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**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

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RECENT ADVANCES IN THE DETERMINATION OF PHOSPHATE IN FERTILISERS

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INTRODUCTION

The official methods used for analysing fertilisers in most European countries have been summarised in "Fertilisers, Methods of Analysis used in O.E.E.C. Countries", published by the Organisation for European Economic Co-operation, 1952. From this, it can be seen that, in effect, there are five methods of extracting the phosphate, which is subsequently determined by one of five procedures. The processes for extracting the phosphate from the fertiliser materials are:-

1. Total phosphate, by strong mineral acids.
2. Soluble phosphate -
 - (a) by water,
 - (b) by Petermann solution (ammoniacal ammonium citrate solution),
 - (c) by neutral ammonium citrate solution,
 - (d) by 2% citric acid.

However brought into solution, the phosphate is finally determined in these official methods by one of the following procedures:-

1. Precipitation as magnesium ammonium phosphate direct from a solution containing citrate (and, occasionally, ferric citrate). This precipitate is calcined to magnesium pyrophosphate and weighed as such.
2. Precipitation as ammonium phosphomolybdate which is
 - (a) oven dried and weighed as such,
 - (b) heated to 550°C and then weighed,
 - (c) dissolved in standard sodium hydroxide and the excess of sodium hydroxide titrated with sulphuric acid,

- (d) dissolved in ammonia to give a solution from which magnesium ammonium phosphate is precipitated, to be washed, calcined to magnesium pyrophosphate and weighed.

It is probable that none of these methods is less than fifty years old, and of course cannot take into account subsequent advances in methods for the determination of phosphate in fertilisers. We have had recent experience with four modern methods, all of which involve considerable changes from the above methods, and which have, or are claimed to have, substantial advantages over the older methods. It is these newer methods that we propose to discuss. Let us emphasise that our aim is not to present a complete review of all published work of recent years on the determination of orthophosphate, but to draw attention to work illustrating present-day trends, which must be considered carefully and objectively before any attempt is made to establish an international method such as is envisaged by the Committee Internationale de Normalisation.

EXTRACTION PROCEDURES.

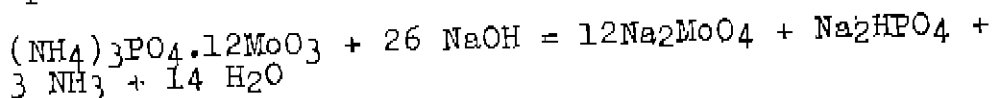
We must also premise that as our work has been done in Great Britain we have only concerned ourselves with British methods of bringing the phosphate into solution, that is, strong acids for "total P₂O₅", 2% citric acid solution for "citric acid soluble P₂O₅" in basic slag, and water for "water soluble P₂O₅". It is time, however, that further consideration be given to this question also. Why are such reagents as Petermann solution, or neutral ammonium citrate used? These reagents are, of course, solvents for calcium ions, not for phosphate. They are supposed to simulate the action of the plant in the soil but they certainly do not act in the same way as plants, and "available" phosphate has come to mean "phosphate extracted by some arbitrary statutory test" without any reference to the type of soil. The neutral ammonium citrate test, for example, was "standardised by pot and field experiments on lightly ammoniated superphosphate and experimental batches of high temperature phosphates using mainly acid soils, at a time when little phosphate was used on neutral soils. But now it may sometimes pay to ammoniate more heavily at the cost of losing some citrate-soluble phosphate I believe that a water-solubility test may have to be introduced in the United States as increasing quantities of fertiliser are used on the neutral or calcareous soils of the West. The ammonium citrate test has not been accepted in the United Kingdom, where we have many conditions requiring water-soluble phosphates. We do, however, need a test for products containing dicalcium phosphate. I suggest that separate statements of the water soluble P and the citric acid soluble P would serve for a wide range of fertilisers." These are not our words; they are not even the words of an analyst, but of one of the most distinguished of British agronomists, the late Dr. B.M. Crowther (Chemistry and Industry, 1954, Nov. 13, page 1409). If Crowther's suggestion were implemented, how it would simplify the life of the agricultural and fertiliser analyst, by saving his time and his reagents! Certainly the dissolution of "available" phosphate merits further extensive enquiry. It seems impossible to devise any one test which will indicate the behaviour of the fertiliser on every type of soil, but would it not be possible for agronomists or analysts and agronomists working in closer collaboration to devise some method less influenced by minor changes of conditions than the present procedures?

EXISTING OFFICIAL METHODS.

Similarly, all the statutory or official methods of determining phosphate in the extracted solutions are open to

criticism in the light of modern work. At a first glance it might appear that precipitation of magnesium ammonium phosphate followed by its ignition to magnesium pyrophosphate, must be an accurate method of analysis, and indeed when the whole of the phosphate is precipitated as $MgNH_4PO_4 \cdot H_2O$ (or $6H_2O$) and no other compound is precipitated, excellent results are obtained. But it is by no means easy to fulfil this condition. Other salts are always present in solution, sometimes in amounts vastly in excess of the phosphate, leading to risk of contamination. On the other hand, if magnesium, ammonium, hydroxyl and phosphate ions only are present in significant amounts, at least three undesirable insoluble salts may occur - $Mg_3(PO_4)_2$, $MgHPO_4$, and $Mg(NH_4)_4(PO_4)_2$, of which the last is the most likely, especially in the presence of excess ammonium salts, but only $MgNH_4PO_4$ will yield $Mg_2P_2O_7$ on ignition. (H. Bassett. "Theory of Quantitative Analysis" pp.81-88). Indeed, Lundell and Hoffman (J.A.O.A.C. 1924, 8. 186) said "Single precipitations as magnesium ammonium phosphate can never give correct results in the analysis of phosphate rock except through fortunate balancing of errors, for the precipitate always contains molybdenum (i.e. after dissolution of the yellow ammonium phosphomolybdate) and is rarely, if ever, of ideal composition." After discussing the effect on the composition of the precipitate of varying the rate and amount of the addition of the precipitate solution, the authors proceed, "It is obvious from the foregoing results that double precipitations of the magnesium ammonium phosphate are absolutely necessary; the loss of phosphorus through repeated precipitation is negligible." A few years later, Epperson in a model investigation (J.A.C.S. 1928, 50, 321) confirmed that a double precipitation is essential if accurate results are to be obtained. Even in the presence of citrate it is very difficult to obtain the correct result by one precipitation; correct results probably only occur through a compensation of errors, citrate tending to increase the solubility of the magnesium ammonium citrate at the same time as it lessens positive errors caused by the co-precipitation of other phosphates (lime, iron, etc.). (See, for example, Annals of Frauds and Falsifications, No. 311, Nov. 1934). Yet no official methods legislate for the purification of the magnesium ammonium phosphate before it is ignited.

A similar state of affairs is found when we examine the methods based directly on ammonium phosphomolybdate. The composition of this substance was a matter of controversy for many years, and the older literature abounds in such formulae as $(NH_4)_3PO_4 \cdot 12MoO_3 \cdot 2HNO_3$. The evidence is confused, no two authors being of the same opinion as to the composition of the precipitate or the "best" conditions for precipitation. The composition of the precipitate is known to be greatly influenced by the presence of sulphate ions. Falk and Sugiura (J.A.C.S. 1915, 37, 1507) even suggested that a definite compound was formed, to which they assigned the formula $(NH_4)_{14}(PO_4)_4SO_4 \cdot 53MoO_3$, a formula which no doubt fits the composition of the precipitate obtained under their conditions. For long it was considered that the precipitate contained nitric acid, but a note by Bourdon and Cotte (Bull. Soc. Chim. France 1949, 16, 428) showed that the precipitate did not contain nitric acid, although under the conditions prescribed by Lorenz it contained such an excess of molybdate as is equivalent to approximately 2 moles HNO_3 per mole. Consequently instead of consuming 52 equivalents of $NaOH$ per mole, to correspond with the equation:-



one mole of " P_2O_5 " corresponds, after allowing for eliminating the NH_3 liberated, to upwards of 54 moles of $NaOH$ according to

circumstances. True, the authors say that on dissolving the precipitate in ammonia and re-precipitating with nitric acid in the presence of ammonium nitrate, a compound of ideal composition is obtained, but this is never done in practice. Recent work shows that the composition of the precipitate approximates to but never reaches $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot x\text{H}_2\text{O}$, and the precipitate always contains excess of MoO_3 but not nitric acid. This excess varies with the acidity of the solution, the concentration of other ions present, and the concentration (i.e. the excess) of molybdate present. M. Frey (Bull. Soc. Chim. France 1950, 17, 685) states that only by precipitating in the cold, in a very narrow range of conditions, can a precipitate of ammonium phosphomolybdate of the correct equivalent weight be obtained.

The facts can all be accommodated within the framework of the hypothesis that the yellow precipitate is a solid solution of MoO_3 in $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot n\text{H}_2\text{O}$, and that there is a partition coefficient between the two phases, solid and solution. Thus under constant conditions of the solution there will be a constant excess of MoO_3 in the precipitate; any change will upset this state of affairs and lead to a different composition of precipitate. For example, sulphate ions in solution decrease the solubility of " MoO_3 " in the aqueous phase, and hence proportionately more appears in the solid phase - an effect akin to "salting out." All these phenomena confirm the view expressed by the late Dr. Bernard Dyer in 1931: "As regards fertilisers ... which contain large percentages of phosphate, the liability of the precipitate to variation under different circumstances make any modification of the volumetric method inadequate when really accurate results are required." (Lunge and Keane "Technical Methods of Chemical Analysis" 2nd Ed. Vol. III, 1931, pp. 536-538).

IDEAL OFFICIAL METHOD.

We have so far criticised the various "official" methods by implication; consider now the undesirable and desirable features of methods of analysis for referee purposes.

For such methods mere precision (i.e. reproducibility) within a restricted range of circumstances is not enough. Perhaps if all analysts in a country use a method that gives the same answer, and the answer is in error, nobody is seriously perturbed, but as soon as a transaction takes place across the border of the country and another method of analysis is in use, there can be trouble, delay and unnecessary expense. Our ideal referee method must be accurate as well as reproducible.

It must not be empirical and depend on standardisation under very closely defined conditions, because any unavoidable departure from the conditions - sure to occur sooner or later in dealing with unfamiliar materials - will lead to unsuspected errors. It ought to be based on clearly understood reactions proceeding to completion, and leading either to the precipitation of compounds of known composition and negligible solubility, or to the formation in solution of highly stable complexes. It should not be subject to "corrections" to allow either for losses due to solubility of precipitates, or gains due to impure precipitates.

It should not depend for its results on compensation of errors, and it should be flexible enough to allow it to be used on a large variety of samples without much, if any, change in procedure. It should not be influenced by those slight changes in manipulation which are summarised in the term "personal factors".

Finally, though this is not a matter of chemistry, it is desirable that it should be simple in manipulation, and of reasonable rapidity.

None of the "official" methods fulfils any of these conditions, but the mere fact that they are "official" has tended to surround them with an atmosphere almost of sanctity, blinding many analysts to their shortcomings. The economic necessities of recent years have, however, stimulated research into the determination of phosphates, into attempts to devise methods that would be more accurate and less time-consuming. Recent developments in the design of spectrophotometers enable the colour of a solution to be measured with the same accuracy as its titre, acid or alkali as the case may be. A better understanding of the fundamentals of volumetric analytical processes now permit the devising of volumetric methods fully as accurate as the classical gravimetric procedures; indeed, it can be maintained a priori that volumetric methods are potentially more accurate than gravimetric.

RECENT WORK

We have had experience over recent years of four methods, two volumetric, one gravimetric, and one colorimetric, which were thought to be worth considering as potential standard methods of analysis. They are:-

- (i) The method of Kassner, Crammer and Ozier,
(Anal. Chem. 1948, 20, 1052).
- (ii) The method of Wilson (Analyst 1951, 76, 65 and
Analyst 1954, 79, 535).
- (iii) The method of de Saint Chamant and Vigier,
(Bull, Soc. Chim. France, 1954, p.180).
- (iv) The Vanado-Molybdate Colorimetric method,

Misson	(Chem. Zeitung, 1908, <u>32</u> , 663),
Kitson and Mellon	(Ind. Eng. Chem. Anal. 1944, <u>16</u> , 379)
Barton	(Ibid, 1948, <u>20</u> , 1068)
Hanson	(J. Soc. Food and Agric. 1950, <u>1</u> , 172)
Gericke and Kurmies	(Zeit. Anal. Chem. 1952, <u>137</u> , 15)

These methods illustrate the current trends in chemical analysis very clearly. We propose to summarise and discuss them individually in relation to our experimental findings. In a few cases our results relate to only one laboratory but mostly they relate to those obtained in collaborative trials carried out in the laboratories of our three firms.

KASSNER, CRAMMER AND OZIER METHOD

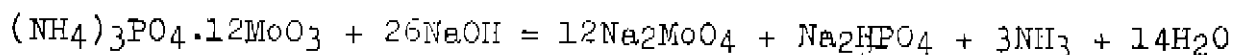
This paper is important because it is the first for many years in which any attempt is made to modify the properties of the molybdate reagent by adding a complexing reagent. The authors add citric acid to a fairly conventional "nitro-molybdate" solution, "the molybdate solution has been stabilised, and conditions for precipitation have been established which give an ammonium phosphomolybdate precipitate of uniform composition".

The yellow precipitate is dissolved in excess of standard alkali solution and the excess back-titrated, and the authors say that by their procedure it is no longer necessary to standardise empirically (but see over). Unfortunately, they nowhere

state what they assume to be the true formula of the ammonium phospho-molybdate and they give no results from which this can be calculated. It is unfortunate also that all their results were obtained on phosphate rock, and apparently they carried out no experiments in the presence of sulphate, which so profoundly influences the composition of the precipitate obtained in the usual way.

Their intention in adding the citric acid to their reagent was to "stabilise" it, that is to prevent the precipitation of "molybdic acid" and they quote earlier authors who have used similar reagents. They note also that the phosphomolybdate is formed (at the boiling point) in a coarsely crystalline condition, but they have apparently paid no attention to the mechanism whereby these results are obtained. The citric acid in fact forms a complex (or rather a series of complexes) with the molybdic acid, so that there is effectively less molybdic acid in solution; hence the precipitate is formed more slowly and has a smaller excess of MoO_3 . We shall see below that a further increase in citric acid concentration can prevent precipitation of ammonium phosphomolybdate.

In testing this method, the experimental procedure we have followed varies very slightly from the original and is given in the Appendix. Our results with pure recrystallised potassium dihydrogen phosphate indicated that the titration was not according to the theoretical reaction:-



and that it was necessary to use an empirical factor of:-

$$1 \text{ ml N/1 NaOH} \approx 3.051 \text{ mg P}_2\text{O}_5$$

With this factor, the method has been used for a large number of a variety of samples. The following is a summary of the results:- *

Number of results	80
Average P_2O_5	24.89% sol. P_2O_5
Standard Deviation	0.26
Coefficient of Variation	1.04

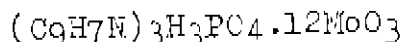
* In presenting our findings in all these tests, it will not be practicable to table all our results but only a summary. For example, more than 700 analyses by the Wilson Method have been carried out in 15 laboratories, and only mean results and variations will be reported. There are several ways of representing variation or reproducibility of a method, but we consider this to be most conveniently shown as "Standard Deviation", taking account of all results rather than by a range of results. Knowing the standard deviation, it is possible to give the approximate limits within which a stated proportion of the errors will lie. The chances are nineteen to one against any single result being in error by an amount which is greater than twice the standard deviation. In a series of samples of widely differing composition, the standard deviation may be misleading, and in this case we have brought the results to a common basis by using "coefficients of variation", i.e. the standard deviation expressed as a percentage of the arithmetical mean of the results.

These results were all obtained in one laboratory. As will be seen from later results, the method would appear to be somewhat less precise than the Wilson or the St. Chamant and Vigier methods. The method is fairly rapid, as the precipitate may be filtered off almost immediately instead of allowing a minimum of three hours for the completion of the precipitation as in the older methods. It is useful for routine work but lacks the essential prerequisite of the ideal referee method in that it involves a nonstoichiometric factor.

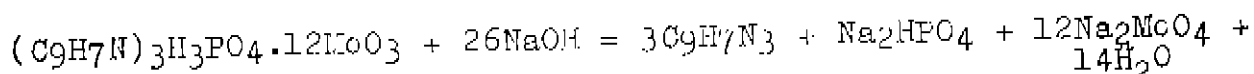
WILSON METHOD

The two papers by Wilson describe a new approach to the preparation of a phosphomolybdate of constant composition - a composition that corresponds exactly to the ratio $PO_4 : 12MoO_3$. The author was seeking for a rapid method, free from the disadvantages of known procedures. He considered the reactions available for the determination of phosphate, and concluded that the phosphomolybdate was most suitable as it was most free from interferences by other elements, but that it must be so modified as to avoid the undesirable features common to all the methods based on ammonium phosphomolybdate. He thought it preferable to form the 12 molybdiphosphoric acid first, and then precipitate it, as this would be likely to produce a more pure precipitate. He considered that ammonium was not the ideal cation to use since, as a base it is too strong and has an effect in blurring the sharpness of the end-point in the back titration of the excess sodium hydroxide; a base so weak that it had only a negligible effect on the pH of the solution would be preferable.

Quinoline in the form of a dilute solution in hydrochloric acid was chosen as precipitant. The quinolinium salt of 12 molybdiphosphoric acid is exceedingly insoluble in aqueous acids; if carefully precipitated it filters well, and has exactly the composition indicated by the formula:-



It obstinately retains traces of water (not water of crystallisation) and so is rather difficult to dry. Ten or twenty milligrams can be dried at 105° and weighed, thus giving an excellent micro method for phosphorus as the factor of 0.0321 for converting the weight of precipitate to weight of P_2O_5 is most advantageous. For larger amounts it is better to dissolve the precipitate in an excess of sodium hydroxide solution free from carbonate and titrate with N/2 hydrochloric acid. The reaction:-



is absolutely quantitative, and by titrating to a pH of 8.4 (thymol blue/phenolphthalein mixed indicator) accurate results are obtained. The composition of the precipitate is unaffected by any of the usual components of fertilisers (except soluble silica and ammonia (see below)). Large amounts of sulphuric acid cause abnormal and high results through the precipitation of "molybdic acid". Hence hydrochloric acid, aqua regia or perchloric acid must be used to dissolve the sample. The precipitation of the quinolinium phosphomolybdate takes place in a solution about 1.5N with regard to hydrochloric acid, but the exact strength is not critical. The precipitate is not of cubic structure, like the ammonium salt, but of a much lower order of symmetry (monoclinic or triclinic), and it may be that it owes its freedom from excess of MoO_3 to the inability of the crystal lattice to accommodate any excess.

This method was subjected to a most thorough and extensive series of collaborative trials both by the authors of this paper and by the British fertiliser industry in general. We believe that few, if any, new analytical methods have ever been subjected to such a searching examination.

The method was checked against the British Official method described in the Regulations to the Fertilisers and Feeding Stuffs Act*. This is Jorgensen's procedure of precipitation as ammonium phosphomolybdate which is dissolved in ammonia to give a solution from which magnesium ammonium phosphate is precipitated and then calcined to magnesium pyrophosphate and weighed. This method was not chosen as standard primarily for its accuracy but because it is the method on which is based all commercial fertiliser transactions in Britain. In all, eighteen samples were tested in fifteen laboratories and it was shown that the new method was significantly more precise than the Official method.

It was, however, deduced from these results that the new method was less precise for "total P_2O_5 " than for "water soluble P_2O_5 ". At the same time, the criticism was brought forward that silica in solution would interfere. The method was then modified, as detailed in Wilson's second paper and explained below, to overcome the interference of silica. Improvements were also made in the method of dissolving the samples prior to determination of total P_2O_5 and in eliminating the effect of ammonium salts.

Soluble silica in any form is converted by molybdic acid to 12 molybdisilicic acid, which is exactly analogous to the corresponding phosphoric acid and is titrated by sodium hydroxide, leading to high results. Ammonium ion causes the precipitation of a certain amount of the ammonium salt instead of the quinolinium salt, causing a tendency to low results. It is quite easy to remove silica by dehydration and to destroy ammonium salts with hypobromite, nitrite or aqua regia, but much time can be saved in the course of the analysis if these steps can be omitted. Further, in the determination of "citric acid soluble P_2O_5 " in basic slag almost the whole of the silica present dissolves in the citric acid, and its removal from the citric acid solution would be very awkward. It was known that the addition of tartaric acid or "certain other substances" completely inhibits the reaction between silica and molybdic acid, and this reaction has been successfully applied to the volumetric method by incorporating citric acid in the reagent. This reagent is made by dissolving molybdic anhydride in the minimum quantity of sodium hydroxide solution, and pouring into a solution of citric and hydrochloric acids in water. The reagent is stable.

The hypothesis was put forward that the citric acid forms a complex with the molybdic acid. Molybdic acid reacts with hydrogen ions to form " MoO_3 " and water. The " MoO_3 " in turn reacts with the silica or phosphoric acid to produce the 12-molybdiheteroacid. If sufficient citric acid is present to lower the concentration of "free" MoO_3 below that required for the substantial formation of silico-molybdic acid (which is less stable than phosphomolybdic acid) not enough silico-molybdic acid will be formed to exceed the solubility product of quinolinium silicomolybdate, and this will therefore not be precipitated. Of course if very large amounts of citric acid are present, the formation of phosphomolybdic acid also will be delayed or inhibited.

* The methods in these Regulations are summarised in "Fertilisers, Methods of Analysis used in C.E.E.C. Countries", published by the Organisation for European Economic Co-operation 1952.

As ammonium phosphomolybdate is much more soluble than the quinolinium salt, it can be seen that the concentration of citric acid can be adjusted so that even in the presence of moderate amounts of ammonium salts, ammonium phosphomolybdate is not precipitated. Thus the quinoline citric molybdic method is virtually free from interferences and can be applied to a very large variety of substances with but little modification and without prior separation of silica. Basic slag, for example, may be dissolved completely in dilute mineral acid and the phosphate determined on a suitable aliquot of the solution.

These modifications incorporated in the method, working details of which are given in the Appendix, were then tried out in a further series of collaborative trials.

In this second series we analysed a variety of samples, including basic slag. The experimental work was not restricted to exceptionally skilled analysts, but arranged so that competent analysts of average experience should participate. Every result was to be reported and duplicate determinations were to be truly independent and not carried out in parallel by the same person on the same day. One exception was made to the request for independent tests, in that for basic slag, aliquots of the same citric extract were to be analysed by the old and new methods, the whole being repeated for the second determination.

Some of the laboratories were not able to complete their tally of determinations; others, however, supplied more than two results on some of the samples. The following tables show the bias and precision of the method. Samples 1, 2 and 3 are compound fertilisers of different types, 4 is a representative Morocco rock, 5-8 are basic slags. The basic slags were tested particularly to determine the effect of silica. Samples of superphosphate were not included as it was considered that the determination of P_2O_5 in compound fertilisers is more difficult, and that the results with compounds could be applied to superphosphate analysis. The extraction procedure for "soluble P_2O_5 " is that of the Statutory Regulations to the Fertilisers and Feeding Stuffs Act, with water as solvent for the compound fertilisers and 2% citric acid for the basic slags. Although results are reported to four significant figures, the methods are obviously not of this accuracy, but it was desirable for statistical purposes to calculate the results to this degree.

TABLE I

Sample	No. of Partic. Labs.	Total No. of Results	Soluble P_2O_5			Total P_2O_5		
			Av. by Official Method	Av. by Wilson Method	Bias	Av. by Official Method	Av. by Wilson Method	Bias
1. Comp. Ferts.	15	101	8.319	8.296	-.023	8.958	9.001	-.056
2.	15	92	7.278	7.267	-.011	8.995	9.001	+.006
3.	14	50	11.95	11.91	-.04			
4. Morocco Phos.	15	54				33.41	33.48	+.07
5. Basic Slag	14	97	7.93	7.88	-.05	9.40	9.60	+.20
6.	12	81	17.57	17.49	-.08	19.78	19.71	-.07
7.	14	93	15.26	15.09	-.17	16.38	16.26	-.11
8.	13	86	15.37	15.27	-.10	16.44	16.42	-.02
Average Bias					-.07			+.002

TABLE Ia

Precision of Methods expressed as Standard Deviations

Sample No.	Soluble P ₂ O ₅		Total P ₂ O ₅	
	S.D. Statutory Method	S.D. Wilson Method	S.D. Statutory Method	S.D. Wilson Method
1	0.085	0.072	0.099	0.075
2	0.098	0.073	0.164	0.081
3	0.169	0.111		
4			0.228	0.250
5	0.237	0.123	0.289	0.177
6	0.227	0.193	0.320	0.178
7	0.212	0.190	0.261	0.169
8	0.227	0.219	0.276	0.144

TABLE Ib

Precision of Methods expressed as Coefficients of Variation

Sample No.	Soluble P ₂ O ₅		Total P ₂ O ₅	
	C. of V. Statutory Method	C. of V. Wilson Method	C. of V. Statutory Method	C. of V. Wilson Method
1	1.022	0.869	1.111	0.842
2	1.346	1.004	1.823	0.900
3	1.414	0.924		
4			0.682	0.747
5	2.988	1.560	3.075	1.843
6	1.291	1.103	1.618	0.903
7	1.389	1.259	1.594	1.039
8	1.476	1.434	1.679	0.877

In every case except "total P₂O₅" in Morocco phosphate, the new method is appreciably more precise than the old. In the case of phosphate rock, the difference has no practical significance. Both methods tend to be less accurate in the analysis of basic slag than of compound fertilisers; the difference is less marked in Wilson's method.

DE SAINT CHAMANT AND VIGIER METHOD

These writers also made a fresh approach to an old problem - the quantitative precipitation of pure magnesium ammonium phosphate. They divided their work into two parts:-

- (a) The quantitative production of well crystallised pure ammonium magnesium phosphate,
- (b) The masking of all ions that can interfere.

They claimed that their technique could be applied to a variety of samples and that its precision was good.

They carefully studied the precipitation of magnesium ammonium phosphate, and showed that it was complete at pH 8. They also showed by microphotographs that by addition of sufficient non-ethanolamine to a somewhat acid solution containing ammonium ions, magnesium ions and phosphate ions, they obtained

a well crystallised precipitate in contrast to the precipitates obtained in the usual way. Their precipitate is slightly deficient in P_2O_5 (and correspondingly carries an excess of MgO) but the deviation from the ideal composition is very small. Other variables affecting the precipitation were also studied, and included the concentrations of ammonium chloride, magnesium chloride and mono-ethanolamine, the volume of solution, the effect of temperature change and the quantity of phosphate which should be present. It was shown that for each variable there was a fairly wide range over which good results were obtained, and the best conditions were finally established. There is a tendency for minute amounts of phosphate (of the order of 0.4 mg. P_2O_5) to escape precipitation, hence one should avoid applying the method to aliquots containing less than 100 mg. P_2O_5 , the preferred quantity being from 100 mg. to 400 mg. Finally, it was claimed that precipitation was complete in 30 minutes.

Many previous attempts have been made to precipitate magnesium ammonium phosphate in the presence of other elements (e.g. calcium, aluminium, iron), by using citric acid or ammonium citrate to inhibit interference but correct results are obtained only through compensation of errors in particular circumstances. Calcium is not completely prevented from forming an insoluble phosphate, and precipitation of magnesium phosphate is incomplete (but see Hoffman and Lundell. J. Res. Nat. Bur. Standards. 1937, 19, 59.) For these reasons the authors investigated other complexing agents, in particular ethylenediaminetetraacetic acid (E.D.T.A.), used as its ammonium salt, and lactic acid.

E.D.T.A. forms a series of very stable anionic complexes, particularly with divalent metals; the complex with calcium is more stable than that with magnesium, particularly at pH 8-10. This property permits the complete precipitation of magnesium ammonium phosphate from a solution in which calcium phosphate is not formed. Calcium is a common component in fertilisers and the best conditions for suppressing its interference were carefully studied. It was proved that in the recommended procedure up to 400 mg. Ca are without effect.

Aluminium, iron and titanium were not satisfactorily masked by E.D.T.A., and it was already known that citric or tartaric acids were not entirely satisfactory masking reagents. After considering various possibilities, lactic acid was selected, and found to be satisfactory for dealing with amounts of iron and aluminium provided less than 40 mg. are present. If more is present so much lactic acid must be used that precipitation of the magnesium ammonium phosphate becomes slow and incomplete. It is interesting to note that results (on 185 mg. P_2O_5) tend to be high by about 0.5 mg. This is because the filter paper absorbs and retains minute amounts of the substances present in solution, particularly magnesia (average 0.40 mg. MgO).

Fairly large variations in the quantities of the reagents used are without effect on the results.

Finally the authors described in detail their procedure (see Appendix) and concluded with a note on the precision obtained in their laboratory.

We have subjected this method to a collaborative trial, confined to highly skilled analysts, for the analysis of phosphate rock. For comparison the samples were also analysed by the British Official method, to which we have already referred. A summary of the results is shown on the next page.

TABLE II

Sample	Number of Laboratories	Number of Analyses	Av. result by St. Chamant & Vigier Method (a)	Av. Result by British Official Method (b)	Difference (a) - (b)
Gafsa Phosphate	6	20	28.18	28.31	-0.13
Morocco Phosphate	6	22	32.81	32.85	-0.04

TABLE IIa

	Standard Deviation		Coefft. of Variation	
	St. Chamant & Vigier	British Official	St. Chamant & Vigier	British Official
Gafsa	0.21	0.12	0.75	0.42
Morocco	0.26	0.09	0.80	0.28
Combined	0.23	0.10	0.76	0.32

The results show that for phosphate rock analysis it is less reproducible than the much slower British Official method. It is slow compared to Wilson's Method.

For other samples we have done only a few tests, the results of which tend to suggest that it is not so satisfactory a method for mixed fertilisers as it is for phosphate rock.

VANADO-MOLYBDATE COLORIMETRIC METHOD

The reaction on which this elegant, simple and accurate method is founded was first described by Misson, in 1908, (Chem. Zeit. 1908, 32, 663) for the determination of phosphorus in steels, and it is curious that until the last few years it seems to have been undeservedly neglected. It is possible that its potentialities were only appreciated when accurate and reliable spectrophotometers became available. Two or three papers dealing with it were published in America. Barton was the first to apply it to phosphate rock and to combine vanadate and molybdate in one reagent. In England, it was first put forward as a method of fertiliser analysis by Hanson in 1950. In Germany, an excellent review was published by Gericke and Kurat in 1952.

In this reaction the acid solution containing orthophosphate is reacted upon by an acid solution of molybdic acid containing vanadic acid. Instead of 12 molybdiphosphoric acid there is formed a vanadi-molybdiphosphoric acid, whose formula is $H_3PO_4 \cdot VO_3 \cdot 11MoO_3 \cdot 2H_2O$. In many ways this substance resembles the familiar 12 molybdiphosphoric acid, e.g. in its ready formulation and its solubility in esters, but it has an intense orange colour. The maximum light absorption of the solution is at about 3300Å, but it is not necessary to measure the absorption of the solution at this point; for ordinary analytical purposes the wavelength to be chosen is not critical and depends to some extent on convenience. We have found that measurement in the region 4200 - 4800Å is satisfactory. The light, however, must be sensibly monochromatic.

The vanado-molybdate method is the best colorimetric method for phosphate; it is not influenced by reasonable amounts of

hydrochloric, sulphuric, acetic or citric acids. Fluorides retard the development of the colour, but not when present in the amounts normally found in fertilisers. Silica forms a similar compound, but the colour is much weaker, and develops much more slowly, so that after five minutes 1 mg. of silica per 100 ml. of solution has developed no colour, whereas the reaction with phosphate is complete. The method is most suitable for quantities of phosphate between 0.25 and 10 mg., so that for ordinary fertilisers it is convenient to dilute a solution to a known bulk and take an aliquot. Check calibrations of the photometer need not cover more than two or three points, provided that it gives light that is monochromatic as the coloured solution obeys the Beer-Lambert laws.

The most accurate way of using colorimetric analysis is by the "differential method", that is, comparison between the colour given by an accurately known solution and the unknown, or in practice by measuring the difference between the two colours. The theory is fully discussed in the references given below. To use the method, the standard solution should have a high optical density and the difference between the two solutions should be small. In practice the concentration of the standard solution is limited by the sensitivity of the spectrophotometer, and in analysing a range of samples one must depart to some extent from measuring only small differences. They should, however, be relatively small, compared with the concentration of the standard. Thus if the standard was a solution containing 5 mg. P_2O_5 , it would be preferable for the unknown solution to contain between 5 and 6 mg. P_2O_5 .

Much of the work reported below was carried out using an instrument with a glass prism and with optics such that sensibly monochromatic light is obtained. Hence, within the range of concentration measured, the graphs relating optical density to concentration of phosphate are straight lines. Other spectrophotometers can, of course, be used even if their light is not quite monochromatic, provided that the sensitivity and reproducibility are sufficient. However, in this case the graphs will not be straight lines and will deviate from linearity the more as the colour deepens. The overall accuracy will not be quite as good.

It may be thought that the colorimetric method, though no doubt an excellent routine method, is not suitable for consideration in a paper devoted to procedures of the highest accuracy, but this is not so. Let us consider this further. The formation of $H_3PO_4 \cdot VO_3 \cdot 11MoO_3$ is complete, as complete as the formation of $H_3PO_4 \cdot 12MoO_3$, probably more complete and reproducible than the customary precipitation of $NH_4MgPO_4 \cdot 6H_2O$. Our knowledge of the laws relating to light absorption is now amply adequate for purposes of accurate quantitative analysis, and the present day spectrophotometer made by a first class manufacturer is capable of measurements of optical density of a high degree of accuracy - the same order of accuracy or better than the measurement of volume, e.g. from a burette. If measurements are made differentially the results compare favourably with those obtained by any analytical process whatever. (Bastain and Hiskey, *Anal. Chem.* 1949, 21, 1441; 1950, 22, 160 and 1464; 1951, 23, 506 and 580; Neal, *Analyst* 1954, 79, 403; Milner and Phennah, *Ibid.* 414). There seems then to be no reason why a photometric method of analysis founded upon the quantitative formation of a compound that obeys the Beer-Lambert laws should not be as eligible a referee method as a gravimetric or volumetric method. Experience shows that this particular method can give results of the highest order of accuracy.

The following typical results drawn from the experience of our three firms illustrate the advantages of differential measurements and the use of a first-class spectrophotometer. The results have been obtained by comparing determinations made on many samples by both the colorimetric and a reference method of known reproducibility. Series 1 and 2 refer to the analysis of superphosphate and series 3 to a compound fertiliser.

1. Non-Differential Measurement - Filter Instrument

Test	Standard Deviation	Bias	Mean	Coefficient of Variation
w/s P ₂ O ₅	0.12	+ 0.165	18.16	0.66
Total P ₂ O ₅	0.16	+ 0.09	19.64	0.81

2. Differential Measurement - Filter Instrument

Test	Standard Deviation	Bias	Mean	Coefficient of Variation
w/s P ₂ O ₅	0.044	- 0.04	17.27	0.255
Total P ₂ O ₅	0.084	- 0.12	19.34	0.435

3. Differential Measurement - Monochromator Spectrophotometer

Test	Standard Deviation	Bias	Mean	Coefficient of Variation
w/s P ₂ O ₅	0.032	- 0.014	11.9	0.274

Note. The standard deviation of colorimetric determination has been calculated from the variance of the difference between a colorimetric determination and determination by a standard method, and the previously ascertained variance of the standard method.

AN APPRECIATION OF THE ABOVE METHODS IN LABORATORY PRACTICE

Previous sections of this paper have been confined to the chemical factors involved in the choice of a satisfactory analytical method for phosphate determination. Not only must that method have a high precision, but it must also be accurate. We have seen some estimates of the relative merits of the various methods discussed in both these respects.

We would further suggest, as a third criterion, that any method selected must preferably be simple in its application. There are probably two main reasons for which an analysis is required:-

- (a) Process control, production and materials usage,
- (b) Commercial transactions, which may be legally enforced in some countries.

This paper is not concerned with the former, but it may be said that for process control, any method which is known to give consistent results is acceptable, providing that any bias is known and small, and it is capable of giving quick results. For commercial transactions a method should be universally acceptable as a standard, especially if it is enforceable by law.

In addition, the cost of carrying out an analysis must be considered. This is not necessarily confined to the chemicals

involved plus the equipment required. The most costly item in any laboratory is operator time. In assessing the value of a method, we should therefore consider not only the time taken by a method of analysis to produce the result, but the operator time involved in its production.

The time necessary for the preparation of the solution from which an aliquot is taken for the actual phosphate determination varies with the procedures in use in different countries. Therefore in the comments which follow we have only considered the times involved after the phosphate has been extracted.

Kassner, Crammer and Ozier Method

At least 50 minutes are required to obtain a result and an operator will be almost continually engaged during this time. The washing of the precipitate obtained is more difficult and requires a higher degree of operator skill than the quinoline-based precipitate obtained in the Wilson method.

Wilson Method

We estimate that, having obtained the required solution, results can be available in 45 minutes, of which the operator portion is about 20 minutes. In other words, three samples can be completed within one hour and we consider that this is about the optimum number of samples that one operator can handle satisfactorily at any one time. This method requires a higher degree of operator skill and technique than the colorimetric method, but certainly less than that required by the de Saint Chamant and Vigier method.

De Saint Chamant and Vigier Method

This is the slowest method of those discussed and would require some 4 hours in overall time for total P_2O_5 determination and approximately $3\frac{1}{2}$ hours after sample preparation for a water soluble phosphate estimation. The operator times are, respectively, 80 and 45 minutes. A feature of this method is the high degree of skill and experience required from the operator carrying out the tests. We should not consider it possible for an operator to carry on more than three determinations at a time.

Colorimetric Method

After the extracted solution has been prepared, the overall time to obtain a result by the differential method is 17 minutes, of which 7 minutes are operator time. Once the solutions have been obtained little operator skill is required, but the highest attention must be paid to cleanliness of equipment especially with the colorimetric cells.

Summary

We estimate that an experienced laboratory assistant, provided with a satisfactorily ground sample and all the necessary reagents and standard solutions, can analyse the following number of samples (for both water soluble and total P_2O_5) per day:-

Colorimetric	12 samples
Wilson	8 samples
Kassner, Crammer & Ozier	4 samples
De St. Chamant & Vigier	3 samples

The relative costs of the methods for one determination have been estimated for a typical British laboratory to be as follows:-

<u>Method</u>	<u>Salary or wages cost</u>	<u>Chemical and apparatus cost</u>	<u>Total cost</u>
Colorimetric	3/-	6d.	3/6d.
Wilson	4/6d.	2/2d.	6/8d.
Kassner, Crammer & Ozier	9/-	11d.	9/11d.
De St. Chamant & Vigier	12/-	2/7d.	14/7d.

The salary costs, in addition to direct wages, include administrative costs, pensions, etc.

CONCLUSIONS

These four new methods illustrate present trends; each is a departure from conventional procedures, each is capable of giving results at least as accurate and as precise as any of the older "official" methods. The longest can be completed in about 4 hours, the volumetric methods in about one hour after dissolution of the sample, and three are virtually free from interference. Our results, which were obtained in a large number of laboratories in what was probably a unique collaboration between three firms in the fertiliser industry, show that the methods are worthy of consideration for official or international methods.

Industry today cannot afford the time nor the manpower to plough through dreary and lengthy "official" methods fifty or more years old, nor can it afford to take the risk of using shortened "approximate" methods for commercial transactions, though these no doubt may have their place in plant control laboratories. We have shown that there exist analytical procedures almost free from errors caused by "interferences", of greater accuracy and reproducibility than the British Statutory methods, and which we can expect will be superior to any of the other statutory methods. They are, moreover, rapid. Not being endowed with the gift of prophecy, we cannot state how long it will be before the existence of these methods is officially recognised. We earnestly recommend that the Fertiliser Industry should continue to urge the adoption of these new techniques.

Finally, we would like to thank the Directors of Fisons Limited, Imperial Chemical Industries Limited and Scottish Agricultural Industries Limited for their encouragement of the extensive collaborative work necessary to investigate these new methods and for their permission to publish this paper.

A P P E N D I XOPERATING DETAILS OF PHOSPHATE METHODS1. Kassner, Crammer and Ozier Method

The procedure we followed was slightly modified from the original and was as follows:-

Reagents.

Indicator. Triturate 0.100 gm. phenol red with excess NaOH, and when dissolved adjust pH with HNO₃ to 7.5 and dilute to 250 ml. in graduated flask. Similarly with bromothymol blue. Mix 40.0 ml. bromothymol blue solution with 25.0 ml. phenol red solution.

Citromolybdate reagent. A. Dissolve in 1360 ml. H₂O without heating, 54 gm. NH₄NO₃, 52.5 gm. citric acid, 68 gm. ammonium molybdate, i.e. (NH₄)₆Mo₇O₂₄.4H₂O.

B. Dilute 253 ml. HNO₃ (sp. Gr. 1.42) with 310 ml. H₂O. Pour solution A into solution B.

NaOH. 0.3N, carbonate free, standardised against A.R. potassium hydrogen phthalate using phenolphthalein.

HCl. 0.25N, not standardised.

Phosphate sample should contain 18 - 46 mg. P₂O₅ in not more than 50 ml. of solution. To this, in a 250 ml. beaker, add 80 ml. citric molybdate reagent; heat to boiling; boil gently for three minutes; allow to stand for 15 - 30 minutes and filter with suction through an asbestos packed Gooch crucible. Wash the precipitate by decantation 5 times, each with 20-25 ml. cold water; transfer the precipitate to the filter and wash 5 times; transfer filter pad and precipitate to original beaker, washing crucible with the minimum quantity of cold water. From a burette run in 0.3 N sodium hydroxide with stirring until the yellow precipitate is completely dissolved and add about 12 ml. in excess. Add 10 drops of indicator and titrate with 0.25 N hydrochloric acid to a pale yellow colour. Dilute with CO₂-free water to 150 ml. approximately. In good daylight or in the light from a fluorescent daylight lamp back titrate with 0.3 N sodium hydroxide to a permanent light purple colour.

To determine the equivalence of the sodium hydroxide and hydrochloric acid solution, carry out a blank titration of 30 ml. sodium hydroxide with hydrochloric acid to the yellow end point of the indicator and back titrate to the purple colour with sodium hydroxide.

1 ml. NaOH \equiv 3.051 mg. P₂O₅.

2. WILSON METHODReagents

Citric-Molybdate Reagent. Stir 54 gm. molybdic anhydride (MoO₃) Analar with 200 ml. of water, add 11 gm. of sodium hydroxide Analar and stir whilst heating until the molybdic anhydride dissolves. This will take 20-30 minutes. Dissolve 60 gms. of pure citric acid in about 250-300 ml. of water, add 140 ml. of pure hydrochloric acid (sp. gr. 1.18). Pour the molybdate solution into the acid solution stirring throughout the addition. Then cool, and filter through a pulp pad if necessary. Dilute to 1 litre. This solution is slightly green or blue in colour, and the colour deepens on exposure to light.

(ii)

Add drop by drop a dilute (0.5 or 1%) solution of potassium bromate until the green colour is discharged. This solution is now stable if kept in the dark.

Quinoline Solution. Measure 50 ml. conc. hydrochloric acid and 300 or 400 ml. of water into a litre beaker and warm to 70 or 80°C. Pour 50 ml. of "synthetic" pure quinoline (free from reducing agents) in a thin stream into the dilute acid, whilst stirring. When the quinoline is dissolved, cool, dilute to 1 litre and filter through pulp. Note. Quality of quinoline. "Synthetic" quinoline is usually suitable. To purify impure quinoline, a satisfactory method is to dissolve in hydrochloric acid, and with an excess of zinc chloride dissolved in dilute hydrochloric acid, precipitate the double zinc chloride $(C_9H_7N_3)_2ZnCl_4$. This crystallises well, is washed with cold dilute acid, the quinoline regenerated with excess of sodium hydroxide, dried and distilled.

Indicator Solution. Mix 3 volumes of an 0.1% solution of thymol blue (dissolve 0.1 gm. in 2.2 ml. N/10 sodium hydroxide and 50 ml. in ethyl alcohol and dilute to 100 ml. with water) with 2 volumes of an 0.1% solution of phenolphthalein in 60% alcohol.

Water soluble P₂O₅.

Prepare the aqueous solution exactly according to the Regulations of the Fertilisers and Feeding Stuffs Act, but avoid the use of alcohol to disperse the sample, as it may cause some reduction of molybdate at a later stage. After filtration take an aliquot which will contain less than 70 mg. P₂O₅ and preferably about 50 mg., and transfer it to a stoppered conical flask, marked at 150 ml. Dilute the aliquot to 150 ml., add 50 ml. of the citric molybdate reagent, heat to incipient ebullition and maintain at this temperature for 3 minutes, then raise to the boiling point. Add from a burette with a coarse jet 25 ml. of the quinoline reagent. The reagent should be added dropwise for the first few ml. then in a slow stream, with constant swirling throughout to ensure a precipitate of the maximum particle size. Time spent in the precipitation will be more than saved in the filtration.

Allow to stand on a boiling water bath for 5 minutes, cool to room temperature in running water and filter on a pulp pad. Wash with cold distilled water until free from acid. Transfer the pulp pad and precipitate to the original flask, using not more than 100 ml. of water. Shake vigorously to disperse the pulp and precipitate - this is essential - add an excess of N/2 NaOH solution (CO₂-free), shake to dissolve the precipitate, then examine carefully to make sure that no yellow particles remain, and back titrate with N/2 HCl, using mixed phenolphthalein/thymol blue indicator.

1 ml. N/2 NaOH solution = 1.366 mg. P₂O₅

Carry out a "blank" test on all reagents, but use N/10 acid and alkali for the titration. The "blank" should be very small.

Total P₂O₅

Weigh out 5 gm. sample, finely ground into a 400 ml. beaker, stir thoroughly with 100 ml. of water and boil. Add slowly a thin stream of 10 ml. conc. hydrochloric acid, followed by 10 ml. of conc. nitric acid to the boiling solution. Boil gently for 10 minutes, cool, transfer to a 500 ml. volumetric flask, and adjust the volume to the mark. Filter through a dry paper, discarding the first 10 or 20 ml., and transfer a suitable aliquot

(iii)

of the filtrate to a 500 ml. stoppered conical flask. If the sample does not contain calcium add 100 - 200 mg. of pure calcium carbonate, then sodium hydroxide until a slight permanent precipitate is formed. Do not use an indicator, as this is very liable to be absorbed on the final precipitate and interfere with the final titration.

Dissolve the precipitate by dropwise addition of dilute hydrochloric acid, dilute to 150 ml. with water and proceed as above.

Note. The addition of a minute amount of a solution of a surface active agent, e.g. sodium alkylbenzene sulphonate, to the quinoline phosphomolybdate and water before shaking, will assist in the dispersion of the precipitate.

3. DE SAINT CHAMANT AND VIGIER METHOD

Reagents

1. Nitric Acid. (Sp. Gr. 1.33)
2. 30% perchloric acid (Sp. Gr. 1.250)
3. A solution of distilled water acidified with 1% perchloric acid (Sp. Gr. 1.61)
4. Magnesium chloride, $MgCl_2 \cdot 6H_2O$.
5. Ammonium chloride, NH_4Cl .
6. Magnesia mixture: 3 litres of solution containing:-

$MgCl_2 \cdot 6H_2O$ (4)200 gm.
 NH_4Cl (5)450 gm.

7. Ammonia, Sp. Gr. = 0.925 : 20% solution.
8. Methyl red, 2% solution in 60% ethyl alcohol.
9. Crystallised ethylenediaminetetraacetic acid.
10. Lactic Acid.
11. Complexing solution prepared as follows:

A mixture containing 80 gm. of ethylenediaminetetraacetic acid (9) and 200 ml. of lactic acid (10) previously brought to 500 ml. with distilled water, is neutralised by ammonia solution (7), in the presence of about 15 ml. of methyl red, until the colour change. After neutralisation, the solution is made up to 1 litre with distilled water.

12. Monoethanolamine : 1/5 volume solution.
13. Ammoniacal solution of ammonium chloride containing 5 gm. of ammonium chloride (5) and 125 ml. of ammonia solution (7) per litre.

Method.

1 gm. of the sample is weighed to 1 mg. in a nickel dish. The sample is placed into a 250 ml. beaker, the last traces of phosphate from the nickel dish being brushed in with a fine brush; the beaker is covered with a watch glass.

The sample contained in the beaker is moistened with 2 - 3 ml. of distilled water. 2 ml. of nitric acid (1) are added. After effervescence has finished, the whole is heated on the sand bath to dryness at a temperature of about $130^{\circ}C$. When no more liquid remains, the temperature is raised and the whole is heated strongly until the N_2O_4 fumes completely disappear.

The beaker is removed from the sand bath, and, after cooling, the residu is taken up in 20 ml. of perchloric acid (2). The whole is boiled gently until a white residu and a clear supernatant liquid are obtained (which should normally coincide with the appearance of the first white fumes of perchloric acid).

(iv)

On cooling; 50 ml. of distilled water are added and the whole is gently digested for 20 minutes. The watch glass is rinsed with distilled water. After filtering with an ordinary pleated filter paper, collecting the filtrate in the 500 ml. beaker, the beaker and filter are carefully washed with the acidified distilled water, (3).

The total volume of the filtrate should be about 150 ml. and perfectly clear.

60 ml. of the magnesia mixture are added (6) and then 50 ml. of the complexing solution (11). The whole is neutralised with the ammonia solution (7) until the methyl red changes to yellow. This neutralisation:-

- (a) must be done quickly in order to avoid the precipitation of the ethylenediaminetetraacetic acid which is insoluble in acid, and is very difficult to dissolve.
- (b) must not be taken beyond the colour change, so as to avoid a rapid precipitation of the ammonium magnesium phosphate.

The precipitation of the ammonium magnesium phosphate is then done in the following way by the addition of 20 ml. of the monoethanolamine solution (12):-

The solution is stirred with a glass rod, without touching the sides of the beaker and the reagent is introduced drop by drop. The crystalline precipitate forms without difficulty. When the precipitation is well started, the reagent is added faster.

The beaker is covered with a watch glass and is left standing for $1\frac{1}{2}$ hours, with occasional shaking.

The whole is filtered, using ashless filter paper of diameter 110 mm. and of a medium filtration speed; the precipitate is washed by decantation, and then the beaker and filter with ammoniacal solution of ammonium chloride (13), 120 to 150 ml. of the washing liquid being used.

While washing the filter, it is recommended to direct the jet of the wash bottle on to the upper edges of the filter paper in order to eliminate the ammonium perchlorate.

If this precaution is neglected, decrepitation, leading to loss of product, may occur on calcination.

The filter paper is removed from the funnel, dried gently on the bath and then placed into a platinum crucible previously brought to red heat and weighed.

The crucible is placed on the edge of the furnace with the door open, and the paper is allowed to char without flaming; the crucible is then placed into the interior of the furnace. The door is left open for a few seconds to allow a satisfactory oxidation of the paper. The temperature is raised to 1000° and kept there until a perfectly white precipitate of constant weight is obtained.

The crucible is allowed to cool in the desiccator and is weighed.

Calculation of the results

Calculate the P₂O₅ content of the sample from the relationship:-

1 gm Mg₂P₂O₇ corresponds to 0.6377 gms. P₂O₅

(v)

4. VANADO-MOLYBDATE COLORIMETRIC METHOD

The detailed instruction that follows applies to the determination of water soluble P_2O_5 in a fertiliser that contains 11 or 12% P_2O_5 . It is equally applicable to a "total P_2O_5 " determination of about 11 or 12% P_2O_5 . Note 4 explains the dilution and aliquots to be taken for other percentages of P_2O_5 .

Reagent

Dissolve 20 gms. ammonium molybdate in water. Dissolve 1 gm. ammonium vanadate in water. Mix, acidify with 140 ml. of concentrated nitric acid and dilute to 1 litre.

Preparation of Graph

Dry some pure potassium hydrogen phosphate, dissolve 1.9173 gms. (=1.0 gm. P_2O_5) in distilled water and dilute to 1 litre, (1 ml. = 1.0 mg. P_2O_5). Prepare a five-fold dilution by pipetting 50 ml. into a 250 ml. flask and diluting to the mark, (1 ml. = 0.200 mg. P_2O_5). From a burette measure into a series of 100 ml. graduated flasks 25.0, 26.0, 27.0 31.0 ml. (i.e. 5.0, 5.20, 5.40 6.2 mg. P_2O_5). This series of measurements is of the greatest importance, and too much care cannot be taken, particularly over the 5 mg. standard, as all measurements are made by difference.

Make sure that the temperature of the reagent and the dilution water are $20^{\circ}C$, or other selected temperature add 25 ml. of reagent to each flask, dilute to the mark with water and shake well. Allow to stand for ten minutes.

Check that the spectrophotometer is set to the correct wavelength, say 4200 Å, fill two 1 cm. cells with the 5 mg. solution, and ascertain that there is no difference in optical density, (i.e. check the identity of the cells). Errors can arise through incorrect placing of the cells.

Note 1. It will be appreciated that as in volumetric analysis all volumetric glassware must be of the highest quality, and should be calibrated before use. The temperature of the final solutions must be kept constant or allowances made for differences from $20^{\circ}C$. The photometric cells must match; the cell has a nominal thickness of 1 cm.; obviously an error of 0.01 mm. will cause an error in the optical density measurement of 1%. It does not matter whether the cells used are exactly 1.00 cm. in thickness, but if several cells are in use, they must be alike; if a new cell is used a new calibration graph must be drawn. It will usually be sufficient to check two points on the graph if it is a straight line in the instrument. Take care that the cell is in the correct position, always the same way round. Successively measure the difference between the optical density of the 5 mg. standard and the other standard solutions. From time to time refill the comparison cell with fresh "5 mg." solution to avoid errors caused by temperature changes. In some photometers the solutions warm up.

Record the differences in optical density, and plot them on large scale graph paper. The points should lie on a straight line. Calculate the slope of the line in terms of difference in optical density and mg. P_2O_5 .

Thus: Difference x Factor = y mg. P_2O_5

Analysis of Sample

Prepare the aqueous solution in the usual way, by agitating 20 gms. of the sample for 30 minutes with 800 ml. water and then diluting to 1 litre. Mix and filter. Pipette 50 ml. into a 500 ml. flask, dilute to the mark with water, mix well, withdraw 25 ml. and transfer to a 100 ml. volumetric flask. At the same time, transfer 25 ml. of the 0.2 mg. P_2O_5 /ml. standard solution to a second 100 ml. flask. Add 25 ml. of reagent to each, dilute to 100 ml. with water, mix well and after ten minutes measure the difference in optical density between the two solutions.

Multiply by the factor to find the mg. P_2O_5 present in the aliquot taken for analysis. This represents 20 gms./20 x 20 = 50 mg., so that $mg. P_2O_5/2y =$ percentage of water soluble P_2O_5 in the sample.

Note 2. If the monochromator of the spectrophotometer is not quite efficient enough to give a linear calibration graph, a simple factor cannot be applied. The instrument can still be used by referring to the calibration graph for every analysis. Alternatively, the line is fitted by an equation of the form:-

$$mg. P_2O_5 = aE + bE^2$$
 where E is the optical density,

a is the slope of the tangent to the curve at its origin,
 b is an empirically determined constant.

Note 3. When the calibration graph is a straight line, much calculation can be saved by selecting the wavelength. In the example given above, where a 50 mg. aliquot was finally measured 5 mg. P_2O_5 represents 10% on the sample. Select such a wavelength that the 5 mg. standard solution has an optical density of exactly 1.00. Then 6 mg. - i.e. the amount of P_2O_5 in a 12% P_2O_5 sample - will have a density of 1.20, the difference reading being 0.200, and so forth. So the percentage of P_2O_5 in the sample = 10 + (optical density x 10).

Note 4. Using the reagents and method given above, it will be found that 5.00 mg. of P_2O_5 will give a final solution whose optical density, measured in a 1 cm. cell at a wavelength of 4200A, is about 1.0. At shorter wavelengths it is denser, at longer wavelengths it is less dense. This is very convenient for the measurement of solutions containing about 5.5 - 6.0 mg. P_2O_5 , and an aliquot containing this quantity is readily prepared, e.g. for a fertiliser containing 11 or 12% of water soluble P_2O_5 one extracts 20 gms. with 1 litre of water as usual and after filtering measures an aliquot of 50 ml. (i.e. 1.00 gm. of original sample) by means of a pipette into a 500 ml. flask and dilutes to the mark with water. A 25 ml. aliquot of this solution represents 50 mg. of the original sample, that is 5.5 mg. P_2O_5 . At the wavelength indicated, the difference between standard and sample will correspond to an optical density of about 0.10 which is quite convenient.

It can readily be seen that this system of dilution can be applied to any sample and the standard can be altered to meet a particular case. Let us consider the analysis of samples of "triple superphosphate" with about 47% of water soluble P_2O_5 . From the usual solution (20 gms. to 1 litre), a 25 ml. aliquot is taken (= 235 mg. approx. of P_2O_5), and diluted again to 1 litre. A 25 ml. aliquot of this solution will contain 5.75 mg. approx. of P_2O_5 - a convenient amount. A sample containing 18% soluble P_2O_5 could be dealt with by taking from 1 litre a

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50 ml. aliquot (180 mg. P_2O_5) diluting to 500 ml. and taking a 20 ml. aliquot of the dilute solution (= 7.2 mg.). In this case, it would be more accurate to use a standard solution containing 6 mg. P_2O_5 but not essential.

The presence of a small amount of acid in the final aliquot makes no difference to the colour development, so from the above discussion, it should be quite easy to decide the quantities to be used in the analysis of any fertiliser for either total or water soluble P_2O_5 .