Fundamental Conditions and Reaction Mechanisms in Formation of Phosphomolybdenum Blue

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Fundamental studies of the color development of phosphomolybdenum blue are essential for establishing the method for determining micro amounts of phosphate. Strickland[1] has extensively studied the condition of the formation and reduction of silicomolybdate, which is similar to phosphomolybdate. Only a few studies, however, have been made of the reduction mechanism of phosphomolybdate. Bolz et al.[2] tried a polarographic study and found two reduction stages in the reduction process of phosphomolybdate, but the half-wave potential for each stage was not clearly given.

The studies described in this paper were undertaken in order to establish the optimum conditions for the determination of phosphate and to explain the mechanism of phosphomolybdenum blue formation.

The effect of acidity and the concentration of molybdate, which affect the formation of phosphomolybdate remarkably, have been extensively studied; the results obtained will be graphically shown. Many photometric methods proposed for the determination of phosphate by the formation of phosphomolybdate are explained by the graph obtained.

The reduction products obtained in the process of phosphomolybdenum blue development have been studied photometrically by measurements of its absorption spectra. Useful information concerning the chemical properties of the development of phosphomolybdenum blue has thus been obtained.

1) J. D. H. Strickland, *J. Am. Chem. Soc.*, **74**, 862, 868 (1952).
2) D. F. Boltz, T. De Vries and M. G. Mellon, *Anal. Chem.*, **21**, 563 (1949).

Conditions for the Formation of Phosphomolybdenum Blue

Acidity and Molybdate Concentration. — The acidity and concentration of molybdate, which remarkably affect the formation of phosphomolybdenum blue, were examined in detail. To a solution containing 50 μg. of phosphate, different amounts of 10 N sulfuric acid and a 2.5% ammonium molybdate solution were added. After the solution had been diluted to about 40 ml., 0.25 ml. of a 2% stannous chloride solution in hydrochloric acid (1+9) was added, and then the solution adjusted to 50 ml. with water. The absorbance of the solution was measured at 10 min. after the addition of the reagents. The measurement was made by use of a Kotaki, AKA-type photoelectric photometer, with a 10-mm. cell and a 660 mμ filter. The temperature of the solution was kept at 25°C throughout the experiment. The results are given in Fig. 1.

The effect of the acidity, with reference to curves 4 and 4′ in Fig. 1, for example, the final concentration of 0.15% ammonium molybdate, may be summarized as follows:

(1) When the acidity is lower than 0.5 N, the excess molybdate reagent is also reduced to form a blue color.

(2) With acidity from 0.5 to 0.8 N, a nearly identical intensity of the blue color is always obtained.

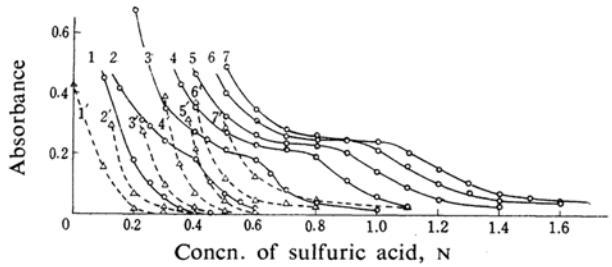

Fig. 1. Effect of concentration of sulfuric acid and ammonium molybdate
PO_4 (1)—(7), 1.0 p.p.m.; (1')—(7'), 0
Ammonium molybdate
1,1'; 0.025% 2,2'; 0.05% 3,3'; 0.10% 4,4'; 0.15%
5,5'; 0.20% 6,6'; 0.25% 7,7'; 0.30%

(3) With acidity more than 0.8, but lower than 1.1 N, the intensity of the blue color is affected by a slight change in acidity.

(4) When the acidity is higher than 1.1 N, no blue color is develops.

Therefore, the suitable acidity for the determination is considered to be in a range of 0.5 to 0.8 N, with 0.15% of ammonium molybdate.

With another concentration of ammonium molybdate, the effect of acidity upon color formation on the curves in Fig. 1 was also examined. Figure 2 indicates the relationship, showing domains, divided by curves, which the author calls "phosphomolybdenum blue color fields." The conditions shown by field 1 in Fig. 2 have been further investigated in order to establish the optimum conditions, and 0.65 N sulfuric acid and 0.15% ammonium molybdate were selected. A mixed solution of sulfuric acid (6.5 N)-ammonium molybdate (1.5%) was then prepared for practical use.[3]

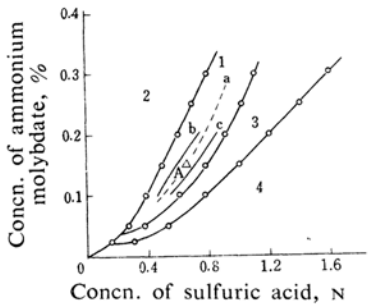

Fig. 2. Phosphomolybdenum blue color field.
1 : Suitable condition for determination
2 : Not applicable condition for determination, blue color formed in the absence of phosphate
3 : Unsuitable condition, color intensity affected by slight change in acidity
4 : Not usable, no color formed
Point A : Optimum condition proposed by author
Line a : Good condition
Line b : Absorbance 0.235 with 1 p.p.m. PO_4 in this study
Line c : Absorbance 0.215 with 1 p.p.m. PO_4 in this study

An Interpretation of the Phosphomolybdenum Blue Color Field.—When blue color is developed under the conditions given by fields 1 and 2 in Fig. 2, approximately the same absorbance values, after correction for blank values, are obtained. This fact indicates that under these conditions all the phosphate is converted to phosphomolybdate and all of the latter is reduced to phosphomolybdenum blue. Therefore, phosphomolybdenum blue color fields may be explained as follows.

Fields 1 and 2: All the phosphate is converted to phosphomolybdate and then reduced to phosphomolybdenum blue. Under the conditions given by field 2, however, molybdate added in excess is also reduced to a blue color.

Field 3: A part of the phosphate is converted to phosphomolybdate, which is reduced to phosphomolybdenum blue.

Field 4: No phosphomolybdate is formed.

These fields are obtained in 10 min. of reaction time at 25°C. The acceleration of the reaction at an elevated temperature would probably result in the complete formation of phosphomolybdate and then phosphomolybdenum blue, even in field 3.

An Examination of Methods for the Photometric Determination of Phosphate by the Formation of Phosphomolybdate.—The photometric determination of phosphate by the formation of phosphomolybdate is carried out by the following different methods:

1) Phosphate in an aqueous solution is converted to phosphomolybdate.

2) The color of phosphomolybdenum blue is developed in an aqueous solution.

3) Phosphomolybdate is extracted by some organic solvents and, after the extraction, the color of phosphomolybdenum blue is developed.

4) Phosphomolybdenum blue is extracted by

3) F. Kawamura and H. Namiki, *Japan Analyst (Bunseki Kagaku)*, **7**, 238 (1958).

some organic solvents.

The acidity and ammonium molybdate concentrations proposed by many authors[4-21] for these procedures are plotted in a phosphomolybdenum blue color field in Fig. 4. Other molybdate is calculated to an equivalent amount of ammonium molybdate. Many conditions have been proposed, as may be seen in Fig. 3; however, a reasonable interrelation between the concentrations of acid and ammonium molybdate in the above methods can easily be obtained from the interpretation of the phosphomolybdenum blue color field.

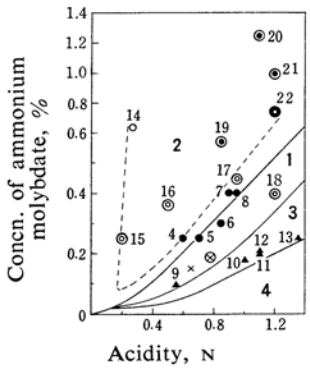

Fig. 3. Color developing conditions for photometric method by formation of phosphomolybdate and phosphomolybdenum blue.

- ● Phosphomolybdenum blue (room temperature)
- ▲ Phosphomolybdenum blue (heating)
- ○ Phosphomolybdate
- ◎ Extraction of phosphomolybdate
- ◉ Reduction of extracted phosphomolybdate
- ⭘ Dissolution of extracted phosphomolybdate
- × Phosphomolybdenum blue by author
- ⊗ Extraction of phosphomolybdenum blue by author

Area in dotted line shows good condition reported by Ishibashi and Tabushi for extraction of phosphomolybdate. Number in Figure shows the number of literatures.

The Phosphomolybdate Method, The Phosphomolybdate Extraction Method and The Method of Reducing Extracted Phosphomolybdate to a Blue Color.—All these methods depend on the complete conversion of phosphate to phosphomolybdate. The condition given by fields 1 and 2 in Fig. 3 are, therefore, suitable. Under the conditions given by field 1, however, standing for 10 min. or warming is required in order to complete the reaction. No. 18 in Fig. 3 corresponds to field 1. In this case extraction is made after accelerating the reaction by warming the solution. The conditions reported by many authors correspond to field 2, however. Extensive work by Ishibashi and Tabushi[16] on the extraction of phosphomolybdate also show a good agreement with this explanation.

The Phosphomolybdenum Blue Method and Its Extraction Method.—As has been discussed field 1 is suitable for these methods when the reactions take place at room temperature. If the color is developed by heating, the conditions shown by field 3 are also applicable. The conditions plotted in Fig. 3 show good agreement with this explanation.

The Reducing Agent.—In old works, various reducing agents were proposed in an attempt to effect the selective reduction of phosphomolybdate only. However, the control of acidity and of the concentration of molybdate is more important for this purpose. When these concentrations meet field 1 conditions, an excess of the molybdate reagent does not form a blue complex. (The details will be given in the next section.) The use of weak reducing agent sometimes limits the reduction of the molybdate reagent, even under the conditions in field 2.[4,5,8] Nevertheless, in this case only a part of the phosphomolybdate formed is often reduced to a blue color. The intensity of the resultant color, therefore, is liable to be affected by time and by temperature.

There is a procedure using weak reducing agents for determining more than 10 p.p.m. of phosphate by the phosphomolybdenum blue method.[8,23] With this procedure, only a part of the phosphate may be converted to phosphomolybdenum blue; therefore, the results are considered to be affected by the time, the temperature and other factors. The stannous chloride solution used as the reducing agent

4) P. S. Chen, Jr., T. Y. Toribara and H. Warner, *Anal. Chem.*, **28**, 1756 (1956).
5) K. D. Fleischer, B. C. Southworth, T. H. Hodecker and M. M. Tuckerman, ibid., **30**, 152 (1958).
6) S. R. Dickman and R. H. Bray, *Ind. Eng. Chem., Anal. Ed.*, **12**, 665 (1940).
7) P. Goodloe, ibid., **9**, 527 (1937).
8) M. S. Scherman, ibid., **14**, 182 (1942).
9) F. F. Hoffman, L. C. Jones, Jr., O. B. Robbins, Jr., and F. R. Alsberg, ibid., **30**, 1334 (1958).
10) D. F. Boltz and M. G. Mellon, *Anal. Chem.*, **19**, 873 (1947).
11) O. R. Gates, *Ind. Eng. Chem., Anal. Ed.*, **26**, 730 (1954).
12) W. J. Boyer, *Proc. Am. Soc. Testing Materials*, **44**, 774 (1944).
13) H. L. Katz and K. L. Proctor, *Ind. Eng. Chem., Anal. Ed.*, **19**, 612 (1942).
14) D. F. Boltz and M. G. Mellon, *Anal. Chem.*, **20**, 749 (1948).
15) M. A. De Sesa and L. B. Rogers, ibid., **26**, 1381 (1954); **26**, 1278 (1954).
16) M. Ishibashi and M. Tabushi, *Japan Analyst (Bunseki Kagaku)*, **8**, 588 (1959).
17) C. Wadelin and M. G. Mellon, *Anal. Chem.*, **25**, 1668 (1958).
18) M. Ura, *Japan Analyst (Bunseki Kagaku)*, **7**, 420 (1958).
19) S. Yokosuka, ibid., **5**, 395 (1956).
20) W. A. Pons, Jr., and J. D. Guthrie, *Ind. Eng. Chem., Anal. Ed.*, **18**, 184 (1946).
21) C. H. Lueck and D. F. Boltz, *Anal. Chem.*, **28**, 1168 (1956).
22) C. H. Lueck and D. F. Boltz, ibid., **30**, 183 (1958).
23) L. S. Stoloff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 636 (1942).

for the procedure recommended by the author is superior in that even considerable deviations from the specified amount do not affect the color intensity and in that it can be used for a long time.

The Reaction Mechanism for the Development of Phosphomolybdenum Blue

The Valency of Molybdenum in a Phosphomolybdenum Blue Complex.—Phosphate solutions containing 1, 2, 3, 4 and 6 p. p. m. (0.105×10^{-4}, 0.211×10^{-4}, 0.316×10^{-4}, 0.421×10^{-4} and 0.632×10^{-4} M respectively) were reduced to molybdenum blue by the use of various amounts of a diluted stannous chloride solution, in the optimum concentration of sulfuric acid and ammonium molybdate as described in a previous section. The absorbance of a colored solution at 700 mμ was measured with a Shimadzu photoelectric spectrophotometer, type QB-50, using a 10-mm. cell and water as a reference. The results obtained are shown in Fig. 4. Each of the five curves shows good linearity and has a sharp deflection point, indicating the quantitative reaction of phosphomolybdate with stannous chloride under such conditions. The equivalent mole of stannous

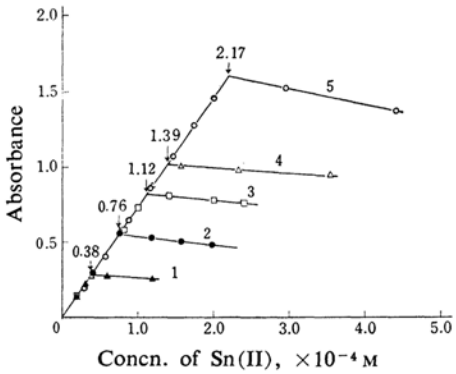

Fig. 4. Intensity of phosphomolybdenum blue vs. Sn(II) concentration.

1: PO_4 1.0 p.p.m. (0.105×10^{-4} M)
2: PO_4 2.0 p.p.m. (0.211×10^{-4} M)
3: PO_4 3.0 p.p.m. (0.316×10^{-4} M)
4: PO_4 4.0 p.p.m. (0.421×10^{-4} M)
5: PO_4 6.0 p.p.m. (0.632×10^{-4} M)

chloride can be found by each deflection point to be 3.62, 3.60, 3.18, 3.30 and 3.43 mol. for each curve, to 1 mol. of phosphate. It has already been reported that, under these conditions, the total amount of phosphate in the solution is completely converted to phosphomolybdate. It is also generally known[24,25] that one molecule of phosphomolybdate contains one atom of phosphorus and 12 atoms of molybdenum. Therefore, according to the reaction ratio described above, it is presumed that in this first step of the reduction seven of the molybdenum atoms in phosphomolybdate are reduced from molybdenum(VI) to molybdenum(V).

The Reduction by Stannous Chloride in Excess Amounts.—A phosphate solution of 2 p. p. m. was reduced to blue with varying amounts of stannous chloride solution in excess. The absorbance of the colored solutions at 700 mμ is given in Fig. 5, while the absorption spectra of these solutions are shown in Figs. 6 and 7. The curve in Fig. 5 shows a horizontal line between the concentration of stannous chloride from 0.74×10^{-4} M (equivalent mole to phosphate) to 3×10^{-4} M. It seems that the same blue product of the first stage of the reduction of phosphomolybdate is always formed in this range of stannous chloride concentration. The blue product obtained within this concentration

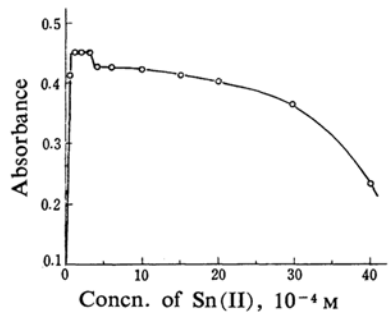

Fig. 5. Intensity of phosphomolybdenum blue v.s. Sn(II) concentration (by filter type photometer).
PO_4: 2.0 p.p.m. (0.211×10^{-4} M)

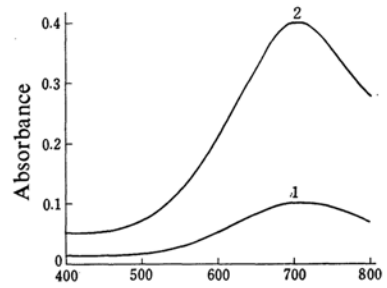

Fig. 6. Change in absorption spectra of phosphomolybdenum blue with different concentration of Sn(II).
PO_4: 2.0 p. p. m. (0.211×10^{-4} M)
Concn. of Sn(II)
1: 0.15×10^{-4} M, 2: 0.55×10^{-4} M

24) H. Remy, "Lehrbuch der Anorganischen Chemie," II, John Wiley and Sons Inc., New York (1952), p. 183.

25) H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," George Routledge and Sons, London (1940), p. 181.

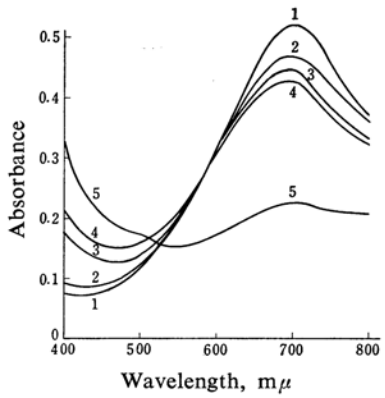

Fig. 7. Change in absorption spectra of phosphomolybdenum blue with different concentration of Sn(II).
PO_4: 2.0 p.p.m. (0.211×10^{-4} M)
Concn. of Sn(II)
1: 1.5×10^{-4} M 2: 5.0×10^{-4} M
3: 20×10^{-4} M 4: 30×10^{-4} M
5: 40×10^{-4} M

range of stannous chloride is hereafter called "normal phosphomolybdenum blue" in this paper. The absorption spectra of the normal phosphomolybdenum blue are given by curves 1 and 2 in Fig. 6 and also by curve 1 in Fig. 7, the characteristics of all of which show good agreement.

To return to Fig. 5, the absorbance falls slightly and sharply between the concentration of stannous chloride of 3×10^{-4} M and that of 4×10^{-4} M. This seems to indicate the occurrence of a second-step reduction. More exact research is required into this interesting phenomenon; the present author has not studied it further since the decrease in absorbance is slight and does not seriously affect his studies in analytical chemistry. The absorption spectra of the blue solution obtained with 5×10^{-4} M of stannous chloride closely resemble that obtained for normal phosphomolybdenum blue, shown by curve 2 in Fig. 7. Therefore, it is also thought to be normal phosphomolybdenum blue in this paper.

The absorbance at 700 mμ decreases gradually with very high concentrations of stannous chloride. This phenomenon is considered to indicate that the third step of the reduction takes place slowly in these solutions and that a part of normal phosphomolybdenum blue is reduced further to a lower valency. Curves 3—5 in Fig. 7 indicate the absorption spectra of these solutions; these spectra differ considerably from the curve for normal phosphomolybdenum blue. Such solutions usually appear green.

The absorbance decrease at 700 mμ is regarded as due to the third step of the reduction; however, the absorbance increase at 400 mμ is not considered due to the same reason. The quantity of phosphomolybdate at the third step of the reduction is considered too small to cause the large change in the absorbanc at 400 mμ shown by curves 3—5 in Fig. 7. The absorbance increase at 400 mμ is regarded by the author as being caused by a reduction of the molybdate reagent added in excess. This consideration is confirmed by the experiments described below.

Examination by the Extraction of Phosphomolybdenum Blue. — It has been generally known[26] that in an acid solution molybdenum is reduced from molybdenum(VI) to molybdenum(V) at the first step of the reduction and from molybdenum(V) to molybdenum(III) at the second step. Some observers think that only a few of the molybdenum atoms constituting the molybdate ion are reduced to molybdenum(V) at the first step of the reduction. The two solutions containing molybdenum(V) and molybdenum(III) are said to show blue and reddish brown, respectively. As was seen in the previous section, the reduction of the molybdate reagent with a blue color development has been observed at low acidity or at a high molybdate concentration. This phenomenon can be prevented when the concentration of reagents is adjusted to proper values. In the presence of strong reducing agents or a large amount of stannous chloride, the molybdate solution is reduced directly to a final reddish-brown solution, showing no intermediate blue stage. Figure 8 gives the absorption spectra of two solutions, containing 0 and 2 p. p. m. phosphate respectively, reduced by shaking them with a 2% zinc-mercury amalgam for a proper length of time. In this case a part of the molybdate reagent has been reduced. The same operation is applicable to the volumetric determination of molybdenum, and molybdenum is known to be reduced to

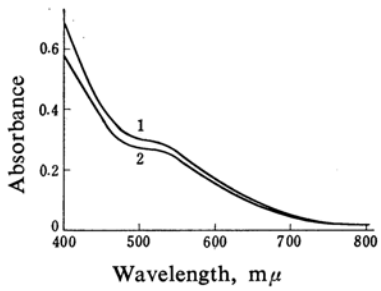

Fig. 8. Absorption spectra for low valency molybdenum reduced with Zn-Hg amalgam.
1: PO_4 2.0 p.p.m. 2: PO_4 0

26) W. M. Latimer "The Oxidation States of the Elements and their Potentials in Aqueous Solution," 2nd Ed., Prentice Hall, Englewood Cliffs, N. J. (1959), p. 251.

TABLE I. CONCENTRATION OF Sn(II) CONSUMED FOR FORMATION OF LOW VALENCY MOLYBDENUM

Concn. of phosphate $\times 10^{-4}$ M	Concn. of Sn(II), $\times 10^{-4}$ M			
	Initial	After color developing	Consumed for reduction	Consumed for reduction to low valency Mo
0[a]	20	20	0	0
0	10	7.3	2.7	2.7
0	40	24.3	15.7	15.7
0.211[b]	10	5.2	4.8	4.1
0.211	20	8.4	11.6	10.9
0.211	30	14.8	15.2	14.5
0.211	40	16.5	23.5	22.8

a) Sulfuric acid only was added, no ammonium molybdate used.
b) Sn(II) equivalent to 0.211×10^{-4}M of phosphate is 0.74×10^{-4} M.

molybdenum(III) in this process. The author has studied these reduction process by the use of various amounts of stannous chloride in excess. The blue color complex obtained was extracted by shaking it with an equal volume of *n*-butyl alcohol for 5 to 10 sec.* The absorption spectra of the solvent and aqueous phase, and also of the original solution are given in Figs. 9 and 10.

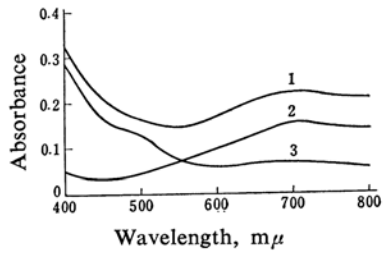

Fig. 9. Absorption spectra of colored complexes in various phases.
10 ml. of colored solution was extracted with 10 ml. of *n*-butyl alcohol
PO_4: 2.0 p.p.m. (0.211×10^{-4} M)
Sn(II) : 40×10^{-4} M
1 : Original solution
2 : *n*-Butyl alcohol phase
3 : Aqueous phase

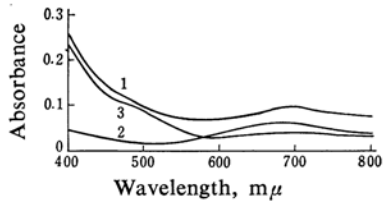

Fig. 10. Absorption spectra of colored complexes in various phases.
10 ml. of colored solution was extracted with 10 ml. of *n*-butyl alcohol
PO_4: 0, Sn(II) : 40×10^{-4} M
1 : Original solution
2 : *n*-Butyl alcohol phase
3 : Aqueous phase

* Prolonged shaking resulted in a blank color development, and also in an alteration of the absorption spectra.

The accurate comparison of the absorption curves in these figures was difficult because of the slight volume change which took place in the course of the extraction, the incomplete extraction, and the effect of the solvent on the absorption spectra. Nevertheless, curve 3 in both Figs. 9 and 10 is similiar to that in Fig. 8 at a shorter wavelength range. It is also notable that curve 2 in Fig. 9 is similar to that for normal phosphomolybdenum blue. Therefore, it has been concluded that the complex remaining in the aqueous phase consists of molybdenum reduced to a lower valency, probably molybdenum(III), and that the complex extracted with *n*-butyl alcohol is phosphomolybdenum blue. The appearance of a green color in a solution reduced with a large amount of stannous chloride is considered to be due to the co-existence of these two complexes.

Examination by the Titration of the Stannous Chloride Remaining Unreacted.—The amounts of stannous chloride remaining unreacted in the aqueous phase after the solvent extraction described above can be determined iodometrically with starch as an indicator, and this titration can be carried out without being affected by molybdenum of a lower valency. The data of determination are given in Table I. The top line in Table I is a blank test conducted without the addition of molybdate reagent. It is confirmed that stannous chloride is not lost during this operation, either with air oxidation or with dissolution into the solvent.

The amounts of stannous chloride consumed by reduction to low valency molybdenum are calculated from the amounts of stannous chloride initially added and equivalent to the existing phosphate. As Table I shows, considerable amounts of stannous chloride, approximately half of the amounts originally

added, are consumed in the formation of low valency molybdenum. In other words, a very large amount of low valency molybdenum is formed. In spite of the fact described above, the fading of the blue color is not as prominent as in Fig. 7. This indicates that the reduction of molybdate reagent to form a low valency of molybdenum takes place more easily than the reduction of normal phosphomolybdenum blue to color fading. Earlier in this paper, it was described that reduction with stannous chloride in an amount less than a mole equivalent to phosphate results in the reduction of phosphomolybdate only.

In the presence of excess stannous chloride, therefore, reduction takes place in the following order:

(1) Phosphomolybdate → Normal phosphomolybdenum blue
(2) Molybdate reagent → Low valency of molybdenum
(3) Normal phosphomolybdenum blue→Low valency of phosphomolybdenum blue

The reactions do not always proceed in this sequence, however. With an excess of stannous chloride, reaction 3 proceeds partially via reactions 1 and 2, resulting in a decrease in the intensity of blue. However, with a slight excess of stannous chloride, reaction 3 is negligible because excess stannous chloride is quickly diminished by reaction 2.

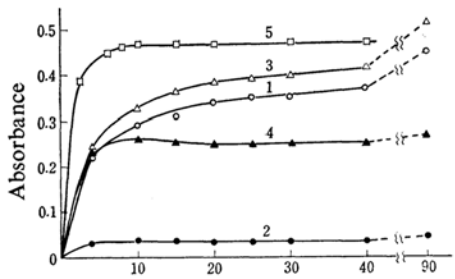

Fig. 11. Reduction rate for phosphomolybdate and molybdate with excess Sn(II).
1 PO_4 0, Sn(II) 40×10^{-4} M, 400 mμ
2 PO_4 0, Sn(II) 40×10^{-4} M, 700 mμ
3 PO_4 2.0 p.p.m., Sn(II) 40×10^{-4} M, 400 mμ
4 PO_4 2.0 p.p.m., Sn(II) 40×10^{-4} M, 700 mμ
5 PO_4 2.0 p.p.m., Sn(II) 5×10^{-4} M, 700 mμ

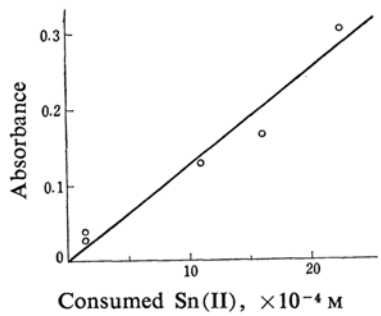

Fig. 12. Absorbance of low valency molybdenum compound v.s. Sn(II) consumed (Measured 10 min. after addition of reagents).

This view will be explained further by the following experiments. Figure 11 shows changes in the absorbance with time at 400 mμ and 700 mμ measured on solutions, containing 0 and 2 p.p.m. of phosphate; these solutions were treated in the same way as in the experiments for Figs. 9 and 10. Figure 12 shows the relation between the absorbance at 400 mμ of low valency molybdenum and the amounts of stannous chloride consumed for its formation. The relation was obtained from data in Table I and Figs. 6, 7, 9 and 10. The consumption of stannous chloride with time shown in Fig. 11 is obtained from the absorbance at 400 mμ and Fig. 12. The amounts of unreacted stannous chloride can be obtained by subtracting the amount consumed from the amounts added initially. For example, by means of curves 1 and 3 in Fig. 11* the amounts of unreacted stannous chloride are found to be 20×10^{-4}, 17×10^{-4}, 16×10^{-4} and 10×10^{-4} M after 5, 7.5, 15 and 30 min. respectively. Stannous chloride in an amount less than $10\sim15\times10^{-4}$ M does not cause the remarkable fading of phosphomolybdenum blue shown in Fig. 5. Thus, the reaction which takes place in Fig. 11 is explained as follows: Through the range of reaction, in the first 10 min. after the addition of the reagent, reactions 1, 2 and 3 progress simultaneously. All the phosphomolybdate is reduced in this period, and then some part of it is further reduced to that of a lower valency with less color intensity than normal phosphomolybdenum blue. After 10 min., the amount of stannous chloride decreases to approximately 16×10^{-4} M, where reaction 3 ceases and the blue color becomes stable.

Summary

The effects of acidity and molybdate concentration on the development of phosphomolybdenum blue have been studied in detail and the relationships among these three factors shown by a graph, called a "phosphomolybdenum blue color field" by the author. A further investigation was undertaken in order to explain the mechanisms of color development and the fundamental properties of reaction products under the optimum conditions established by the author for the determination

* The difference between curves 1 and 3 is due to the absorbance of phosphomolybdenum blue at 400 mμ.

of phosphate. The acidity and molybdate concentration in the graph was divided into 4 fields, the fields denoting the concentration conditions given below.

Field 1: All phosphate forms phosphomolybdate, and then forms phosphomolybdenum blue. No blue color due to the reagent blank is obtained. This field is suitable for the phosphomolybdenum blue method.

Field 2: All phosphate forms phosphomolybdate, and then forms phosphomolybdenum blue. However, the reagent blank also becomes blue. This field is suitable for the phosphomolybdate method.

Field 3: Only a part of the phosphate forms phosphomolybdate and then phosphomolybdenum blue. Heating promotes the reaction, making it suitable for the phosphomolybdenum blue method.

Field 4: No phosphomolybdate is formed. This field is not applicable for determinations.

When the reaction of phosphomolybdenum blue development is carried out in a solution containing 0.65 N sulfuric acid and 0.15% ammonium molybdate, which is optimum for the determination of phosphate, phosphate is completely converted to phosphomolybdate, which in turn is quantitatively reduced by stannous chloride to form phosphomolybdenum blue. At the first stage of the reduction, one phosphomolybdenum blue molecule is regarded as possessing seven molybdenum atoms that have been reduced to molybdenum(V). Reduction by the use of excess amounts of stannous chloride proceeds in the following order:

(1) Phosphomolybdate → Phosphomolybdenum blue
(2) Molybdate reagent → Molybdenum of low valency
(3) Phosphomolybdenum blue → Phosphomolybdenum blue of a low valency

The reduction product in reaction 2 is probably a molybdenum(III) compound. A large excess of stannous chloride fades the blue color of the solution by means of reaction 3. Reaction 3 is negligible compared with reactions 1 and 2 in solutions containing a slight excess of stannous chloride. Under the conditions established by the author for color development, no blue product is formed as a results of the reduction of the molybdate reagent. Molybdate is considered to have been reduced directly to reddish brown molybdenum(III).

The knowledge obtained from these experiments is thought to be enough for the performance of the phosphomolybdenum blue method, although it is still insufficient for a complete explanation of the properties of the reactions and the reaction products.

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