

Spectrophotometric Microchemical Phosphorus Determination
A Quantitative Oxygen Flask Procedure Applicable to Problem
Organophosphorus Compounds

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Numerous methods have been proposed for the oxidative decomposition of organophosphorus compounds. These include Carius, Parr bomb, oxygen bomb, oxygen-flask, and catalytic combustion. All convert the phosphorus present to the orthophosphate which is quantitatively determined by various gravimetric, volumetric, or spectrophotometric methods. The most popular combustion method in microanalysis today is the oxygen-flask procedure of Schöniger (2, 3, 6, 7). This has been used successfully in the analysis of many organophosphorus compounds. The author, however, has encountered some phosphorus-containing materials which did not burn properly using the normal combustion techniques. Some materials exhibited excessive sparking during combustion, some produced sooty fumes and deposits, while others either volatilized partially without decomposition or were too refractory. These behaviors, of course, lead to poor accuracy and precision. Consequently, a more generally applicable oxygen-flask combustion procedure was sought.

One requirement placed on the method was that the resulting solution containing the orthophosphate permit the spectrophotometric determination of the phosphorus by the molybdenum blue procedure (1, 4, 8, 9). The molybdenum blue method was chosen because of its sensitivity and the frequent need to determine trace amounts of phosphorus in agricultural products. Conditions for optimum color development and stability were studied as were conditions for the absorption of the phosphates formed during combustion and the treatment of the resulting solution prior to color development. The method

finally developed combines a modified Schöniger (7) oxygen-flask method with a modified AOAC (1) molybdenum blue procedure.

APPARATUS AND REAGENTS

A. Apparatus

Arthur H. Thomas¹ Infrared Igniter for oxygen flask combustions, 1000-ml combustion flask, sample carrier, black paper sample wrappers, Burrell "wrist-action" shaker and Beckman B spectrophotometer with 2.5 cm Pyrex absorption cells.

B. Reagents

Potassium chloride, fuming nitric acid, oxygen, concentrated sulfuric acid and the following solutions:

Ammonium molybdate solution. (a) Dissolve 5 g of ammonium molybdate in 60 ml of water. (b) Add 15 ml of concentrated sulfuric acid to 40 ml of water and add to solution (a).

Hydroquinone. Dissolve 5 g of hydroquinone in water in a 100-ml volumetric flask and dilute to volume.

Sodium sulfite. Dissolve 20 g of sodium sulfite in water in 100-ml volumetric flask and dilute to volume.

Phosphorus standard. Solution I: Place 0.4394 g of KH_2PO_4 in a 1-liter volumetric flask; dilute to volume with water.

Solution II: Dilute 50 ml of solution I to 1 liter.

PROCEDURE

Accurately weigh a sample containing approximately 0.5 mg of phosphorus onto a black sample wrapper. Fold the wrapper and place it in a platinum sample carrier (basket). The baskets are cleaned prior to use in the usual manner by flaming them to red heat over a Meeker burner using platinum tipped tongs. When necessary, the baskets are first boiled in concentrated nitric acid.

To prepare the combustion flask unit, suspend a platinum wire, approximately 3.5 cm long, from the hook of the combustion flask head and hang the platinum basket with its sample on the other end of the platinum wire.

To a 1-liter combustion flask add 10 ml of distilled water and approximately 100 mg of KCl. Fill the flask with oxygen. Introduce 0.5 ml of fuming HNO_3 into the top of the flask and quickly insert the prepared stopper unit. Seal the ball joint with water and secure the stopper unit with a spring-type clamp. Perform sample ignition, then place the flask on the wrist-action shaker for 30 minutes. Remove the flask from the shaker, tilt, and slowly rotate to rinse its walls with absorption solution and to drop the basket into the solution. Place the closed flask in an oven at 100°C for 5 minutes and then allow it to cool (or allow the flask to stand 24 hours at room temperature).

Open the flask and immediately rinse the stopper, platinum wire, platinum basket, and flask wall with water. After letting the flask walls drain, transfer the sample solution to a 100-ml beaker rinsing the flask 5 times and evaporate to dryness on a steam bath. Transfer the residue to a 100-ml volumetric flask using at least 5 rinsings and dilute to volume.

Place a 5-ml aliquot of the above solution in a 25-ml volumetric flask. Prepare 3 standards containing 0.025, 0.05, and 0.075 mg of phosphorus by diluting 5, 10, and 15 ml of the standard KH_2PO_4 solution II to 25 ml in volumetric flasks. Use a fifth 25-ml flask for the reagent blank.

Treat each 25-ml volumetric flask as follows: Add 2 ml each of the ammonium molybdate, hydroquinone, and sodium sulfite solutions in the order listed and rotate to mix after each addition. Dilute to volume with distilled water, stopper, and shake well. Remove the stopper and place on a steam bath with medium steam flow for 5 minutes, or in a boiling water bath for 2 minutes, then allow to cool to room temperature (approximately 45 minutes).

Read the absorbance of each solution successively in the spectrophotometer at $650\text{ m}\mu$ using the prepared blank as reference.

RESULTS AND DISCUSSION

Four changes in the usual procedure were made which increased the efficiency of the degradative-oxidation phase of the oxygen-flask procedure. First, the extension of the sample depth in a 1-liter combustion flask by suspending the platinum basket from a length of platinum wire enabling the basket proper to be at least 6 cm from the glass hook of the flask head. This prevented the partially decom-

Calculations:

$$K = \frac{\frac{\text{absorbance of standard}}{\text{cell length}}}{\text{mg of phosphorus in color standard; }^2}$$
$$\% \text{ phosphorus} = \frac{\frac{\text{absorbance of sample}}{\text{cell length} \times K} \times \frac{\text{volume}}{\text{aliquot}}}{\text{sample weight (mg)}} \times 100.$$

posed sample (or sample products) from contacting the cool glass surface during combustion. Second, the addition of fuming nitric acid to the absorption solution liberates nitrogen oxide fumes which retard sparking. Third, potassium chloride was added to the absorption solution to prevent loss of phosphorus, particularly during steam bath evaporation. Fourth, heating the closed flask for a 5-minute period in an oven at 100°C increased the efficiency of the absorption. If the closed flask was not heated, it was necessary to allow it to stand at room temperature for 24 hours.

It was confirmed that the sensitivity of the spectrophotometric method based on the molybdenum blue procedure depended on the reaction conditions existing when the color reagents are added. Thus, a deviation from Beer's Law was produced by the presence of excess acid, base, or even salt. At a high pH the point of reduction of the phosphomolybdic acid complex is close to that of the molybdate causing the molybdenum blue intensity to be disproportionate to the phosphorus concentration. Moreover, a signal excess of acid causes a decrease in color intensity. To overcome the inhibiting effect of excess nitric acid in the absorbing solution, the solution could be neutralized with ammonium hydroxide in the presence of phenolphthalein and reacidified to colorless. However, better precision was obtained using steam-bath evaporation to remove the excess acid from the solution. Slight variation in molybdate, hydroquinone, and sulfite concentration and in pH do not greatly affect the color intensity. The best proportions for the three color reagents have already been established (1).

Temperature affected the rate and amount of color development. Previously we had used an overnight standing period for the molybdenum blue color development and stabilization as the most

TABLE I
REPRESENTATIVE EXPERIMENTAL RESULTS

Compound	Theoretical (% P)	Found (% P) Determinations	Average	Standard devia- tion	Standard error	
Syntropan:						
3-diethylamino 2,2- dimethyl propyl tropate phosphate	7.64	7.63 7.62 7.56	7.64 7.63 7.54	7.60	0.04	0.016
Ilidar phosphate:						
6-allyl-6,7-dihydro- 5H-dibenz (c,e)- azepine phosphate	9.29	9.26 9.20 9.26	9.31 9.19 9.14	9.23	0.06	0.024
3,4-Dichlorobenzyl- triphenylphosphonium chlorine	6.74	6.68 6.70 6.56	6.58 6.70 6.59	6.64	0.06	0.024
Triphenyl phosphine	11.83	11.49 11.79 11.82	11.84 11.79 11.79	11.75	0.13	0.053
Diphenyl cyclo hexylamine phosphate	9.35	9.31 9.26 9.35	9.18 9.28 9.30	9.28	0.06	0.024
Triphenyl phosphate	9.51	9.43 9.39 9.52	9.50 9.44 9.40	9.45	0.08	0.033
Octadecyl phosphate	8.6	8.62 8.58 8.53	8.59 8.55 8.50	8.56	0.04	0.016

precise and accurate method. This was modified by placing the solution on a steam bath with medium steam flow for exactly 5 minutes. A 4-minute period produced low results while 6 minutes produced high and erratic results. A 2-minute period in a boiling water bath may also be used. Although the sample and color standards must be treated and measured in the same time interval, the color developed is sufficiently stable so that a difference in reading time of 15-20 minutes does not affect the accuracy. If the concentration of phos-

phorus in the unknown differed from the standard by more than 35%, an error was introduced because of a slight deviation from Beer's Law. Although the absorbance value for only 1 standard was used, 3 standard solutions were prepared at the same time the color was developed in the sample solution so as to bracket the optimum sample absorption range.

This procedure has been successfully used in this laboratory for the determination of phosphorus content in various compounds including some of those whose quantitative degradation and oxidation have been difficult to accomplish by the previously used oxygen-flask method. Table 1 illustrates the accuracy and precision attained.

SUMMARY

A modified oxygen-flask combustion procedure has been developed for the determination of phosphorus in organic materials difficult to oxidize by conventional flask methods. Combustion takes place in a mixture of oxygen and nitrogen oxides and absorption and hydrolysis to orthophosphate are aided by heating the flask and contents before opening. The orthophosphate formed is determined spectrophotometrically as the molybdenum blue complex. Color development and stability are aided by heating the solution briefly after adding the color reagents. Data are presented to show the accuracy and precision of the method.

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¹ Mention of company or trade names does not imply endorsement by the U. S. Department of Agriculture over others not named.

² Use absorbance of standard closest to that of sample.