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ANALYTICAL PROCEDURES FOR SUPERPHOSPHATE

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1. INTRODUCTION

The aim of this paper is to present details of some analytical procedures which have been developed or modified in our laboratories and which we feel may be of general interest. In addition some suggestions are included as to modification of the existing standard methods.

Total P₂O₅. The differential spectrophotometric method, as advocated by Donald et al. (1) has been found highly satisfactory and could probably be adopted as standard. A procedure for dissolving the sample with elimination of silica is given.

Water Soluble P₂O₅. a) It is suggested that a standard procedure be adopted for preparation of the extract of water soluble P₂O₅.

b) A rapid alkalimetric method suitable for process control is given in which interference from calcium is eliminated by addition of oxalate. (2)

Moisture and water of crystallisation. Azeotropic distillation, capable of determining the above separately is described (3).

Acid balance. A method is given for checking the degree of acidulation of the rock, which is independent of time of curing of the sample.

2. DISCUSSION AND DESCRIPTION OF THE METHODS

(1) Total P₂O₅ - differential spectrophotometric method.

Each of the standard methods included in the publications of O.E.E.C. (4) and AOAC (5) must be regarded as satisfactory for the determination of P₂O₅ if properly carried out. Each method was adopted as standard only after experience had shown that it gave reproducible and reliable results.

To illustrate this, several methods were used to analyse a sample of Negev Phosphate Rock and excellent agreement was obtained with the Lorenz, A.O.A.C., $MgNH_4PO_4$ double precipitation, Wilson and differential spectrophotometric methods.

However, it would clearly be preferable if two or three methods could be accepted as standard throughout the O.E.E.C. countries. These methods should be accepted on account of their high accuracy, reproducibility and convenience. Two or three methods should be adopted rather than one, to allow for cross-checking in case of doubt and to permit individual laboratories to choose the method which fits in best with their overall programme of work.

Many of the advantages of the differential spectrophotometric method were outlined by Donald et al. (1). We fully agree with their findings and recommend that this method take its proper place among the other standard methods. Two additional advantages not stressed by the authors are: 1) any fault in apparatus or reagent is automatically discovered as a deviation from the expected optical densities of the standards, and 2) treatment of almost any sample to obtain the solution for spectrophotometric analysis is simple and convenient.

The following procedure is that used in our laboratories:-

Reagents.

- a) Colour reagent: 1) 3.4 g NH_4VO_3 is dissolved in 4N- H_2SO_4 to volume of 1 litre
- 2) 64 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ is dissolved in water to 1 litre

Equal volumes of solutions 1) and 2) are mixed immediately before use.

- b) Standard P_2O_5 solution: $Na_2HPO_4 \cdot 2H_2O$ p.a. is dried to constant weight at $105^\circ C$ to determine its content of Na_2HPO_4 . A calculated quantity of $Na_2HPO_4 \cdot 2H_2O$, to contain 0.8872 g Na_2HPO_4 , is weighed and dissolved in 10 ml conc. H_2SO_4 and water to 1 litre.

Apparatus.

Beckman DU Cells 1.00 cm. Corex. Filter for 320-400 m μ . Blue phototube.

Preparation of solution.

A representative sample containing 260 ± 40 mg P_2O_5 is weighed and transferred to a 500 ml volumetric flask. 10 ml H_2O , 5 ml HNO_3 and 5 ml H_2SO_4 are added and heated on a sand bath to appearance of white fumes of H_2SO_4 . The flask is removed to cool, then water is added to mark, shaken and solids allowed to settle.

Determination.

To a 100 ml volumetric flask, 10 ml of the test solution is added followed by 10 ml of the mixed reagent and water to mark. Two further solutions are prepared as above but with exactly 10 and 12 mls. of the standard P_2O_5 solution in place of the test solution. Solutions are allowed to stand 20 minutes. Apparatus is adjusted to read zero absorbance for the 10 ml standard at 390 m μ ; the 12 ml sample gives 0.440. Absorbance of test solution is then measured.

$$\text{mg } P_2O_5 \text{ in sample} = 222 + 100.8 \times \text{absorbance.}$$

(2) Water soluble P₂O₅.

a.) Preparation of water soluble extract.

The summary in Fertilizers (4) p. 11, shows that different methods work with or without grinding, with ratios of water to rock of 1/20 to 1/100 and different times of agitation. We have found the official U.K. method to be convenient and reproducible. The ratio 1/50 lies midway between the values used in other procedures.

b.) The Oxalate method.

For accurate work any of the standard methods may be used for determining P₂O₅ in the extract. However for routine control work, where an accuracy of better than ±1.2% is not required, the following method has been found to give very rapid and reliable results. The method takes 3 minutes after preparation of solution and has been in use in our laboratories for nearly 2 years.

Reagents. NaOH N/10 (CO₂ free). Potassium oxalate, 25% solution, neutral to phenolphthalein. Mixed indicator: 23 mg Methyl red, 67 mg Bromocresol Green, 10 mg Cresol Purple, 100 mg Phenolphthalein in 200 ml 50% ethanol.

Procedure. To a 1 l flask add 20 gms superphosphate, 800 ml water and shake for 30 mins. Fill to mark, shake and filter. Place 50 ml of the filtrate, 150 ml water and 1 ml mixed indicator in a 300 ml Erlenmeyer. Neutralise with 0.1-N NaOH to a grey colour without any red tint.

Add 5 ml potassium oxalate solution and titrate with NaOH to a violet colour with a distinct red tint (a ml).

$$\% P_2O_5 \text{ water soluble} = a \times 0.71$$

Remark. A more rapid procedure, useful for immediate check control of production by the plant manager, is as follows :-

150 ml water are added to 1 g superphosphate and shaken for 30 seconds. 1 ml mixed indicator is added and the method continued as above.

(3) Water determination.

This determination is included in A.O.A.C. (5) but not in Fertilizers (4). Total water is determined by drying at 100° ± 1°C for 5 hrs., free water by passing dry air through the sample at 60°C or by desiccating at room temperature for 16-18 hrs. Gericke (6) extracts with alcohol, washes with ether and dries at 120°C. Nunn and Dee (7) determine total water by drying at 100°C for 4 hrs, and free water at 50°C under vacuum to constant weight. Hill et al (8) show that total water is expelled in 2 hrs at 130°C. At 100°C (and in some cases at 60°C) some water of crystallisation is expelled together with free water; this is especially pronounced in acid samples such as superphosphate. The only one of these methods that appears reliable for free water is desiccation at room temperature for 16-18 hrs.

The azeotropic method (3) is proposed because of its speed and accuracy. Distillation from benzene in the presence of CaCO₃ gives free water. Xylene gives total water.

Procedure.

a.) Free water. Weigh a 40 g sample into a 300 ml flask of a Dean and Stark apparatus. Add 5 gm CaCO₃ and 130 ml benzene. Assemble and distil at reflux rate of 90-120 drops per minute. Measure volume of water distilled after 40 minutes reflux.

% free water = 2.5 x vol. water distilled.

b.) Total water. Proceed as above, but omit the CaCO₃ and use xylene in place of benzene.

(4) Degree of acidulation of superphosphate.

The acid requirement of phosphate rock for superphosphate may be determined analytically (9), (10), (11), or experimentally (12). All methods give a more or less accurate measure of acid requirement.

Having produced the superphosphate it is necessary to check that correct acidulation has in fact been achieved. The method that has been introduced by Mr. A. Strauchen for control in our laboratories is based on analysis of total, water soluble and free acid P₂O₅ in the cured superphosphate. The formula for correct acidulation used is :-

$$\% P_2O_5 \text{ Free acid} = 1 + 1.5 (\% P_2O_5 \text{ total} - \% P_2O_5 \text{ w.s.})$$

A second method (11) for determining degree of acidulation is as follows :-

Weigh 5 g of a representative sample, transfer to a 250 ml volumetric flask and add 30 ml HCl, 5 ml HNO₃ and 100 ml water. Heat till solubles have dissolved, cool and fill to mark. Evaporate a 10 ml aliquot to dryness in a dish on the waterbath; add 2 ml water and exactly 10 ml 0.1-N H₂SO₄, evaporate to dryness and leave on the waterbath for a further 30 mins. Add 50 ml water, mix and decant the solution to a 500 ml flask. Crush the CaSO₄ crystals with a rubber bung held in a glass tube. Transfer to beaker, dilute to 300 ml and stir till CaSO₄ has dissolved. Add 1 ml mixed indicator (as used in oxalate method) and titrate with 0.1-N NaOH. End point is grey without any red tint.

$$\text{Acid deficiency } D_c = 12.3 \frac{10 - a}{w} - 2.07 \times \% F \text{ in superphosphate.}$$

Remarks: 1) 2.07 is an experimental factor based on an effective equivalent of 0.8 for the fluorine.

2) The value of D_c may be positive or negative dependent on whether shortage or excess acid has been used.

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