A New Method for the Colorimetric Determination of Hypophosphate Ions with the Molybdenum(V)-Molybdenum(VI) Reagent

By Norimasa Yoza and Shigeru Ohashi

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This work was undertaken to establish a method for the colorimetric determination of hypophosphate ions in the presence of hypophosphite, phosphite, and orthophosphate ions. No colorimetric methods specific to hypophosphate ions have yet been reported. Hypophosphate ions can be determined indirectly by oxidizing them to orthophosphate ions and then by employing conventional method for the colorimetric determination of orthophosphate ions. However, this procedure can not be employed in the presence of hypophosphite or phosphite ions. In a previous paper[1] it has been mentioned that hypophosphoric acid does not give any colored products when it is treated with ammonium molybdate(VI) in a perchloric acid solution.

Lucena-Conde and Prat[2] have proposed a new reagent for the colorimetric determination of orthophosphate ions. This reagent is an acid solution of a mixture of molybdenym(V) and molybdenum(VI) and reacts with orthophosphoric acid to form a blue complex. In the present paper this reagent is called the molybdenum(V)-molybdenum(VI) reagent. During the course of a series of investigations of lower oxo acids of phosphorus, it was found that hypophosphoric acid reacts with this molybdenum(V)-molybdenum(VI) reagent to form a blue complex and that this reaction can be applied to the colorimetric determination of hypophosphate ions in the presence of hypophosphite, phosphite, and orthophosphate ions. The properties and composition of the blue complex due to hypophosphoric acid were compared with those of the blue complex due to orthophosphoric acid by means of spectrophotometry and the solvent extraction method.

The term "heteropoly blue" has commonly been used for the blue complex of orthophosphoric acid with molybdenum.[3] For the sake of convenience, the present authors employ the term "hypophosphoric heteropoly blue" for the blue complex produced by the reaction of hypophosphoric acid with the molybdenum molybdenum(VI) reagent and the term "orthophosphoric heteropoly blue" for the blue complex due to orthophosphoric acid.

Experimental

Apparatus.—A Shimadzu photoelectric spectrophotometer, QB-50, with 1.00 cm. cells was employed.

Reagents.—Disodium dihydrogen hypophosphate hexahydrate was supplied by Blaser and Worms. Sodium hypophosphite monohydrate, disodium phosphite pentahydrate, potassium dihydrogen orthophosphate, and the other reagents used were commercial reagents of the purest grade. The molybdenum(V)-molybdenum(VI) reagent was prepared by the procedure described by Lucena-Conde and Prat.[2] The concentrations of the constituents of this reagent were 0.08 M for molybdenum(V), 0.12 M for molybdenum(VI), 10 N for sulfuric acid, and 3 N for hydrochloric acid.

The Procedure for the Determination of Hypophosphate.—A suitable amount of an approximately neutral solution of a given sample was placed in a 25 ml. volumetric flask and diluted to about 20 ml. with water. After 2 ml. of the molybdenum(V)-molybdenum(VI) reagent had been added, the solution was shaken well. Then, the volume was adjusted to the mark with water and again the solution was well shaken. After the solution had been kept at room temperature for 30 min., the absorbance at 670 mμ was measured. A reagent blank was used as a reference solution.

The Procedure for the Determination of Molybdenum in Organic Extracts.—The molybdenum contained in "hypophosphoric and orthophosphoric heteropoly blue" extracted in an organic phase was determined by Lueck and Boltz's method.[4] An *n*-butyl alcohol phase which separated from an aqueous phase was washed three times with an equal volume of 1 N sulfuric acid to remove an excess of molybdate in the organic phase. By shaking the organic phase with a buffer solution of 0.5 M aqueous ammonia and 0.5 M ammonium chloride, the molybdate in the organic phase came into the aqueous phase. The absorbance at 230 mμ due to molybdate(VI) ions was measured.

Results and Discussion

Reactions at 95°C.—Lucena-Conde and Prat have investigated the color reaction of ortho-

1) S. Ohashi and N. Yoza, This Bulletin, **36**, 707 (1963).
2) F. Lucena-Conde and L. Prat, *Anal. Chim. Acta*, **16**, 473 (1957).
3) D. F. Boltz, "Colorimetric Determination of Nonmetals," Interscience Publishers, Inc., New York (1958), p. 33.
4) C. H. Lueck and D. F. Boltz, *Anal. Chem.*, **30**, 183 (1958).

phosphoric acid with the molybdenum(V)-molybdenum(VI) reagent and its application to the determination of orthophosphate ions. In this case it is necessary to heat a test solution at 95°C for 1 hr. in order to ensure complete color development. Under the same conditions, the reactions of hypophosphorous, phosphorous, and hypophosphoric acid with the molybdenum(V)-molybdenum(VI) reagent were examined. As is shown in Fig. 1, hypophosphorous and phosphorous acid do not give any color reactions, while hypophosphoric acid gives "hypophosphoric heteropoly blue," the absorption spectrum of which has two maximums, at 590 and at 670 mμ. "Orthophosphoric heteropoly blue" gives a spectrum, with a maximum at 820 mμ, which is identical with the spectrum of the well-known blue complex produced by the reduction of molybdophosphoric acid. Curve D in Fig. 1 was obtained for a mixture of orthophosphoric and hypophosphoric acid, the quantities of which are equal to those used in the cases of curves B and C respectively. The sum of the absorbances of curves B and C is quite identical with curve D. It is well known that hypophosphoric acid is hydrolyzed by heating it with mineral acid to form phosphorous and orthophosphoric acid.[5] However, the facts mentioned above indicate that hypophosphoric acid is not hydrolyzed by heating it in an acid solution at 95°C for 1 hr. if the molybdenum(V)-molybdenum(VI) reagent is also present.

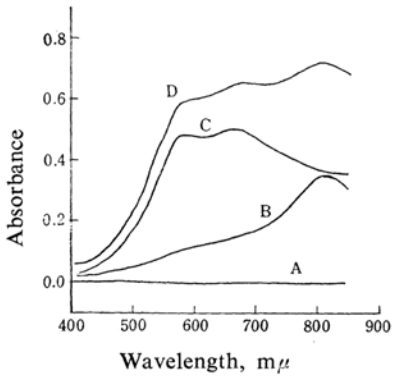

Fig. 1. Absorption spectra of reaction products between oxo acids of phosphorus and the molybdenum(V)-molybdenum(VI) reagent.
A: Hypophosphorous and phosphorous acid, each 62.0 μg. as P in 25 ml.
B: Orthophosphoric acid, 12.4 μg. as P in 25 ml.
C: Hypophosphoric acid, 25.9 μg. as P in 25 ml.
D: A mixture of orthophosphoric acid, 12.4 μg. as P, and hypophosphoric acid, 25.9 μg. as P in 25 ml.
Reaction temp.; 95°C, Reaction time; 1 hr.

Reactions at Room Temperature.—The reactions of hypophosphorous, phosphorous, hypophosphoric, and orthophosphoric acid with the molybdenum(V)-molybdenum(VI) reagent at room temperature were examined. As was to be expected, hypophosphorous and phosphorous acid do not cause any color reactions. Hypophosphoric acid forms "hypophosphoric heteropoly blue." As is shown in Fig. 2, there is no difference among the shapes of absorption spectra of "hypophosphoric heteropoly blue" produced from hypophosphoric acid of various concentrations at room temperature (curves A, C, E, and F) and at 95°C (curves B and D). Therefore, it has been concluded that the species of "hypophosphoric heteropoly blue" produced under the various conditions mentioned above are quite identical with one another. Orthophosphoric acid gives a faint blue color (curve G in Fig. 2), the intensity of which is highly dependent on the reaction temperature.[2]

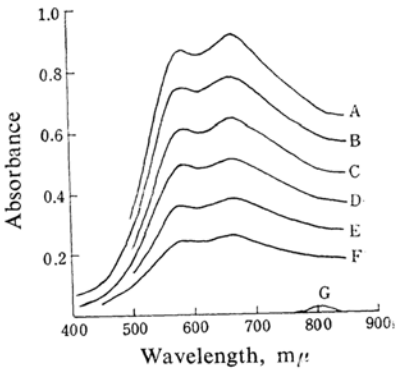

Fig. 2. Absorption spectra of "hypophosphoric heteropoly blue" produced under various conditions and an absorption spectrum of "orthophosphoric heteropoly blue" produced at room temperature.
A, C, E, and F: Hypophosphoric acid, 45.5, 32.5, 19.5, and 13.0 μg. as P in 25 ml., respectively. Reaction temp.; room temp. Reaction time; 30 min.
B, and D: Hypophosphoric acid, 39.0 and 26.0 μg. as P in 25 ml., respectively. Reaction temp.; 95°C, Reaction time; 1 hr.
G: Orthophosphoric acid, 12.4 μg. as P in 25 ml. Reaction temp.; room temp. Reaction time; 30 min.

The Effect of Reagent Concentration.—Varying quantities of the molybdenum(V)-molybdenum(VI) reagent and hypophosphoric acid, 32.4 μg. as phosphorus, were allowed to react at room temperature for 30 min. When the reagent amount was 0.5, 1.0, 2.0 or 4.0 ml., the

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

absorbance at 670 mμ was 0.551, 0.620, 0.620, or 0.621 respectively. Hence, 2 ml. of the reagent is sufficient to ensure the color development.

The Effect of Acid Concentration.—If 2 ml. of the molybdenum(V)-molybdenum(VI) reagent is added to an approximately neutral solution of a sample and diluted to 25 ml. with water, the final acidity will be 1.04 N. The reaction of hypophosphoric acid with the reagent at room temperature was studied at various final acidities, which were regulated by the addition of sulfuric acid or sodium hydroxide. When a final acidity is lower than 0.3 N, a reagent blank is blue. On the other hand, the higher a final acidity is, the lower the reaction rate becomes. For instance, when a final acidity is 2.0 N, it took about 2 hr. for the complete color development. When a final acidity lies between 0.6 and 1.4 N, the complete color development is attained within 30 min. The resulting blue color is stable for at least 3 hr.

A recommended procedure for the determination of hypophosphate ions is described in the experimental section. A calibration curve obtained by this procedure follows Beer's law, as Fig. 3 shows. A molar extinction coefficient of "hypophosphoric heteropoly blue" at 670 mμ is 3.04×10^4 on the assumption that a molecule of the blue complex contains a molecule of hypophosphoric acid.

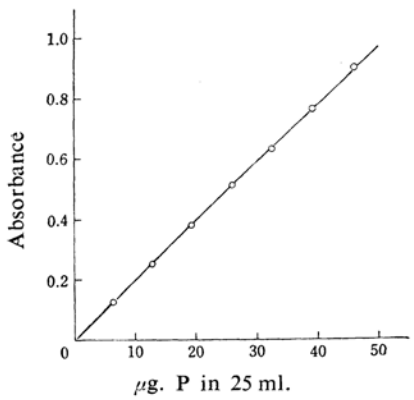

Fig. 3. Calibration curve for hypophosphate ions, at 670 mμ.

Interference.—The effect of several ions on the determination of hypophosphate ions is indicated in Table I. The presence of a large excess of hypophosphite, phosphite, orthoarsenate, and metasilicate ions caused no interference. The presence of orthophosphate ions likewise caused no serious interference if its quantity was less than or comparable with the quantity of hypophosphate ions. Wolframate ions caused a serious interference because they form a blue product by reaction with the reagent.

TABLE I. THE EFFECT OF SEVERAL IONS ON THE DETERMINATION OF HYPOPHOSPHATE IONS

Hypophosphate ions, 30.2 μg. as P in 25 ml.

Coexistent substance			Absorbance	Error
Formula	Amount μg.			%
None	—		0.5884	—
$NaH_2PO_2\cdot H_2O$	350	as P	0.5884	0.00
$Na_2HPO_3\cdot 5H_2O$	335	as P	0.5901	+0.29
KH_2PO_4	6.22	as P	0.5884	0.00
KH_2PO_4	15.6	as P	0.5884	0.00
KH_2PO_4	31.1	as P	0.5918	+0.57
$Na_2WO_4\cdot 2H_2O$	500	as W	0.8153	+38.6
H_3AsO_4	500	as As	0.5867	−0.12
Na_2SiO_3	500	as Si	0.5850	−0.60

The Solvent Extraction of "Hypophosphoric and Orthophosphoric Heteropoly Blue."—"Hypophosphoric and orthophosphoric heteropoly blue can be extracted into *n*-butyl alcohol, isobutyl alcohol, tributyl phosphate, or cyclohexanone. Chloroform, carbon tetrachloride, hexane, benzene, xylene, cyclohexane, *n*-butyl acetate, and ethyl ether are not good extractants for both heteropoly blues. "Orthophosphoric heteropoly blue" produced by the reduction of molybdophosphoric acid shows a similar behavior in the solvent extraction.[6] When aqueous solutions of "hypophosphoric and orthophosphoric heteropoly blue" produced by reaction with the molybdenum(V)-molybdenum(VI) reagent are shaken with an equal volume of *n*-butyl alcohol, the blue complexes are completely extracted into the organic phase. When *n*- or iso-butyl alcohol diluted with benzene is used as an extractant, the difference between the extractability of the two heteropoly blues can be observed as is illustrated in Fig. 4. "Hypophosphoric heteropoly blue" is less extractable than "orthophosphoric heteropoly blue." Absorption spectra of both heteropoly blues in *n*-butyl alcohol are shown in Fig. 5.

Lueck and Boltz[4] have described a method for the determination of the molybdenum(VI) content in an organic extract of molybdophosphoric acid. This method was applied in the present investigation to the determination of molybdenum combined with hypophosphoric acid and orthophosphoric acid in both heteropoly blues. When organic extracts of both heteropoly blues were shaken with a buffer solution of ammonia and ammonium chloride, the blue colors disappeared. It was found that no molybdenum remains in the organic phase after this

6) M. Miyamoto, *Japan Analyst* (*Bunseki Kagaku*), **12**, 32 (1963).

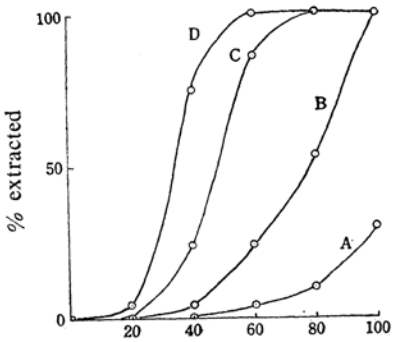

Fig. 4. Extractability of "hypophosphoric and orthophosphoric heteropoly blue."
"Hypophosphoric heteropoly blue"
A; Isobutyl alcohol-benzene
B; *n*-Butyl alcohol-benzene
"Orthophosphoric heteropoly blue"
C; Iso butyl alcohol-benzene
D; *n*-Butyl alcohol-benzene

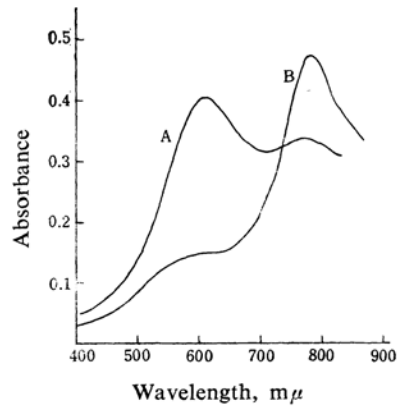

Fig. 5. Absorption spectra of "hypophosphoric and orthophosphoric heteropoly blue" in *n*-butlyl alcohol.
A; "Hypophosphoric heteropoly blue," 24.8 μg. as P in 25 ml.
B; "Orthophosphoric heteropoly blue," 18.7 μg. as P in 25 ml.

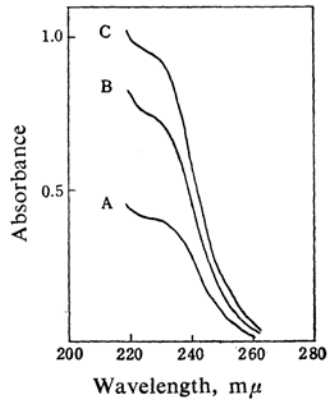

Fig. 6. Absorption spectra of molybdate(VI) ions.
A; Molybdate(VI) ions back extracted from an *n*-butyl alcohol phase containing "hypophosphoric heteropoly blue", 13.0 μg. as P in 25 ml.
B; Ammonium molybdate, 13.4 ppm of molybdenum(VI), as a standard solution
C; Molybdate(VI) ions back-extracted from an *n*-butyl alcohol phase containing "orthophosphoric heteropoly blue", 12.4 μg. as P in 25 ml.

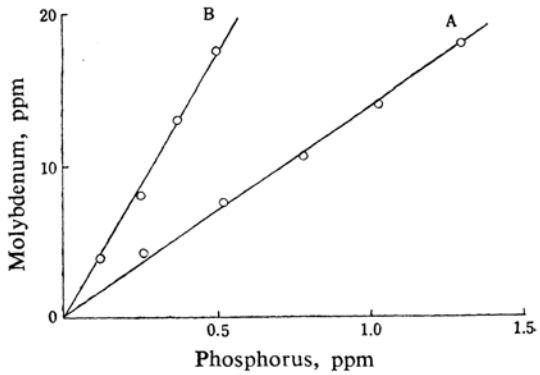

Fig. 7. Relations between contents of molybdenum and phosphorus in "hypophosphoric and orthophosphoric heteropoly blue."
A; "Hypophosphoric heteropoly blue"
B; "Orthophosphoric heteropoly blue"

treatment and that molybdenum(V) is oxidized to molybdenum(VI) by shaking it with the buffer solution in air. The resulting molybdenum(VI) in the aqueous solution can be determined by measuring the absorbance at 230 mμ (Fig. 6). The relations between the contents of molybdenum and phosphorus in both heteropoly blues are shown in Fig. 7. From these data, the mole ratios of molybdenum (a sum of molybdenum(V) and molybdenum(VI)) to hypophosphoric and orthophosphoric acid in both heteropoly blues were calculated to be approximately 9 and 12 respectively.

Summary

It was found that hypophosphoric acid reacts with the molybdenum(V)-molybdenum(VI) reagent at room temperature as well as at 95°C to form a blue complex, the absorption spectrum of which has maximums at 590 and 670 mμ. Although orthophosphoric acid reacts with this reagent at 95°C to form a blue complex, it gives only a faint blue color at room temperature. Hypophosphorous and phosphorous acid do not give any colored products when treated with this reagent. Therefore, the

reaction of hypophosphoric acid with this reagent at room temperature can be applied to the colorimetric determination of hypophosphate ions in the presence of hypophosphite, phosphite, and orthophosphate ions. The differences in the absorption spectra and solvent extraction behavior between the two blue complexes due to hypophosphoric and orthophosphoric acid (" hypophosphoric heteropoly blue " and " orthophosphoric heteropoly blue ") have been described. The mole ratios of molybdenum to hypophosphoric and orthophosphoric acid in the blue complexes were found to be approximately 9 and 12 respectively.

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Department of Chemistry
Faculty of Science
Kyushu University
Hakozaki, Fukuoka