

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

ON THE DETERMINATION OF PHOSPHORIC ACID
AS MAGNESIUM PYROPHOSPHATE.¹

BY HUGO NEUBAUER.

TRANSLATED AND ABSTRACTED BY K. P. MCELROY.

AFTER giving a brief history of the molybdenum method for the determination of phosphoric acid, Herr Neubauer states his reasons for thinking this method undeserving of its high repute for accuracy. He next gives the results of a long investigation of the sources of error inherent in the method.

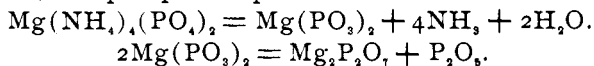
As a standard silver orthophosphate was employed, this salt being chosen partly because of its perfectly definite composition, partly because of the ease with which the base could be estimated. Magnesium ammonium phosphate was rejected for this purpose because it was not thought proper to have the same salt serve as both the beginning and the end. Disodium phosphate was rejected because, of its tendency to absorb carbonic acid. In the first series of experiments on the molybdate method (Wagner's modification), the amount of phosphoric acid found was a trifle less than that known to have been used, the discrepancy ranging from 0.3 mgm. on 84.2 mgms. P_2O_5 to 2.7 mgms. on 166.8 mgms. P_2O_5 . Two explanations could be made of this loss—either that the precipitations were not complete or that volatilization of the phosphoric acid occurred during the ignition of the magnesium salt previous to weighing. Neubauer rejected the former explanation in favor of the latter, adducing a series of

¹ Presented to the World's Chemical Congress, Chicago, August 22, 1893.

experiments in favor of his view. The lid of a platinum crucible was covered with a layer of magnesium hydroxide on the under side and ignited till magnesium oxide was formed and the weight of the lid remained constant. A filter containing magnesium phosphate was then burned in the crucible and after the combustion of the paper, the lid was placed in position and the salt ignited to constant weight. The lid was found to have increased in weight in amounts varying from 0.2 mgm. to 3.8 mgms. The smaller amount was found where the phosphoric acid was directly precipitated and also in a case where magnesium ammonium phosphate reputed to be chemically pure was directly ignited. The largest increase in weight was found in cases where large quantities (five grams) of ammonium chloride or molybdate were added previous to the precipitation of the double phosphate. In the precipitate obtained by the Wagner process (in this method the ammoniacal solution of the yellow precipitate is not neutralized previous to adding the magnesia mixture) the increase varied from 0.5 mgm. to 2.0 mgms. On solution of the magnesia layer on the lid, phosphoric acid was detected by the molybdate reaction. The observation is made that precipitates exposed to the heat of a common Bunsen burner are but little below the truth, while the weights of large precipitates obtained by the molybdate method are often several milligrams too low after strong ignition. The argument is made that the molybdic acid cannot be responsible for this peculiar behavior, since the precipitate when washed till the chlorine reaction disappears contains but an insignificant amount of this substance. Magnesium ammonium phosphate covered before ignition with a weighed amount of lime or magnesia, weighs more than a similar precipitate ignited without this addition, in case an excess of ammonium salts has been present during the precipitation. If the washed precipitate of magnesium ammonium phosphate is dissolved in a very little hydrochloric acid, ammonia in excess added and then two cc. of magnesia mixture, the double precipitated salt will weigh more than it would have done otherwise in case much ammonium molybdate was originally present.

From these facts the conclusion is drawn that in the presence of an excess of ammonium salts, the magnesian precipitate is not

pure dimagnesium ammonium phosphate (MgNH_4PO_4), but contains more or less monomagnesium ammonium phosphate ($\text{Mg}(\text{NH}_4)_2(\text{PO}_4)_2$). This latter salt decomposes on ignition into magnesium metaphosphate, ammonia, and water. On further ignition, this phosphate becomes converted into pyrophosphate, and phosphorus pentoxide is set free and volatilized.



The greater the concentration of the ammonium salts, the larger the amount of monomagnesium salt which will be formed. For this reason the prevailing ideas relative to the concentration of the solutions to be precipitated are erroneous and more accurate results can be obtained by greater dilution.

Two chances of error exist in the determination of phosphoric acid by the magnesian method—first, that the precipitate may contain too much magnesia, second, that it may contain too little. The second error is readily detected by the method already given. The other may be detected by Tollen's method (*J. Landw*, 1882, **30**, 48), which consists in suspending the ignited phosphate in water, adding a little dilute solution of silver nitrate and heating. In the presence of an excess of magnesium, silver orthophosphate is formed and recognized by its yellow color. The reaction is sufficiently sensitive.

Experiments were made with solution of pure magnesium ammonium phosphate containing various amounts of ammonium chloride. In one solution containing 300 mgms. of the chloride, half a milligram of magnesia was found in the filtrate after precipitation by ammonia, and the same quantity of phosphorus pentoxide was volatilized on ignition of the precipitate. In another case where 2.5 grams of ammonium chloride were present, the loss in magnesia and phosphoric oxide were respectively 1.1 and 1.6 mgms. In a third where five grams were employed, the losses were 3.2 and 4.4 mgms. respectively. Finally, phosphoric acid (44.8 mgms.) was precipitated in the presence of 200 cc. of approximately saturated solution of ammonium chloride. The losses reached the large figures of 12.7 and 15.6 mgms. respectively for MgO and P_2O_5 . The filtrate contained phosphoric acid in amount sufficient to permit its recognition by molybdate, but there was not enough to determine.

Even in the absence of an excess of magnesium chloride the phosphoric acid is wholly precipitated, although ammonium chloride may be present in large amount. The precipitate thus obtained is, however, never of the correct composition. It invariably contains an excess of phosphoric acid and this excess is proportional to the amount of sal ammoniac present. This error is not counteracted by the presence of an amount of magnesium chloride sufficient to form a precipitate of the proper composition.

In the presence of an excess of magnesium chloride the precipitate invariably contains at least enough magnesia to form the normal salt, even in the presence of an excess of ammonium salts. A pure precipitate is, however, only obtained when the amount of free ammonia present is just sufficient for its formation. Any excess of the base causes the precipitate to contain too much magnesia. When ammonia is allowed to slowly flow into a solution containing phosphoric acid and a magnesium salt in excess, the precipitate formed has the normal composition, provided that the rate of flow has been so regulated that the precipitation has taken place in neutral solution. Of course an excess of ammonia must be finally added in order to secure complete precipitation, but this excess is not injurious after the precipitate has once formed.

Various attempts were made to secure a process giving reliable results and yet not too clumsy for practice. Ammoniacal solution of phosphomolybdic acid was neutralized with hydrochloric acid till the yellow precipitate no longer disappeared on stirring and no smell of ammonia could be detected, neutral magnesium chloride solution containing ammonium chloride added, and then dilute ammonia, till a precipitate began to appear. The solution was allowed to stand for awhile, a trifle more ammonia added, and finally, after another wait, an excess of ammonia. By this process correct results were occasionally obtained, but usually the precipitate was a trifle (0.0 to 1.5 mgms.) too heavy and gave Tollen's reaction. For many purposes the results are sufficiently close.

It is probable that in the presence of excess of magnesium chloride and of ammonia some trimagnesium phosphate is

formed, for it is not likely that the excess of magnesia in the precipitate is due to oxide mechanically carried down in the precipitate when quickly formed.

When hydrochloric acid is added to an ammoniacal solution of phosphomolybdate till the precipitate redissolves with difficulty on stirring, the solution reddens blue litmus paper and probably contains free phosphomolybdic acid. On now adding first magnesium chloride in excess and then ammonia, ammonium phosphomolybdate is probably first formed, and then this salt gradually breaks up as more ammonia is added, forming magnesium ammonium phosphate with the magnesia already in solution.

Precipitates obtained from solutions approximately neutral often contain noticeable proportions of molybdic acid in the free state. This is caused by the decomposition of phosphomolybdic acid by ammonia and magnesium chloride. As molybdic acid is not particularly soluble in water, it is deposited simultaneously with the magnesium ammonium phosphate and is enclosed by the latter salt to some extent, and so shielded from the solvent action of the excess of ammonia later added. This separation of free molybdic acid, of course, does not occur in the presence of free ammonia.

The difficulty of preparing the pure double phosphate is not so great in the absence of molybdate and when the excess of magnesium chloride is not large. Washed magnesian precipitates dissolved in hydrochloric acid containing a slight amount of magnesium chloride, and carefully reprecipitated with ammonia, gave better results than had been hitherto obtained. The process is, however, too dependent on the skill of the operator to be reliable.

Magnesium ammonium phosphate can be obtained in three different conditions:

(1) The precipitate is formed in neutral or ammoniacal solution containing no excess of magnesium salt. The result of this is that the precipitate contains less than the normal amount of magnesia, and phosphoric oxide is volatilized on ignition. Therefore weights come out too low.

(2) The precipitate is formed in the presence of an excess of

magnesium salt, but during its formation ammonia is not present in excess. As a result the precipitate possesses the normal constitution and the weights obtained are correct.

(3) The precipitate is formed in the presence of an excess of both ammonia and magnesium salts. The result is that the precipitate contains an excess of magnesia and the weights afforded are consequently too high.

Viewing in the light of these results the method for the precipitation of phosphoric acid (that of Abesser, Jani and Maercker), in which the ammoniacal solution of the yellow precipitate is approximately neutralized with hydrochloric acid, magnesia mixture then added, and subsequently an excess of ammonia, it is readily seen that the following sources of error exist:

A. The whole precipitate is formed as is indicated under (1). This occurs when the amount of ammonia present in the magnesia mixture is so large that precipitation of the phosphoric acid is at once effected when the reagent is slowly added and the liquid stirred, excess of magnesia not being present during the precipitation. Subsequent addition of excess of magnesium chloride or of ammonia is of no avail. The results are similar to those obtained by Wagner's process (in which the neutralization with hydrochloric acid is not practiced).

B. In the formation of the precipitate all three conditions successively occur. This is the case when the amount of ammonia in the magnesia mixture is such that when the reagent is added, drop by drop, stirring constantly, precipitation begins while there is no excess of magnesia, but continues after an excess has been added. Under these circumstances the errors may nearly balance. It is not practicable to form the precipitate wholly of the composition given under (2).

C. When magnesia mixture and ammonia are added drop by drop, stirring constantly, the precipitate formed generally has the composition given under (2) and (3). The 2.5 per cent. ammonia of the usual magnesia mixture is so weak that the precipitate begins to form when magnesia is in excess. The results are consequently too high, and the quicker the precipitation has been effected the higher the results are likely to be, from the

fact that a smaller portion of the precipitate is formed in neutral solution.

D. The precipitate is exclusively of the composition given under (3) only when magnesia mixture and ammonia are too quickly added. The results are in this case even higher than those just referred to under C.

These theoretical conclusions were confirmed by direct experiment.

The common citrate method gives approximate results which is due to the fact that two sources of error counterbalance each other. On the one hand the precipitate invariably contains lime and on the other the phosphoric acid is not completely precipitated. When magnesia mixture is slowly added to an ammoniacal solution of phosphoric acid containing ammonium citrate but no bases forming insoluble salts with phosphoric acid, the precipitate forms mostly in the condition given under (1) and but little in that given under (3), inasmuch as most of it is formed in the absence of an excess of magnesium chloride. This view was confirmed by experiment, but it was also shown that even when the magnesia was rapidly added, some phosphoric acid was volatilized during the subsequent ignition of the precipitate. This is due to the fact that from solutions of phosphoric acid containing no lime salts the precipitate is formed with tolerable rapidity even where citrate was present, so that on the addition of the magnesia mixture a portion of the precipitate is formed in the absence of an excess of magnesium chloride.

The general conclusion drawn from the results of a number of determinations made by various modifications of the molybdate method and by the citrate method is that none of these methods is particularly accurate. It appears practically impossible to completely convert phosphoric acid into pure magnesium pyrophosphate under analytical conditions, where the molybdate method is employed. The exact amount of phosphoric acid in a substance can therefore only be obtained by correcting the results analytically found by a factor, assuming that the errors of analysis are constant for a given amount of phosphoric acid.

Results obtained, where the neutralization with hydrochloric acid is practiced, are oftener nearer the truth than where this

precaution is omitted. However, results thus obtained are dependent on so many sources of error that it is difficult to make parallel analyses. Besides this the method is rather inconvenient. The molybdic acid occurring in the precipitate is a nuisance. Its complete removal by ignition requires skill and practice, and often as much time as the expulsion of the volatile phosphoric acid from the precipitate formed where neutralization is omitted (Wagner's modification). On the other hand the latter modification of the method is very convenient in practice and the attendant relations are so simple, that duplicates must agree where simple precautions are observed.

A systematic determination was made of the errors attendant on Wagner's method and from the results a table constructed, the use of which is recommended for phosphate determinations. The source of error in this method lies exclusively in the loss of phosphoric acid by volatilization. The magnesia-covered crucible lid offers a very good control of this error and its use is recommended to the analyst. Of course, the presence of sulphur in the gas used for ignition is liable to disturb this check.

The following course of procedure in the determination of phosphoric acid can be recommended:

Separate the phosphoric acid in the form of the yellow precipitate and wash this latter in the usual way. Too high a heat should not be employed, nor should the solutions be allowed to stand too long lest excess of molybdic acid separate. Dissolve the phosphomolybdate in 100 cc. of cold 2.5 per cent. ammonia and add as many cc. of the usual magnesia mixture (fifty-five grams magnesium chloride and seventy grams ammonium chloride dissolved in a liter of 2.5 per cent. ammonia) as there are centigrams of phosphoric acid present. Addition should not be made faster than ten cc. per minute. Stir during the addition. After the precipitation stir briskly once more and then allow to stand at least three hours. Wash with 2.5 per cent. ammonia till the chlorine reaction disappears, dry the filter and introduce into a well-cleaned crucible which has been thoroughly ignited. Place the lid at an angle, carbonize the filter and gradually raise the heat, though not higher than a medium red heat, till the pyrophosphate becomes completely white. When

this happens bring the blast into action and ignite to constant weight. The weight finally accepted must not change even after half an hour's ignition. Upon this requirement especial stress must be laid. Pure magnesium pyrophosphate does not suffer any loss even after several hours' ignition, nor does a good platinum crucible. To the weighed amount of pyrophosphate add the correction given in the table. Multiplication of the sum by 64 gives the amount of phosphoric acid in the weight taken for analysis.

CORRECTION FOR PHOSPHORIC ACID DETERMINATION.

Found, Mg ₂ P ₂ O ₇ in grams.	Lost, milligrams Mg ₂ P ₂ O ₇ .	Found, Mg ₂ P ₂ O ₇ in grams.	Lost, milligrams Mg ₂ P ₂ O ₇ .
0.10	0.6	0.24	4.0
0.12	0.8	0.25	4.2
0.14	1.2	0.26	4.6
0.15	1.4	0.27	5.0
0.16	1.6	0.28	5.5
0.17	2.4	0.29	6.1
0.18	2.6	0.30	6.8
0.19	3.2	0.31	7.6
0.20	3.5	0.32	8.6
0.21	3.6	0.33	9.6
0.22	3.8	0.34	10.6

When phosphoric acid is to be estimated as pyrophosphate it must always be first separated as molybdate, even when the original solution contained no bases capable of forming insoluble phosphates, as otherwise these corrections will not be applicable.

Using these corrections, the estimation of phosphoric acid becomes one of the most accurate of known analytical methods.

EXPERIMENTS ON A FERRO-TUNGSTEN.

BY JAMES S. DE BENNEVILLE.

Received February 28, 1894.

IN making an analysis of a ferro-tungsten rich in tungsten the chemical behavior of a residue insoluble in acids and apparently not decomposed by fused solvents led me to believe that it was metallic tungsten. The time available was limited and the few experiments made were hasty and at intervals, and in a private communication describing the method pursued in analy-