

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

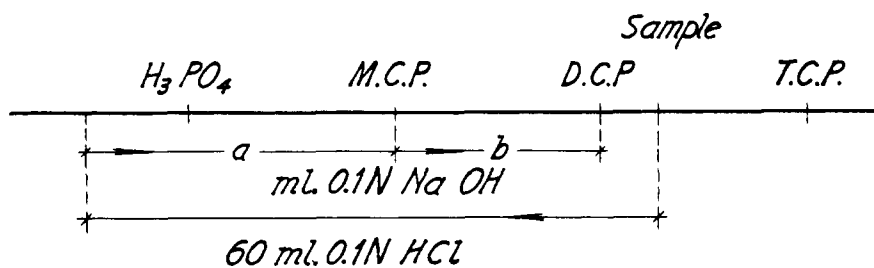


Figure 2. Titration scheme for the determination of total phosphorus pentoxide in dicalcium phosphate

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

until reaction is complete. Ash overnight at 450° C. in a muffle furnace. Dissolve the ash in 6 ml. of concentrated hydrochloric acid and sufficient water to give a final volume of 25 ml. Filter.

Analytical Procedure. Make analyses in duplicate.

Place a 3-ml. aliquot of sample or standard solution in each test tube, add 2 ml. of dipropylene glycol reagent, and mix thoroughly, then, at once, add 5 ml. of barium chloride reagent and again mix thoroughly.

Let mixture stand for 15 minutes to 1 hour and read transmittance at 720 m μ , using reagent blank as reference sample. Determine concentration of sulfur from standard curve.

If a smaller aliquot is used, enough zero sulfur standard should be added to make a volume with the aliquot of 3 ml.

Reading the transmittance at about 410 m μ increases sensitivity about two- or threefold.

Discussion

Comparison with Gravimetric Method. Results obtained by the proposed method are in good agreement with those obtained by the official AOAC method (3), as shown in Table I.

Analysis of variance showed no significant differences due to method of chemical analysis. There was an interaction, barely significant at the 5% level, between sulfur level in the sample and the method of analysis. The proposed method gave slightly higher values than the official method on samples containing about 0.2% sulfur and slightly lower values on samples containing 0.4% sulfur. The method gave equally good results with oily material of the seed and the nonoily root material.

Use of Alcoholic Magnesium Nitrate Solution. Alcoholic magnesium nitrate was used instead of the aqueous solution described in the official AOAC method to give better penetration of oily materials such as soybean meal.

Effect of Added Salts. The presence of magnesium and chloride ions at the high levels contained in the ash solution increases the absorbance by a factor of about 1.8 following addition of barium to a sulfate solution. It was therefore necessary to include magnesium chloride reagent in the standard solutions.

Table I. Results Obtained with Proposed Method and with AOAC Method

Sample No.	Material	Sulfur, %		Mean Difference		
		Proposed Method	Official Method	Proposed Method	Official Method	
1	Seed	0.20	0.20	0.21	0.22	-0.015
2	Seed	0.21	0.22	0.20	0.19	+0.02
3	Seed	0.23	0.23	0.21	0.22	+0.015
4	Seed	0.28	0.27	0.28	0.28	-0.005
5	Seed	0.27	0.28	0.28	0.28	-0.005
6	Roots	0.30	0.30	0.30	0.32	-0.01
7	Roots	0.39	0.38	0.40	0.41	-0.02
8	Roots	0.39	0.38	0.38	0.38	+0.005

The increase in turbidity with the addition of magnesium chloride reagent was not due to traces of sulfate, as the same amount of reagent was added to each standard, nor was it due specifically to either magnesium ions, chloride ions, or pH as the addition of sodium chloride, hydrochloric acid, or nitric acid had similar effects. In agreement with Toennies and Bakay (4), the effect of added salts was found to be small at low sulfur concentrations.

The amount of salts in the ash solution originating from the sample itself was small compared to that which was added. Variations of salt concentration of the magnitude owing to differences in ash content of the samples were found to have no effect on turbidity. The addition of phosphate to the standards to give concentrations higher than would be found in the ash solutions had no effect.

In the presence of only moderate concentrations of salts it is possible to determine sulfate volumetrically. Asghar, Quayyum, and Rana (7) have recently published a rapid method in which sulfate is precipitated as barium sulfate and the excess barium is titrated with the disodium salt of (ethylenedinitrilo)tetraacetic acid. However, the high concentration of magnesium necessary to prevent the loss of sulfur during ashing of plant materials would result in too high a blank for good accuracy with this method.

Spectrophotometry. Reading transmittance of 720 m μ gave satisfactory sensitivity over a wide range of sulfur concentrations, so that it was seldom necessary to change aliquot size. Greater sensitivity is possible at 410 m μ , but aliquot size must then be varied according to the expected percentage of sulfur. However, if the sample con-

tains less than about 200 γ of sulfur, the greater sensitivity at the lower wave length is worth while.

Commercially available reagents were used except in the case of magnesium nitrate and no difficulty was experienced due to the trace of sulfur which the reagents may have contained. Deionized water prepared by passing distilled water through a column of Amberlite Monobed No. 3 resin proved very satisfactory.

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- (2) Assoc. Offic. Agr. Chemists, Washington, D. C., "Official Methods of Analysis," 7th ed., p. 8, 1950.
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Endrin Content of Milk and Body Tissues of Dairy Cows Receiving Endrin Daily in Their Diet—Correction

On page 520 [Kiigemagi, Ulo, Sprowls, R. G., Terriere, L. C., *J. Agr. Food Chem.* **6**, 518 (1958)], in Table V, the heading of the fourth column should read "Ratio, Output/Intake."

Enzymic Hydrolysis of Naringin in Grapefruit—Correction

On page 548 [*J. Agr. Food Chem.* **6**, 546 (1958)], in the legend of Figure 5, the broken line should be the hydrolyzed sample and the solid line the original sample. S. V. TING

INSECT ATTRACTANTS

Esters of 6-Methyl-3-cyclohexene-1-carboxylic Acid as Attractants for the Mediterranean Fruit Fly

ATTRACTANTS are useful in the control and eradication of insect pests. In combination with a toxicant, they may

lure insects to their doom, or traps may be baited with them to determine the location and extent of insect infestation (1),

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so that control measures may be applied only when and where needed. Attractants are particularly helpful in detecting