

SOLUBLE PHOSPHATE ASSAY

Rapid Determination of Water-Soluble Phosphorus Pentoxide in Superphosphate and Total Phosphorus Pentoxide in Dicalcium Phosphate

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A volumetric method determines water-soluble phosphorus pentoxide in superphosphate extract to $\pm 1\%$ in 5 minutes. Addition of potassium oxalate at the inversion point of the primary salt precipitates calcium oxalate and makes possible the titration of dihydrogen phosphate with sodium hydroxide. The amount of hydroxide used is equivalent to the phosphoric acid content of the solution. The method was also applied to the analysis of total phosphoric acid in dicalcium phosphate.

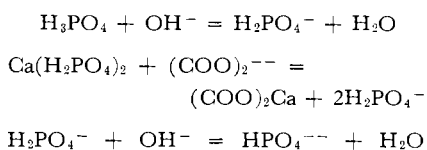
SOME of the more widely used methods for the determination of water-soluble phosphorus pentoxide in superphosphate are the double precipitation as magnesium ammonium phosphate, the Lorenz method, and the AOAC (7) titration method—all of which are reliable but time-consuming. The last one is the most rapid and can be completed within 1 hour. The differential spectrophotometric method of Gee and Deitz (3) combines speed and accuracy, but requires a fairly expensive spectrophotometer.

During production of superphosphate in the authors' plant, a speedy check on the water-soluble phosphorus pentoxide became necessary in order to enable plant supervision to carry out adjustments as fast as possible. To meet this requirement the volumetric method outlined in this paper—oxalate method—was worked out. It demands no special apparatus or expensive reagents and allows the determination of water-soluble phosphoric acid in superphosphate extract within 5 minutes with a maximum error of $\pm 1\%$. The principle has been mentioned by Schucht (6), Kolthoff (4), and Fischer and Kraft (2). In this laboratory, the principle has been applied to the determination of water-soluble phosphorus pentoxide in superphosphate and total phosphorus pentoxide in dicalcium phosphate. For the extraction of water-soluble phosphorus pentoxide from superphosphate, two methods are generally used: the AOAC (7) or the Organisation for European Economic Cooperation (OEEC) (5) method. According to the first one, the weighed superphosphate sample is washed on a filter with a measured amount of water. The OEEC test requires the shaking of the superphosphate sample with water for half an hour with subsequent filtration. In the procedure outlined below, the latter method was employed.

Principle

To the extract containing free phosphorus pentoxide and monocalcium

phosphate, standardized sodium hydroxide is added to pH 4.9, converting thereby the free phosphoric acid into the primary salt. From the amount of sodium hydroxide required to convert the primary phosphate into the secondary one, the phosphorus pentoxide content can be calculated. In order to avoid the precipitation of dicalcium phosphate of varying composition, potassium oxalate is added, which precipitates calcium oxalate and sets free an equivalent amount of monopotassium phosphate. For the determination of the two end points, a suitable mixed indicator is used. It has two turning points: one at 4.9, exhibiting a grayish shade, and one at 9.3, producing a purple-red color. The reactions involved are:



The pH of 4.9, at which the mixed indicator changes color sharply from reddish to grayish green, is somewhat higher than the theoretical one. It provides, however, a very convenient starting point for the second stage of the titration.

As the second end point—violet with a distinct red tint—is not so marked as the first one, the titration is carried out against the color of a standard solution of superphosphate, having a known phosphorus pentoxide content. The phosphorus pentoxide content is determined according to one of the standard methods (Lorenz or differential spectrophotometric), and the corresponding amount of 0.1*N* sodium hydroxide solution required for titration (*b*) amount is calculated as stated in procedure. The amount of sodium hydroxide added is therefore the theoretical one and a true measure of the phosphorus pentoxide content. The solution to be tested is then titrated with 0.1*N* sodium hydroxide against the purple tint obtained with the standard solution.

Figure 1 shows the various stages of the titration.

Procedure

Reagents. Sodium hydroxide, 0.1*N*, free of carbon dioxide.

Potassium oxalate, 25% solution, neutral against phenolphthalein.

Mixed indicator. Solution 1: methyl red, 23 mg.; bromocresol green, 67 mg.; and cresol purple, 10 mg., dissolved in 100 ml. of ethyl alcohol (50%). The mixture of the indicators is leached with small amounts of 50% ethyl alcohol and decanted, and this is repeated until dissolution occurs. A small insoluble residue is filtered off. Solution 2: 0.1% phenolphthalein in 75% alcohol. Solutions 1 and 2 are combined in equal parts. A 4-month supply was completely stable during that period.

Superphosphate standard solution. From 40 grams of a representative superphosphate sample, a solution of 2 liters is prepared in accordance with the procedure described under Determination. The phosphorus pentoxide content of the solution is analyzed according to a standard method (Lorenz or spectrophotometric), and the theoretical amount of sodium hydroxide required for the titration is calculated as follows:

$$b = \frac{\% \text{P}_2\text{O}_5}{0.71}$$

Preparation of Superphosphate Extract.

Superphosphate, 10 grams, is placed in a 500-ml. volumetric flask, 350 ml. of distilled water is added, and the flask is stoppered and placed in a shaking apparatus for half an hour. The flask is then filled up to the mark and the content—without settling—is filtered through a dry, folded filter. The first 20 ml. of the filtrate is discarded.

Determination. Aliquots of 50 ml. of the standard solution and 50 ml. of the test solutions, respectively, are placed separately in 300-ml. Erlenmeyer flasks. To this, 150 ml. of water and 1 ml. of mixed indicator are added. The solutions are titrated with 0.1*N* sodium

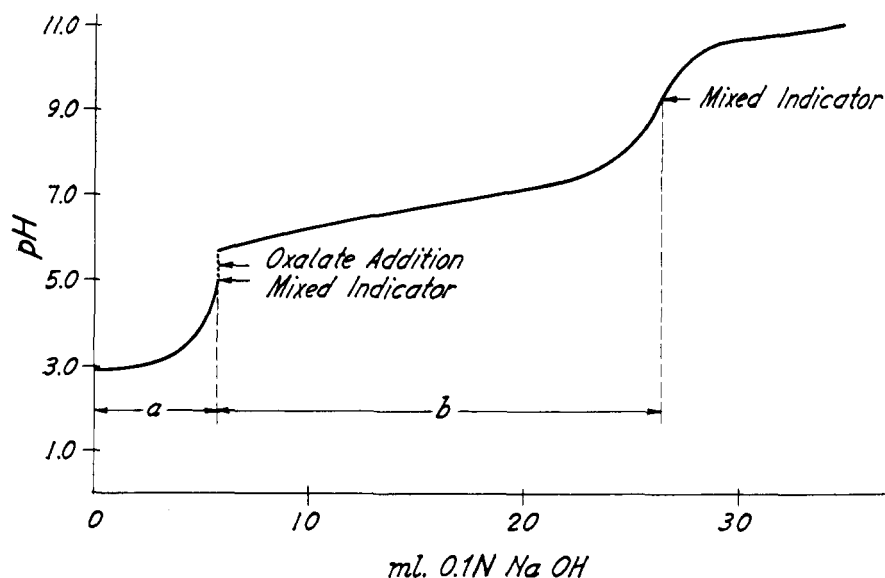


Figure 1. Titration of the superphosphate solution

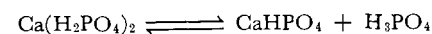
hydroxide to a gray color without any red tint (milliliters of sodium hydroxide added = *a*), and 5 ml. of potassium oxalate solution is then added. The calculated amount of sodium hydroxide solution is added to the standard solution, and purple tint is obtained. Against this tint, all test solutions are then titrated (milliliters of sodium hydroxide added = *b*).

$$\% \text{ P}_2\text{O}_5 \text{ (water soluble)} = b \times 0.71$$

Results and Discussion

Reaction conditions were examined with the aid of reagent grade monocalcium phosphate. The gravimetric analysis of the calcium oxide and phosphate contents indicated an excess of 5.8% free phosphorus pentoxide.

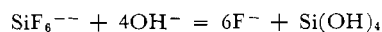
By washing the salt with a mixture of acetone and dioxane, monocalcium phosphate with the right calcium-to-phosphorus ratio was obtained. Without the presence of free phosphorus pentoxide during production, part of the monocalcium phosphate would have dissociated according to



The pH of this purified monocalcium phosphate is 4.6 at the dilution used in the test, the pH of the secondary salt is 9.3 in presence of the oxalate. No combination of indicators was found, which would have satisfactorily duplicated these potentiometrically determined inversion points. The mixed indicator used in the proposed oxalate method changes color at a somewhat higher pH than the theoretical one, 4.9. However, as this end point is very distinct, it was finally adopted for the procedure. The second inversion point was then determined as mentioned above by comparison with the tint of mixed indicator obtained by adding to a

standard solution the theoretical amount of sodium hydroxide required.

At the second stage of the titration, interference by soluble silicofluoride was expected according to reaction

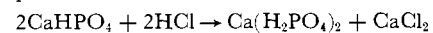


The silicofluoride present in the water extract in concentrations equivalent to 0.1 to 0.5% fluorine was, therefore, removed by adding two drops of perchloric acid to the aliquot and evaporating it on the water bath. However, the results of numerous tests with and without removal of the silicofluoride did not show any divergency. At pH 4.9—the pH of the first titration point in the proposed procedure—the conversion of the silicofluoride may be assumed to be complete. The removal procedure was therefore omitted.

Table I shows satisfactory agreement of the results obtained by the oxalate method with accepted standard methods for the determination of water-soluble phosphorus pentoxide in superphosphate. Samples 4 to 11 were calculated to one decimal only, the accuracy being sufficient for control purposes.

Total Phosphorus Pentoxide in Dicalcium Phosphate

When dicalcium phosphate is dissolved in a measured volume of standardized hydrochloric acid, the composition of the resulting solution is similar to the water extract of superphosphate containing monocalcium phosphate and free acid.



The procedure outlined below is after the acidification and analogous to that described for superphosphate with the difference that a standard solution of dicalcium phosphate is used.

Table II compares the results obtained with the oxalate and Lorenz methods in samples from current production. For preparation of dicalcium phosphate standard solution, a chemically pure product of Riedel de Haën was used.

Procedure. One gram of the sample is dissolved in a 100-ml. measuring flask with 30 ml. of 0.5*N* hydrochloric acid (150 ml. 0.1*N* hydrochloric acid). The sample is heated, if necessary, cooled, and filled up to the mark. An aliquot of 40 ml. is placed in a 300-ml. Erlenmeyer flask, diluted to 200 ml., 1 ml. of mixed indicator is added, and the procedure continues as indicated above for superphosphate.

Dicalcium Phosphate Standard Solution. Dicalcium phosphate, 20 grams, of known percentage of phosphorus pentoxide is dissolved in a 2-liter volumetric flask with 600 ml. of 0.5*N* hydrochloric acid and filled up to the mark.

The percentage of total phosphorus pentoxide contained in dicalcium phosphate is determined by one of the standard methods (Lorenz or spectrophotometric). The amount of sodium hydroxide to be added to the standard solution is calculated as above (see superphosphate). The titration scheme of the oxalate method for dicalcium phosphate is depicted in Figure 2.

By adding a known excess of acid and carrying out two titrations, it is possible to determine not only the phosphorus pentoxide but also the calcium oxide bound to the phosphate (not to sulfate or chloride). In this way, the important

Table I. Comparison of Methods for Determining Water-Soluble Phosphorus Pentoxide in Superphosphate

Sample	Water-Soluble P ₂ O ₅ , %			
	Oxalate	Lorenz	AOAC	Spectrophotometric
1	16.50	16.60	...	16.62
2	16.56	16.60	...	16.64
3	15.91	15.92	...	15.87
4	16.7	...	16.6	...
5	16.1	...	16.1	...
6	16.2	...	16.2	...
7	16.2	...	16.3	...
8	16.6	...	16.5	...
9	16.2	...	16.2	...
10	16.2	...	16.1	...
11	16.2	...	16.2	...

Table II. Comparison of Methods for Analysis of Total Phosphorus Pentoxide in Dicalcium Phosphate

Sample	Total P ₂ O ₅ , %	
	Lorenz	Oxalate
1	43.50	43.65
	43.60	43.65
2	43.80	43.80
	43.50	43.70
3	42.65	42.80
	42.55	42.85
4	44.80	44.75
	44.70	44.80
5	43.80	43.80
	43.95	43.85
6	42.20	41.95
	42.15	42.15

calcium oxide to phosphorus pentoxide ratio can be ascertained. The presence of calcium carbonate and free calcium oxide or hydroxide leads necessarily to a higher ratio. This is related to the "Peterman solubility" of dicalcium phosphate—a higher ratio indicating a decreased Peterman solubility. As the Peterman test is a lengthy one, the ratio determination, shown herewith, offers a useful check on production of dicalcium phosphate.

PLANT ANALYSES

Determination of Sulfur in Plant Materials

A rapid routine modification of the turbidimetric determination of sulfur in plant materials is described. The range is wide enough that it is seldom necessary to vary sample size or aliquot. The use of magnesium nitrate in the ashing process increases sensitivity and prevents loss of sulfur. Turbidity is measured by means of a spectrophotometer, and sensitivity can be varied by reading transmittance at a different wave length.

PRECIPIATION OF SULFUR as barium sulfate is an integral part of many methods for the determination of sulfur. This precipitation in acid solution has high specificity, but the method lacks sensitivity at low sulfur levels and is not rapid enough for routine determinations. Numerous micromethods have been proposed but their extreme sensitivity and narrow range limit their usefulness. The method described has proved satisfactory in the analysis of hundreds of samples of plant materials.

The ashing procedure is a modification of that used in the official AOAC method (3), but subsequent steps utilize the greater sensitivity and speed of the turbidimetric rather than the gravimetric method. The sample is large enough to make micromethods unnecessary.

The use of dipropylene glycol and alcohol as reported by Toennies and

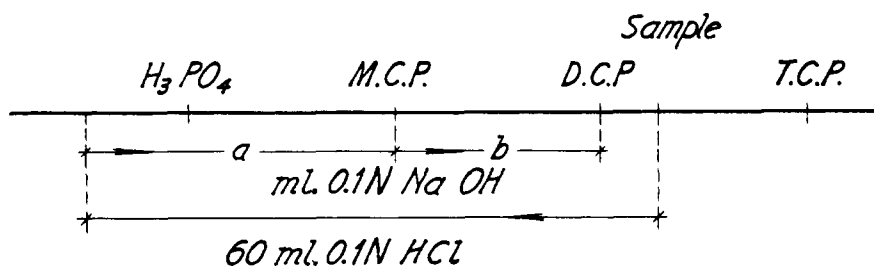


Figure 2. Titration scheme for the determination of total phosphorus pentoxide in dicalcium phosphate

Phosphoric acid in sample.

$$\% \text{P}_2\text{O}_5 = \frac{b \times 0.71}{w}$$

Calcium oxide content.

$$\% \text{CaO} = \frac{(60 - a + b) 0.28}{w}$$

$$\text{Ratio CaO/P}_2\text{O}_5 = \frac{60 - a}{b}$$

where w is weight of sample in aliquot used; a is amount of sodium hydroxide required to obtain monocalcium phosphate; and b is amount necessary for the conversion of monocalcium phosphate to dicalcium phosphate.

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Bakay (4) greatly improved the stability of the barium sulfate suspension.

Reagents

Dipropylene glycol. Mix by volume 55% dipropylene glycol (Eastman Kodak practical grade) and 45% absolute ethyl alcohol.

Barium chloride. Dilute 5 ml. of 1.25M barium chloride stock solution to 100 ml. with water; filter. Add dipropylene glycol reagent to a total volume of 167 ml. Use after 2 hours. This reagent is good for about 40 hours.

Alcoholic magnesium nitrate solution. Prepare magnesium nitrate from magnesium oxide low in sulfur according to the AOAC method (2), but crystallize out. Dissolve 360 grams of the air-dried crystals in 1 liter of 95% ethyl alcohol.

Magnesium chloride. Dissolve 108 grams of magnesium chloride in about

200 ml. of water, add 150 ml. of concentrated hydrochloric acid, and make up to 500 ml.

Precipitation of Standards

Prepare stock solution of potassium sulfate containing 4 mg. of sulfur per ml. Prepare standard solutions containing 50 ml. of magnesium chloride reagent and 0, 1, 2, 3, or 4 ml. of potassium sulfate stock solution in 100 ml. In preparing the standard curve, these solutions correspond to 0, 1, 2, 3, or 4 mg. of sulfur, respectively, in the original sample when the procedure below is followed.

Ashing Procedure. To a 1-gram sample in a No. 2 porcelain crucible, add 10 ml. of alcoholic magnesium nitrate solution. Let the solution stand 30 minutes, then heat on a hot plate