Quantitative Analysis of Phosphoric Acid, Part IV.

Gravimetric and Volumetric Determination as Ammonium Phosphomolybdate

By

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Since L. Sonneschein[1] proposed that the precipitation of phosphoric acid as ammonium phosphomolybdate might be utilized for analysis of the acid, a great many works dealing with this subject have been published by several authors.   F. Hundeshagen[2] assigned the formula $12MoO_3$. PO_4 $(NH_4)_3$. $2HNO_3$. H_2O or $12MoO_3$. $PO_4(NH_4)_3$. $2HCl$. H_2O to the yellow precipitate of ammonium phosphomolybdate which, when heated to a constant weight at 150^0 or at $160^\circ-180^{\circ 3}$, was regarded as taking the composition[4], $12MoO_3$. $PO_4(NH_4)_3$.

Now if the yellow precipitate of ammonium phosphomolybdate changes quantitatively into $(NH_4)_3PO_4$. $12MoO_3$ the amount of P_2O_5 might be calculated from the weight of it by multiplying by the factor 0.0378.   Practically, however, various different factors have been used by different authors, thus

0.0303 (L. Sonneschein)[1]

0.0390 (C. Rammelsberg)[5]

1 J. prak. Chem., (I), **53**, 339 (1851)

2 Zs. anal. Chem., **28**, 141 (1889)

3 R. Finkener: Ber. D. chem. Ges., **11**, 1640 (1878)

4 According to R. Woy {Chem. Ztg., **21**, 442 (1897)} when ammonium phosphomolybdate contained in a Gooch crucible is put in a large nickel crucible and heated till the bottom of the external crucible becomes dark red it may be weighed as having the composition $P_2O_5.24MoO_3$.

5 Ber. D. chem. Ges., **10**, 1776 (1877)

0.0366 (W. Gibbs)[1]

0.03794 (R. Finkener)[3] (P.91)

0.03753 (F. Hundeshagen)[2]

0.0376 (T.S. Gladding)[3]

This clearly shows that quantitative transformation of phosphoric acid into pure ammonium phosphomolybdate of the formula $(NH_4)_3 PO_4 . 12MoO_3$ is very difficult and consequently the application of the reaction to the determination of phosphoric acid can not be expected to give satisfactory results. For this reason, precipitation of phosphoric acid as ammonium phosphomolybdate is generally used only as a means of separating phosphoric acid from other substances, and in order to make a quantitative estimation the phosphomolybdate is dissolved in ammonia water, and from this solution phosphoric acid is precipitated as magnesium ammonium phosphate and weighed as magnesium pyrophosphate. This very tedious process would, however, be greatly simplified, if we could find out the condition under which ammonium phosphomolybdate of a definite composition is precipitated unaccompanied by any impurities and also the temperature at which it takes a definite form suitable for weighing. Moreover, for the determination of a minute quantity of phosphoric acid the phosphomolybdate method will be found far more suitable than the magnesium pyrophosphate method, because the percentage of phosphoric acid in $(NH_4)_3PO_4 . 12MoO_3$ is only 3.78 while that in $Mg_2P_2O_7$ is about 17 times greater, that is, 63.79. The present work was undertaken in the hope of finding such a condition and after several experiments it was confirmed that quite satisfactory results can be obtained in the following way : Ammonium phosphomolybdate is precipitated from a nitric acid solution containing some excess of ammonium nitrate at a high temperature, and the precipitate is filtered with a quartz filter crucible and washed with 2% nitric acid. When it has been thoroughly washed, a filter crucible is placed in a large porcelain crucible and heated gradually first for ten minutes and then strongly at 250°–300° for about thirty minutes. The crucible is then cooled in a desiccator over freshly prepared fused calcium chloride or phosphorus pentoxide. The amount of P_2O_5 is simply obtained from the weight of ammonium phosphomolybdate by multiplying by the theoretical factor 0.0378.

To ascertain how amounts of ammonium molybdate and ammonium

1   Chem. News, **45**, 31 (1882)

2   Zs. anal. Chem., **32**, 144 (1893)

3   J. Amer. Chem. Soc., **18**, 23 (1896)

nitrate effect the precipitation of ammonium phosphomolybdate and how acidity of the solution and temperature influence the accuracy of the analysis several experiments, described below, were carried out.

Experimental

I. Gravimetric Method

In all the experiments ammonium phosphate, ammonium molybdate, ammonium nitrate and nitric acid were taken as the solution prepared in the following way :

1. Ammonium phosphate solution was prepared by dissolving 1.000 gram of Kahlbaum's ammonium phosphate "Zur Analyse mit Garantieshein" to one litre.
2. Thirty five grams of pure ammonium molybdate $(NH_4)_6MoO_7O_{21}.4H_2O$ obtained from Merck were dissolved to one litre. One ml of such a solution corresponds to 0.001 gram of P_2O_5.
3. Ammonium nitrate solution was prepared by dissolving 400.3 grams of ammonium nitrate to one litre (5 normal).
4. Nitric acid solutions of 5 normal and 0.4 normal (2 %).

Table I

No.	Temperature	Time of heating	$(NH_4)_3PO_4.12MoO_3$	P_2O_5 (53.77%)	Differce
		min.	grm.	%	%
1	40°—45°	10	0.3553	53.72	−0.05
2	40°—45°	10	0.3553	53.72	−0.05
3	50°—55°	5	0.3558	53.79	+0.02
4	50°—55°	5	0.3557	53.78	+0.01
5	60°—63°	5	0.3560	53.83	+0.06
6	60°—63°	5	0.3559	53.81	+0.04
7	70°—73°	5	0.3565	53.90	+0.13
8	70°—73°	5	0.3570	53.97	+0.20
9	70°—73°	30	0.3652	55.22	+1.45
10	boiling	5	0.3609	54.57	+0.80
11	boiling	5	0.3621	54.75	+0.98

1. *Influence of Temperature on the Precipitation of Ammonium Phosphomolybdate*

In each experiment here described, ammonium phosphate was precipitated in the following manner : 25 ml of ammonium phosphate solution were diluted with 100 ml of water and to this were added 50 ml of the ammonium nitrate solution and 25 ml of the ammonium molybdate solution.   To this mixture 25 ml of 5 normal nitric acid were added at temperatures varying from $45°$ to $100°$ and then cooled for 3 hours, when the precipitation of ammonium phosphomolybdate was found completed, no trace of phosphoric acid being left in the filtrate.   The results are as summarized in Table I.

From the table it is seen that a rather large positive error always accompanies the value of phosphoric acid when the working temperatures are higher than $70°$.   This is evidently due to the formation of a hydrated molybdenum trioxide of the formula $MoO_3 2H_2O$.

Table II

No.	5N–HNO$_3$		Time of standing	$(NH_4)_3PO_4.12MoO_3$	P_2O_5	Diffce	Phosphate in filtrate
	ml	Narmality for total volume		grm.	%	%	
1	100	2.5	over night	0.0483	7.30	−46.47	distinct
2	50	1.7	„ „	0.3412	47.56	−6.18	little
3	50	1.7	„ „	0.3499	52.90	−0.87	trace
4	32	1.3	„ „	0.3555	53.75	−0.02	none
5	32	1.3	„ „	0.3553	53.72	−0.05	„
6	25	1.0	„ „	0.3558	53.79	+0.02	„
7	25	1.0	„ „	0.3556	53.77	±0.00	„
8	25	1.0	3 hours	0.3558	53.79	+0.02	„
9	25	1.0	3 hours	0.3555	53.75	−0.02	„
10	15	0.7	over night	0.3561	53.84	+0.07	„
11	15	0.7	„ „	0.3557	53.78	+0.01	„
12	13	0.6	„ „	0.3571	53.98	+0.21	„
13	13	0.6	„ „	0.3567	53.92	+0.15	„
14	10	0.5	„ „	0.3639	55.02	+1.25	„
15	10	0.5	„ „	0.3617	54.69	+0.92	„

2. Influence of Concentration of Nitric Acid

For the precipitation of ammonium phosphomolybdate, 25 ml of the ammonium phosphate solution were made to react upon 25 ml of the ammonium molybdate solution in the presence of 50 ml of the ammonium nitrate solution the strength of the nitric acid being varied from 2.5 to 0.5 normal.

From Table II it will be seen that when nitric acid is more concentrated than 1.7 normal, the precipitation of ammonium phosphomolybdate is always incomplete (No. 1—No. 3), while in the solution in which the concentration of the nitric acid is smaller than 0.6 normal the value of phosphoric acid is found to be higher owing to the precipitation of ammonium nitromolybdate $NH_4NO_3.4MoO_3$.[1] According to the present writer's experiments ammonium nitromolybdate is easily formed in a dilute nitric acid solution containing ammonium nitrate and ammonium molybdate as silky needles insoluble in dilute nitric acid of 1—2% concentration, but soluble both in concentrated nitric acid and in pure water.

To learn the influence of dilution, a solution containing ammonium phosphate, ammonium molybdate and ammonium nitrate in the same quantities as in the previous case was diluted with various quantities of water and 25 ml of 5 normal nitric acid were added. The results are shown in Table III.

Table III

No.	Water added	HNO_3	Time of standing	$(NH_4)_3PO_4.12MoO_3$	P_2O_5	Diffce	Phosphate in filtrate
	ml	Normality for total volume	hour	grm.	%	%	
1	50	0.7	3	0.3558	53.79	+0.02	none
2	50	0.7	„	0.3559	53.81	+0.04	„
3	100	0.6	„	0.3562	53.86	+0.09	„
4	100	0.6	„	0.3565	53.90	+0.13	„
5	150	0.5	„	0.3566	53.91	+0.14	„
6	150	0.5	„	0.3570	53.97	+0.20	„
7	200	0.4	„	0.3583	54.17	+0.40	„
8	200	0.4	„	0.3606	54.52	+0.75	„

1 J. Clarens: Zs. anal. Chem., **57**, 463 (1918)
   M. S. Posternak: C. R., **170**, 932 (1920)

The positive error due to the formation of ammonium nitromolybdate in a dilute nitric acid solution becomes less when the dilution of the solution is made greater.

From the results shown in Table II and Table III it may be concluded that the most suitable concentration of nitric acid lies between 0.7 and 1.3 normal.

3. *Influence of Amount of Ammonium Nitrate*

For analysis 25 ml of the ammonium phosphate solution with various quantities of ammonium nitrate added were treated with 25 ml of the ammonium molybdate solution the normality of the nitric acid being maintained between 0.7 and 1.3. The results are shown in Table IV.

Table IV

No.	Water	NH$_4$NO$_3$ solution		5N–HNO$_3$		Time of standing	(NH$_4$)$_3$PO$_4$·12MoO$_3$	P$_2$O$_5$	Diffce
	ml	ml	Normality	ml	Normality	hour	grm.	%	%
1	/	5	0.4	10	0.8	3	0.3585	54.20	+0.43
2	/	5	0.4	10	0.8	,,	0.3580	54.13	+0.36
3	70	20	0.6	25	0.8	,,	0.3557	53.78	+0.01
4	70	20	0.6	25	0.8	,,	0.3560	53.83	+0.06
5	/	10	0.7	15	1.0	,,	0.3557	53.78	+0.01
6	/	10	0.7	15	1.0	,,	0.3560	53.83	+0.06
7	70	50	1.3	25	0.7	,,	0.3558	53.79	+0.02
8	70	50	1.3	25	0.7	,,	0.3559	53.81	+0.04
9	/	20	1.6	25	1.3	,,	0.3560	53.83	+0.06
10	/	20	1.6	25	1.3	,,	0.3558	53.79	+0.02
11	/	50	2.0	25	1.0	,,	0.3558	53.79	+0.02
12	/	50	2.0	25	1.0	,,	0.3556	53.77	±0.00
13	/	75	2.5	30	1.0	,,	0.3557	53.78	+0.01
14	/	75	2.5	30	1.0	15	0.3557	53.78	+0.01
15	/	115	2.8	40	1.0	3	0.3545	53.60	−0.17
16	/	115	2.8	40	1.0	15	0.3552	53.71	−0.06
17	/	250	3.3	70	0.9	15	0.3483	52.66	−1.11
18	/	250	3.3	70	0.9	15	0.3495	52.84	−0.93

It is thus seen from the table that the normality of ammonium nitrate must be kept between 0.6 and 2.5.

4. *Influence of Amount of Ammonium Molybdate*

Ammonium phosphomolybdate was precipitated from a solution containing 25 ml of the ammonium phosphate solution and 20 ml of the ammonium nitrate solution and also of 5 normal nitric acid. The total volume of the solution was so adjusted that the concentration of both nitric acid and ammonium nitrate was nearly one normal. The solution containing the precipitate after having been heated for about 5 minutes at 50°–60° was left to cool for 3 hours and filtered. The results of the experiments are shown in the following table.

Table V

No.	Water	Amm. Molybdate		$(NH_4)_3PO_4.12MoO_3$	P_2O_5	Diffce
	ml	ml	Mol. ratio to $(NH_4)_2HPO_4$	grm.	%	%
1	20	15	1.3	0.3541	53.54	−0.23
2	20	15	1.3	0.3549	53.66	−0.11
3	18	17	1.5	0.3557	53.78	+0.01
4	18	17	1.5	0.3555	53.75	−0.02
5	15	20	1.8	0.3556	53.77	±0.00
6	15	20	1.8	0.3559	53.81	+0.04
7	10	25	2.2	0.3558	53.79	+0.02
8	10	25	2.2	0.3557	53.78	+0.01
9	/	35	3.1	0.3560	53.83	+0.06
10	/	35	3.1	0.3560	53.83	+0.06
11	/	40	3.5	0.3567	53.93	+0.16
12	/	40	3.5	0.3566	53.91	+0.14
13	/	50	4.4	0.3596	54.37	+0.60
14	/	50	4.4	0.3606	54.52	+0.75

The above table shows that the molar ratio of ammonium molybdate to ammonium phosphate should be maintained at 1.5—3.0. When less is used, it gives a negative error, when more, a positive.

5. Suitable Amounts of the Phosphate to be taken for Analysis

As ammonium phosphomolybdate is 14 times heavier than ammonium phosphate, if we take several decigrams of the latter for analysis of phosphoric acid we have to treat with several grams of ammonium phosphomolybdate. This makes the process very tedious and the result of analysis inaccurate.

To determine what is the most suitable quantity of ammonium phosphate to be taken for analysis several experiments were performed twice as much ammonium molybdate being used as theory requires and the concentration of ammonium nitrate and of nitric acid being always kept at one normal. The precipitate of ammonium phosphomolybdate was heated at 50°—60° for five minutes with the mother liquor and left to stand over night, when the precipitation of phosphoric acid was observed to have taken place completely. The precipitate was ignited at 250°—300° for 20—120 minutes according to its amount. The results are shown thus :——

<p align="center">Table VI</p>

No.	$(NH_4)_2HPO_4$	$(NH_4)_3PO_4.12MoO_3$	P_2O_5	Diffce
	grm.	grm.	%	%
1	0.2500	3.7183	56.22	+2.45
2	0.2500	4.3660	66.01	+12.24
3	0.1250	1.7755	53.69	−0.08
4	0.1250	1.7760	53.73	−0.04
5	0.0625	0.8886	53.74	−0.03
6	0.0625	0.8886	53.74	−0.03
7	0.0250	0.3557	53.78	+0.01
8	0.0250	0.3555	53.75	−0.02
9	0.0100	0.1424	53.83	+0.06
10	0.0100	0.1421	53.71	−0.06

The most favourable quantities of ammonium phosphate which are to be taken for analysis were thus found to lie between 0.01 and 0.13 grams $\{(NH_4)_3PO_4.12MoO_3, 0.14—1.78$ grams$\}$. When more ammonium phosphate was taken than this limit, the value of phosphoric acid was found to

be remarkably high (No. 1—No. 2). This is probably due to the formation of ammonium nitromolybdate.

6. The Best Procedure for Precipitating Ammonium Phosphomolybdate, Composition of Phosphomolybdate and how to Dry it

From what we have so far learned, the best procedure for precipitating phosphoric acid as ammonium phosphomolybdate may be established as follows :—

To a neutral solution containing 0.006—0.07 grams of P_2O_5, ammonium molybdate is added in an excess (about twice the theoretical quantity). The total volume of the solution should then be about 60 ml. Now 20 ml of 5 molar ammonium nitrate solution and of 5 normal nitric acid are added, whereupon the solution becomes distinctly yellow and begins to precipitate ammonium phosphomolybdate. The solution is then heated to $50°$—$60°$ in a water bath for about five minutes with occasional stirring and left to cool for three hours. The precipitate is transferred into a quartz filter crucible and quickly washed with 2% nitric acid[1] under suction till the filtrate ceases to give the reaction of molybdenum. The filter crucible is placed in a large porcelain crucible containing some glass wool, and heated gradually for the first ten minutes and then at $250°$—$300°$ till its weight becomes constant. For the precipitate amounting 0.3—0.5 grams ignition for about 30 minutes is quite sufficient. The ignited filter crucible is then cooled in a desiccator containing phosphorus pentoxide or $CaCl_2.1\tfrac{1}{5}H_2O$ and weighed. The weight of the precipitate multiplied by the theoretical factor $0.0378^{[2]}$ gives the amount of P_2O_5.

The composition of ammonium phosphomolybdate ignited at a temperature of $250°$—$300°$ is $(NH_4)_3PO_4.12MoO_3$. This anhydrous substance is exceedingly hygroscopic and gradually changes into the hydrated form $(NH_4)_3PO_4.12MoO_3.3H_2O$ even in a desiccator containing $CaCl_2.2H_2O$. This

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1 The precipitates of ammonium phosphomolybdate is generally washed with water, ice water, alcohol or 1% nitric acid. With these treatments, however, the precipitate was observed to become partly colloidal and to pass through the filter. It was found safest to wash with 2% nitric acid.

2 Strictly speaking the theoretical factor is 0.03784. But as the thoroughly dried precipitate is very hygroscopic it absorbs some moisture while it is being weighed even though the weighing is done as promptly as possible. Perhaps for this reason the factor 0.0378 gives better results.

hydrated phosphomolybdate is also obtained by thoroughly washing ammonium phosphomolybdate, precipitated from a nitric acid solution, with water or dilute potassium nitrate solution. To prove this, the following experiments were performed :

After washing the yellow precipitate of ammonium phosphomolybdate with water till the filtrate no longer gave the nitric acid reaction, it was dried in the open air for a few days and then placed in a desiccator over $CaCl_2$. $2H_2O$. When its weight became constant it was ignited at $250°—300°$ for 30 minutes and cooled in another desiccator containing P_2O_5 or $CaCl_2.1\frac{1}{5}H_2O$. The ratio of its weights after and before ignition was as follows :

After ignition	Before ignition	Ratio	$\dfrac{(NH_4)_3PO_4.12MoO_3}{(NH_4)_3PO_4.12MoO_3.3H_2O}$
0.2431 grm.	0.2503 grm.	0.9712	0.9720
0.2935 ,,	0.3020 ,,	0.9719	,,
0.3904 ,,	0.4012 ,,	0.9731	,,

The dried phosphomolybdate was next dissolved in dilute ammonia water and nearly neutralized with dilute hydrochloric acid and from this solution phosphoric acid was precipitated as magnesium ammonium phosphate according to the writer's method[1] and determined as magnesium pyrophosphate.

$(NH_4)_3PO_4.12MoO_3.3H_2O$	$Mg_2P_2O_7$	P_2O_5	$\dfrac{P_2O_5 \times 100}{(NH_4)_3PO_4.12MoO_3.3H_2O}$
4.0910 grm.	0.2354 grm.	3.67 %	3.68
3.4834 ,,	0.2001 ,,	3.67 ,,	,,
3.0812 ,,	0.1776 ,,	3.68 ,,	,,

The formula $(NH_4)_3PO_4.12MoO_3.2HNO_3.H_2O$ given by A. Neumann[2] and Z. Shibata[3] to ammonium phosphomolybdate thoroughly washed with water seems to be erroneous.

As was stated before, anhydrous ammonium phosphomolybdate is so hygroscopic that it changes into the trihydrate in a desiccator containing $CaCl_2.2H_2O$. Even when it is kept long over $CaCl_2.1.2H_2O$ or concentrated sulphuric acid (1.84) it gradually absorbs moisture and becomes partially hydrated as is shown by the following experiments :

0.1805 grams of anhydrous ammonium phosphomolybdate, when kept for 50 days over $CaCl_2.1.2H_2O$, became 0.1818 grams. This increase in weight shows the formation of hydrate, $(NH_4)_3PO_4.12MoO_3.2.25H_2O$.

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1 These Memoirs, **12**, 23 (1929)

2 Zs. anal. Chem., **42**, 791 (1903)

3 J. Chem. Soc., Japan, **47**, 242 (1926)

0.2826 grams of the trihydrate lost 0.0062 grams after standing for 50 days over concentrated sulphuric acid (1.84). The loss corresponds to 1.03 H_2O, so that the hydrate newly formed is expressed by $(NH_4)_3PO_4.12MoO_3$ $1.97H_2O$.

When exposed in the open air the trihydrate takes up more moisture and the weight is thus increased about 1.27%.

Trihydrate grm.	Weight increase grm.	%
4.0910	0.0520	1.27
3.4834	0.0441	1.27
3.0812	0.0392	1.27

The weight of moisture corresponds to 1.4 molecules of water and therefore the hydrate thus formed may be expressed by $(NH_4)_3PO_4.12MoO_3.4.4H_2O$.

Ammonium phosphomolybdate washed with dilute nitric acid (about 2.5 normal) and kept for 50 days over $CaCl_2.2H_2O$ was also observed to absorb moisture in the open air. The results of experiments carried out to confirm its composition before and after absorption of moisture, were as follows:

a = weight of the molybdate dried over $CaCl_2.2H_2O$

b = the weight after ignition at 250°—300°

c = the weight after keeping ignited molybdate over $CaCl_2.2H_2O$ for 12 hours

a grm.	b grm.	$\dfrac{b \times 100}{a}$	$\dfrac{(NH_4)_3PO_4.12MoO_3 \times 100}{(NH_4)_3PO_4.12MoO_3.HNO_3.2H_2O}$
0.2556	0.2426	94.91	94.99
0.2654	0.2520	94.95	,,
0.3421	0.3252	95.06	,,

b grm.	c grm.	$\dfrac{b \times 100}{c}$	$\dfrac{(NH_4)_3PO_4.12MoO_3 \times 100}{(NH_4)_3PO_4.12MoO_3.3H_2O}$
0.2426	0.2497	97.16	97.20
0.2520	0.2583	97.56	,,
0.3252	0.3337	97.45	,,

Percentage of phosphoric acid in the molybdate dried over $CaCl_2.2H_2O$ was determined:

Molybdate grm.	$Mg_2P_2O_7$ grm.	P_2O_5 %	$\dfrac{P_2O_5 \times 100}{2(NH_4)_3PO_4.12MoO_3.HNO_3.2H_2O}$

3.9260	0.2210	3.59	3.60
1.9518	0.1095	3.58	,,
2.8413	0.1591	3.57	,,

From the above result there is absolutely no doubt that ammonium phosphomolybdate washed with dilute nitric acid and dried over $CaCl_2.2H_2O$ has the composition represented by the formula $(NH_4)_3PO_3.12MoO_3. HNO_3. 2H_2O$. The formula, $(NH_4)_3PO_4.12MoO_3.2HNO_3.H_2O$ first given by Hundeshagen[1] and hitherto accepted as true must be corrected.

This phosphomolybdate containing a molecule of nitric acid and two molecules of water has also a tendency to absorb water in the open air. The increase in weight thus produced was found by measurement to amount to 2.79% which nearly corresponds to three molecules of water. The formula of the molybdate after absorbtion of water may therefore be expressed by $(NH_4)_3PO_4.12MoO_3.HNO_3.5H_2O$.

As there are many varieties of ammonium phosphomolybdate differing from each other in the degree of hydration, and some of them take up moisture even in an ordinary desiccator, strict attention should be paid to their dehydration before weighing.

It may be mentioned here that the sensibility of the reaction by which phosphoric acid is precipitated as ammonium phosphomolybdate was examined by treating 0.0001 grams of ammonium phosphate (0.000054 grams of P_2O_5) with 10 ml of the ammonium molybdate solution in a solution containing 10 ml of the ammonium nitrate solution and of 5 normal nitric acid together with 20 ml of water. The yellow precipitate began to appear after 30 minutes and became distinct after an hour. Sensibility is, therefore, expressed by 0.000054 (P_2O_5) : 50 or 1 : 1,000,000. Even with 0.00001 grams of ammonium phosphate (0.0000054 grams of P_2O_5) the precipitate of ammonium phosphomolybdate could still be observed after a night's standing, from which sensibility as small as 1 : 10,000,000 is deduced.

7. Influence of Various Substances on the Precipitation of Ammonium Phosphomolybdate

In order to see the influence of various acids and salts on the precipitaion of ammonium phosphomolybdate, 25 ml of the ammonium phosphate solution were treated with 25 ml of the ammonium molybdate solution in the presence of 20 ml of the ammonium nitrate solution and also of 5 normal nitric acid and 10 ml of a solution of the substance to be tested.

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1 Loc. cit.

Table VII

No.	Substance mixed		Time of standing	$(NH_4)_3PO_4.12MoO_3$	P_2O_5	Diffce	Phosphate in filtrate
	Name	grm.		grm.	%	%	
1	HCl	2.6	over night	0.3493	52.81	−0.96	trace
2	„	1.3	„ „	0.3545	53.20	−0.57	trace
3	„	0.9	„ „	0.3559	53.81	+0.04	none
4	„	0.9	„ „	0.3555	53.75	−0.02	„
5	H_2SO_4	1.9	5 hours	0.3627	54.84	+1.07	„
6	„	0.9	5 hours	0.3582	54.15	+0.38	„
7	CH_3COOH	4.2	over night	0.3555	53.75	−0.02	„
8	„	2.1	„ „	0.3556	53.77	±0.00	„
9	Tartaric acid	1.5	„ „	0.3129	47.31	−6.46	distinct
10	Citric acid	1.5	„ „	0.1405	21.24	−32.53	distinct
11	Oxalic acid	1.0	„ „	no precipitation takes place			
12	$NaNO_3$	3.0	„ „	0.3549	53.66	−0.11	none
13	„	3.0	„ „	0.3550	53.67	−0.10	„
14	KNO_3	3.0	„ „	0.3550	53.67	−0.10	„
15	„	2.0	„ „	0.3553	53.72	−0.05	„
16	$Ca(NO_3)_2$	2.0	„ „	0.3553	53.72	−0.05	„
17	„	1.0	„ „	0.3553	53.72	−0.05	„
18	$FeCl_3$	1.0	„ „	0.3539	53.51	−0.26	trace
19	„	0.3	„ „	0.3547	53.63	−0.14	trace

Hydrochloric acid.—The precipitation of ammonium phosphomolybdate from a solution containing more than I gram of hydrogen chloride in every 100 ml is incomplete (No. 1—No. 2).

This incompleteness can easily be removed by adding ammonium molybdate in large excess. But as this treatment becomes the cause of a positive error (see Table V) the precipitate thus formed must be dissolved and reprecipitated once again.

Sulphuric acid.—This acid becomes a cause of positive error which, however, may be got rid of by double precipitation.

Acetic acid.—No influence.

Tartaric acid and citric acid.—Both these acids have the effect of lowering the value of phosphoric acid, perhaps owing to the formation of some soluble complex molybdate whose complexity is nearly of the same degree as that of the phosphomolybdate. Though this hindrance may be removed by using ammonium molybdate in a large excess another hindrance causing positive error is thus introduced, so that, the precipitate must be redissolved in dilute ammonia and again precipitated.

Oxalic acid.—Not only is the precipitation of ammonium phosphomolybdate entirely obstructed but the precipitate once formed is also dissolved by oxalic acid to no small extent. Perhaps the complexity of the compound[1] formed by molybdic acid and oxalic acid is greater than that of the phosphomolybdate complex. This hindrance may also be removed in a manner similar to that used in the case of tartaric acid.

Sodium nitrate, potassium nitrate and calcium nitrate.—These all show almost no bad influence.

Ferric chloride.—This makes the precipitation of phosphomdlybdate somewhat incomplete. This hindrance may be removed in the same way as in the case of tartaric, citric and oxalic acids.

II. Volumetric Method

The following five methods for volumetrically determining phosphoric acid precipitated as ammonium phosphomolybdate are known :

1. The precipitate is dissolved in a known excess of a standard alkali solution and alkali remaining as excess is titrated with an acid.

2. The precipitate is boiled with a concentrated alkali solution and the amount of ammonia evolved is determined volumetrically.

3. The precipitate is treated with a known quantity of a standard alkali solution and after driving off ammonia the excess of alkali left unchanged is titrated.

4. The dark greenish brown or brown solution obtained by reducing ammonium phosphomolybdate is titrated with potassium permanganate.

5. Iodine liberated from potassium iodide by the action of the molybdate is titrated.

By tracing these methods and comparing the results obtained the

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1 A. Rosenheim : Zs. anorg. Chem., **4**, 352 (1893)

A. Rosenheim u. A. Bertheim : Ibid., **34**, 427 (1903)

R. F. Weinland u. K. Zimmermann : Ibid., **108**, 248 (1919)

F. Feigl : Zs. anal. Chem., **74**, 386 (1928)

present writer found the first method to be the best.

H.Pemberton[1] thought that ammonium phosphomolybdate thoroughly washed with water or ammonium nitrate just reacts with alkali according to the equation given below, and the excess of alkali left unchanged may be exactly titrated with an acid, phenolphtalein being used as indicator.

$$2(NH_4)_3PO_4.12MoO_3 + 46NaOH = 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 22H_2O$$
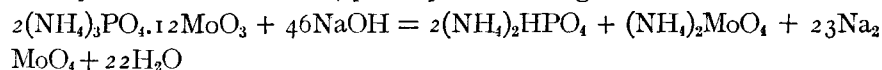
If this view is correct 1ml of $\dfrac{N}{10}$—NaOH used up must correspond to 0.0003089 grams of P_2O_5. The results of the present writer's experiments turned out somewhat different.

Ammonium phosphomolybdate well washed with water and dehydrated over $CaCl_2.2H_2O$ was analysed and the percentage of P_2O_5 {theoretical value calculated for $(NH_4)_3PO_4.12MoO_3.3H_2O$, 3.68 %} was calculated.

Amm.phosphomolybdate grm.($=a$)	$\dfrac{N}{10}$-NaOH ml($=b$)	P_2O_5 $\% \left(=\dfrac{b \times 0.0003089 \times 100}{a}\right) \%$	Diffce %
0.1286	15.58	3.74	0.06
0.1167	14.14	3.74	0.06
0.1846	22.39	3.75	0.07
0.2822	34.19	3.74	0.06
0.1464	17.89	3.76	0.08

The value of phosphoric acid is thus found constant but always about 0.06 % higher. The main cause of this constant error may be attributed to the fact that the end point indicated by phenolphtalein in the last titration of alkali is not what we really want to determine. For the P_H value of the solution containing diammonium hydrogen phosphate, ammonium molybdate and sodium molybdate exactly in the proportion of $2(NH_4)_2HPO_4$, $(NH_4)_2MoO_4$ and $23Na_2MoO_4$ was found to be 6.8 — 7.2 while that of the solution in which red phenolphtalein is decolourized is 8.3. Use of other indicators such as neutral red, bromthymol blue, bromcresol purple and cresol red, however, was found less reccommendable, for the end point shown by them was not quite so sharp as to give a constant result. After many trials it was finally found that the method giving the best and most constant result is to use phenolphtalein in the titration of alkali as Pemberton did and to multiply the number of mls of $\dfrac{N}{10}$-NaOH found by the factor 0.0003030 instead of the theoretical number 0.0003089, as is shown in the experiments described below.

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1 J. Amer. Chem. Soc., **15**, 382 (1893); **16**, 378 (1894)

Experimental

Procedure.—Ammonium phosphomolybdate prepared from a definite quantity of ammonium phosphate according to the manner described in the part dealing with gravimetric method is transferred to a filter by decantation and washed with 1 % potassium nitrate solution till the filtrate reacts neutral to litmus paper. The filter containing the precipitate is now put in a beaker into which an excess of $\frac{N}{10}$-NaOH solution is then poured, the beaker being shaken all the time. When the precipitate of ammonium phosphomolybdate is completely dissolved the excess of alkali is titrated with $\frac{N}{10}$-HCl, phenolphtalein being used as indicator. Though the presence of filter paper does not interfere with the accuracy of titration still it will be found convenient to select as small a filter as possible.

Experiment I

Ammonium phosphomolybdate was precipitated from a solution containing 0.0250 grams of ammonium phosphate, 25 ml of the ammonium molybdate solution, 20 ml of the ammonium nitrate solution, 20 ml of 5 normal nitric acid and 35 ml of water. The results of titration are as follows :—

$\frac{N}{10}$ — NaOH	Factor	P_2O_5	Diffce
ml		%	%
	0.0002842	50.50	−3.27
	0.0002960	52.59	−1.18
44.42	0.0003089	54.89	+1.12
	0.0003030	53.84	+0.07
	0.0002842	50.42	−3.35
	0.0002960	52.52	−1.25
44.36	0.0003089	54.81	+1.04
	0.0003030	53.76	−0.01

$\dfrac{N}{10}$ — NaOH	Factor	P_2O_5	Diffce
	0.0002842	50.50	−3.27
	0.0002960	52.59	−1.18
44.42	0.0003089	54.89	+1.12
	0.0003030	53.84	+0.07
	0.0002842	50.53	−3.24
	0.0002960	52.63	−1.14
44.45	0.0003089	54.92	+1.15
	0.0003030	53.87	+0.10
	0.0002842	50.41	−3.36
	0.0002960	52.50	−1.27
44.34	0.0003089	54.81	+1.04
	0.0003030	53.74	−0.03

If the precipitate of ammonium phosphomolybdate after thorough washing is of the composition $(NH_4)_3PO_4.12MoO_3.2HNO_3.H_2O$ or $(NH_4)_3 PO_4.12MoO_3.HNO_3.2H_2O$ the factors by which to multiply the number of ml of $\dfrac{N}{10}$—NaOH must be 0.0002842 and 0.0002960 respectively. The fact that both factors fail to give satisfactory results, as is seen in the table, may be taken as another evidence against such compositions.

Experiment 2

To prepare ammonium phosphomolybdate 0.0100 grams of ammonium phosphate, 10 ml of the ammonium molybdate solution, 10 ml of the ammonium nitrate solution and also of 5 normal nitric acid and 20 ml of water were employed. The results of titration are tabulated thus :

$\dfrac{N}{10}$ — NaOH	Factor	P_2O_5	Diffce
ml		%	%
17.77	0.0003030	53.84	+0.07

$\frac{N}{10}$ —NaOH	Factor	P_2O_5	Diffce
17.75	,,	53.78	+0.01
17.75	,,	53.78	+0.01
17.77	,,	53.84	+0.07

Experiment 3

To learn how far this method is applicable for the determination of a minute quantity of phosphoric acid, ammonium phosphomolybdate prepared from 0.0050 grams of ammonium phosphate was analysed with the following results :—

$\frac{N}{10}$ —NaOH	Factor	P_2O_5	Diffce
ml		%	%
8.90	0.0003030	53.93	+0.16
9.85	,,	53.63	−0.14
9.85	,,	53.63	−0.14
8.88	,,	53.81	+0.04

Experiment 4

With the aid of a micro-burette giving readings of 0.0001 ml, ammonium phosphomolybdate formed from 0.0025 grams of ammonium phosphate was analysed.

$\frac{N}{10}$ —NaOH	Factor	P_2O_5	Diffce
ml		%	%
4.502	0.0003030	54.56	+0.79
4.432	,,	53.69	−0.08
4.485	,,	54.36	+0.59
4.455	,,	53.99	+0.22

Summary

1. In order to ascertain the conditions essential for the precipitation of phosphoric acid quantitatively as ammonium phosphomolybdate, the influence on the reaction of

    a) Temperature
    b) Concentration of nitric acid
    c) Amount of ammonium nitrate
    d) Amount of ammonium molybdate
    e) Quantity of the phosphate taken for analysis were examined.

2. The composition of ammonium phosphomolybdate after thorough washing was determined, and the behaviour of anhydrous ammonium phosphomolybdate both in the open air and in desiccators was minutely examined. As a consequence of this, all the points concerning its dehydration and its cooling after ignition were made clear.

3. The sensibility of the reaction in which phosphoric acid is precipitated as ammonium phosphomolybdate was calculated.

4. The influence of various acids and salts on the precipitation of ammonium phosphomolybdate was closely studied.

5. As the result of the investigation the method of determining phosphoric acid as ammonium phosphomolybdate was greatly improved, making it, for the first time, practically applicable.

6. The volumetric method hitherto proposed for determining phosphoric acid precipitated as ammonium phosphomolybdate was carefully traced, and an improved method giving an accurate result not inferior to the gravimetric method was also established.