

# Quantitative Analysis of Phosphoric Acid, Part III. Determination as Zinc Ammonium Phosphate

By

Masayoshi Ishibashi

(Received October 30, 1928)

---

Since the method of precipitating zinc as zinc ammonium phosphate and determining it as the pyrophosphate was first proposed by H. Tamm<sup>1</sup> the investigation into this method has been undertaken by many authors<sup>2</sup>. As to the application of the reaction for determining phosphoric acid no investigation has yet been published, but judging from the analogy of zinc with magnesium and manganese such an application may be expected to be quite possible.

As the results of experiments carried out by the present writer it was made clear that the reaction of precipitating phosphoric acid as zinc ammonium phosphate can also be applied for determination of the acid, if strict care be paid regarding the acidity of the solution. The writer also tried to find some means by which zinc ammonium phosphate can be used for volumetric analysis of phosphoric acid, and found that the method<sup>3</sup> of estimating zinc in zinc ammonium phosphate indirectly by changing it first into the oxalate and titrating oxalic acid combined with

---

<sup>1</sup> Chem. News **24**, 148 (1871); Zs. anal. Chem., **13**, 320 (1874).

<sup>2</sup> G. Lösekann u. T. Meyer: Chem. Ztg., **10**, 729 (1886); Zs. anal. Chem., **26**, 78 (1887); T. Meyer u. M. Austin: Zs. anorg. Chem., **22**, 212 (1900); H. D. Dakin: Zs. anal. Chem., **39**, 273 (1900); K. Voigt: Ibid., **49**, 613 (1910); P. Artmann: Ibid., **54**, 89 (1915); **62**, 8 (1923); D. Balarew: Ibid., **60**, 442 (1921).

<sup>3</sup> H. L. Ward: Amer. Jour. Sci., [4], **33**, 334; Gooch: Methods in Chemical Analysis p. 187 (1912).

zinc with potassium permanganate is applicable here and gives a tolerably good result, though the way may appear at first sight too roundabout.

## Experimental

The following solutions were used in the experiments described below.

Phosphate solution.—10.0000 grams of Kahlbaum's ammonium phosphate "Zur Analyse mit Garantieschein" were dissolved in 1 litre.

Zinc chloride solution (about 1 molar).—136.3 grams of the salt were dissolved in water and diluted to 1 litre; white turbidity, if produced, was dissolved in dil. hydrochloric acid.

Ammonium chloride solution (about 5 molar).—A conc. solution containing 268 grams of the salt after having been made ammoniacal was left to stand for 2 or 3 days and then filtered. The filtrate was now made slightly acidic with hydrochloric acid and diluted to 1 litre.

Ammonia water.—About 2.5 % solution.

### I. Gravimetric Method

After having conducted the experiment in many different ways the procedure described below was found to give the most satisfactory result in precipitating phosphoric acid as zinc ammonium phosphate. The important points are (1) the temperature at which precipitation takes place, (2) the acidity of the solution containing phosphoric acid, zinc chloride and ammonium chloride from which zinc ammonium phosphate is to be precipitated by addition of ammonia, (3) a constant agitation of the solution while precipitation is going on and (4) the acidity of the solution at the time when the precipitation is just completed.

Procedure.—To the phosphate solution an excess of zinc chloride and a still greater excess of ammonium chloride are added, and the acidity of this mixture is so regulated that either none or only a small quantity of zinc ammonium phosphate separates out at this point. The solution is then heated nearly to boiling point and well agitated till the amorphous precipitate completely changes into crystalline. Now ammonia water is slowly added while the mixture is well agitated, care being taken not to add the second drop before the precipitate formed by the first drop has become crystalline and also not to add more than to impart a slight yellow colour to p-nitrophenol previously added. As zinc ammonium phosphate is soluble both in acid and alkali it is of the utmost importance to restrict the acidity of the solution accurately. The  $P_{H}$  value of the

solution in which zinc ammonium phosphate is most insoluble was found to lie between 5—6.5 and such a point can be indicated by p-nitrophenol ( $P_H=5-7.9$ ; ammonia is added till a slightly yellow colour is produced), bromocresolpurple ( $P_H=5.2-6.8$ ; ammonia is added till an intermediate yellowish violet colour is produced) or neutral red ( $P_H=6.8-8.0$ ; ammonia is added till a slightly red colour, not a yellowish red colour, is produced). On cooling, the precipitate is filtered and washed with cold pure water, dried and ignited. For ignition a porcelain crucible is preferred, because zinc pyrophosphate often becomes fused when ignited in a platinum crucible.

It may be mentioned that the melting point of zinc pyrophosphate was determined to be  $962^\circ$  by the present writer.

### ***Relation of Quantities of Phosphoric Acid, Zinc Chloride and Ammonium Chloride to each other***

In order to find out the suitable quantities of zinc chloride and ammonium chloride which should be taken for precipitation of zinc ammonium phosphate and also to learn the most suitable molecular relation between these two precipitants, a series of experiments were carried out, the results of which are shown in Table I.

It was shown in the preliminary experiment that the amount of zinc chloride does not much effect the accuracy of the analysis if other conditions are favourable. In the table this relation is shown quantitatively (No. 22—No. 26). All the other experiments from No. 1 to No. 21 were, therefore, carried out always with the molar ratio of zinc chloride to the phosphate maintained at 2.6.

The molar ratio of ammonium chloride to zinc chloride may be selected in a wide range, that is, between 50 and 100 without much effecting the result, as is seen in No. 1—No. 21. But the concentration of ammonium chloride has a more important bearing on the accuracy of the analysis. When the concentration is less than 2.0 Normal the value of phosphoric acid is found higher owing to the precipitation of normal zinc phosphate,  $Zn_3(PO_4)_2$ , whose presence in zinc pyrophosphate was proved by Tollen's reaction (No. 6—No. 8). If on the contrary its concentration is greater than 3.6 Normal it dissolves some zinc ammonium phosphate and consequently the result comes out somewhat lower (No. 13—No. 21).

Table I

For each experiment 25 ml of  $(\text{NH}_4)_2\text{HPO}_4$  solution were taken.

No.	Water added		ZnCl <sub>2</sub>		NH <sub>4</sub> Cl			Time of standing hrs	Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> gram.	P <sub>2</sub> O <sub>5</sub> %	Diff. %	Phos- phate in filtrate
	ml	ml	gram.	Mol. ratio to $(\text{NH}_4)_2\text{HPO}_4$	ml	gram.	Mol. ratio to ZnCl <sub>2</sub>					
1	—	5	0.681	2.6	30	7.8	30	15	0.2879	53.68	-0.09	trace
2	100	"	"	"	"	"	"	"	0.3402	63.43	+9.66	none
3	—	"	"	"	50	13.4	50	"	0.2882	53.73	-0.04	none
4	—	"	"	"	"	"	"	"	0.2881	53.71	-0.06	none
5	20	"	"	"	"	"	"	10	0.2882	53.73	-0.04	none
6	50	"	"	"	"	"	"	10	0.2885	53.79	+0.02	none
7	100	"	"	"	"	"	"	10	0.2893	53.99	+0.22	none
8	200	"	"	"	"	"	"	10	0.2902	54.11	+0.34	none
9	—	"	"	"	60	14.1	60	15	0.2881	53.71	-0.06	none
10	30	"	"	"	"	"	"	10	0.2884	53.77	±0.00	none
11	50	"	"	"	"	"	"	10	0.2887	53.83	+0.06	none
12	100	"	"	"	"	"	"	10	0.2895	53.98	+0.21	none
13	—	"	"	"	75	19.6	75	15	0.2880	53.70	-0.07	none
14	50	"	"	"	"	"	"	15	0.2880	53.70	-0.07	none
15	—	"	"	"	100	26.8	100	15	0.2878	53.66	-0.11	trace
16	—	"	"	"	"	"	"	50	0.2877	53.64	-0.13	trace
17	50	"	"	"	"	"	"	20	0.2880	53.70	-0.07	trace
18	—	"	"	"	150	40.2	150	50	0.2874	53.59	-0.18	trace
19	100	"	"	"	"	"	"	50	0.2880	53.70	-0.07	trace
20	—	"	"	"	200	53.6	200	50	0.2860	53.43	-0.34	little
21	100	"	"	"	"	"	"	50	0.2881	53.71	-0.06	trace
22	—	3	0.409	1.6	30	7.8	50	15	0.2882	53.73	-0.04	none
23	—	5	0.681	2.6	50	13.4	50	15	0.2882	53.73	-0.04	none
24	—	10	1.363	5.3	100	26.8	50	15	0.2883	53.75	-0.02	none
25	—	20	2.726	10.6	200	53.6	50	15	0.2881	53.71	-0.06	none
26	100	20	2.726	10.6	200	53.6	50	15	0.2881	53.71	-0.06	none

**Influence of various Salts present**

The influence exerted by sodium chloride, potassium chloride, sodium sulphate, sodium nitrate, sodium acetate, ammonium tartrate, ammonium citrate and ammonium molybdate were examined and the results summarized in the following table were obtained.

Table II  
For each experiment 25 ml of  $(\text{NH}_4)_2\text{HPO}_4$  solution were taken.

No.	Salt mixed		$\text{Zn}_2\text{P}_2\text{O}_7$		$\text{P}_2\text{O}_5$	Diff.	Phosphate in filtrate
	Name	gram.	gram.	colour	%	%	
1	NaCl	3.0	0.2885	white	53.79	+0.02	none
2	$\text{NaNO}_3$	3.0	0.2884	white	53.77	$\pm 0.00$	none
3	$\text{Na}_2\text{SO}_4$	1.0	0.2884	white	53.77	$\pm 0.00$	none
4	"	2.0	0.2887	white	53.83	+0.06	none
5	$\text{C}_2\text{H}_3\text{O}_2\text{Na}$	4.0	0.2880	white	53.70	-0.07	trace
6	"	2.0	0.2883	white	53.75	-0.02	trace
7	KCl	4.0	0.3045	white	56.78	+3.01	none
8	"	2.0	0.2967	white	55.32	+1.55	none
9	Am. tartrate	2.5	0.2850	grayish brack	53.88	+0.11	none
10	Am. citrate	2.5	0.2765	grayish brack	51.55	-2.22	none
11	Am. molybdate	2.4	0.2956	white	55.11	+1.34	little
12	"	1.2	0.2942	white	54.85	+1.08	little

$\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ .—No influence (No. 1—No. 4).

$\text{C}_2\text{H}_3\text{O}_2\text{Na}$ .—It makes the precipitation of phosphoric acid somewhat incomplete, trace of it being left in the filtrate (No. 5—No. 6).

KCl.—Some zinc potassium phosphate is formed together with zinc ammonium phosphate, so that the precipitate fuses more easily when ignited, and the ignited residue shows Tollen's reaction. This bad effect can be got rid of to a certain degree by double precipitation (No. 7—No. 8).

Ammonium tartrate.—This is adsorbed in the precipitate of zinc ammonium phosphate, but can be easily taken off by double precipitation.

Ammonium citrate.—Its effect is rather curious. Though it does not interfere with the precipitation of zinc ammonium phosphate, it causes a

remarkably great negative error (No. 10). By repeating precipitation twice this bad effect may also be avoided.

Ammonium molybdate.—Accurate determination of phosphoric acid in the presence of molybdate is impossible, as the bad effect of the latter can not be prevented in any of the usual ways.

## II. Volumetric Method

Indirect determination of phosphoric acid by titrating zinc in zinc ammonium phosphate was attempted. Of all the volumetric methods for determining zinc hitherto known, only H. L. Ward's oxalate method<sup>1</sup> was found to give fairly good results, though it may be felt too indirect to be applied for the determination of phosphoric acid.

Experiment 1.—Zinc ammonium phosphate was precipitated from a solution consisting of 25 ml of ammonium phosphate solution (0.2500 grm. of  $(\text{NH}_4)_2\text{HPO}_4$ ), 5 ml of zinc chloride solution and 50 ml of ammonium chloride solution according to the procedure described before. The precipitate was filtered after a night's standing and well washed with cold water, and then converted into zinc oxalate by treating it with oxalic acid. After adding some sodium acetate and glacial acetic acid the solution in which zinc oxalate is precipitated was heated for a few minutes nearly to boiling point and left to stand for about 3 hours. Zinc oxalate was now filtered with a glass filter, washed several times with a small quantity of water and dissolved in hot dil. sulphuric acid. The sulphuric acid solution thus obtained was warmed in a water bath and titrated with  $\frac{N}{10}$ - $\text{KMnO}_4$ .

COOH   COOH	CH <sub>3</sub> COOH (glacial)	$\frac{N}{10}$ - $\text{KMnO}_4$ (ml)		P <sub>2</sub> O <sub>5</sub>	Diff.
		calc.	found		
grm.	ml			%	%
2.0	60	37.84	37.85	53.76	-0.01
3.0	100	37.84	37.82	53.73	-0.04
3.0	100	37.84	37.84	53.77	±0.00

Experiment 2.—25 ml of the solution containing 0.1250 grm. of ammonium phosphate, 3 ml of zinc chloride solution and 30 ml of ammonium chloride solution were used for precipitation of zinc ammonium phosphate.

<sup>1</sup> Loc. cit.

$\begin{array}{c} \text{COOH} \\   \\ \text{COOH} \end{array}$	$\text{CH}_3\text{COOH}$ (glacial)	$\frac{N}{10} - \text{KMnO}_4$ (ml)		$\text{P}_2\text{O}_5$	Diff.
		calc.	found		
gram.	ml			%	%
1.5	50	18.92	18.85	53.57	-0.20
2.0	60	18.92	18.87	53.62	-0.15
2.0	60	18.92	19.00	53.99	+0.22

Experiment 3.—25 ml of the solution containing 0.0625 gram. of ammonium phosphate, 1.3 ml of zinc chloride solution and 15 ml of ammonium chloride solution were employed. In this experiment a micro-burette was used for titration.

$\begin{array}{c} \text{COOH} \\   \\ \text{COOH} \end{array}$	$\text{CH}_3\text{COOH}$ (glacial)	$\frac{N}{10} - \text{KMnO}_4$ (ml)		$\text{P}_2\text{O}_5$	Diff.
		calc.	found		
gram.	ml			%	%
1.5	50	9.461	9.470	53.82	+0.05
1.0	50	9.461	9.450	53.71	-0.06
1.0	50	9.461	9.480	53.88	+0.11

### Summary

1. A new gravimetric method for determining phosphoric acid as zinc pyrophosphate was established.
2. The most favourable relation between the quantities of zinc chloride and ammonium chloride which are to be taken for precipitation of phosphoric acid and also their relation to the amount of phosphoric acid taken for analysis were studied.
3. The hydrogen ion concentration of the solution necessary for the complete precipitation of zinc ammonium phosphate was determined.
4. The influence of various salts such as sodium chloride, potassium chloride, sodium sulphate, sodium nitrate, sodium acetate, ammonium tartrate, ammonium citrate and ammonium molybdate was examined.
5. It was also confirmed that with fairly good results phosphoric acid may indirectly determined by titrating zinc in zinc ammonium phosphate according to the oxalate method of H. L. Ward.

The writer wishes here to express his sincere thanks to Professor M. Matsui under whose kind guidance and encouragement the work was carried out.

---