

## Rapid Determination of the Sulfate Content of Wet-Process Phosphoric Acid by Phototurbidimetric Titration

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A rapid routine control procedure is described for the determination of sulfate in wet-process phosphoric acid using a phototurbidimetric titration technique. The titration and mechanical stirring are carried out in a photocolormeter cell to a point where no increase in absorbance is detected after titrant addition. Impurities normally present in wet-process acids do not interfere. The sulfate content of the sample may be determined accurately within 20 minutes of receipt of sample.

PRIOR to the commissioning of a wet-process phosphoric acid plant, it became necessary to evaluate all available published methods for determining the sulfate content of phosphoric acid. A knowledge of this content is very important for plant control, and the method chosen had to be rapid and sufficiently accurate for this purpose.

The classical gravimetric barium sulfate method, although probably the most accurate, if carefully carried out, had to be ruled out as the analysis time is too lengthy. The questionable accuracy of the rapid gravimetric method has been shown (5), and although this is the most used process control method, it still requires about 2 hours to complete one determination. Several modifications of this method have been used including centrifuging techniques, but all depend on several critical factors, and deviations from these result in even greater inaccuracies.

Turbidimetric methods have been used for determining sulfate ions in various solutions, including phosphoric acid (3-5), but the conditions under which turbidity is developed must be controlled closely if reproducible barium sulfate suspensions are to be achieved. Also, variations in the phosphate content of the acid can affect the accuracy of the sulfate determination (7). Thus additions of standard phosphate solution must be made to the aliquots to bring them up to a constant predetermined phosphate concentration. This, of course, complicates the procedure and further increases the analyses time.

Direct and indirect titrimetric methods for the determination of sulfate ions have been reviewed (6). These methods have the advantage of speed but, unfortunately, phosphate interferes seriously and must be removed if reasonable results are to be obtained. Prior separation of phosphate introduces further steps in the procedures with a corresponding increase in analysis time.

A Russian paper (2) relates that a

phototurbidimetric titration technique was used to determine the sulfate content of wet-process phosphoric acid. Attractive features of the method were its apparent independence of the phosphate concentration in the final aliquot and its nonreliance on particle size reproducibility. This method, then, was chosen for further study.

### Analytical Procedures

**Reagents.** BARIUM CHLORIDE (0.01 *M*). Dissolve 2.443 grams of reagent grade barium chloride dihydrate in distilled water and make up to 1 liter.

HYDROCHLORIC ACID, 20% v/v. Dilute 200 ml. of hydrochloric acid (sp. gr. 1.16) to 1 liter with distilled water.

**Apparatus.** PHOTOCOLORIMETER. Bruno Lange Model J, with No. 805 cuvettes.

LABORATORY STIRRER. Multifix, with flexible shaft drive and special stirring device.

**Dissolution of Sample.** Weigh 5 ml. of filtered phosphoric acid, and transfer to a 500-ml. graduated flask. Add 25 ml. of 20% hydrochloric acid, and dilute to the mark with distilled water.

**Dilution and Titration.** Transfer a 30-ml. aliquot to the titration cell, add 25 ml. of ethanol and 20 ml. of distilled water. Place this cell in the right-hand side holder and a similar cell containing distilled water in the left. Position the stirrer in one corner of the cell, away from the light path, and switch on the motor, adjusting the stirring speed to 800 r.p.m. Set the instrument to zero using the right side iris control, with the sensitivity controls set to the middle position. Add approximately half the volume of titrant required, allow equilibrium to be attained, and then reset the instrument to zero with the left side control. Finish the titration by adding increments of titrant at regular intervals, allowing equilibrium to be obtained each time before resetting to zero. At the end point, no further increase in absorbance will be detected with the addition of titrant, and the absorbance will start to decrease with further titrant additions because of the dilution effect of excess

titrant. The sensitivity controls can be turned to the maximum setting near the finish of the titration, resulting in sharper end points. The volume of titrant is recorded, and the sulfate content of the sample obtained by reference to the calibration curve, previously prepared from standards.

### Experimental

Adaptation of this method to the apparatus available in this laboratory required some changes in the original procedure. The optical cells used for titration in the photocolormeter available required a solution depth of at least one and a half inches for the light beam to be below the surface. This meant that the final volume taken for titration had to be increased to 75 ml.

It was desirable to be able to cover the range of sulfate contents expected, with a single aliquot size. It was determined experimentally that the range from 0 to 7% sulfate content could be covered adequately with a 30-ml. aliquot, which is equivalent to approximately 0.40 gram of sample. To keep the percentage of ethanol at the 30 to 35% level, 25 ml. of ethanol was added to the aliquot, and the final volume was then made up to 75 ml. with distilled water before titration. The strength of the barium chloride titrant was changed to 0.01*M*, and, when using the dilution and aliquot size outlined in the procedure, 1 ml. is equivalent to approximately 0.2% sulfate in the original sample.

Having then departed from the original conditions outlined as regards cell size and shape, titration volume, and its sulfate content, some experimentation was necessary to determine the most efficient stirrer design and speed. Several types of stirrer paddles were fabricated, including the spiral type used in the original reference. The design chosen, after evaluation of the different types in situ, is shown in Figure 1. At the determined stirrer speed, no tendency of the precipitate to layer out was noticeable. As such, when equilibrium in the reaction between the titrant and sulfate ions was attained, needle fluctuations were barely perceptible.

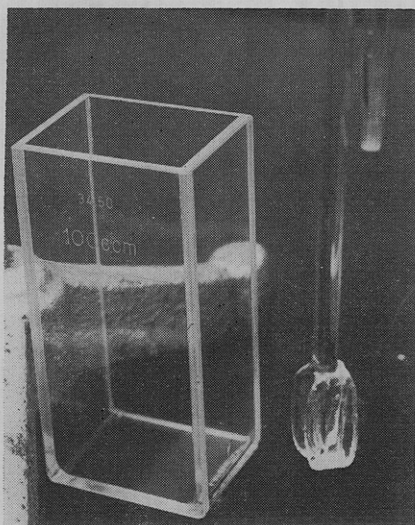


Figure 1. Stirring device and cuvette

Other modifications to the original procedure were the use of a green filter in the colorimeter, and the technique of setting to zero using distilled water in the second cell. It was considered that any errors, owing to the dilution by titrant of the background color in the process acids, would be minimized by using a green filter rather than a colorless matt filter. In actual practice, this final background is slight, but varies (in intensity and color) with the origin of the phosphate rock used in the process.

This possible source of error is not eliminated by the use of a second aliquot in the reference cell, as in the Russian

article. In fact, when the aliquot is made up to final volume with ethanol and water, entrapped bubbles appear from time to time on the optical surfaces of the cells. A stirring action is necessary to remove these bubbles, and this effect is achieved only in the titration cell. Thus, the use of distilled water in the reference cell was adopted.

For the purposes of calibration, synthetic standards were made up from phosphoric acid and standard sulfate solution to cover the range from 0 to 7%. The use of synthetic standards has the advantage that the final results on the assays are not dependent on the accuracy of gravimetric determinations. The calibration graph obtained appears to be linear over the range investigated, and the reaction between titrant and sulfate ions is, to all intents, stoichiometric.

Samples of process acid made from Nauru rock were analyzed by this method, and the results obtained were in close agreement to those obtained by the classical gravimetric procedure. Results of tests by the authors showed that the method is tolerant of impurities found in wet-process acid. The calcium oxide, fluoride, iron oxide, and aluminum oxide contents can vary over a wider range than would be normally encountered, without any significant effect on the results of the sulfate determination. The results are also independent of the phosphorus pentoxide contents of the filtrate acid.

In the early stages of the study, some work was done using protective agents, not to achieve repro-

ducible particle size but to minimize layering effects at the higher ranges. Use of these agents is necessary for turbidimetric measurements where absorbance is related to sulfate content (7, 2, 6), but as pointed out earlier, this method does not depend on reproducible particle size. The early work showed that, with the stirrer design and speed used, no advantage was gained by using these protective agents, and accordingly their use was not incorporated in the method.

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#### Literature Cited

- (1) Bentata, A., I.C.I.A.N.Z., Melbourne, private communication, 1965.
- (2) Chepelevetskii, M. L., Makarevich, V. M., *Zavodsk. Lab.* **30** (8), 935 (1964).
- (3) Claudy, H. N., Karasek, F. W., Ayers, B. O., Skinner, J. G., *Anal. Chem.* **31**, 1255 (1959).
- (4) Gassner, K., Friedel, H., *Z. Anal. Chem.* **152**, 420-4 (1956).
- (5) Nelson, G., *Proc. Fertilizer Soc.* **79**, 30 (1963).
- (6) Puschel, R., Lassner, E., *Chemist-Analyst* **49**, 90 (1960).

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## IMPURITIES FROM PHOSPHORIC ACID

# Precipitated Impurities in Fertilizers Prepared from Wet-Process Phosphoric Acid

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Ammoniation of wet-process phosphoric acid precipitates the metallic elements that were dissolved from the phosphate rock or added as micronutrients. The nature and solubility of the precipitates change as the acid is concentrated to the superphosphoric acid range and condensed phosphate species are introduced. The optical properties and x-ray patterns of 26 of the most common precipitates are described.

WET-PROCESS phosphoric acid contains soluble impurities, mostly iron and aluminum, that were dissolved from the gangue minerals in the phosphate rock from which the acids were prepared. In the concentration of these acids to merchant-grade (24% P, 54%  $P_2O_5$ ) or superphosphoric acid (about 33% P, 75%  $P_2O_5$ ), some of the impurities precipitate during storage as crystalline compounds (9) that interfere seriously with mechanical handling of the acid and immobilize some of the

phosphate. Considerable amounts of these impurities—iron, aluminum, calcium, and magnesium—remain in solution or as suspended solids, particularly when additives are introduced during production of the acid to stabilize suspended solids or delay their formation until the acid is processed into other fertilizers.

The preparation of fertilizers from wet-process phosphoric acid usually entails ammoniation of the acid; the acid or its ammoniation product often is concen-

trated, and many of the products thus contain condensed phosphates as well as orthophosphate. Addition of salts of potassium to prepare complete fertilizers and of micronutrients increases the amount of metal cations that may take part in precipitation processes.

The change in pH during ammoniation and the introduction of condensed phosphate species by concentration steps result in precipitation of the dissolved metallic impurities; these crystallization processes usually require an induc-