of acid to be dependent on the cryolite content of the system. Our results seem to agree with this expectation and the data in Table I, illustrates the degree of inaccuracy encountered in conventional fluoride method. From the general trend of the results, it appears that :—

The net occlusion/sorption of the acid increases with the increase in aluminium ion concentration. However, there is no linear relationship between the two.

It was also observed that in general in solutions of low aluminium content and high acidity the colour of the indicator gradually faded away on standing accompanied by a gradual decrease in the pH of the solution. This is probably due to desorption of sorbed acid from cryolite.

The fact that occlusion occurs even in neutral aluminium salts was shown by a series of experiments (Table I part A). The negative values obtained seem to indicate apparent alkalinity but not real. Similar results obtained by Verma et al[14] were however reported as real alkalinity. In our opinion this apparent alkalinity is due to the occlusion in the cryolite of a significant fraction of acidity liberated on account of the hydrolysis of the salt in aqueous solution, an equivalent amount of aluminium hydroxide goes into solution which subsequently reacts with potassium fluoride and liberates alkalinity. The net alkaline reaction, therefore, in samples which do not contain initial alkalinity can be explained. The recommendation of Verma et al[14] to adopt the conventional fluoride method would also yield low results irrespective of the efficiency of the mixed indicator.

Suppression of occlusion/Sorption by hexamine and formaldehyde

The results show that if hexamine is added to the system before the addition of fluoride then the occlusion/sorption is inhibited. This modification leads to accurate results if the free acidity is upto 2% and the titration is completed within 3 minutes (Table I parts B & C). If however the titration is delayed or the acid concentration is high the results are low. This is attributed to an acid hydrolysis of hexamine according to the following reaction whose effect is not so marked in low acid concentration or when the titration is completed in a short time.

$$(CH_2)_6N_4 + 2\,H_2S0_4 + 6\,H_20 \rightleftharpoons 2(NH_4)_2SO_4 + 6\,HCHO$$

The above view was confirmed by carrying out experiments in presence of both hexamine and formaldehyde, the latter being used to retard the hydrolysis of hexamine.

The extent of hydrolysis in the absence of formaldehyde and therefore, the percentage error in both low as well as high acid concentrations will depend upon the time interval between the addition of hexamine and completion of titration. However, to avoid any possibility of error due to hydrolysis of hexamine, addition of 2 to 3 ml of formaldehyde (neutral) prior to the addition of hexamine is recommended in all titrations, except in case of ammonium alum, since its ammonium component will react with formaldehyde liberating free acid. In such cases deferred titration method (method C) is recommended.

Our observations above are in complete agreement with the potentiometric titration results (Fig. 1). Dotted curved arrows  in curve A indicate a decrease in pH of the solution and fading of the indicator colour at the end point.

Potassium fluoride as complexing agent—Different authors have proposed different quantities of potassium fluoride required to form a stable nonhydrolysable complex with aluminium salt. Thus Scott and Furman[10] has recommended a molar ratio of potassium fluoride to aluminium as 160 : 1 as against 37 : 1 of Verma et al [14] and 30: 1 of Graham [13]. These ratios appear to be either on the higher or on the lower side. The data obtained by the authors is summarised in Table IV and shows the critical concentrations of potassium fluoride for various concentrations of aluminium. It will be seen that the combining ratio is not stiochiometric.

Role of hexamine—Hexamine behaves as a weak monobase. It forms addition compounds with acids, both free as well as those derived from hydrolysis of hydrolysable salts like aluminium sulphate etc. The acid in the addition compound can be quantitatively titrated with a strong alkali provided the interference due to hydrolysable salt can be avoided by suitable fixing agents.

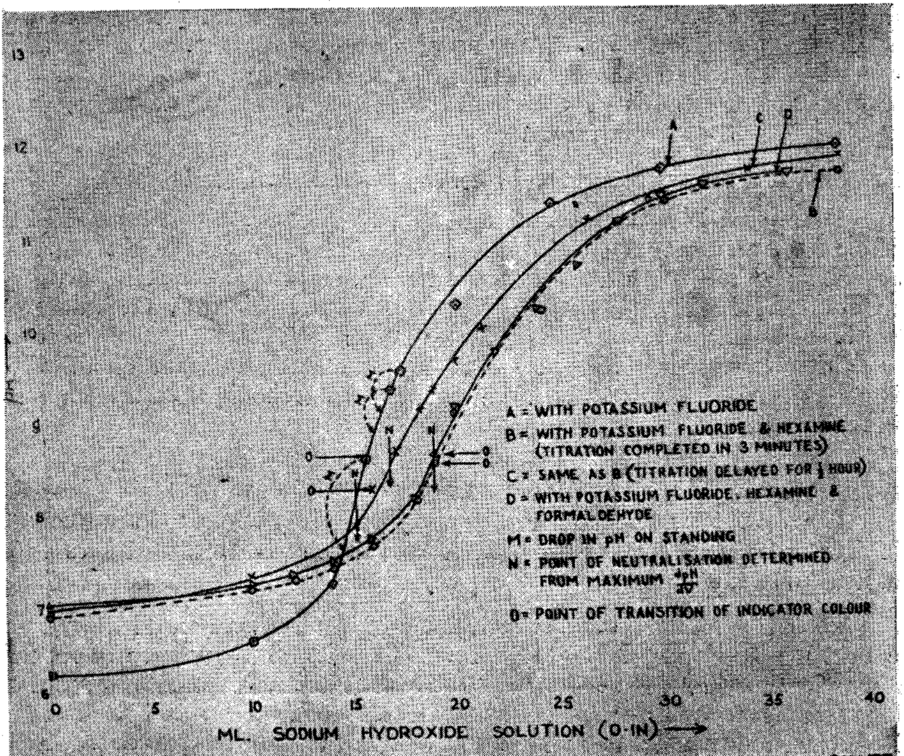

FIG. 1. POTENTIOMETRIC DETERMINATION OF FREE ACID IN ALUMINIUM SULPHATE

FIG. 1

Thus in the estimation of free acidity or alkalinity in aluminium sulphate, the reaction with hexamine may be written as follows assuming that free acid if present exists as H_2S0_4 and free alkali as Al $(OH)_3$. KF has been added to fix aluminium.

$$\text{(i) } Al_2\ (SO_4)_3+H_2SO_4\ \text{(Free)}+2(CH_2)_6\ N_4+12KF+6KF \longrightarrow 2K_3\ Al\ F_6+[(OH_2)_6\ N_4]_2\ \overline{H_2SO_4}+3K_2SO_4$$

$$\text{(ii) } Al_2\ (SO_4)_3+Al(OH)_3\ \text{(free)}+18KF \longrightarrow 3K_3\ Al\ F_6+3\ \overline{KOH}+3K_2SO_4$$

The precise mechanism by which hexamine prevents occlusion/adsorption has not been investigated; however, it appears that this reagent being basic in character has great affinity to bind acid than the relatively weaker Vander-wall forces capable of producing sorption of the acid on the cryolite. Further the occlusion of relatively large size hexamine—sulphuric acid addition compound in the comparatively small cryolite crystal is rather improbable. From the above it also follows that for accurate work addition of hexamine must be made prior to potassium fluoride.

Table IV gives the critical concentrations of hexamine for various concentrations of the salt solution. It will be seen that stiochiometry is only approximately maintained above a concentration of 0·5 gm of the aluminium salt, while below this limit hexamine required is approximately double the stiochiometric amount. Further it depends on 'H' ion concentration of the system. Accuracy of the result is not affected when hexamine is added in excess to the critical concentration; however inaccurate results are obtained if it is added below the critical concentration.

Choice of indicator—An examination of the potentiometric curves shows that in the titration of free acidity by the conventional fluoride method, the end point lies near pH 7·85, whereas, in the case of the methods developed the end point lies near pH 8·5. In view of these observations several indicators covering a pH range of 7·5 to 9·5 were examined for their suitability. From the results of Table V it will be seen that a fairly large number of indicators can be used. However, in view of author's experience, the mixed indicators [Table V.) S. No. 8] is recommended because of its better performance in respect of sharp change of the colour at the end point. The indicator recommended by Verma et al[14] was not found to give sharp end point with hexamine-fluoride method.

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TABLE I

Recoveries of Free Acidity by different Methods

Serial No.	Ml of aluminium sulphate solution 5% (W/V) taken	Ml of 0·1N H_2SO_4 solution added	Ml of potassium fluoride solution (25% W/V) added	% Recovery by conventional fluoride Method (Method D)	Hexamine-Fluoride Method		Formaldehyde Hexamine-Fluoride Method	Remarks
					Ml of hexamine solution (20% W/V) added (Method A)	% Recovery	(Formaldehyde added-5 ml in each case, Hexamine same as in case of Hexamine-fluoride method) % Recovery (Method B)	
					PART A			
1	10·0	*Nil*	12·5	—0·25	7·5	*Nil*	..	Negative values of recovery by conventional fluoride method indicate apparent alkalinity.
2	20·0	*Nil*	25·0	—0·50	7·5	*Nil*	..	
3	40·0	*Nil*	35·0	—0·60	18·0	*Nil*	..	
4	50·0	*Nil*	40·0	—1·05	25·0	*Nil*	..	
					PART B			
1	5·0	2·0	6·5	80·0	4·0	99·0	100·0	Titrations in case of hexamine-fluoride method completed within 3 minutes.
2	10·0	2·0	12·5	75·0	7·5	100·0	98·5	
3	20·0	2·0	25·0	64·0	7·5	98·5	100·0	
4	30·0	2·0	30·0	61·0	12·5	100·0	100·0	
5	40·0	2·0	35·0	52·5	18·0	102·5	100·0	
					PART C			
1	20·0	2·66	25·0	..	7·5	99·6	99·6	Do.
2	20·0	4·25	25·0	..	7·5	100·0	100·0	
3	20·0	4·50	25·0	..	7·5	98·9	100·0	
4	20·0	6·40	25·0	..	7·5	98·6	99·1	
5	20·0	8·52	25·0	..	7·5	99·8	99·8	
6	20·0	10·65	25·0	..	7·5	100·0	99·5	
7	20·0	15·98	25·0	..	7·5	99·5	99·5	
					PART D			
1	1·0	1·0	5·0	85·0	1·0	95·0	100·0	Low recoveries in case of hexamine fluoride method are due to delayed titration (10—15 mts) and high acid concentration.
2	1·0	5·0	5·0	91·0	3·0	95·0	100·0	
3	1·0	10·0	5·0	93·3	3·0	93·5	100·0	
4	1·0	15·0	5·0	93·0	3·5	93·0	100·0	
5	1·0	30·0	5·0	95·9	4·0	92·0	100·0	

TABLE II

Comparative results obtained by the method recommended by Verma et al[14]*, Hexamine-Fluoride method and Formaldehyde-Hexamine-Fluoride method*

Serial No.	Aluminium Compound taken	Amount taken in gram	Ml. of 0.1N H_2SO_4 solution added	Ml. of Potassium fluoride (25%) solution added	Percent recovery by fluoride method Verma et al[14]	Hexamine-Fluoride method		Percent recovery by Formaldehyde-Hexamine-Fluoride method (2ml of 40% Formaldehyde added in each case)
						Ml. of 20% Hexamine solution added	Percent recovery	
1	$Al_2(SO_4)_3$ 18 H_2O	1·0	9·3	20	96·8	20	99·1	99·46
2	Do.	1·5	6·1	25	95·7	20	98·3	100·8
3	K_2SO_4 $Al_2(SO_4)_3$ $24H_2O$	3·0	9·3	40	96·02	40	99·0	99·5
4	$(NH_4)_2SO_4$ $Al_2(SO_4)_3$ $24H_2O$	3·0	11·15	40	96·8	40	99·7	Not applicable.

TABLE III

Effect of mode of addition of reagents on recovery of free acidity (25 ml of 25% potassium fluoride solution and 7·5 ml of 20 % hexamine solution were added in each case)

Serial No.	Ml of aluminium sulphate 5%(W/V) solution taken	Ml of 0·1 N H_2SO_4 solution added	Mode of addition of reagents	Percent recovery of the acid
1	20	4·5	Hexamine & Potassium fluoride solutions were mixed and added.	92·2
2	20	5·4	Do.	92·6
3	20	7·2	Do.	94·5
4	20	8·1	Do.	94·5
5	20	5·3	Potassium fluoride added prior to hexamine	84·7
6	20	6·4	Do.	85·2
7	20	8·5	Do.	87·7

TABLE IV

Critical concentrations of Potassium fluoride and hexamine required for the estimation of free acidity

Serial No.	Ml of aluminium sulphate ($Al_2(SO_4)_3$ $18H_2O$) solution 5% (W/V) taken	Ml of N/10 H_2SO_4 added	Minimum volume of potassium fluoride solution (25%W/V) required to complex aluminium in Ml	Minimum volume of hexamine solution (20% W/V) required to bind acid in Ml	Percent recovery of the acid
1	10	10	12·5	7·5	99·5
2	20	10	25	7·5	99·7
3	30	10	30	12·5	99·4
4	40	10	35	18·0	99·7
5	50	10	40	25	99·3
6	70	10	50	37·5	99·6

TABLE V

Serial No.	Indicator	Colour change (from acidic to alkaline medium at end point)	Volume of indicator necessary for colour change	Remarks
1	Phenolphthalein (0·1% Alcoholic solution)	Colourless to pink	1 ml	End point not sharp in ordinary light but sharp in fluorescent light.
2	O-Cresol-phthalein (a solution obtained from B.D.H. Ltd. was used)	Do.	Do.	End point sharp.
3	Quinizarin Sulphonic acid (a solution obtained from B.D.H. was used)	Yellow/Orange yellow to violet	Do.	End point not sharp.
4	A mixture of equal volume of:— (*i*) Quinizarin Sulphuric acid (*ii*) O-Cresol-phthalein (*iii*) Phenolphthalein	Yellow/Orange yellow to Pink.	3 ml	Do.

TABLE V—*contd.*

Serial No.	Indicator	Colour change (from acidic to alkaline medium at end point)	Volume of indicator necessary for colour change	Remarks
5	Thymolphthalein in (0·1 % Alcoholic solution)	Colourless to blue	1 ml	End point sharp.
6	A mixture of equal volume of—			
	(i) Phenolphthalein	Colourless to violet	3 ml	Do.
	(ii) Thymolphthalein			
	(iii) O-Cresol-phthalein			
7	A mixture of—			
	(i) Phenol Red (0·1 alcoholic solution)	Green to blue	*(i)* 1 drop *(ii)* 2 drops	End point not sharp with hexamine-fluoride method but sharp with fluoride method.
	(ii) Methylene blue (0·02% aqueous).			
8	A mixture of equal volume of—			
	(i) B.D.H. 9011 (a solution obtained from BDH Ltd.)	From red through yellow to orange red	3 ml	End point sharp.
	(ii) Phenolphthalein			
	(iii) Thymolphthalein			
9	A mixture of equal volume of—			
	(i) Thymol blue (a solution obtained from BDH Ltd.)	Pink through yellow to violet	3 ml	Do.
	(ii) Thymolphthalein			
	(iii) Phenolphthalein			