

Table I. Recovery of Azide from Sodium Azide

| Sample, Mg. | Azide Nitrogen, Mg. | | |
|-------------|---------------------|--------------------|-------|
| | Taken | Found | Error |
| 5.21 | 3.37 | 3.47 | +0.10 |
| 5.72 | 3.70 | 3.62 | -0.08 |
| 6.17 | 3.97 | 3.98 | +0.01 |
| 6.43 | 4.15 | 4.10 | -0.05 |
| 6.53 | 4.22 | 4.21 | -0.01 |
| 7.90 | 5.10 | 5.15 | +0.05 |
| 8.22 | 5.31 | 5.25 | -0.06 |
| 8.85 | 5.72 | 5.60 | -0.12 |
| 9.28 | 5.99 | 6.04 | +0.05 |
| 9.44 | 6.10 | 6.12 | +0.02 |
| | | Av. ± 0.06 | |
| | | Standard deviation | 0.07 |

Table II. Analysis of Lead Azide

| Sample, Mg. | Azide Nitrogen, Mg. | | |
|-------------|---------------------|--------------------|-----------|
| | Calculated | Found | Deviation |
| 12.9 | 3.54 | 3.58 | +0.04 |
| 14.8 | 4.06 | 4.04 | -0.02 |
| 15.0 | 4.11 | 4.12 | +0.01 |
| 15.4 | 4.22 | 4.20 | -0.02 |
| 16.0 | 4.39 | 4.43 | +0.04 |
| 17.0 | 4.66 | 4.73 | +0.07 |
| 21.1 | 5.79 | 5.65 | -0.14 |
| | | Av. ± 0.05 | |
| | | Standard deviation | 0.07 |

ceric sulfate. Mix well to decompose the azide and evaporate to dryness on a water bath or in an electric oven at 110° C. Cool and proceed as above eliminating the addition of the thiosulfate.

As only one third of the azide nitrogen is recovered, the per cent azide can be calculated from the following equation

$$\% \text{ azide} = 4200 N \left(\frac{V}{S} - \frac{v}{s} \right)$$

where N = normality of the standard acid, V = ml. of acid used for total nitrogen, v = ml. of acid used for protein nitrogen, S = sample weight for total nitrogen, and s = sample weight for protein nitrogen.

DISCUSSION

Sodium azide was used to test the method.

Eastman technical grade sodium azide was purified by recrystallization. The sodium azide was dissolved to make a saturated solution and filtered through Whatman No. 42 filter paper. The filtrate was diluted with an equal volume of 95% ethyl alcohol and the sodium azide was precipitated by adding an excess of diethyl ether. After an hour, the salt was filtered through Whatman No. 42 filter paper on a Büchner funnel and dried for 1 hour at 110° C. Only one recrystallization was used, because repeated recrystallizations resulted in decomposition of the azide.

Table I gives the recoveries from the purified sodium azide and indicates the accuracy of the method. With 5- to 10-mg. samples the average deviation from the theoretical quantities of azide was ± 0.06 mg. with a standard deviation of 0.07 mg.

The data in Table II were obtained with a sample of lead azide containing a proteinaceous material as a stabilizing agent. Because of the large molecular weight of lead azide, slightly larger sample weights were used in order to obtain amounts of nitrogen equivalent to the data in Table I. As the sample was not pure lead azide, the data in column 2 were calculated from the mean per cent azide and the data in Table II are therefore indicative of the precision of the method. An average deviation of ± 0.05 mg. and a standard deviation for precision of 0.07 were obtained, which are practically identical with the error statistics for sodium azide.

It is essential to add the thiosulfate first, so that a reducing agent is present when the hydrazoic acid is liberated. Experiments in which the thiosulfate was added after the sulfuric acid invariably gave low results.

The digestion step is imperative, whether carbonaceous material is present or not. Experiments in which the sample of sodium azide was weighed in platinum boats and no heat applied resulted in the recovery of less than 1% of the theoretical amounts of nitrogen. Since the perchloric acid digestion is so short (~ 20 minutes), the use of cigarette paper, which acts as an additional reducing agent during the digestion step, is advocated.

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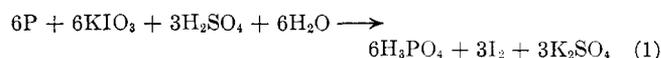
RECEIVED for review June 29, 1951. Accepted October 8, 1952. Based on work performed at Los Alamos Scientific Laboratory of the University of California under Government Contract W-7405-eng-36.

Determination of Elementary (Red) Phosphorus by Potassium Bromate

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THE use of potassium iodate in the volumetric determination of elementary phosphorus has been investigated by Buehrer and Schupp (1). This method is based on the oxidation and subsequent conversion of phosphorus into phosphoric acid. Iodine liberated during the process or/and the unreacted iodate after the completion of the reaction is estimated iodometrically and the amount of phosphorus is calculated from the following reaction mechanism:



Experience, however, showed that the accuracy of the results depended on a series of experimental precautions and necessitated the use of special apparatus. Numerous quantitative oxidation processes involving the use of potassium bromate show that its oxidizing property is almost equivalent to that of potassium

iodate (2-6). Available information in the literature about the quantitative oxidation of phosphorus by potassium bromate is, however, meager. The addition of acidified potassium bromate solution to phosphorus leads to its gradual disappearance accompanied with a rapid evolution of bromine. The present work was undertaken to investigate the factors affecting this reaction and to determine its utilizability for the determination of elementary phosphorus.

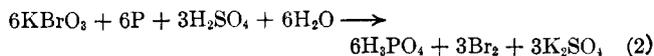
EXPERIMENTAL

Red phosphorus of British Drug House reagent grade quality was purified initially by Buehrer and Schupp's method (1). It was then added to an excess of concentrated solution of Merck's extra pure copper sulfate and boiled for a few minutes. The copper phosphide thus obtained was washed thoroughly and decomposed with pure dilute nitric acid. The liberated phos-

phorus was freed from copper nitrate by repeated washing and was dried in a vacuum desiccator. The analysis of this sample by the usual magnesium pyrophosphate method showed only negligible quantities of impurity.

An accurately weighed amount of dry phosphorus was taken in a Kjeldahl-type flask, to which a known excess of standard potassium bromate solution was added, followed by 5 to 10 ml. of carbon tetrachloride or chloroform. The flask was fitted with a ground-glass seal condenser; its contents were diluted to about 100 ml. and acidified with 10 ml. of 4 *N* sulfuric acid. The system was heated gradually in a water bath and refluxed for about an hour till all the red particles of phosphorus disappeared completely. The condenser was removed and the solution was boiled gently to expel the bromine from the carbon tetrachloride (or chloroform) layer. A slow stream of air was drawn through the hot solution to ensure the complete removal of free bromine. The flask was removed from the water bath and cooled to room temperature and the unreacted potassium bromate was determined iodometrically by standard thiosulfate (?).

By analogy with the P-KIO₃ reaction, the interaction of phosphorus with potassium bromate may be represented by the equation:



The difference in the quantity of potassium bromate added initially to phosphorus and that left over after the completion of the reaction should correspond to the amount utilized in the oxidation of phosphorus.

Since according to Equation 2, 1 mole of potassium bromate is equivalent to one of phosphorus, a knowledge of the quantity of potassium bromate utilized in the reaction is useful for the direct determination of phosphorus.

The agreement between the calculated and weighed quantities of phosphorus (cf. Table I) proves the stoichiometry of the reaction.

The influence of acidity on the total reaction was studied by varying the concentration of the known volume (10 ml.) of the acid added to the system from 0.2 to 10 *N* and also by refluxing red phosphorus only with aqueous potassium bromate. Experiments 12 and 13 (Table I) refer to results obtained by acidifying the bromate solution with 10 ml. of 8 *N* sulfuric acid.

In a purely aqueous medium the rate of reaction was found to be appreciably slow; a brisk evolution of bromine and rapid disappearance of phosphorus were, however, observed when the total acidity of the system was increased progressively above 2 *N*.

While the high results obtained on exceeding the acid concentration above a certain limit (Experiments 12 and 13) may be attributed to the decomposition of more of potassium bromate than is actually necessary to oxidize phosphorus according to Equation 2, its incomplete oxidation and subsequent conversion

Table I. Determination of Elementary (Red) Phosphorus by Potassium Bromate

| Expt. No. | Phosphorus Taken Gram | Wt. of KBrO ₃ Grams | KBrO ₃ Unreacted Grams | KBrO ₃ Reacted Gram | Phosphorus Found Gram | Error % |
|-----------|--------------------------|-----------------------------------|--------------------------------------|-----------------------------------|--------------------------|---------|
| 1 | 0.03100 | 0.9182 | 0.7522 | 0.1660 | 0.03082 | -0.58 |
| 2 | 0.03100 | 1.7586 | 1.5850 | 0.1730 | 0.03120 | +0.96 |
| 3 | 0.03220 | 1.1286 | 0.9605 | 0.1681 | 0.03215 | -0.15 |
| 4 | 0.03560 | 0.8912 | 0.7001 | 0.1911 | 0.03546 | -0.39 |
| 5 | 0.03680 | 0.9188 | 0.7224 | 0.1964 | 0.03647 | -0.89 |
| 6 | 0.03780 | 1.0962 | 0.8921 | 0.2041 | 0.03788 | +0.21 |
| 7 | 0.04500 | 1.2192 | 0.9790 | 0.2401 | 0.04458 | -0.90 |
| 8 | 0.04600 | 0.9796 | 0.7841 | 0.2455 | 0.04558 | -0.90 |
| 9 | 0.04900 | 0.8156 | 0.5514 | 0.2642 | 0.04403 | +0.07 |
| 10 | 0.05020 | 1.1462 | 0.8777 | 0.2685 | 0.04985 | -0.68 |
| 11 | 0.1050 | 1.6201 | 1.0590 | 0.5611 | 0.1042 | -0.76 |
| 12 | 0.1096 | 1.3370 | 0.7037 | 0.6333 | 0.1176 | +8 |
| 13 | 0.0588 | 0.8622 | 0.5200 | 0.3422 | 0.06353 | +8 |
| 14 | 0.1180 | 1.3894 | 0.7789 | 0.6105 | 0.1130 | -3.5 |
| 15 | 0.0926 | 2.1071 | 1.6490 | 0.4581 | 0.0806 | -8 |
| 16 | 0.1019 | 1.4410 | 0.9517 | 0.4893 | 0.0984 | -11 |
| 17 | 0.0912 | 1.6232 | 1.1760 | 0.4472 | 0.07929 | -12 |

into phosphoric acid in an aqueous medium may lead to the large negative error as observed in Experiments 14 to 17 (Table I).

These results suggest, therefore, that acid concentration is an important determinant in the present method of estimating phosphorus and that under the given experimental conditions it is possible to get quantitative results by maintaining the overall acidity of the system at or about 0.5 *N* sulfuric acid.

ACKNOWLEDGMENT

Grateful thanks of the authors are due to S. S. Joshi for facilities and kind interest in the work and to the National Institute of Sciences of India for award of a research fellowship to one of the authors (G.S.D.).

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RECEIVED for review April 28, 1951. Accepted November 2, 1951.

Acidimetric Determination of Vicinal Hydroxyl by Means of Sodium Periodate

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IN RECENT years the Malaprade reaction (3) has found wide application to the analysis of numerous compounds containing vicinal hydroxyl groups (5). Perhaps the most generally used analytical adaptation of this reaction is the iodometric procedure, whereby periodate equivalent to glycol in the sample is measured as the relatively small difference between the iodine liberated from periodate in the blank and that from iodate and excess periodate remaining after reaction. Because of this, considerable practice is necessary to obtain good precision. In addition, the iodometric procedure is time-consuming and requires large volumes of standard solutions.

It seemed likely that a more direct and rapid procedure could be devised by utilizing the acidimetric titration of sodium paraperiodate to disodium paraperiodate as described by Smith (5) and suggested in the earlier work of Malaprade (2). However, the inflection at pH 9.7 is not sharp and requires potentiometric titration to a fixed pH for concordant results. In a recent article, Crouthamel and coworkers (1) have demonstrated that a considerable increase in the inflection slope at pH 9.7 can be effected

by reducing the temperature of the solution to about 0° C. (Figure 1). In the present method, advantage has been taken of this temperature effect to provide a rapid and precise method involving only titration of the reaction mixture and a blank with standard alkali to an indicator end point.

ANALYTICAL METHOD

Reagents. Sodium metaperiodate (NaIO₄), analytical reagent grade, aqueous 0.1 *M* solution.

Mixed indicator, 0.2% thymolphthalein and 0.1% 1-naphtholbenzen in 90% ethyl alcohol.

Sodium hydroxide, 0.1 *N*, standardized and carbonate-free.

Procedure. Accurately weigh a sample of the glycol sufficient to give 20 me. of vicinal hydroxyl into a 250-ml. volumetric flask. Calculate the number of equivalents from the following reactions:

