Quantitative Analysis of Phosphoric Acid, Part II. New Gravimetric and Volumetric Methods

By

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The method of determining manganese as its pyrophosphate was studied by W. Gibbs[1] and by F. A. Gooch and Martha Austin[2], and it is now practically used for analysis. The reaction of precipitating phosphoric acid as manganous ammonium phosphate, however, has long been regarded as unapplicable for the determination of phosphoric acid, because manganese undergoes spontaneous oxidation in an alkaline solution and is partly precipitated as brown manganous acid. According to the present writer's experiment the formation of manganous acid can never be prevented by the addition of an excess of ammonium chloride. In one experiment the molar ratio of ammonium chloride to manganous chloride was made as high as 400, and still it was not effective; the manganous acid was observed to begin its precipitation after about two hours.

After having made several trials the present writer finally succeeded in finding out that the formation of manganous acid could entirely be prevented by the addition of a small quantity of hydroxylamine, and as a consequence the precipitation of phosphoric acid as manganous ammonium phosphate could be utilised as a new gravimetric method for its determination. It was also found that the manganese in manganous ammonium phosphate can be exactly titrated with potassium permanganate, and this process may be employed as an excellent volumetric method for analysis of phosphoric acid.

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1   ZS. anal. Chem., **7**, 101 (1868).

2   ZS. anorg. Chem., **18**, 339 (1893); ZS. anal. Chem., **38**, 784 (1900).

Experimental

I. Gravimetric Method

In the experiments described below the following solutions were employed :

(a) Diammonium phosphate solution containing 10.0000 grams of Kahlbaum's ammonium phosphate " Zur Analyse mit Garantieshein " in one litre.

(b) A molar manganous chloride solution prepared by dissolving 198 grams of the crystalline salt in one litre.

(c) Ammonium chloride solution prepared by dissolving 268 grams of the chloride in water was made alkaline by the addition of a small quantity of conc. ammonia and diluted to one litre. After standing for 2 or 3 days it was filtered and acidified with hydrochloric acid till its reaction to methyl red was acid. This solution is nearly 5 molar and its P_H is about 5.

(d) 10 % hydroxylamine hydrochloride solution.

(e) The solution used for washing the precipitate was prepared as follows : to 500 ml of 1 molar ammonium chloride solution, 1 ml of the hydroxylamine solution above stated was added and the mixture was made alkaline with ammonia till phenolphthalein added to it beforehand, became distinctly red.

(f) Ammonia waters of 20 % and 1 %.

Procedure for precipitating manganous ammonium phosphate :—

To the phosphate solution, manganous chloride and ammonium chloride are added in an excess together with a small quantity of hydroxylamine hydrochloride and well stirred. The acidity of the solution should be such that the precipitate of manganous ammonium phosphate is produced only in a small quantity. If, therefore, the precipitate is produced in a large quantity, it must be redissolved in hydrochloric acid. Now the solution in which either none or a small quantity of the precipitate is suspended is heated nearly to boiling point, and dilute ammonia water is added drop by drop, the solution being well agitated all the while, when a crystalline precipitate with silky lustre is produced. Some conc. ammonia water is now added to make the solution strongly alkaline and the whole is left to cool for about 2 hours and filtered. The precipitate is washed with the washing solution above stated and then with 1 % ammonia water, and finally dried, ignited and weighed as usual. It must be remembered that if the reaction of precipitating manganous ammonium phosphate is conducted at ordinary temperature the precipitate takes a

colloidal form and contains no small quantity of $Mn_3(PO_4)_2$. If this normal phosphate is once formed in a solution containing manganous chloride in an excess it can never be transformed into manganous ammonium phosphate by mere heating. If, however, the manganese present is just equivalent to the phosphoric acid or less, the transformation can be brought about completely by heating, and this may be counted as another reason why phosphoric acid could not hitherto be determined as manganous pyrophosphate.

1. Relative Amounts of Manganous Chloride and Ammonium Chloride

To find out the most suitable amounts of manganous chloride and ammonium chloride which should be taken for precipitation of manganous ammonium phosphate and also to learn the influence of dilution of the sample solution, a series of experiments were carried out the results of which are shown in Table I.

Table I

For each determination 25 ml of the ammonium phosphate solution and 0.3 ml of the hydroxylamine hydrochloride solution were taken.

| No. | Water added ml | MnCl$_2$ | | | NH$_4$Cl | | | Mn$_2$P$_2$O$_7$ grm. | P$_2$O$_5$ (53.77%) | |
		ml	grm.	Mol. ratio to (NH$_4$)$_2$HPO$_4$	ml	grm.	Mol. ratio to MnCl$_2$		%	Diff.
1	75	5	0.629	2.6	25	6.9	25	0.2750	55.04	+1.27
2	50	,,	,,	,,	50	13.4	50	0.2699	54.02	+0.25
3	25	,,	,,	,,	75	19.6	75	0.2686	53.76	−0.01
4	10	,,	,,	,,	90	24.1	90	0.2686	53.76	−0.01
5	—	,,	,,	,,	100	26.8	100	0.2687	53.78	+0.01
6	—	,,	,,	,,	125	33.5	125	0.2688	53.80	+0.03
7	—	,,	,,	,,	150	40.2	150	0.2688	53.80	+0.03
8	—	,,	,,	,,	200	53.6	200	0.2682	53.69	−0.08
9	—	3	0.378	1.6	60	16.1	100	0.2686	53.76	−0.01
10	—	5	0.629	2.6	100	26.8	100	0.2687	53.78	+0.01
11	—	10	1.259	5.3	200	53.6	100	0.2687	53.78	+0.01
12	—	20	2.518	10.6	400	107.2	100	0.2687	53.78	+0.01
13	100	5	0.629	2.6	100	26.8	100	0.2688	53.80	+0.03
14	200	5	0.629	2.6	100	26.8	100	0.2692	53.88	+0.11
15	300	5	0.629	2.6	100	26.8	100	0.2710	54.24	+0.47

From the above results we can draw the following conclusions :

1. Complete precipitation of phosphoric acid takes place when the molar ratio of ammonium chloride to manganous chloride lies between 75 and 125. Deficiency of ammonium chloride becomes a cause of positive error, phosphoric acid being partly precipitated in the form of normal manganous phosphate, while too great excess of this reagent produces negative error, as it tends to dissolve manganous ammonium phosphate (No. 1—No. 8).

2. The amount of manganous chloride does not much effect the exactness of analysis if it be present in an excess as is seen in No. 9—No. 12.

3. Analysis with too dilute solution is to be avoided, because from such solutions the value of phosphoric acid is often found too high owing to the precipitation of normal manganous phosphate (No. 13—No. 15).

2. Influence of Various Salts on the Analysis

The influence of various salts such as sodium chloride, potassium chloride, sodium sulphate, sodium nitrate, sodium acetate, ammonium citrate, ammonium tartrate and ammonium oxalate was examined. In each experiment, 25 ml of the phosphate solution were mixed with a definite quantity of the salt and this solution was treated with 5 ml of manganous chloride, 100 ml of ammonium chloride and 0.3 ml of hydroxylamine solution in the manner described before. The results are shown in Table II.

Table II

No.	Salt mixed		Time of standing	$Mn_2P_2O_7$		P_2O_5	Diff.	
	Name	grm.	hours	grm.	colour	%	%	
1	NaCl	3.0	2	0.2687	pale rose	53.78	+0.01	
2	KCl	2.0	2	0.2688	„	53.80	+0.03	
3	Na_2SO_4	2.0	2	0.2688	„	53.80	+0.03	
4	$NaNO_3$	3.0	2	0.2688	„	53.80	+0.03	
5	$C_2H_3O_2Na$	2.0	20	0.2686	„	53.76	−0.01	
6	Am. citrate	5.0	2	0.2511	„	50.26	−3.51	
7	„	2.5	2	0.2630	„	52.70	−1.07	
8	Am. tartrate	5.0	2	0.2806	grayish brown	56.16	+2.39	Phosphate was detected in the filtrate
9	„	2.5	3	0.2681	pale rose	53.66	−0.11	„
10	„	5.0	3	0.2676	„	53.56	−0.21	„
11	Am. oxalate	1.0	2	0.2717	„	54.32	+0.55	Phosphate was detected in the filtrate and in $Mn_2P_2O_7$
12	„	1.0	20	0.2797	„	55.98	+2.21	No phosphate in the filtrate
13	„		3	0.2687	„	53.78	+0.01	

NaCl, KCl, Na_2SO_4, $NaNO_3$.——These salts have no influence as is seen in No. 1—No. 4.

$C_2H_3O_2Na$.——This seems to retard the precipitation of manganous ammonium phosphate, so that the precipitate should be left to stand for a long time before filtration (No. 5).

Ammonium citrate.——This seems mainly to dissolve manganous ammonium phosphate (No. 6—No. 7).

Ammonium tartrate.——The action of this salt is twofold: tartrate is occluded (perhaps as manganous tartrate) in the precipitate of manganous ammonium phosphate so as to make the value of phosphoric acid very high (No. 8) and at the same time it has the effect of making the precipitation incomplete (No. 9 and No. 10). When therefore ammonium tartrate is added after the precipitation of manganous ammonium phosphate is completed, the value of phosphoric acid is found remarkably low.

Ammonium oxalate.——It retards the precipitation of manganous ammonium phosphate and forms some other phosphate which does not change into pyrophosphate. The former hindrance may be got rid of by long standing, but at the same time the latter hindrance becomes greater (No. 11—No. 12). The two hindrances may only be cleared away by means of double precipitation (No. 13).

3. *Influence of Ammonium Molybdate*

To examine the influence of ammonium molybdate on this method of phosphoric acid determination and to find out a convenient process by which its bad effect, if any, may be well prevented was a very interesting work for the present writer.

In an analysis conducted preliminarily with a phosphate solution containing 1.20 grams of ammonium molybdate, the precipitate was found to contain a considerable quantity of $MnMoO_4$. Though manganous molybdate dissolves in concentrated ammonia its complete separation from manganous ammonium phosphate could not be effected by merely washing with ammonia.

So the precipitation of the phosphate from a solution previously made strongly ammoniacal was tried in the hope that manganous molybdate would not separate out together with it from such a solution. To 25 ml of the phosphate solution made strongly ammoniacal 100 ml of the ammonium chloride solution, 2.4 grams of ammonium molybdate and 0.3 ml of hydroxylamine solution were added, and after heating the solutin

nearly to boiling point about 1 ml of the manganous chloride solution was added to it and well agitated, whereupon the precipitate formed became crystalline. Now a second 1 ml of manganous chloride solution was then added and agitated, and this process was repeated several times till the total quantity of manganous chloride attained the required excess. Sometimes manganous ammonium phosphate begins to become yellowish coloured. As this shows the formation of manganous molybdate, concentrated ammonia water must, in such a case, be again poured in to prevent its precipitation. Now the precipitate of manganous ammonium phosphate was filtered after about 2 hours' standing and treated as usual. Though all this was done with the utmost care, the precipitate was always faintly yellowish and the value of phosphoric acid was found 0.23–0.35 % higher.

It was therefore thought necessary to make double precipitation and for this purpose manganous ammonium phosphate was dissolved in dilute hydrochloric acid, and to this solution 2 ml of manganous chloride, 100 ml of ammonium chloride and 0.3 ml of hydroxylamine solution were again added and from this solution manganous ammonium phosphate was precipitated for the second time. The result was now quite satisfactory.

II. Volumetric Method

Titration of manganese with potassium permanganate according to the reaction

$$3Mn^{..} + 2MnO_4 + 2H_2O = 5MnO_2 + 4H^{.}$$
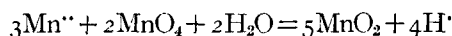
is now practically used for analysis as Guyard-Volhard's or Volhard-Wolff's method. In order to precipitate manganese completely as MnO_2, zinc sulphate or zinc oxide has generally been added to manganese solution. Recently B. Reinitzer and P. Conrath[1] stated that sodium acetate may replace the zinc salt or oxide with far better results, precipitating MnO_2 quicker and more completely.

Now it occurred to the present writer that if the above method could be applied for determining manganese in manganous ammonium phosphate it might conveniently be utilised as an indirect method for analysis of phosphoric acid. The result of experiments carried out with the purpose of confirming this view showed that phosphoric acid can thus be determined rapidly with an average error of ±0.1 % even when the acid is present in the small quantity of a few milligrams, as is described below.

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1 ZS. anal. Chem., **68**, 130 (1926

Procedure

Manganous ammonium phosphate produced from a known quantity of ammonium phosphate is dissolved in water acidified with 2 or 3 drops of sulphuric acid and after adding a suitable quantity of sodium acetate $\left(\text{about 2 grams for each 10 ml of }\dfrac{N}{10}\text{—KMnO}_4\text{ required}\right)$ diluted with 200—400 ml of water. The solution is now heated to $80°$—$90°$ and at this temperature it is titrated with $\dfrac{N}{10}$—KMnO$_4$. In the neighborhood of the end point the beaker containing the liquid is removed for a short time from the sand bath in order to make manganese dioxide subside, and the colour of the liquid is observed. At the end point the colour of the solution becomes permanent for 2 or 3 minutes.

Experiment 1

Manganous ammonium phosphate used for analysis was prepared from 0.0625 grams of (NH$_4$)$_2$HPO$_4$, 1 ml of MnCl$_2$ solution, 25 ml of NH$_4$Cl solution, 0.3 ml of NH$_2$OH · HCl solution and 45 ml of water.

Water added	Sod. acetate	$\dfrac{N}{10}$ —KMnO$_4$		P$_2$O$_5$		Diff.
ml	grm.	calc. ml	found ml	grm.	%	%
350	4.0	15.77	15.75	0.03357	53.71	−0.06
350	4.0	15.77	15.80	0.03367	53.88	+0.11
350	4.0	15.77	15.80	0.03367	53.88	+0.11

Experiment 2

The manganous ammonium phosphate used for this analysis was prepared from 0.03125 grams of (NH$_4$)$_2$HPO$_4$, 0.5 ml of MnCl$_2$ solution, 15 ml of NH$_4$Cl solution, 0.2 ml of NH$_2$OH · HCl solution and 35 ml of water.

Water added	Sod. acetate	$\dfrac{N}{10}$ —KMnO$_4$		P$_2$O$_5$		Diff.
ml	grm.	calc. ml	found ml	grm.	%	%
400	2.0	7.88	7.88	0.01679	53.77	±0.00
300	2.0	7.88	7.86	0.01675	53.60	−0.17
200	2.0	7.88	7.90	0.01684	53.88	+0.11

Experiment 3

The manganous ammonium phosphate used for analysis was prepared from 0.015625 grams of $(NH_4)_2HPO_4$, 0.3 ml $MnCl_2$ solution, 10 ml of NH_4Cl solution, 0.1 ml of $NH_2OH \cdot HCl$ solution and 30 ml of water. In this and the next experiment a micro-burette was used for titration.

Water added	Sod. acetate	$\frac{N}{10}$ —KMnO₄		P₂O₅		Diff.
ml	grm.	calc. ml	found ml	grm.	%	%
200	1.0	3.942	3.950	0.008418	53.88	+0.11
300	1.0	3.942	3.950	0.008418	53.88	+0.11
300	1.0	3.942	3.945	0.008408	53.81	+0.04

Experiment 4

The manganous ammonium phosphate used for analysis was formed from 0.0078125 grams of $(NH_4)_2HPO_4$, 0.2 ml of $MnCl_2$ solution, 5 ml of NH_4Cl solution, 0.1 ml of $NH_2OH \cdot HCl$ solution and 27 ml of water.

Water added	Scd. acetate	$\frac{N}{10}$ —KMnO₄		P₂O₅		Diff.
ml	grm.	calc. ml	found ml	grm.	%	%
200	1.0	1.971	1.975	0.004209	53.88	+0.11
200	1.0	1.971	1.968	0.004194	53.69	−0.08
200	1.0	1.971	1.968	0.004194	53.69	−0.08

Summary

1. Quantitative precipitation of phosphoric acid as $MnNH_4PO_4$ was made possible by the addition of a small quantity of hydroxylamine hydrochloride, and as a conseqence, new methods for determining phosphoric acid both gravimetrically and volumetrically were established.

2. The appropriate quantities of manganous chloride and ammonium chloride to be taken for the precipitation of phosphoric acid were determined.

3. The influence of various salts such as sodium chloride, potassium

chloride, sodium sulphate, sodium nitrate, sodium acetate, ammonium citrate, ammonium tartrate and ammonium oxalate upon the precipitation were studied. The bad effect of ammonium molybdate and how to prevent it were carefully examined.

4. It was confirmed that the volumetric determination of manganese in manganous ammonium phosphate affords an excellent means for estimating minute quantities of phosphoric acid rapidly.