The Color Reactions of Lower Oxoacids[1] of Phosphorus with Molybdate and their Application to Colorimetric Determinations of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ *and* $(-\overset{3}{P}-)_6$*-Acid[2]*

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In the last ten years a number of salts of new, lower oxoacids of phosphorus have been reported[3]. Blaser and Worms[4,5] have synthesized a series of alkali salts of lower oxoacids by the oxidation of red phosphorus. Some of them, such as $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ and $(-\overset{3}{P}-)_6$-acid, are compounds in which more than two phosphorus atoms are bound directly. The former has a chain structure, while the latter has a ring structure. More recently two compounds, $\overset{4}{P}-\overset{4}{P}-O-\overset{4}{P}-\overset{4}{P}-$ and $(-\overset{4}{P}-\overset{4}{P}-O-)_2$-acid, which are obtained by the polymerization of $\overset{4}{P}-\overset{4}{P}$-acid have been reported[6].

It is well known that the $\overset{5}{P}$-acid reacts with molybdate in a mineral acid solution to produce molybdophosphate and that the resulting yellow salt produces a blue color in the presence of a reducing agent. In this paper the authors describe the color reactions of lower oxoacids of phosphorus with molybdate in

1) In this paper the authors use the term "lower oxoacids of phosphorus" for oxoacids of phosphorus with a lower oxidation number than 5.

2) These acids do not yet have chemical names. The authors use the notations proposed by Blaser and Worms for these two acids as well as for other oxoacids of phosphorus because of their simplicity. The Arabic numerals attached to the phosphorus atoms represent the oxidation numbers of the phosphorus atoms. See B. Blaser and K.-H. Worms, *Z. anorg. u. allgem. Chem.*, **300**, 225 (1959). The structural formulas of lower oxoacids of phosphorus represented by the notations are shown in Table I.

3) Reviewed by S. Ohashi, *Kagaku-no-Ryoiki* (*Tokyo*), **15**, 926 (1961).

4) B. Blaser and K.-H. Worms, *Z. anorg. u. allgem. Chem.*, **300**, 250 (1959).

5) Ibid., **300**, 237 (1959).

6) Ibid., **311**, 313 (1961).

TABLE I. COLOR REACTIONS OF OXOACIDS OF PHOSPHORUS WITH MOLYBDATE IN THE NEUTRAL AND THE ACID SOLUTION

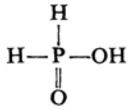
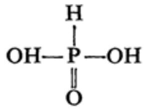
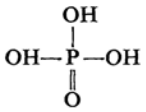
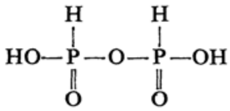
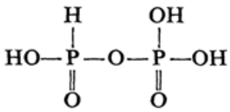
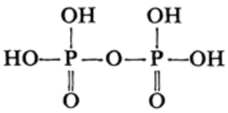
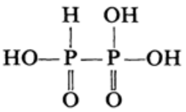
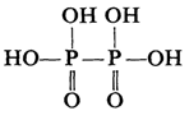
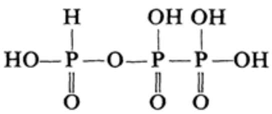
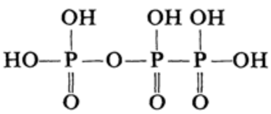
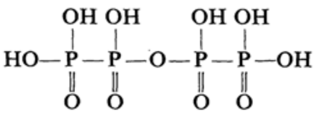
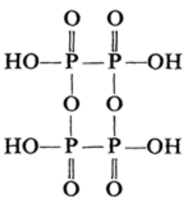
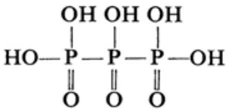
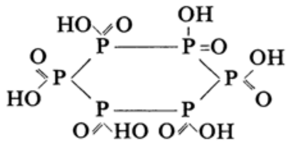
Oxoacids		In the neutral solution	In the acid solution	
Abbreviated formulas	Structural formulas		No reducing agent	In the presence of amidol
$\overset{1}{P}$-Acid		No	No	No
$\overset{3}{P}$-Acid		No	No	No
$\overset{5}{P}$-Acid		No	Yellow	Blue
$\overset{3}{P}$-O-$\overset{3}{P}$-Acid		No	No	No
$\overset{3}{P}$-O-$\overset{5}{P}$-Acid		No	Yellow	Blue
$\overset{5}{P}$-O-$\overset{5}{P}$-Acid		No	No	Blue
$\overset{2}{P}$-$\overset{4}{P}$-Acid		No	Bluish green	Blue
$\overset{4}{P}$-$\overset{4}{P}$-Acid		No	No	Blue
$\overset{3}{P}$-O-$\overset{4}{P}$-$\overset{4}{P}$-Acid		No	No	Blue
$\overset{5}{P}$-O-$\overset{4}{P}$-$\overset{4}{P}$-Acid		No	Yellow	Blue
$\overset{4}{P}$-$\overset{4}{P}$-O-$\overset{4}{P}$-$\overset{4}{P}$-Acid		No	No	Blue
(-$\overset{4}{P}$-$\overset{4}{P}$-O-)$_2$-Acid		No	No	Blue

Table I. (Continued)

Oxoacids: Abbreviated formulas	Oxoacids: Structural formulas	In the neutral solution	In the acid solution: No reducing agent	In the acid solution: In the presence of amidol
$\overset{4}{\mathrm{P}}$-$\overset{3}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-Acid		No	Bluish green	Blue
$(-\overset{3}{\mathrm{P}}-)_6$-Acid		Bluish green (unstable)	Bluish green	Blue

neutral or acid solutions. Samples include twelve lower oxoacids as well as $\overset{5}{\mathrm{P}}$– and $\overset{5}{\mathrm{P}}$–O–$\overset{4}{\mathrm{P}}$–acid.

The authors found that three of the fourteen oxoacids, $\overset{2}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$–, $\overset{4}{\mathrm{P}}$–$\overset{3}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$– and $(-\overset{3}{\mathrm{P}}-)_6$–acid, show characteristic color reactions with molybdate; i. e., the three oxoacids react with molybdate in acid solutions to produce a blue color without any reducing agent. These chemical properties give a means for the analysis of these compounds, especially for colorimetric determinations of $\overset{4}{\mathrm{P}}$–$\overset{3}{\mathrm{P}}$–$\overset{4}{\mathrm{P}}$– and $(-\overset{3}{\mathrm{P}}-)_6$–acid.

Experimental

Materials and Equipment.—An aqueous solution of guaranteed reagent-grade ammonium molybdate tetrahydrate and an amidol (1-amino-2-naphthol-4-sulfonic acid) solution for a reducing agent were prepared by Nakamura's method[7].

Sample solutions of salts of fourteen oxoacids of phosphorus were prepared; $NaPH_2O_2 \cdot H_2O$ was used for $\overset{1}{\mathrm{P}}$-acid, $Na_2PHO_3 \cdot 5H_2O$ for $\overset{3}{\mathrm{P}}$-acid, $Na_2HPO_4 \cdot 12H_2O$ for $\overset{5}{\mathrm{P}}$-acid, $Na_2P_2H_2O_5$ for $\overset{3}{\mathrm{P}}$-O-$\overset{3}{\mathrm{P}}$-acid, $Na_3P_2HO_6 \cdot 4H_2O$ for $\overset{3}{\mathrm{P}}$-O-$\overset{5}{\mathrm{P}}$-acid, $Na_4P_2O_7 \cdot 10H_2O$ for $\overset{5}{\mathrm{P}}$-O-$\overset{5}{\mathrm{P}}$-acid, $Na_3P_2HO_5 \cdot 12H_2O$ for $\overset{2}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-acid, $Na_2H_2P_2O_6 \cdot 6H_2O$ for $\overset{4}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-acid, $(CN_3H_6)_4P_3HO_8 \cdot$aq. (guanidinium salt) for $\overset{3}{\mathrm{P}}$-O-$\overset{4}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-acid, $(NH_4)_5P_3O_9 \cdot$aq. for $\overset{5}{\mathrm{P}}$-O-$\overset{4}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-acid, $Na_6P_4O_{11} \cdot$aq. for $\overset{4}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-O-$\overset{4}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-acid, $Na_4P_4O_{10} \cdot 4H_2O$ for $(-\overset{4}{\mathrm{P}}-\overset{4}{\mathrm{P}}-O-)_2$-acid, $Na_5P_3O_8 \cdot 14H_2O$ for $\overset{4}{\mathrm{P}}$-$\overset{3}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$-acid, $(K(Na)PO_2)_6 \cdot$aq.[8] for $(-\overset{3}{\mathrm{P}}-)_6$-acid. The salts of $\overset{1}{\mathrm{P}}$-, $\overset{3}{\mathrm{P}}$-, $\overset{5}{\mathrm{P}}$- and $\overset{5}{\mathrm{P}}$-O-$\overset{5}{\mathrm{P}}$-acid were commercial reagents, while the others were supplied by Blaser and Worms. It was confirmed by paper chromatography that all of these compounds were pure.

Measurements of absorbances were carried out with a Shimadzu spectrophotometer QB-50, with glass cells 1.00 cm. in width.

Paper Chromatography.—An ascending technique was employed. A basic solvent recommended by Thilo and Heinz[9] was made by mixing 150 ml. of 2-methyl-1-propanol, 190 ml. of ethanol, 225 ml. of water, and 3 ml. of concentrated aqueous ammonia. A spray reagent was made according to the method of Hanes and Isherwood[10] by mixing 5 ml. of 60% perchloric acid, 1 ml. of concentrated hydrochloric acid, and 1 g. of ammonium molybdate tetrahydrate, and diluting it to 100 ml. with distilled water. Rectangular battery jars and Toyo No. 51A filter papers were used.

Color Reactions and Measurement of Absorbances. — Three series of 10 ml. of 1% ammonium molybdate solutions were prepared. One of them was neutral (only dissolved in distilled water), and the others were 1 N acid solutions in relation to perchloric acid. One milliliter of the respective sample solutions (about 10^{-2} M) was added to each series of the molybdate solutions, and 1 ml. of an amidol solution was added to one of the series of acid solutions. They were shaken well, and the color reactions were observed for an hour at room temperature.

Five milliliters of the 10% ammonium molybdate solution and 10 ml. of a 5 N perchloric acid solution were added to a 50 ml. volumetric flask. It was diluted to 30 ml. with distilled water, and then each sample solution was added. The concentration of the sample, $\overset{4}{\mathrm{P}}$-$\overset{3}{\mathrm{P}}$-$\overset{4}{\mathrm{P}}$- or $(-\overset{3}{\mathrm{P}}-)_6$-acid, was adjusted to $10^{-3} \sim 10^{-5}$ M. The volume was brought up to the 50 ml. mark with distilled water. The mixture was shaken well and, after 30 min., the absorbances were measured in the range of 400 to 800 mμ wavelength, using a reagent solution as a reference.

Determination of Total Phosphorus.—All the phosphorus in a sample was converted into $\overset{5}{\mathrm{P}}$-acid and determined colorimetrically. Five milliliters of aqua regia were added to a 25 ml. flask containing

7) M. Nakamura, *J. Agr. Chem. Soc. Japan* (*Nippon Nogei Kagaku Kaishi*), **24**, 1 (1950).

8) This salt is mainly composed of the potassium salt of $(-\overset{3}{\mathrm{P}}-)_6$-acid, but it contains a small amount of the sodium salt of the acid.

9) E. Thilo and D. Heinz, *Z. anorg. u. allgem. Chem.*, **281**, 303 (1955).

10) C. S. Hanes and F. A. Isherwood, *Nature*, **164**, 1107 (1948).

1 ml. of the sample solution. It was evaporated gently on the water bath so as to decompose and oxidize the lower oxoacid. The residue was dissolved and then diluted to 25 ml. with distilled water. An aliquot of the solution was transferred to a 25 ml. volumetric flask, and 10 ml. of the 5 N perchloric acid solution, 5 ml. of the 10% ammonium molybdate solution, 20 ml. of distilled water, and 5 ml. of the amidol solution were added. It was brought up to the mark with distilled water, shaken well and, after 30 min., the absorbance at 780 mμ, using a reagent solution as a reference.

Results and Discussion

The color reactions of fourteen oxoacids of phosphorus with ammonium molybdate were tested. The results are summarized in Table I, $\overset{1}{P}$-, $\overset{3}{P}$- and $\overset{3}{P}$-O-$\overset{3}{P}$-acid give no color reaction in either the neutral or the acid solutions, even in the presence of the reducing agent.

It is well-known that $\overset{5}{P}$-acid does not show any color change in a neutral solution but does give a yellow color in an acid solution, and that the yellow heteropoly acid changes into a blue compound in the presence of a reducing agent such as amidol. $\overset{3}{P}$-O-$\overset{5}{P}$- and $\overset{5}{P}$-O-$\overset{4}{P}$-$\overset{4}{P}$-acid show the same behavior as $\overset{5}{P}$-acid does, because they are readily hydrolyzed in the acid solution to produce $\overset{5}{P}$-acid. $\overset{5}{P}$-O-$\overset{5}{P}$-Acid gives no detectable yellow color in the acid solution because of the slower rate of hydrolysis of the $\overset{5}{P}$-O-$\overset{5}{P}$-acid in comparison with the other compounds containing a $\overset{5}{P}$-unit.

Four compounds which contain a $\overset{4}{P}$-$\overset{4}{P}$-unit and no $\overset{5}{P}$-unit show a blue color only in the presence of amidol. This may be because of the hydrolysis of $\overset{4}{P}$-$\overset{4}{P}$-acid into $\overset{3}{P}$- and $\overset{5}{P}$-acid in the acid solution[11].

$\overset{2}{P}$-$\overset{4}{P}$-Acid produces a faint bluish green color (absorbance, about 0.04) in the acid solution, when the concentration of the $\overset{2}{P}$-$\overset{4}{P}$-acid is 10^{-3} M. In the concentrations more than 10^{-3} M, it colors semiquantitatively, but the reproducibility is not good. It was shown by paper chromatography that a main product of the reaction is $\overset{3}{P}$-acid due to the hydrolytic decomposition of the $\overset{2}{P}$-$\overset{4}{P}$-acid. The bluish-green coloration may be due to the redox reaction between molybdenum(VI) and the $\overset{2}{P}$-$\overset{4}{P}$-acid, where a part of the $\overset{2}{P}$-$\overset{4}{P}$-acid is oxidized into $\overset{4}{P}$-$\overset{4}{P}$-acid and a part of the molybdenum(VI) is reduced to molybdenum(V).

$\overset{4}{P}$-$\overset{3}{P}$-$\overset{4}{P}$-Acid shows a bluish-green color reaction only in the acid solution. (-$\overset{3}{P}$-)$_6$-Acid produces bluish-green colors in both the neutral and the acid solution. However, the bluish-green color caused by the (-$\overset{3}{P}$-)$_6$-acid in the neutral solution is very unstable; its intensity diminishes rapidly with time.

By paper chromatography distinct spots of $\overset{3}{P}$- and $\overset{4}{P}$-$\overset{4}{P}$-acid and a faint spot of $\overset{5}{P}$-acid were detected in the reaction products of the $\overset{4}{P}$-$\overset{3}{P}$-$\overset{4}{P}$-acid and molybdate in the acid solution. It appears reasonable to consider the following scheme for this reaction:

$$\overset{4}{P}\text{-}\overset{3}{P}\text{-}\overset{4}{P}\text{-Acid} \begin{cases} \xrightarrow{A} \overset{3}{P}\text{-Acid} + \overset{4}{P}\text{-}\overset{4}{P}\text{-Acid} \\ \xrightarrow{B} \overset{5}{P}\text{-Acid} + \overset{4}{P}\text{-}\overset{4}{P}\text{-Acid} \end{cases}$$

Path A is the hydrolysis of the $\overset{4}{P}$-$\overset{3}{P}$-$\overset{4}{P}$-acid, and path B is the oxidation of the acid by molybdate. The larger part of the $\overset{4}{P}$-$\overset{3}{P}$-$\overset{4}{P}$-acid is decomposed by path A and the smaller part of the acid by path B.

The reaction between (-$\overset{3}{P}$-)$_6$-acid and molybdate in the acid solution seems to be more complicated. Unfortunately, paper chromatographic identification of the reaction products was not certain. On the paper chromatogram a spot of $\overset{3}{P}$-acid was observed, but spots of other species were spread near the initial point.

The authors found that the bluish-green color produced by the reaction of $\overset{4}{P}$-$\overset{6}{P}$-$\overset{4}{P}$- or (-$\overset{3}{P}$-)$_6$-acid with molybdate in the acid solution is quite stable, at least in the range of

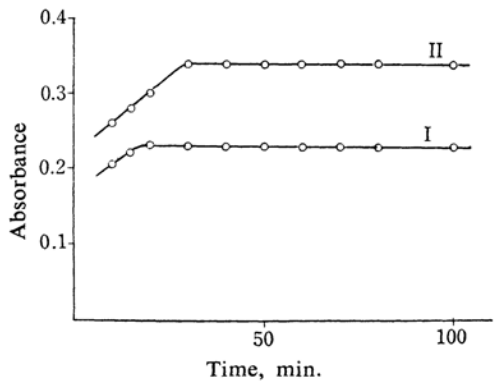


Fig. 1. Stability of bluish green color.
I $\overset{4}{P}$-$\overset{3}{P}$-$\overset{4}{P}$-acid, 4.42×10^{-4} M
II (-$\overset{3}{P}$-)$_6$-acid, 6.41×10^{-5} M

11) J. R. Van Wazer, "Phosphorus and its Compounds", Interscience Publishers, Inc., New York (1958), p. 410.

TABLE II. SIMULTANEOUS DETERMINATIONS OF $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ AND $(-\overset{3}{P}-)_6$-ACID

No.	Taken, mol./l.		Found, mol./l.			
	$\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-Acid	$(-\overset{3}{P}-)_6$-Acid	$\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-Acid	Error, %	$(-\overset{3}{P}-)_6$-Acid	Error, %
1	—	4.85×10^{-5}	—	—	4.81×10^{-5}	0.8
2	4.51×10^{-4}	—	4.52×10^{-4}	0.22	—	—
3	1.80×10^{-3}	4.85×10^{-5}	1.83×10^{-3}	1.6	4.20×10^{-5}	13
4	9.02×10^{-4}	4.85×10^{-5}	8.87×10^{-4}	1.4	4.80×10^{-5}	1.0
5	4.51×10^{-4}	4.85×10^{-5}	4.51×10^{-4}	0.00	4.83×10^{-5}	0.41
6	4.51×10^{-4}	9.70×10^{-5}	4.55×10^{-4}	0.89	9.77×10^{-5}	0.72
7	1.50×10^{-4}	1.62×10^{-4}	1.51×10^{-4}	0.66	1.60×10^{-4}	1.2
8	1.50×10^{-5}	1.62×10^{-4}	1.89×10^{-5}	25	1.60×10^{-4}	1.2

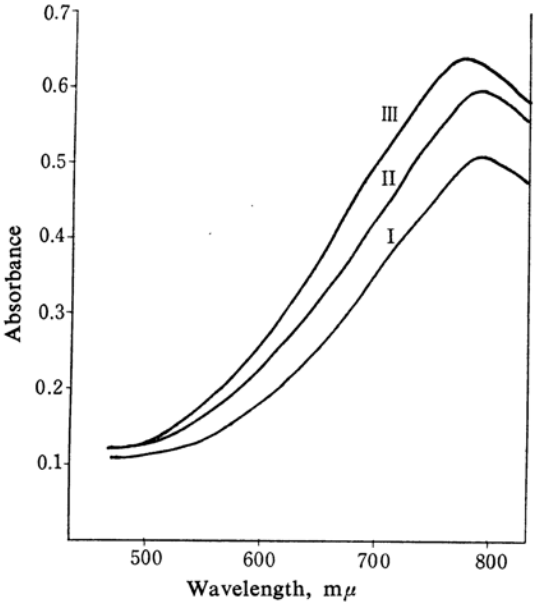


Fig. 2. Absorption curves of bluish green solutions.

I $\overset{2}{P}-\overset{4}{P}$-acid, 7.4×10^{-3} M

II $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid, 1.21×10^{-3} M

III $(-\overset{3}{P}-)_6$-acid, 1.21×10^{-4} M

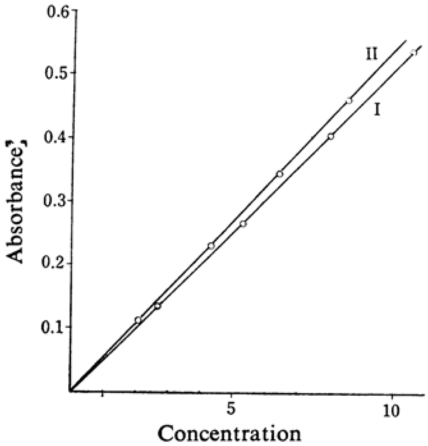


Fig. 3. Calibration curves for $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ and $(-\overset{3}{P}-)_6$-acid at 780 mμ.

10^{-4} M unit for $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}$-acid (I)

10^{-5} M unit for $(-\overset{3}{P}-)_6$-acid (II)

30~100 min., as is shown in Fig. 1. The absorption curves of the bluish-green colors due to $\overset{2}{P}-\overset{4}{P}-$, $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ and $(-\overset{3}{P}-)_6-$ acid are shown in Fig. 2. The curves are similar to one another, having their maxima at 780~785 mμ. An absorption curve of so-called heteropoly blue[12] produced by the reduction of molybdophosphate has a shape similar to the curves of Fig. 2, but it has its maximum at 830 mμ.

The molar extinction coefficients for $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ and $(-\overset{3}{P}-)_6$-acid at 780 mμ are 5.09×10^2 and 5.30×10^3 respectively. As is shown in Fig. 3, they comform well to Beer's law at 780 mμ.

Experimental results show that $\overset{1}{P}-$, $\overset{3}{P}-$, $\overset{5}{P}-$, $\overset{4}{P}-\overset{4}{P}-$ (10^{-2} M, respectively), and $\overset{2}{P}-\overset{4}{P}$-acid (less than 5×10^{-4} M) do not inhibit the quantitative color development of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ or $(-\overset{3}{P}-)_6$-acid in the acid solution. $\overset{2}{P}-\overset{4}{P}$-Acids more than 10^{-3} M increase distinctly the absorbance of the bluish-green color.

The methods described above are satisfactory when one component, either $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ or $(-\overset{3}{P}-)_6-$ acid, is present, accompanying other oxoacids of phosphorus, in a given sample, but it is not applicable if the two components are both present. When both $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ and $(-\overset{3}{P}-)_6$-acid are present in a given sample, the problem is resolved by combining this method with another procedure in which lower oxoacids are converted into $\overset{5}{P}$-acid and the total phosphorus is

12) D. F. Boltz, "Colorimetric Determination of Nonmetals", Interscience Publishers, Inc., New York (1958), p. 33.

determined by the usual heteropoly blue method. The concentrations of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ and $(-\overset{3}{P}-)_6$-acid are obtained by calculating the absorbances measured by both methods. In this case it should be noted that three and six moles of $\overset{5}{P}$-acid are produced by the oxidation of one mole of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ and $(-\overset{3}{P}-)_6$-acid respectively. The experimental results are shown in Table II. The errors for the components of the lower concentrations in Nos. 3 and 8 of Table II are so large that the application of apply this method most be avoided in cases where the differences between the concentrations of the two components are large.

Summary

The color reactions of twelve lower oxoacids of phosphorus, as well as of $\overset{5}{P}-$ and $\overset{5}{P}-O-\overset{5}{P}-$ acid with molybdate, have been described. Of these compounds, $\overset{2}{P}-\overset{4}{P}-$, $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ and $(-\overset{3}{P}-)_6$-acid react with molybdate in the acid solution to produce a bluish-green color without any reducing agent.

The bluish-green color caused by $\overset{2}{P}-\overset{4}{P}$-acid is not reproducible. Since the colors caused by $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ and $(-\overset{3}{P}-)_6$-acid are stable and since their intensities are proportional to their concentrations, one can detect and determine minute amounts of $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ or $(-\overset{3}{P}-)_6-$ acid colorimetrically in the presence of the other oxoacids of phosphorus. When both $\overset{4}{P}-\overset{3}{P}-\overset{4}{P}-$ and $(-\overset{3}{P}-)_6$-acid are present in a given sample, one can determine each component by combining the method described above with the usual heteropoly blue method for the total phosphorus.

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