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THE DIFFERENTIAL ENTHALPIMETRIC DETERMINATION OF PHOSPHATES IN FERTILISERS

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The phosphate contents of fertilisers of various types have been determined enthalpimetrically using a measure of the heat of precipitation of zirconium phosphate in a strongly acidic medium, for the calculation. The use of a sulphuric acid medium obviates the necessity for removal of calcium ions; the apparatus compensates for heats of mixing of the reagents. The precision for this rapid method is 2.5% at the mg level.

The advantages of thermometric and enthalpimetric methods for the routine determination of coloured industrial samples have been previously discussed [1], and the potential of these methods for automation has already been acknowledged by the production of commercial apparatus for this purpose. An area where the use of these techniques is commercially desirable is in the rapid determination of the phosphate content of fertilisers, when the emphasis is on acceptable accuracy and not on highly precise results.

All of the various phosphate fertilisers are made from the basic phosphate rock. Some of the most important fertilisers are the so called super-phosphates, which are obtained by the action of sulphuric acid on phosphate rock; the chief fertiliser constituent is monocalcium phosphate containing about 8.5% w/w available phosphorus. Triple super-phosphate, generally obtained by treating phosphate rock with phosphoric acid contains between 20 and 24% w/w available phosphorus. Another type of commonly used phosphate fertilisers is the ammonium phosphates. These contain both nitrogen and phosphorus and hence are in great demand; they are generally obtained by the reaction of ammonia and phosphoric acid. Depending on the manufacturing process there are four main types of ammonium phosphate fertilisers: (*a*) (11-48-0) which is 11% nitrogen and 21% phosphorus and is predominantly mono-ammonium phosphate; (*b*) (16-48-0) containing 16% nitrogen and 21% phosphorus and which is a mixture of mono-ammonium and di-ammonium phosphates; (*c*) (21-53-0) containing 21% nitrogen and approximately 23% phosphorus; (*d*) (18-46-0) an impure di-ammonium phosphate containing 18% nitrogen and 20% phosphorus.

In the USA a further product is obtainable containing between 26% and 28% available phosphorus; this material known as calcium metaphosphate has been manufactured by the TVA by burning elemental phosphorus in a combustion chamber, with finely divided phosphate rock.

The water solubility of the various phosphate materials varies; the ammonium phosphates are practically completely soluble; the mono-calcium phosphates have about 80% water solubility whilst the calcium metaphosphates are usually under 5% water soluble; rock phosphate is not water soluble.

The calcium phosphates may be effectively solubilised by metathesis with sodium carbonate, or by treatment with sulphuric or nitric acid, and for the most purposes, the phosphate content of a fertiliser is best determined as a soluble phosphate.

Sajó and Sipos [2] have described two methods for the rapid analysis of fertilisers by a direct reading thermometric method. In the absence of magnesium ions, the phosphate ions are precipitated with a magnesia mixture in an ammoniacal medium. Under suitable conditions the precipitation is rapid and the heat of precipitation is sufficient to be used for measurement purposes. However, in the presence of calcium ions, which form a precipitate with the phosphate when the solution is made alkaline, it is necessary to add oxalate ions to remove the calcium before the addition of alkali.

In the presence of magnesium, ammonium phospho-molybdate is precipitated by addition of a known and excess amount of molybdate reagent, and the excess of the molybdate is determined by reaction with hydrogen peroxide. This method has the disadvantage that the heat of mixing of the various solutions makes the method have a relatively low sensitivity, especially if the phosphate has been solubilised using sulphuric acid, which in the present authors' view is the preferred method, being more rapid and more convenient in use.

Preliminary investigations showed that the addition of a solution of zirconyl chloride to an acidified phosphate solution produced a relatively high heat of reaction, and that the kinetics of the precipitation reaction are sufficiently fast to enable the method to have potential use as a direct injection enthalpimetric titration. However, due to the high heat of mixing of the zirconyl chloride, only low sensitivity for phosphate could be obtained, since the overall signal registered, whilst large, had only a small component due to the heat of precipitation, especially for low concentrations of phosphate ion, since there was the same heat of dilution/mixing for the addition of the zirconyl chloride in all cases; and in practice it is essential to keep the heat pulse signal within the compass of the recorder.

Various workers have attempted to compensate for the heat of mixing of titrants by chemical means, but numerous attempts to compensate by such methods were unsuccessful, partially because addition of organic solvents such as glycerol (endothermic heat of mixing) resulted in solubility problems with the zirconyl chloride, and the addition of large amounts of ammonium chloride caused precipitation by common ion effects.

Previous work using differential or subtractive enthalpimetry has been successfully applied when the heat of mixing of the titrant could not be compensated for by chemical means [3] and preliminary experiments using the apparatus mentioned, indicated that the differential method can be applied successfully, if an aqueous solution of zirconyl chloride is injected into phosphates contained in a sulphuric acid medium. When hydrochloric or nitric acids were used as the solubilising acid, difficulties arose, mainly caused by variations in the amount of acid present after the solubilization process, which involves boiling and consequent losses of the volatile acids.

Experimental

Apparatus

The titration assembly was essentially as previously described [3]. The titration assembly consists of two identical glass syringes joined to two glass bulb pipettes of nominal capacity 1 ml. These pipettes deliver the titrant to two vessels, one of which contains the sample and the other the same volume of a 'blank' solution. The titration vessels are thick walled polyethylene bottles having a nominal capacity of 30 ml. Each vessel is surrounded by suitable thermal insulation so that the apparatus will give adiabatic or quasi-adiabatic conditions over the time of the determination. One of a pair of matched 10 Kohm thermistors is installed in each vessel and these thermistors are connected into opposing arms of a d.c. Wheatstone bridge. The voltage imbalance of the Wheatstone bridge caused by a temperature difference between the two solutions surrounding the thermistors is measured and recorded on a potentiometric recorder of sensitivity such that 1 mV imbalance gives a pen deflection of 200 mm.

Procedure

Calibration graph

Transfer a known amount of the sample solution containing phosphate to the reaction vessel (*A*), add 10 ml of 2 *M* sulphuric acid to the reaction vessel (*A*) and 20 ml of 2 *M* sulphuric acid to the "blank vessel" (*B*). Make the final volume in *A* to 20 ml adding 2 *M* sulphuric acid or distilled water so that the sulphuric acid concentration in each vessel is 2 *M*. Place each vessel in the insulation block.

Immerse the two pipettes, filled with 50% w/w zirconyl chloride solution, and the matched thermistors in *A* and in *B*. Stir the solution, allow the system to come to thermal equilibrium (as shown by the chart trace). Adjust the bridge to zero voltage imbalance. Inject the zirconyl chloride simultaneously into *A* and *B*. Record and measure the reaction temperature pulse.

Prepare a calibration graph by using known amounts of di-sodium hydrogen phosphate, in procedures similar to that described. (In practice, the voltage applied to activate the bridge was adjusted so that 0.5 mg of P_2O_5 per 1 ml of titration solution gave a deflection of 1 mm.)

Procedure for an unknown sample

(a) *Ammonium phosphate fertilisers*

Dissolve a known weight (1.00 g) in 2 *M* sulphuric acid, make the volume of the solution to 100 ml with 2 *M* sulphuric acid. Use 20 ml portions of this solution for the titration sample. Proceed as in calibration procedure.

(b) *Calcium phosphate fertilisers*

(a) *Determination of soluble phosphate*

Suspend a known weight (ca. 2 g) of the dry and powdered calcium phosphate fertilisers in water (50 ml) and boil the mixture for 5 min. Filter the mixture, wash the residue with 2 × 10 ml portions of boiling water. To the combined filtrate and washings add sulphuric acid to give a final volume of 100 ml of solution which is 2 *M* with respect to sulphuric acid. This is then the prepared sample.

(b) *Determination of total phosphate*

Suspend a known weight (ca. 1.0 g) of the dry powdered fertiliser in 4 *M* sulphuric acid (ca. 40 ml). Boil the mixture for 5 – 10 minutes, dilute with 20 ml water. Filter the mixture, wash the residue with 2 *M* sulphuric acid (2 × 5 ml); add sufficient distilled water to the combined filtrate and washings to give a total volume of 100 ml and a solution which is 2 *M* with respect to sulphuric acid. This solution is the prepared sample.

Comparison of methods

The amounts of phosphate in a series of samples were determined using the proposed method, colorimetrically using a standard method involving the forma-

Table 1

Assay of phosphate samples by various methods

Method *A* – Enthalpimetric method
Method *B* – Gravimetric method
Method *C* – Colorimetric method

Amount of phosphate as P_2O_5 added, mg	7.10	14.20	21.30	28.40	35.50	42.60
Amount recovered,* mg	7.20	14.0	20.9	29.0	36.5	41.6
Method *A*, mg%	101.4	98.6	98.2	102	102.8	97.6
Amount recovered,* mg	7.15	14.15	21.2	28.6	36.0	42.2
Method *B*, mg%	100.7	99.6	99.5	100.7	101.4	99.1
Amount recovered,* mg	7.00	14.4	20.9	29.2	36.8	41.3
Method *C*, mg%	98.5	101.4	98.2	102.8	103.6	96.9

Recoveries: Method *A* 100.1 2.5%
Method *B* 100.1 0.6%
Method *C* 100.2 3.1%

* Average of duplicate determinations

tion of molybdenum blue using ascorbic acid as the reductant [4] and gravimetrically as the quinolinium phospho-molybdate complex [5]. The results obtained are given in Table 1.

Reproducibility of the methods

A series of 10 aliquots of a prepared solution were assayed by the proposed method. The standard deviation was calculated (see Table 2).

Table 2

Reproducibility of the method

Amount of phosphate taken (as mg P_2O_5) 25.5 mg					
Amounts found	25.25 25.50	24.70 26.00	25.50 25.50	24.50 26.15	25.25 24.80

Standard deviation 0.536 mg.
Relative mean deviation 1.64%

Discussion and results

The proposed method is more rapid than the gravimetric technique and gives results, which for routine analysis of phosphate fertilisers are analytically acceptable. The case of making the apparatus into a direct reading instrument, which may be linked to a digital print out via an operational amplifier, make the method of great potential for automation.

The proposed precipitant has several advantages over those previously reported; the unusually low solubility of zirconium phosphate in strong mineral acids [6], and the solubility of other phosphates in these acids, mean that the presence or absence of magnesium and/or calcium have no effect on the reaction. The effect of the common ions, which may be present in a fertiliser sample have been ascertained. Known amounts of various ions, Ca (40 mg), Mg (24 mg), K (20 mg), Na (20 mg), Al (15 mg), N_2 (10 mg as NH_4Cl), Fe(III) (12 mg) have been added individually with phosphate (as 28.4 mg of P_2O_5) and no interferences have been noticed from any one of them. Anions such as sulphate and chloride obviously do not interfere. If Fe(III) is present in amounts more than 1 mg/ml of sample solution, then there is some interference.

The method is fairly rapid, 15–20 determinations using a single bridge circuit can easily be done per hour; the number depends upon the amount of time necessary to obtain thermal equilibrium during the preparation of the sample. The differential apparatus adequately compensates for any effects due to heats of mixing of the various solution.

References

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RÉSUMÉ — On a déterminé par enthalpimétrie la teneur en phosphate de divers types d'engrais chimiques, en utilisant pour le calcul la mesure de la chaleur de précipitation du phosphate de zirconium en milieu fortement acide. En milieu acide sulfurique, il n'est pas nécessaire d'éliminer les ions calcium; l'appareil contrebalance la chaleur de mélange des réactifs. La précision de cette méthode rapide est de 2.5% à l'échelle du mg.

ZUSAMMENFASSUNG — Der Phosphatgehalt verschiedener Typen von Kunstdünger wurde enthalpimetrisch bestimmt, wobei zur Berechnung die Messung der Fällungswärme von Zirkoniumphosphat in stark saurem Medium eingesetzt wurde. Bei Einsatz eines schwefelsauren Mediums erübrigt sich die Entfernung der Calcium-Ionen; das Gerät kompensiert die Mischungswärmen der Reagenzien. Die Genauigkeit dieser Schnellmethode liegt im mg-Bereich bei 2.5%.

Резюме — Содержание фосфата в различного типа удобрениях было определено энтальпиметрически, используя для вычисления меру теплоты осаждения фосфата циркония в сильно кислой среде. Использование серной кислоты, устраняет необходимость удаления ионов кальция. Аппарат компенсирует теплоты смешения реагентов. Точность этого быстрого метода составляет 2,5% при степени содержания в мг.