Precipitation of Molybdenum with Silver Nitrate, Barium Chloride and Hexammine Cobaltic Chloride

It is evident from a consideration of the oxidation potentials involved that iron will interfere in the above method for the determination of molybdenum. Application to the determination of molybdenum in the presence of large amounts of iron is practicable only if a method can be found to separate molybdenum from iron in a form readily dissolved in hydrochloric acid. We have therefore studied the separation of molybdate from iron by precipitation in the presence of acetic acid–acetate buffers with silver nitrate[5] and hexammine cobaltic chloride.[12] It was found, however, that neither reagent gave a precipitate free from iron at a *p*H high enough to allow complete precipitation of the molybdate. We have also studied the precipitation of barium molybdate from alkaline tartrate and citrate solutions. Although quantitative precipitation is obtained in the absence of citrates and tartrates, the presence of sufficient amounts of these substances to prevent precipitation of iron also prevents the quantitative precipitation of molybdate. Moderate amounts of iron may, of course, be separated from molybdate by double precipitation with ammonia.

Summary

1. In 2 *M* hydrochloric acid solution and at a temperature of 60–80°, molybdenum is reduced quantitatively by the silver reductor to the quinquivalent state.

2. The reduced solution may be titrated with ceric sulfate using the *o*-phenanthroline ferrous complex indicator.

3. It is shown that these reactions lead to a precise and rapid method for the determination of molybdenum in the absence of other reducible substances.

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[12] Parks, Dissertation, Columbia University, 1930.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Coprecipitation of Ammonium Silicomolybdate and Ammonium Phosphomolybdate. An Improved Volumetric Method for the Determination of Phosphorus[1]

BY NATHAN BIRNBAUM AND GEORGE H. WALDEN, JR.

The development of rapid and precise methods[2] for the determination of molybdenum has led us to investigate the determination of phosphorus by analysis of the ammonium phosphomolybdate precipitate. There are several methods based upon the composition of the yellow precipitate which depend upon empirical mole ratios of molybdenum to phosphorus.[3] This ratio has received much attention and values ranging widely from the theoretical 12.00:1 have been reported.[4] We have found that an important factor affecting the composition of the precipitate is the presence of small amounts of silica. The interference of silicates has been reported previously,[5] but the extent of the interference is not generally recognized. As little as 0.25 mg. of silica in the presence of 6 mg. of phosphorus causes a measurable excess of molybdenum to be retained by the ammonium phosphomolybdate precipitate. Alkaline solutions of ammonium molybdate become significantly contaminated with silicate in about four weeks when stored at room temperature in Pyrex bottles. We have not investigated the solubility of glass in acid molybdate solutions but the yellow color which they rapidly develop suggests that they also attack the glass.

Reagent grade ammonium molybdate free from detectable traces of silicate is obtainable. By precipitating with freshly prepared solutions of this reagent precipitates containing the correct mole ratio of molybdenum to phosphorus can be obtained consistently. Alkaline ammonium

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[1] From a dissertation submitted by Nathan Birnbaum in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] (a) Furman and Murray, THIS JOURNAL, **58**, 1689 (1936); (b) Birnbaum and Walden, *ibid.*, **60**, 64 (1938).

[3] (a) Lundell and Hoffman, *Ind. Eng. Chem.*, **25**, 44 (1933); (b) Baxter, *Am. Chem. J.*, **28**, 298 (1902); (c) Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, Inc., New York, 1931, p. 224.

[4] For bibliographies on this subject see: (a) Hibbard, *Ind. Eng. Chem.*, **5**, 998 (1913); (b) Johann, Dissertation, Columbia University, 1921.

[5] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 562.

molybdate solution does not appear to deteriorate when kept in non-silicate containers.

Apparatus and Reagents.—Jena fritted glass filters (No. 3G4) were used in filtering the ammonium phosphomolybdate precipitates.

Standard phosphate solutions were prepared from dried, thrice recrystallized potassium dihydrogen phosphate. The purity of the salt was checked by ignition of several samples to the metaphosphate. The solutions were also analyzed for phosphorus by double precipitation of magnesium ammonium phosphate and ignition to the pyrophosphate. The following results are typical of the data obtained: (a) calculated from weight of potassium dihydrogen phosphate, 0.4101 g. phosphorus per liter; (b) precipitation as magnesium ammonium phosphate, 0.4099 g. phosphorus per liter; (c) ignition to potassium metaphosphate, 0.4092 g. phosphorus per liter.

The ceric sulfate solutions were standardized against Bureau of Standards sodium oxalate by the method of Walden, Hammett and Chapman.[6]

The ammonium molybdate solutions used to precipitate the phosphorus were prepared from Merck ammonium heptamolybdate (blue label reagent grade) according to the directions given by Johann.[4b] Solution I contained 100 g. of ammonium heptamolybdate in 400 cc. of water and 80 cc. of ammonium hydroxide; Solution II was made by mixing 400 cc. of 12 *M* hydrochloric acid with 600 cc. of water. When needed for precipitation one volume of Solution I was poured into twice its volume of Solution II; no visible amount of molybdic acid was left on mixing, but as an extra precaution the mixture was always filtered before being added to the phosphate solution. Amounts of Solution I were used which provided more than a five-fold excess of molybdate over that calculated from the stoichiometric relationship.

Experimental

Throughout this investigation molybdenum was determined by the silver reductor method.[2b] It was found that if ammonium phosphomolybdate was precipitated in the presence of nitric acid and ammonium nitrate the precipitate, even after lengthy washing with acid ammonium sulfate wash water, contained enough nitrate to interfere with the determination of molybdenum.[2b] We have therefore made the precipitations in a hydrochloric acid medium and used ammonium chloride in place of ammonium nitrate.[4b] The rapidity and completeness of precipitation compare favorably with that obtained in nitrate solutions. The precipitation is retarded by large amounts of iron but apparently to no greater an extent than occurs in nitric acid solution.[4a]

Two procedures were used in studying the composition of the ammonium phosphomolybdate precipitate.

Procedure I.—Twenty-five-cc. portions of the standard potassium dihydrogen phosphate solution (containing about 6 mg. of phosphorus) were pipetted into 250-cc. Erlenmeyer flasks and diluted with 75 cc. of water; 5 g. of ammonium chloride was added and then the molybdate reagent (15 cc. of Solution I poured into 30 cc. of Solution II). The flasks were shaken for five minutes and allowed to stand for one to three hours. The supernatant liquid was then decanted through the fritted glass filter and the precipitate washed by decantation with 25-cc. portions of acid ammonium sulfate solution (25 cc. 18 *M* sulfuric acid, 15 cc. of 15 *M* ammonium hydroxide and 960 cc. of water). About 15 washings were required before the precipitates were free from impurities.[7] The precipitate was dissolved in 2 *M* sodium hydroxide.[8] The solution was diluted, if necessary, to make the volume 50 cc. and enough 12 *M* hydrochloric acid added to neutralize the sodium hydroxide and make the solution 2 *M* with hydrochloric acid. After adding 3 cc. of sirupy phosphoric acid the molybdenum was determined by the silver reductor method. Precipitation periods of thirty minutes were sufficient to precipitate the phosphorus completely. Completeness of precipitation was established initially by failure of further precipitation to occur in the filtrates on standing; it was eventually confirmed by our success in obtaining correct ratios of molybdenum to phosphorus when known amounts of phosphorus were taken for precipitation.

Procedure II.—Larger samples of ammonium phosphomolybdate were precipitated as in Procedure I. An amount of precipitate sufficient to contain about 160 mg. of phosphorus was dissolved in sodium hydroxide solution and diluted to about 200 cc. Determinations of phosphorus and molybdenum were made in duplicate on portions of the solution withdrawn by calibrated pipets. The mole ratio thus determined depends only upon the analytical data and the volumes delivered by the pipets. Phosphorus was determined by double precipitation of magnesium ammonium phosphate and ignition to magnesium pyrophosphate. The volumes of solution taken for analysis were such that about 20 cc. of ceric sulfate was required to titrate the molybdenum, and magnesium pyrophosphate precipitates weighing about 200 mg. were obtained.

The Variability of the Mole Ratio of Molybdenum to Phosphorus and its Cause

At the beginning of this investigation our data showed the variation in the mole ratio of molybdenum to phosphorus observed by so many. Eventually we were able to correlate increasing values of the ratio with increasing age of the precipitating reagent. This correlation is illustrated by the data in Table I, which were obtained by Procedure II with solutions stored in Pyrex containers.

The determinations were all run in duplicate and an agreement better than one part per thousand was obtained in each case.

It may be seen that the effect of aging is much more rapid at 70° than at 20°. Using Procedure I we have followed systematically the increase of the mole ratio in precipitates prepared with molybdate reagent stored in Pyrex containers at room temperature (about 30°) and at 70°. The results obtained at 70° are shown graphically in Fig. 1. A peculiar feature of the variation is the initial period of several days during which no change was observed.

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[6] Walden, Hammett and Chapman, THIS JOURNAL, **55**, 2649 (1933).

[7] As shown by a negative test for molybdenum in the filtrate with hydrogen sulfide. The zinc–thiocyanate test was always positive, indicating that molybdenum was being slowly washed out of the precipitate.

[8] Sodium hydroxide was used to dissolve the precipitate because with the use of ammonia the yellow precipitate reappeared on acidification with hydrochloric acid.

TABLE I

No.	Description of molybdate soln.	Vol. of soln. for detn. of Mo	Molybdenum found, moles	Vol. of soln. for detn., of P	Magnesium pyrophosphate, g.	Phosphorus found, g.	Ratio moles Mo to moles P
1	Freshly prepared	4.9906	0.002137	49.976	0.1985	0.05530	12.00
2	Aged 4 mon. at 20°	4.9906	.002007	49.976	.1858	.05177	12.05
3	Aged 1 week at 70°	4.9906	.002185	49.976	.2016	.05617	12.08

This effect is quite reproducible and was observed also at 30°, at which temperature the period is extended to about four weeks.

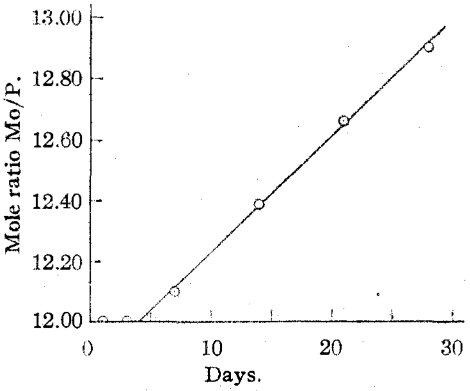

Fig. 1.—Variation of the mole ratio of Mo/P in ammonium phosphomolybdate precipitate with the age of the precipitating agent kept at 70°.

Another correlated observation which furnished the clue to the cause of the variation was that the molybdate reagent, upon acidification, was initially colorless, but became increasingly yellow as the age of the reagent increased. We are greatly indebted to Mr. C. E. Miller for first suggesting to us that this color might be due to the presence of silicomolybdate ion formed from silicate dissolved from the walls of the containers, and that the increase in the mole ratio might be due to precipitation of ammonium silicomolybdate.

To test this hypothesis we mixed a portion of molybdate reagent with powdered Pyrex glass. After five days of standing at 70° the reagent was filtered and a precipitate prepared from it by Procedure I. The reagent became intensely yellow on acidification and the mole ratio found in the precipitate was 12.34. Reference to Fig. 1 shows that a large acceleration of the effect was caused by the powdered glass. In contrast, molybdate reagent stored for seven days at 70° in containers of silver, Beetleware, graphite and iron remained colorless on acidification. A portion stored for eight days at 70° in an iron container formed a precipitate with a mole ratio of 11.98. To decide whether the effect is due to a specific solvent action of the ammonium molybdate reagent or the general solvent action of an alkaline solution, we prepared an ammonia solution containing the same concentration of ammonia as the molybdate reagent. This was mixed with powdered Pyrex glass and kept at 70° for seven days. It was then filtered and molybdate reagent was prepared by dissolving in it solid ammonium heptamolybdate. A precipitate prepared from this reagent by Procedure I had a mole ratio of 12.49, indicating no large specific solvent action of ammonium molybdate.

These experiments demonstrate quite conclusively that the effect is caused by alkali solvent action on the glass container. Since Pyrex glass is a borosilicate glass the increase in mole ratio might be caused by the presence of either borate or silicate. To investigate the effect of borate we made a precipitate with a 15-cc. portion of freshly prepared molybdate reagent in which was dissolved 0.2 g. of boric acid. This solution remained colorless upon acidification and the mole ratio in the precipitate was found to be 12.18. It is evident that borates cause a definite increase in the mole ratio, but the increase is small relative to that produced by a few days' aging of the reagent in the presence of powdered glass. When the relatively large amount of borate present in this experiment is taken into consideration it becomes evident that only a small part of the effect under investigation can be caused by solution of borate. It must therefore be due primarily to the solution of silicate.

To study quantitatively the contaminating effect of silicates we have prepared and analyzed a number of ammonium phosphomolybdate precipitates which were formed in the presence of known amounts of silica. A standard silicate solution was prepared by fusing a weighed amount of selected clear quartz crystal with sodium carbonate in a platinum crucible. The melt was dissolved in water, diluted to volume in a standard flask and stored in a paraffined container. Measured volumes of this solution were added to fresh molybdate solution before acidification. Otherwise the precipitations and analyses were carried out as in Procedure I. The results are shown graphically in Fig. 2.

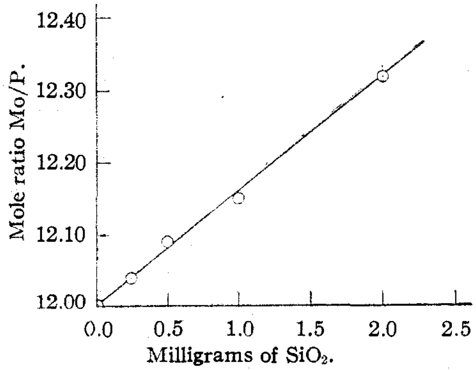

Fig. 2.—Variation of the mole ratio of Mo/P in ammonium phosphomolybdate precipitated in the presence of silicate.

Since there can be little doubt that the immediate formation of a yellow color which we have observed on acidification of aged molybdate solutions is caused by the formation of silicomolybdate ion, we have utilized this color development[9] as a means of following colorimetrically the solution

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(9) Schreiner, THIS JOURNAL, **25**, 1056 (1903); Dienert and Wandenbulcke, *Compt. rend.*, **176**, 1478 (1923).

of silicate from the container. The procedure followed was to place a freshly prepared alkaline molybdate solution in a Pyrex flask which had been cleaned with chromic acid in sulfuric acid. The solution was stored at 70° and from time to time 5-cc. portions were withdrawn by pipet and acidified with nitric acid. The color developed was compared in a Duboscq type colorimeter with that produced by a measured portion of standard silicate solution to which nitric acid and ammonium molybdate were added. The results are represented by the circles plotted in Fig. 3. The curve in Fig. 3 is a plot from the data at 70° in Fig. 1. The values of the mole ratio given in Fig. 1 were converted to amounts of silica present at the time of precipitation by means of the graph in Fig. 2. Although the experimental points do not fall exactly on this curve the correspondence seems as good as could be expected in view of the fact that the rate of solution most certainly depends upon the area and condition of the glass surface in contact with the solution. Neither of these factors could be closely controlled, and we feel that the correspondence is sufficiently close to justify the conclusion that solution of the silica from the glass is entirely responsible for the observed increases in the mole ratio of molybdenum to phosphorus.

With this factor understood we have had no difficulty in obtaining ammonium phosphomolybdate precipitates with the theoretical ratio of molybdenum to phosphorus of 12.00:1 within the precision of the analytical method. Six successive determinations made with fresh molybdate reagent by Procedure I gave mole ratios: 12.00, 12.04, 11.96, 12.00, 12.02, 12.03; mean, 12.01.

Structure of the Silicate Contaminated Precipitate

Silicomolybdate ion is readily formed when excess strong acid is added to a solution containing molybdate and silicate.[10] Ammonium silicomolybdate is considerably more soluble than ammonium phosphomolybdate but it can be precipitated by adding excess ammonium chloride to silicomolybdic acid,[11] or by mixing nitric acid solutions of ammonium molybdate and alkali silicate.[12]

If the increase in the mole ratio of molybdenum to phosphorus is due to contamination by ammonium silicomolybdate, the data in Fig. 2 show that a constant fraction of the silica present is retained by precipitates formed under constant conditions from identical amounts of phosphorus. This is not consistent with the hypothesis that ammonium silicomolybdate precipitates as a separate phase, but suggests, rather, a solubility distribution. The probability of such an occurrence is indicated by the recent work of Illingworth and Keggin,[11] who have compared the crystal structure of ammonium silicomolybdate with that of ammonium phosphomolybdate and have shown the two structures to be identical and the two heteropoly ions to be almost identical in size. Ammonium silicomolybdate, therefore, might be expected to contaminate ammonium phosphomolybdate by extensive solid solution formation.

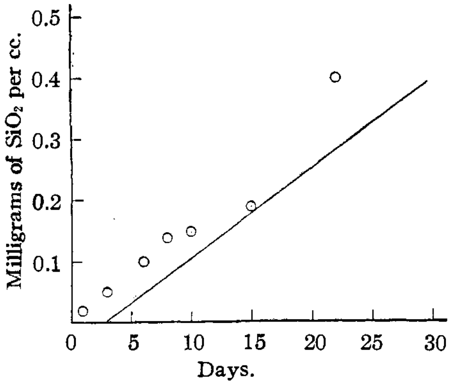

Fig. 3.—Solution of silicate by alkaline ammonium molybdate reagent kept in Pyrex flasks at 70°.

The linear relationship between the mole ratio of molybdenum to phosphorus and the concentration of silica present at the time of precipitation shown in Fig. 2, may indeed be accounted for on this basis. Let x, y and z be, respectively, the moles of silicon, phosphorus, and molybdenum in the precipitate, a and b the moles of silicon and phosphorus present in the solution at the time of precipitation. Under the conditions of the experiment the nearly complete conversion of silica and phosphorus to silicomolybdate and phosphomolybdate was assured by addition of a large excess of molybdate reagent. The requirement for equilibrium will then be given by the ordinary solid solution distribution formula[13]

$$x/(a - x) = Dy/(b - y)$$

where D is the distribution constant. Combination of this equation with the relationship $12\ (x + y) = z$ leads to the expression

$$\frac{z}{y} = 12D\frac{(a - x)}{(b - y)} + 12$$

Now, since the mole fraction of ammonium phosphomolybdate in the precipitates studied was large and did not undergo large percentage variation (1 to 0.93) the quantity $b - y$ remains sensibly constant. With this restriction, the distribution

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(10) Mellor, "Treatise on Inorganic Chemistry," Longmans, Green and Co., New York, N. Y., Vol. VI, p. 869.

(11) Illingworth and Keggin, *J. Chem. Soc.*, 575 (1935).

(12) Parmentier, *Compt. rend.*, **92**, 1234 (1887).

(13) Hahn, "Applied Radiochemistry," Cornell University Press, Ithaca, New York, 1936, p. 77.

law requires that x be proportional to a, and therefore

$$z/y = Ka + 12$$

where K is a constant.

The appearance of a distribution equilibrium in a sparingly soluble precipitate seems rather surprising. It may, however, be noted that these precipitates tend to appear initially in a very finely divided form and require either digestion or vigorous shaking before filtration. In this series of experiments the precipitates were digested for two to three hours, in which time they became coarsely crystalline. Thus conditions similar to those found by Mumbrauer[14] to lead to this type of distribution were present during recrystallization.

It may be observed that since most precipitates coarsen through recrystallization, digestion will tend in all cases of solid solution formation to bring the system to a distribution equilibrium. If solid solutions are formed at the moment of precipitation this process may conceivably lead either to increased or decreased contamination. In the latter event complete elimination of the contamination is possible. Solid solutions of the type observed by Walden and Cohen[15] are probably entirely out of equilibrium with the mother liquor since the precipitates studied by them were not digested sufficiently to cause appreciable recrystallization, and, indeed, the extent of contamination was not found to be related to the concentration of the contaminating ion.

Determination of Phosphorus in the Presence of Iron

By modification of Procedure I we have succeeded in determining phosphorus in the presence of a large amount of iron. The changes are as follows: (1) 3 cc. of 12 *M* hydrochloric acid is added to the solution containing the phosphate and iron before precipitation of the phosphorus; (2) the solution containing the dissolved yellow precipitate is again passed through the fritted glass filter. This is necessary because all the iron is not removed in the washing process and the small amount of ferric hydroxide formed on solution of the precipitate with sodium hydroxide must be separated before acidification. Using this procedure a double separation of the iron is effected, and tests made on the small amount of ferric hydroxide left on the filter showed that no molybdenum is retained by the precipitate.[16] We have confirmed the results obtained by Hibbard[4a] concerning the interference of sulfates; their presence invariably causes high ratios of molybdenum to phosphorus. The results obtained indicate that the amounts of iron usually present in analyses will present no difficulties in the determination of phosphorus. In four successive determinations with 6.157 mg. of phosphorus and 1 g. of iron present the percentage errors were: +0.16, −0.01, +0.40, +0.26.

Determination of Small Amounts of Phosphorus

Approximately 0.01 *M* ceric sulfate solutions were used in these determinations. Blank corrections of almost 0.5 cc. were found to be necessary, caused by the presence of iron in the reagents. The procedure was the same as that described in Procedure I. In six successive determinations with 0.6157 mg. of phosphorus present the percentage errors were: +0.39, −0.75, +0.75, +0.47, +0.07, +1.12.

Attempts to determine 0.6 mg. of phosphorus in the presence of 1 g. of iron did not yield satisfactory results. Erratic positive and negative errors of 5 to 10% were encountered. Further work on this application is now in progress.

Summary

1. The mole ratio of molybdenum to phosphorus in ammonium phosphomolybdate, precipitated with alkaline ammonium molybdate reagent which has been stored in a glass container increases with the age of the reagent.

2. This effect is caused by solution of small amounts of silicate from the glass.

3. Precipitates of ideal composition have been consistently prepared by the use of silicate-free precipitating reagent.

4. A rapid and precise volumetric method for the determination of phosphorus in pure phosphate solution and in the presence of iron has been developed.

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(14) Mumbrauer, *Z. physik. Chem.*, **A156**, 113 (1931).

(15) Walden and Cohen, THIS JOURNAL, **57**, 2591 (1935).

(16) The precipitate was dissolved in hydrochloric acid and tested for molybdenum with hydrogen sulfide and zinc thiocyanate. Neither test was positive.