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RESEARCH ON THE FREE ACID IN SUPERPHOSPHATES.

by A. Graire.

(Etablissements Kuhlmann)

The question of free acid in phosphatic fertilisers has been the subject of much research by the chemist as well as the agronomist.

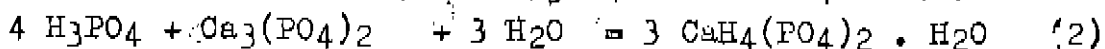
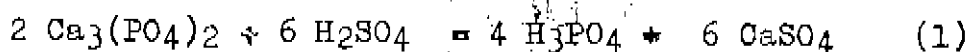
On the one hand the problem was to determine the best conditions for reacting the phosphates using the least amount of acid compatible with good solubilisation of P_2O_5 and as little free acid as possible so that the fertilisers would retain their virtues as dry, free-flowing powders.

On the other hand the problem was to discover the physiological nature of phosphatic fertilisers, their influence on the plants and the soil pH and by other means to establish with the help of field trials, the conditions for their use. So far as "physiological acidity" of phosphatic fertilisers is concerned, we shall recall merely that a large number of trials carried out over the last few years have demonstrated that superphosphate should not have been classed among the acid fertilisers. Even intensive applications do not modify the requirements of the soil for lime and the pH of the soil solution remains virtually constant. The water soluble P_2O_5 of phosphatic fertilisers is rapidly transformed by the action of salts of lime, magnesia, iron or aluminium into neutral compounds of low solubility. The compounds thus obtained through the reversion of phosphoric acid (dicalcium phosphate in non-acid soil, phosphates of iron and aluminium in acid soil) constitute a physiologically neutral fertiliser, the dispersion of which in the soil facilitates its assimilation by plants.

The Chemical Problem of Free Acid.

The chemical problem of the free acid is of a very different nature: it comprises the study of the reactions liable to produce acidity, methods of determining the free acid and the changes that may occur in this acid in the course of fertiliser production.

It is known that the reaction of sulphuric acid with tricalcium phosphate takes place in two stages. In the first, two-thirds of the phosphate is reacted with the formation of free acid. The latter then reacts with the unreacted phosphate, thus:

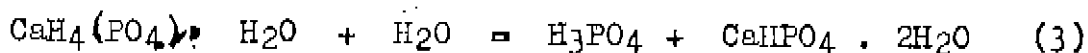


If immediately following one reaction the mass is rapidly diluted with a large volume of water or acetone, 60 - 66% of the phosphoric acid will be found in the filtrate in the free form. But if the same test is repeated after the mass has set, the P_2O_5 will be found mainly in the form of monocalcium salt, the free P_2O_5 not exceeding 25%. Reaction (1) is thus very rapid. Reaction (2) is slower and takes time.

Obviously the reaction of the phosphate depends on the quantity of sulphuric acid used. But it must be noted that free sulphuric acid is never found in a normally manufactured super. In fact, 10 minutes after contact of the acid and the ground phosphate, reaction (1) is practically complete. The use of an excessive amount of sulphuric acid merely has the effect of increasing the amount of free phosphoric acid. In practice, the acidulation is fixed at a certain weight % so the amount of free acid varies within fairly narrow limits. Under these conditions, the phenomena which occur during the production of a freshly prepared superphosphate may easily be discovered.

The high content of free P_2O_5 diminishes progressively, in the course of the curing of the superphosphate, without however disappearing altogether. The tricalcium phosphate is only slowly reacted by the dilute phosphoric acid. In a solid medium containing only traces of acid and $\text{Ca}_3(\text{PO}_4)_2$, this reaction becomes almost impossible because the phosphate and the acid are not in contact. Reaction (2) therefore, is not a complete reaction and we are left with a product containing a little free acid and a little insoluble P_2O_5 .

Moreover, the reversibility of the hydrolytic reaction of monocalcium phosphate does not favour the disappearance of the acidity



Dilution favours the formation of monocalcium phosphate, whilst a strong concentration decomposes it, releasing the acid. This reaction shows why free acid in superphosphate cannot be suppressed completely so long as the super contains monocalcium phosphate.

Solubilisation of di- and tri-calcium phosphates by dilute phosphoric acid.

The determination of free P_2O_5 is carried out generally on the solution obtained by rapid shaking (10 - 15 minutes) of the fertiliser in water. After filtration, an aliquot part of the filtrate is titrated with NaOH in the presence of methyl orange.

One might ask whether such a procedure is strictly correct, and whether there is not reason to fear that the di- and tri-calcium phosphates may be attacked by the free phosphoric acid of the fertiliser. Such a reaction appears not merely possible, but even probable.

In fact it has been known for a long time that methods which involve dissolving the superphosphate in water by means

of shaking yield results which vary with particle-size and length of time shaken, by reason of a slow reaction between the insolubles and the dilute solution of phosphoric acid. Thus, Schucht has shown that if the time the super is shaken in water is extended from 5 minutes to 2 hours, the soluble P₂O₅ rises from 15.94 to 16.16%. Quantitative trials made with precipitated di-calcium and tri-calcium phosphates have shown us that these compounds dissolve very easily in very dilute phosphoric acid, conforming to the reactions stated, thus effecting a reduction in the free P₂O₅.

Here we have the first source of error with low results from the titration of free P₂O₅ in aqueous solutions.

Influence of acid phosphates of iron and aluminium.

It is possible to obtain acid phosphates of iron and of aluminium in the following manner. A known quantity of dilute phosphoric acid of known strength is introduced into a flask, and a variable weight of neutral aluminium phosphate is added. It is then shaken for several minutes and filtered to eliminate excess AlPO₄. A solution of acid phosphate is thus obtained, the free acidity and aluminium content of which may be titrated by means of NaOH to methyl orange. During the titration, the aluminium phosphate is precipitated but it is possible to continue with the addition of NaOH up to the indicator change.

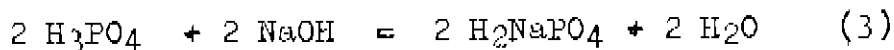
We used a hydrated aluminium phosphate with 68% AlPO₄ and a solution of phosphoric acid containing 25gr/litre of P₂O₅. Increasing amounts of AlPO₄ were shaken for 10 minutes in a 200ml flask containing 150ml water and 20ml phosphoric solution. It was then made up to 200ml filtered and 100ml of the filtrate titrated, (equal to 10ml phosphoric acid).

Test	Crude AlPO ₄	Dissolved Al ₂ O ₃	Total P ₂ O ₅	Free P ₂ O ₅ Actual	Titrated
1	0.250	0.0221	0.2809	0.1888	0.246
2	0.500	0.0395	0.3050	0.1403	0.241
3	1.000	0.0631	0.3379	0.0748	0.238
4	1.500	0.0719	0.3501	0.0503	0.235

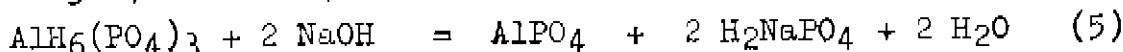
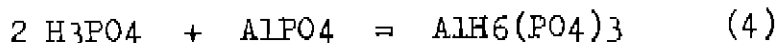
These results show that a considerable proportion of the aluminium of the AlPO₄ can be solubilised in the form of AlH₆(PO₄)₃. The aluminium having been eliminated as AlPO₄ it is shown that the P₂O₅ remaining in solution was equal to the initial P₂O₅ i.e. 0.250 gr. The genuine free P₂O₅ falls thus from 0.250 to 0.0503 owing to the dissolving of the AlPO₄.

However, the titration with NaOH remains substantially constant, whatever the quantity of combined aluminium.

Since the titration of the free acid takes place as follows:



it will be seen that solubilisation and neutralisation of the aluminium phosphate occurs as follows:-



Thus the aluminium phosphate which was dissolved is reprecipitated in the course of the neutralisation. It may well be that the acid phosphate dissociates into $AlPO_4 + 2 H_3PO_4$, and it is this acid which is estimated. Two-thirds of the P_2O_5 of the acid phosphate is titrated by the NaOH.

In the table a slight drop in the P_2O_5 titrated will be noted, which may be explained by the fact that the $AlPO_4$ contained a slight excess of Al_2O_3 in proportion to the P_2O_5 .

We have, on the other hand, studied the influence of dilution of phosphoric acid on the formation and titration of the acid phosphate. To this end we dissolved a constant weight of $AlPO_4$ in solutions of varying concentration, filtered and analysed on 10ml of initial solution:-

Test	10ml solution diluted to	dissolved Al_2O_3	total P_2O_5	free P_2O_5 Actual	P_2O_5 Titrated
5	25ml	0.0560	0.3280	0.0945	0.238
6	50ml	0.0497	0.3193	0.1121	0.240
7	100ml	0.0395	0.3050	0.1403	0.241

Thus the $AlPO_4$ dissolves the more readily the higher the concentration of the acid, or, what amounts to the same thing, the hydrolysis of the acid aluminium phosphate, contrary to that of calcium, is improved by dilution.

In conclusion, it is clear from the preceding tests that the titration of a phosphoric solution with NaOH is not substantially modified by the partial neutralisation of the acid by the $AlPO_4$ i.e. by the intermediate formation of the acid phosphate. But when the watersoluble P_2O_5 from a superphosphate containing aluminium hexaphosphate is titrated, the figure for the free P_2O_5 is increased by two-thirds of the P_2O_5 combined with the aluminium. The determination of free acidity is thus falsified by the presence of this phosphate and the figures found are too high.

Influence of sulphates of iron and aluminium on the titration of the phosphoric acid.

The addition of iron-aluminium sulphate to a phosphoric solution has the effect of modifying the titration of the acid by NaOH. One observes in the course of the neutralisation a precipitation of iron-aluminium phosphate and the colour change of the methyl orange lacks sharpness in the cloudy liquid.

To 10ml of a solution of phosphoric acid (23.6 gr P_2O_5 /litre) were added increasing volumes of a solution of iron alum (35.2 gr Fe_2O_3 /litre). After titration and filtering, the P_2O_5 was determined in the filtrate and in the precipitate.

Test	P_2O_5 used	Alum	Titration N/1 NaOH	P_2O_5 dissolved	$FePO_4$
1	0.236	0ml	3.25ml	0.236	0
2	0.236	2.5	5.3	0.154	0.166
3	0.236	5	7.15	0.076	0.336
4	0.236	10	11.15	0.002	0.603

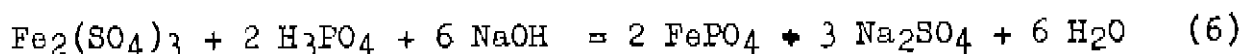
Thus with an addition of iron alum a part of the NaOH is utilised in precipitating the $FePO_4$ and the increase in the titration is proportional to the addition of the iron salts.

(1951)
Transposing the results of test 3 into weights we find:-

P₂O₅ precipitated = 0.160 gr. Fe₂O₃ precipitated = 0.176 gr.
FePO₄ = 0.336 gr.

NaOH corresponding to the remaining free P₂O₅ = 1.05ml.
NaOH corresponding to neutralisation in presence of iron = 6.1ml.
P₂O₅ used in precipitation = 1.009 Mol.
Fe₂O₃ of the alum = 0.99 Mol. FePO₄ precipitated = 2 Mol.

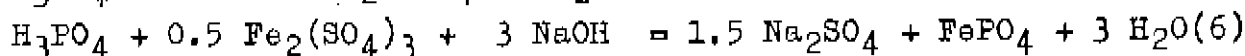
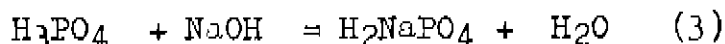
The reaction sought will thus be:-



All the results obtained agree with this equation, except that the volume of NaOH is slightly low, due to the uncertain end-point.

We have verified quantitatively that in the presence of aluminium sulphate an analogous reaction is obtained.

Thus the titration of a phosphoric solution by NaOH in the presence of iron salts gives rise to secondary reactions, whereby the iron is precipitated in the form of neutral phosphate before the free acid is completely neutralised. The excess of NaOH is then proportional to the amount of iron involved.



The phosphoric acid concerned in reaction (6) requires, therefore, three times as much NaOH as compared with the neutralisation according to reaction (3).

Monocalcium phosphate - Action of water and acetone.

The free phosphoric acid can be dissolved in water or in some suitable solvent e.g. ether, alcohol, acetone, ethyl formate. The results obtained by titrating the H₃PO₄ so dissolved will be very different, the lowest figures being obtained with ether and the highest with aqueous solutions. Of the various solvents employed, ether gives the most accurate results. Unfortunately, it is necessary to make a very long extraction with a Soxhlet, which limits its use to special cases. Acetone has the advantage over ether of dissolving the free P₂O₅ very rapidly but the method exercises a noticeable influence on the results.

First of all, we studied the action of water and acetone on the principal constituent of superphosphate, viz: monocalcium phosphate. To this end we prepared a salt as pure as possible, giving the analysis:-

P ₂ O ₅ total	55.40%	equivalent to	0.003902 M
CaO	22.07%	"	0.003936 M
H ₂ O	22.53%		
	100		

This composition corresponds to a mol. ratio CaO/P₂O₅ = 1.008.

If 1 gr. of this phosphate is shaken in 100ml acetone for 10 minutes then filtered, the solvent evaporated and titrated we found

CaO Nil
P₂O₅ free and total Nil

Under the same conditions but using varying quantities of water, we obtained in the presence of methyl orange:-

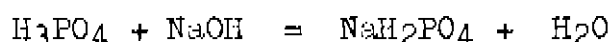
Test	Volume of water	NaOH N/4	Free P ₂ O ₅ per 100 gr. CaH ₄ (PO ₄) ₂
1	20ml	10.1ml	17.9
2	50	2.5	4.44
3	100	0.85	1.51
4	200	0.50	0.89
5	300	0.45	0.80
6	600	0.40	0.70

These results show that even at very high dilutions the aqueous decomposition of CaH₄(PO₄)₂ cannot be avoided.

It is usual to determine the free acid in superphosphate by dissolving 5 gr fertiliser in 200ml water and titrating 100ml of this. We may assume that this 100ml will contain about 1 gr monocalcium phosphate. Therefore, the results of titrating the acid will be too high.

Nevertheless, from tests which would take too long to explain here, we have shewn that by titrating with NaOH a phosphoric solution of monocalcium phosphate at a sufficient dilution, the free acid found in the aqueous solution will be substantially equal to that obtained by extraction with acetone. It thus appears to us that when the acidity is high the titrations are about correct, whereas when the acidity is low or nil the result will be in error.

Now, when a solution of monocalcium phosphate is titrated by NaOH the acid is first saturated with the formation of monosodium phosphate:-



If the hydrolysis of the phosphate cannot then take place, it can be due only to the presence of Na ions in the solution. We may assume that neutral salts such as NaCl would lead to a similar result.

We have, in fact, verified that an aqueous solution of pure monocalcium phosphate is neutral to methyl orange when a few crystals of salt are added.

We are thus led to the conclusion that acetone is suitable for the titration of H₃PO₄ in the presence of monocalcium phosphate. On the other hand, extraction with water gives correct results only in the presence of a sufficient quantity of H₃PO₄ or if salt be added to the solution.

Action of phosphoric acid on di-calcium phosphate in an acetone medium.

We have made numerous tests to obtain evidence of a possible reaction of H₃PO₄ with CaHPO₄ in an acetone medium. Varying amounts of CaHPO₄ and acetone were employed. We will merely indicate the conclusions.

The total P₂O₅ dissolved by acetone remains unchanged, whatever the quantity of di-calcium phosphate employed. Mere traces of lime were detected in the solvent. We may thus conclude that, contrary to what happens when water is used as the solvent, phosphoric acid does not react with di- or tri-calcium phosphate in an acetone medium. Under these conditions, therefore, the separation and determination of the free acid is correct.

Reaction of H₃PO₄ and AlPO₄ in acetone medium

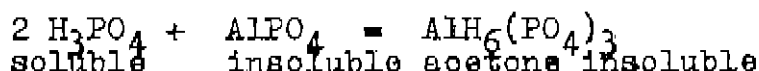
We have seen that in aqueous solution, phosphoric acid reacts with AlPO₄ forming an acid phosphate, the reaction being facilitated by the quantity of AlPO₄ and the concentrations of H₃PO₄. One might well ask whether the same reaction takes place in an acetone medium.

In order to avoid using water, we prepared a solution of H₃PO₄ in acetone and reacted this with increasing amounts of AlPO₄. After filtration, the free P₂O₅ in the acetone was determined by titration and by weight. We then obtained the water insolubles, and titrated the P₂O₅ and the solubilized alumina.

Test	Al ₂ O ₃	NaOH N/4	Free P ₂ O ₅	Total P ₂ O ₅	Soluble Al ₂ O ₃
1	nil	18.10ml	1.321	0.3202	-
2	0.068	17.60	0.312	0.3100	nil
3	0.272	17.15	0.305	0.3036	nil
4	0.680	16.30	0.289	0.2900	nil

Test	Reduction of P ₂ O ₅ in the acetone	P ₂ O ₅ titrated in the water sol. of residue	P ₂ O ₅ sol. of AlPO ₄	Al ₂ O ₃ solubilised
1	-	-	-	-
2	0.0102	0.0089	0.0044	0.0032
3	0.0166	0.0160	0.0080	0.0057
4	0.0302	0.0293	0.0146	0.0105

These tests show that the phosphoric acid has reacted with the AlPO₄ in acetone medium, as follows:-



The H₃PO₄ is less with acetone and becomes partly insolubilised in the form of acid phosphate. No trace of alumina passes into the acetone.

The residue contains AlPO₄ and AlH₆(PO₄)₃. The acid phosphate can be extracted by water, and the P₂O₅ titrated, the acidity being approximately equal to the reduction of the acidity of the acetone.

To summarise, even in acetone medium the H₃PO₄ reacts with the AlPO₄ yielding AlH₆(PO₄)₃, which is insoluble. The free acid thus eliminated can be titrated by taking up the residue in water and determining with NaOH which decomposes the AlH₆(PO₄)₃.

Reaction of acid aluminium phosphate in acetone medium

We study below the opposite of the phenomenon described above. We prepared a very concentrated aqueous solution of acid aluminium phosphate, and worked on 2ml quantities of this solution, which contained:

P ₂ O ₅ of the AlH ₆ (PO ₄) ₃	0.162 gr
Free P ₂ O ₅	<u>0.245</u>
P ₂ O ₅ total	0.407

Mixing this solution with 100 ml acetone produced an immediate precipitate. After filtration and titrating:-

Duration of Contact	P ₂ O ₅ free in Acetone	Acidity of the water solubles	Total acidity
Filtered immediately	0.260	0.095	0.355
after 1 hour	0.283	0.067	0.350
" 18 "	0.299	0.054	0.353

Immediate filtration, though it reduces to a minimum the decomposition of the acid phosphate, does not eliminate it completely. The free acid is, in fact, 0.245gr. After rapid filtration we found 0.260gr, whilst extraction with water gave 0.353gr.

Thus when sesquioxides are present in superphosphate in the form of acid phosphates it is possible, even in acetone, to obtain only approximate titrations. It is advantageous to drain on the filter, but even in this case the acid results are rather high.

Reaction of CaH₄(PO₄)₂ and Al₂(SO₄)₃ in acetone.

In the earlier tests we established that an aqueous solution of monocalcium phosphate and aluminium sulphate becomes acid immediately, and that even during washing on the filter a large quantity of H₃PO₄ is liberated.

We repeated these tests in the presence of 100 ml acetone with 0.5 gr CaH₄(PO₄)₂ and 0.250 gr Al₂(SO₄)₃.

Duration of contact	N/4 NaOH	Free P ₂ O ₅
Washed on the filter	0 ml	0 gr
1 hour	0.2	0.0035
24 "	0.2	0.0035

The release of P₂O₅, which in aqueous medium immediately attains 97.3% of its total value, becomes nil in acetone solution provided the washing on the filter is carried out rapidly.

Methods of Determination.

a. Determination of acid extracted by acetone.

Take 5 gr of superphosphate, or fertiliser based on superphosphate, and place on a 110 mm filter paper in a funnel. Extract on the filter with acetone (neutral) dropwise to a total of 100 ml solvent.

To the filtrate, add 100 ml distilled water, place on a water-bath and evaporate off most of the acetone. Allow to cool. Add a few drops of methyl orange (or methyl yellow) and titrate with an N/2 solution of NaOH to the indicator change.

The sulphuric acid present in the solution can be determined by precipitation with BaCl₂.

b. Determination of acid extracted by water.

1). Choice of indicator. The estimation of the acidity in the aqueous extract corresponds to the neutralisation of the acids and acid salts present; H₃PO₄, H₂SiF₆, FeH₆(PO₄)₃, H₂SO₄.

When the acidity is due exclusively to H₃PO₄, the colour change is sharp, but in the presence of salts of iron and aluminium which are precipitated, it is often difficult to appraise the changing tint of the indicator in the cloudy medium. We have compared the sharpness of the colour change of methyl orange and of methyl red, which are commonly employed together with methyl yellow, the use of which is recommended by the Compagnie Bordelaise and adopted in the preliminary project of the Syndicat des Engrais phosphatés.

Here are the results obtained with three superphosphates, at different stages of curing, with the three indicators. We give the volumes of N/1 NaOH required to neutralise 4 gr of superphosphate, as indicated by the beginning and end of the colour change.

Superphosphate	Methyl Orange	Methyl Red	Methyl Yellow
I	0.80 - 1.00	1.00 - 1.20	0.85 - 0.95
II	2.60 - 3.35	3.85 - 4.35	2.65 - 3.00
III	2.70 - 3.35	5.00 - 5.40	2.75 - 3.05

This table shows that the range of colour change of methyl orange is about twice as great as that of methyl yellow. The colour change of methyl red is sharper but yields results which are too high, the monocalcium phosphate being partially precipitated. These results could of course have been foreseen by a simple examination of the pH limits of the colour change of these three indicators:

Methyl orange	pH 2.0 - 5.0
Methyl red	pH 4.2 - 6.3
Methyl yellow	pH 2.9 - 4.0

It will be seen that the limits for methyl yellow are those which permit the most precise results.

This reagent is prepared as follows: Dissolve 0.050 gr of dimethylamino-nitro benzene in 100 ml alcohol and filter.

2). Procedure. Weigh 5 gr superphosphate (or compound fertiliser) and place in a 250 ml graduated flask. Fill to the mark with distilled water and shake for 10 minutes.

Filter and take 200 ml filtrate (= 4 gr.)

Add 4 drops of methyl yellow and titrate with N/2 NaOH to the indicator change of pink to yellow.

Application in the case of superphosphate.

We have endeavoured to interpret, with the aid of our previous experiments, the results obtained in the analysis of a superphosphate prepared well beforehand and having, in consequence, a low free acidity. The analysis supplied by the factory providing it indicated:

P ₂ O ₅ free	2.17 %
- water soluble	14.13
- water and citrate	16.25
- insoluble	0.38
- total	16.63

a) Acetone soluble

By filtering immediately we found:-

Free P ₂ O ₅ on the acetone soluble	3.30
Free P ₂ O ₅ on the water extract of the insoluble	0.21

b) Water soluble

It can be seen at once that the free P₂O₅ in the water soluble diminishes with the length of time it is exposed to solution: 2.56 for immediate filtration - 2.02 after four hours shaking.

We made two analyses on the product: washed on the filter, and after two hours' shaking, and determined the P₂O₅ in the water and in the insolubles.

Procedure	P ₂ O ₅ free	P ₂ O ₅ soluble in water	P ₂ O ₅ insoluble in water	P ₂ O ₅ total
Washed on filter	2.27	14.64	2.17	16.81
2 hr. shaking	1.99	14.85	1.94	16.79
Difference	- 0.28	+ 0.21	- 0.23	-

The free acid was titrated in the presence of NaCl. It is seen that the reduction in free acidity is more or less equal to the reduction of the insoluble P₂O₅, which shows that the H₃PO₄ has solubilised an equal quantity of dicalcium phosphate.

Moreover, it was found that the iron-aluminium salts are entirely in the citrate soluble, for all these tests. There is thus a reaction of the H₃PO₄ on the (Al.Fe)PO₄. The complete analysis of the citrate soluble gave:

(Fe.Al) PO ₄	1.20
CaH PO ₄	2.75
Ca SO ₄	44.59

Thus the action of the free acid in the aqueous solution was not on the $(Fe.Al)PO_4$ but on the $CaHPO_4$, which was partially solubilised. Thus, in the analysis of an old superphosphate, the acidity extracted by water is less the longer it is shaken because it reacts with the dicalcium phosphate. The quantity of monocalcium phosphate increases by an equivalent amount. On the other hand, the iron-aluminium salts, which are in the form of neutral phosphates, do not affect the determination. In consequence it has been shown that the results obtained remain substantially identical, whether extraction by water or by acetone is adopted.

Application to triple superphosphate.

Experience in the estimation of free acid in triple superphosphate reveals large differences between the water and the acetone methods. Hence, it is interesting to verify, with a concrete example, the conclusions of our study and to establish simultaneously the nature and the composition of this superphosphate.

The conventional analysis of such a superphosphate was as follows:-

P_2O_5 free	5.71
- water soluble	46.82
- soluble in water and citrate...	48.30
- insoluble	0.56
- total	48.86

The conclusions which might be drawn from the above figures, with a view to fixing the composition of such a super will be, as we shall show, completely erroneous.

1) Acetone soluble.

These were obtained for varying periods of contact between fertiliser and solvent. After filtration, the water solubles were extracted and the acidity of the new filtrate determined.

Period of contact	Acidity in		
	Acetone	Water	Total
Immediate filtrate	2.50	3.20	5.70
1 hour	2.76	3.04	5.80
16 hours	3.62	2.16	5.78

The sum of the two acidities remains fairly constant with direct titration. It is seen that, with time, the free P_2O_5 in the acetone increases as a result of the decomposition of the iron-aluminium acid phosphates.

2) Composition of Triple Superphosphate.

We analysed all the elements in the acetone soluble, the water soluble and the citrate soluble, thus:

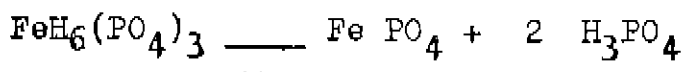
Acetone soluble	}	P ₂ O ₅	2.50 %
		P ₂ O ₅ total	44.64
		CaO	16.52
Water soluble	}	SO ₃	0.65
		(Fe.Al)PO ₄	1.30
		P ₂ O ₅ total	1.81
		CaO	1.46
Citrate soluble	}	SO ₃	1.13
		(Fe.Al)PO ₄	2.04

The constituent salts are thus the following:-

Acetone soluble	H ₃ PO ₄ free	3.24 %			
}	CaSO ₄ = 1.11	SO ₃	0.65		
	}	Fe PO ₄ = 1.30	CaO	0.46	
			Fe ₂ O ₃	0.69	
}	CaH ₄ (PO ₄) ₂ = 67.1	P ₂ O ₅	0.61		
		CaO	16.06		
		P ₂ O ₅	40.72		
	(free P ₂ O ₅ (difference))	3.31		
}	CaSO ₄ = 1.92	SO ₃	1.13		
		}	Fe PO ₄ = 2.04	CaO	0.79
				Fe ₂ O ₃	1.08
}	CaHPO ₄ = 1.63	P ₂ O ₅	0.96		
		CaO	0.67		
		P ₂ O ₅	0.85		

The iron-aluminium phosphates are found mainly as phosphates of iron, which we have expressed as Fe PO₄. It may be noted that the free acidity found (by difference) in the water soluble agrees well with the result of the titration; 3.31 and 3.20 %. This acidity corresponds to the hydrolysis of the acid iron phosphate. A certain part of the neutral phosphate produced by this hydrolysis remains on the filter and will be recovered in the citrate soluble. Another part dissolves but is precipitated in the course of the neutralisation of the aqueous extract.

The total P₂O₅ of the Fe PO₄ (1.57%) enables the P₂O₅ of the corresponding acid phosphate to be calculated in accordance with the formula for the decomposition:



The acid which is freed (2 P₂O₅) should therefore be 3.14. The acid found in the water soluble is actually 3.20. The agreement is as satisfactory as possible, and permits us to

conclude that the iron is entirely in the form of hexaphosphate, $\text{FeH}_6(\text{PO}_4)_3$.

The overall composition of the superphosphate examined is thus as follows:-

Free H_3PO_4	3.24 %
CaSO_4	3.03
$\text{CaH}_4(\text{PO}_4)_2$	67.10
CaHPO_4	1.63
$\text{FeH}_6(\text{PO}_4)_3$	7.67

Thus for this triple superphosphate, the free acid can only be determined by rapid extraction with acetone. The large discrepancies between the true acidity and the acidity found in the water soluble may be attributed to the high content of iron-aluminium acid phosphates and to the hydrolysis of this phosphate in the course of the operations of solubilisation and titration.

SUMMARY, DISCUSSION AND CONCLUSION

The chemical problem of free acid in phosphatic fertilisers consists in the study of the reactions capable of releasing free acid and of the methods of determination to be used. Our study has been limited to a comparison of the phenomena which can accompany the dissolution of the fertiliser in water or in acetone.

The reactions which occur during the manufacture of superphosphate are too well known to require repeating here. They indicate that in the final stage of the process we have a product which is slightly acid and contains a little insoluble P_2O_5 . In a concentrated medium, the disappearance of the acidity is prevented by the hydrolysis of the monocalcium phosphate.

When a super is dissolved in water for the purpose of determining the free P_2O_5 , secondary reactions occur. The dilute solution of phosphoric acid exercises a solubilising action on the insoluble phosphate of lime. The corresponding reduction of free P_2O_5 is more noticeable when the superphosphate is rich in decalcium phosphate, when it is shaken longer, etc.

Another source of error in the analysis of normal phosphatic fertilisers is attributable to the hydrolysis of the monocalcium phosphate, but this reaction is largely counteracted by dilution, by free acid or by the presence of sodium chloride. This means that the error which might affect the determination of free P_2O_5 remains relatively small under normal analytical conditions.

More important are the reactions to which the salts of iron or aluminium are capable of giving rise. Within the fertiliser, these can lead to reversion in the water-soluble P_2O_5 . They may also interfere while it is being dissolved in water or while the solution is being titrated and lead to an erroneous interpretation of the composition of the fertiliser.

The respective proportions of the neutral and acid phosphates of iron and aluminium depend on the reversible reaction :



According to this reaction, an increase in the free phosphoric acid is accompanied by the formation of hexaphosphate. A reduction in the free acid involves the transfer of iron into Fe PO_4 , which is insoluble in water but soluble in ammonium citrate. Similarly, phosphoric acid dissolves the neutral phosphate of aluminium forming a soluble acid phosphate, and the more AlPO_4 is present and the higher the acidity, the more it is dissolved. But if a phosphoric solution of iron-aluminium phosphate is diluted, the hexaphosphate is hydrolysed and the neutral phosphate previously dissolved is re-precipitated.

Similar phenomena occur during the solubilisation of the fertiliser in water or during the titration of the aqueous solution by alkalis. The result is the same in both cases, 2/3rds of the combined P_2O_5 of the hexaphosphate being counted as free acid.

But the reactions of iron salts are not limited to those we have described. Superphosphate can, in fact, contain sulphates, which during extraction with water react with the monocalcium phosphate with a corresponding increase in acidity. On titration with NaOH , 2/3rds of the sulphuric acid in the iron-aluminium sulphate is included as free acid.

Summarising then, the determination of free acid in the aqueous extract of a superphosphate is always accompanied by parasitic reactions. These reactions are of a double nature:-

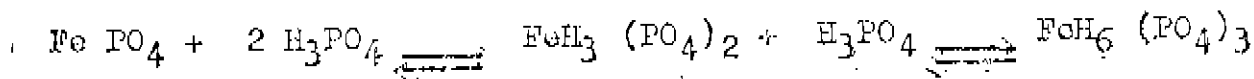
- 1) The reactions of the salts of lime, which lead to a partial saturation of the acid and give figures which are too low.
- 2) The reactions of the iron-aluminium salts, which provoke the phenomena of hydrolysis or double decomposition during extraction and titration and which result in the partial release of the acid combined with the iron and aluminium.

Many laboratories have adopted acetone as the solvent for the phosphoric acid, but although this confidence is justified from some points of view, there can be no question of employing a method of such delicate application and interpretation unless certain precautions are observed. Acetone is a rapid and quantitative solvent for phosphoric and sulphuric acids, and it is enough to wash the fertiliser on the filter for complete solution. Moreover, the acetone does not act upon the monocalcium phosphate. Lastly, saturation of the free acid by dicalcium phosphate does not occur in the presence of acetone.

Unfortunately, acetone does not give complete immunity from the parasitic reactions of iron and aluminium salts, and the characteristic reaction may occur in either direction. In order to prevent decomposition of the acid phosphates of iron and aluminium, it is as well to carry out the extraction

as rapidly as possible. But even with this precaution, the results remain somewhat high. On the other hand, the release of P_2O_5 by the sulphates of iron and aluminium does not occur in acetone solution, even after prolonged contact.

It is interesting to note that, according to circumstances, acetone favours the reaction of iron salts in one or the other direction. Thus one might suppose a tendency towards the formation of a compound intermediate between the neutral phosphate $Fe_2O_3 \cdot P_2O_5$ and the acid phosphate $Fe_2O_3 \cdot 3P_2O_5 \cdot 6H_2O$. This compound would have the composition of a triphosphate $Fe_2O_3 \cdot 2P_2O_5 \cdot 3H_2O$, and the reactions in acetone medium could be represented as follows:-



The phosphate $FeH_3(PO_4)_2$ does indeed exist and has been obtained by Winckler by decomposition of the hexaphosphate in the cold. This salt is not very soluble in water and probably insoluble in acetone.

In view of the preceding remarks, it would seem that all check on the acidity must be regarded as unreliable, since extraction with acetone permits the reaction of phosphates of iron to persist, at least in part.

We have, however, shown, with examples of super and triple super that the results obtained, whether by water or by acetone, can be used with equal profit. We also consider that any fresh research will find it an advantage to make use of both methods.