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THE DETERMINATION OF PHOSPHORUS IN ROCKS CONTAINING VANADIUM

by

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Abstract

This paper describes a rapid routine procedure for the determination of phosphorus in the presence of vanadium. Vanadium is reduced with formic acid prior to precipitation of phosphorus as ammonium phosphomolybdate and the ammonium phosphomolybdate is weighed as such. Ratios of V_2O_5 to P_2O_5 as high as 100 to 1 (the highest tested) give no interference. P_2O_5 in amounts from 0.1 mg to 0.2 g of P_2O_5 may be determined with no changes in conditions or quantity of reagents. The separation of molybdic acid is prevented and the molybdate precipitate has a constant composition.

Introduction

In the determination of phosphorus pentoxide it is common practice to separate the phosphorus first, as the insoluble ammonium phosphomolybdate. The analyst may then either weigh the precipitate, or dissolve the precipitate in standard alkali and back titrate with standard acid, or determine the phosphate as magnesium pyrophosphate. The last method is generally considered to be the most accurate, but the long time required for the analysis more than outweighs the very slight increase in accuracy obtainable.

All these methods presuppose that the separation of phosphorus as the ammonium phosphomolybdate has been quantitative. At least two difficulties are met in the separation of ammonium phosphomolybdate by the usual procedures:

1. The inherent instability of molybdic acid in nitric acid solutions of uncontrolled acidity results too often in a precipitation of molybdic acid. This is serious if the phosphomolybdate is to be weighed or titrated, but is of no consequence if magnesium pyrophosphate is to be weighed.
2. The presence of pentavalent vanadium in solution leads to unreliable results when the concentration of vanadium is about the same or greater than that of phosphate.

The separation of molybdic acid results largely from improper control of the conditions for the precipitation of the phosphomolybdate. These conditions are defined too loosely in common procedures. Conditions that are proper for large amounts of phosphorus cause serious disturbances when small amounts are present. Statements such as "use 10 times excess ammonium molybdate over the theoretical amount needed" are of limited utility, if one does not know how much phosphorus the sample contains.

In the method developed by Kassner, Crammer, and Ozier 1/,

1/ Kassner, J. L., Crammer, H. P., Ozier, Mary A., Determination of phosphorous pentoxide in phosphate rock: Analytical Chemistry, vol. 20, no. 11, p. 1052, 1948.

the precipitation of molybdic acid is prevented by the addition of citric acid. However, the solutions may also be stabilized by proper control of the nitric acid concentration, as is done in this study.

Pentavalent vanadium in solution presents a more serious difficulty. In common with other laboratories, it has been our experience that any of the following conditions may result when vanadium is overlooked, depending on the ratio of V_2O_5 to P_2O_5, and also the amount of phosphorus in the solution.

1. No phosphorus is precipitated when the ammonium molybdate is added. This takes place especially when the phosphorus content of the solution is small and the ratio V_2O_5/P_2O_5 is over 5.
2. The phosphorus is precipitated incompletely.
3. The phosphorus precipitate is contaminated with vanadium.
4. Molybdic acid may precipitate.

We have no data on the performance of the Kassner method in the presence of vanadium. Some of the difficulties are partially reduced by proper control of acidity and molybdate concentrations, but it is doubtful that a useful method could be developed on this basis.

Methods for dealing with vanadium usually involve reduction of the vanadium to the quadrivalent state, and precipitation of the phosphomolybdate at room temperature or colder. Under these conditions little vanadium precipitates and the retarding effect of vanadium on the precipitation of phosphorus is largely overcome. Hillebrand and Lundell [2] advise using $FeSO_4$ and 1 g of iron as ferric nitrate to reduce the vanadium and to prevent subsequent reduction of the molybdenum.

Volatile reducing agents are to be preferred because contamination of the phosphomolybdate precipitate by fixed salts is avoided.

This report deals with the use of formic acid to effect the reduction of vanadium. Proper conditions were developed such that:

1. The phosphomolybdate precipitate obtained is constant in composition.
2. The separation of molybdic acid is prevented.
3. From 0.1 mg to 0.2 g of P_2O_5 may be determined, with no change in conditions, or amounts or types of reagents.

The analyst simply prepares a solution of the sample, adds a fixed amount of reagents, filters, dries, and weighs the precipitate. Thus no guesswork or prior knowledge of the phosphorus and vanadium content is required. The procedure will determine phosphorus with good accuracy when the V_2O_5 to P_2O_5 ratio is as high as 100 to 1, the highest tested. Because of the constant composition of the precipitate, titrimetric procedures may also be used.

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[2] Hillebrand, W. F., and Lundell, G. E. F., Applied inorganic analysis: page 562, New York, John Wiley & Sons, 1929.

Discussion of Procedure

Preliminary investigations by the writers determined optimum conditions for the precipitation of phosphate with ammonium molybdate. These conditions are always used, regardless of the amount of P_2O_5 present up to 0.2 g.

1. The precipitation is done at room temperature.
2. The total volume of solution is 100 ml after all reagents and water are added. It contains 5 ml of formic acid, about 8 g of ammonium nitrate, 15 ml of nitric acid (S.G. 1.42), and 45 ml of the molybdate solution.

These conditions are flexible enough to allow of some variation. The nitric acid content is the most critical factor and should be controlled closely. For example, if the concentration of nitric acid in the final solution is as low as 9 % by volume (i.e. 100 ml of solution contains 9 ml of nitric acid, S.G. 1.42), molybdic acid tends to precipitate. A few tests showed that molybdic acid does not separate out from solutions containing 12 % by volume of nitric acid. The amount of ammonium molybdate is more than enough for precipitation of small amounts of P_2O_5, but to eliminate guesswork on how much to use it is advantageous to keep the amount constant, and this quantity is necessary if 0.2 g of P_2O_5 is to be quantitatively precipitated. Formic acid is necessary to eliminate vanadium interference but is rapidly destroyed by nitric acid if the solution is warmed.

For this reason the nitric acid content of the solution is kept at a minimum prior to the addition of formic acid, and the solution is cooled to room temperature before and after the addition of the nitric acid. If the temperature of the room is high enough to start a slow decomposition of the formic acid, it is preferable to cool the solution to a lower temperature. For uniformity of procedure formic acid is used even when vanadium is absent. Under these conditions, the composition of the phosphomolybdate precipitate when dried at 110°C is $(NH_4)_3PO_4 \cdot 12MoO_3$, and the factor for P_2O_5 is 0.03783.

Procedure

The special reagents needed are formic acid (reagent grade S.G. 1.2, 90 %) and ammonium molybdate solution. The ammonium molybdate solution is prepared by dissolving 16 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, in 90 ml of hot water. Cool the solution and filter if necessary.

I. Preparation of the solution:

1. Phosphate rocks:

   Add 20 ml of (1 + 1) HNO_3 to a 0.5-g sample in a glass container, and evaporate the solution to dryness. Repeat with 20 ml more of (1 + 1) HNO_3. Digest the residue with 20 ml (1 + 3) HNO_3 and filter; wash with water. Reserve the filtrate. Fuse the residue with a minimum of Na_2CO_3 in platinum. Leach the cool melt with water and filter. Wash the precipitate with 1 % Na_2CO_3 solution. Combine the filtrate with the filtrate reserved above. Reject the residue. Add 5 ml HNO_3 and take the combined filtrates to dryness. Add 20 ml of (1 + 3) HNO_3, warm to dissolve the salts, and transfer the solution to a 100-ml volumetric flask, filtering if necessary. For rapid control work the carbonate fusion need not be made and the residue from the initial attack with nitric acid may be rejected. If the sample contains much material that is insoluble in nitric acid, prepare solution as in 2.

2. Siliceous and clayey samples:

Treat a 0.5-g sample in a platinum dish with 10 ml of (1 + 1) HNO_3 and 10 ml of HF. Cover with a platinum cover and digest on the steam bath for 10 minutes. Remove cover and evaporate to dryness. Evaporate twice more with 15 ml of (1 + 1) HNO_3 to remove fluoride. Take up in 20 ml of (1 + 3) HNO_3, digest and filter, washing with water. Reserve the filtrate. Ignite the residue in platinum and fuse with a minimum of Na_2CO_3. Leach the cooled melt with hot water. Filter and wash with dilute Na_2CO_3 solution. Reject the residue.

Combine the filtrate with that reserved previously. Add 5 ml of HNO_3 and take the combined filtrates to dryness. Add 20 ml of (1 + 3) HNO_3, warm to dissolve the salts, and transfer the solution to a 100-ml volumetric flask, filtering if necessary.

II. Determination as ammonium phosphomolybdate:

1. Take an aliquot of the prepared solution, containing 50 mg of P_2O_5 or preferably less, and transfer it to a 150-ml beaker.
2. Neutralize with NH_4OH until methyl red indicator is neutral.
3. Add 5 ml of formic acid and bring the solution just to boiling.
4. Remove from the source of heat immediately, and cool the solution to room temperature in a cold water bath.
5. Add 8 g of NH_4NO_3 (solid) and stir until it dissolves.
6. Add 15 ml of HNO_3.
7. Immediately add 45 ml of ammonium molybdate solution slowly with stirring.
8. Add water to make the total volume 100 ml. Let stand until the precipitate settles. The precipitate is ready to filter as soon as it has settled out.

9. Filter thru a weighed sintered-glass medium filter or Gooch crucible.
10. Wash several times with (1 + 99) HNO_3 solution.
11. Dry the precipitate at 110°C and weigh.

$$\% \; P_2O_5 = \frac{\text{wt. of ammonium phosphomolybdate} \times 3.783}{\text{wt. of sample}}$$

Results of analyses

I. Composition of ammonium phosphomolybdate:

A standard phosphate solution was made from Bureau of Standards sample no. 186 II (Na_2HPO_4) by direct weight and was added to 12 beakers. The first 6 (series A) contained 0.2, 5, 10, 20, 30, and 50 mg of P_2O_5. The second 6 (series B) contained duplicate amounts of P_2O_5 and in addition each had 20 mg of V_2O_5 added as ammonium metavanadate solution. Phosphorus was determined as described in the procedure. The results in table 1 established that the composition of the precipitate dried at 110°C is $(NH_4)_3PO_4 \cdot 12MoO_3$.

II. Analyses of phosphate rocks:

Nitric acid solutions were prepared from three Bureau of Standards standard samples of phosphate rocks:

Sample No.	Rock	% P_2O_5
120	Florida Land Pebble	35.33
56	Tennessee Phosphate	31.33
56a	Tennessee Brown	33.01

Table 1.--Results of analyses of pure solutions

P_2O_5 taken (mg)	P_2O_5 found based on $(NH_4)_3PO_4.12MoO_3$ (mg)
Series A -	
0.2	0.2
5.0	5.0
10.0	10.1
20.0	20.0
30.0	29.8
50.0	50.1
Series B -	
0.2	0.2
5.0	5.0
10.0	10.0
20.0	20.2
30.0	30.1
50.0	50.2

II. Analyses of phosphate rocks. (Cont.)

Six aliquots of each sample were taken in duplicate, representing 5.0, 17.0, and 44.0 mg P_2O_5. No vanadium was added to samples in series A. A 20-mg portion of V_2O_5 was added to each sample in series B. P_2O_5 was then determined according to the procedure. Table 2 lists the results obtained.

Table 2.--Analyses of standard samples

Standard sample no.		P_2O_5 taken (mg)	P_2O_5 found (mg)
120	Series A	5.0	5.1
		17.0	17.2
		44.0	43.8
	Series B	5.0	5.0
		17.0	17.1
		44.0	44.0
56	Series A	5.0	4.9
		17.0	16.8
		44.0	44.1
	Series B	5.0	4.9
		17.0	17.1
		44.0	43.9
56a	Series A	5.0	4.9
		17.0	17.1
		44.0	44.0
	Series B	5.0	5.0
		17.0	17.2
		44.0	44.1

III. Performance of the procedure by other chemists:

Robert Meyrowitz of this laboratory tested the procedure against Bureau of Standards sample no. 120,

III. Performance of the procedure by other chemists. (Cont.)

employing aliquots containing 0.14, 7.1, 17.7, and 35.4 mg of P_2O_5. Table 3 shows the results obtained.

Table 3.--Test of the procedure by Robert Meyrowitz on Bureau of Standards sample no. 120

P_2O_5 taken (mg)	P_2O_5 found (mg)
0.14	0.18
7.1	7.3
17.7	17.8
35.4	35.2

In table 4 Bureau of Standards sample no. 186 II (Na_2HPO_4) was used and aliquots containing 100, 150, and 200 mg of P_2O_5 were analyzed by Robert Meyrowitz.

Table 4.--Test of the procedure by Robert Meyrowitz on Bureau of Standards sample no. 186 II

P_2O_5 taken (mg)	P_2O_5 found (mg)
100	99.8
150	150.3
200	200.8

The results show that when up to 50 mg of P_2O_5 is present, the maximum error is ± 0.2 mg of P_2O_5. For greater amounts of P_2O_5 (i.e. 0.2 g of P_2O_5) the maximum error may be ± 0.8 mg. Although this latter figure seems large, it is actually a small percentage of the total phosphorus present.