

Quantitative Analysis of Phosphoric Acid, Part I. Determination as Magnesium Pyrophosphate

By

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(Received October 30, 1928)

Since the method of determining phosphoric acid as magnesium pyrophosphate was proposed by B. Fresenius¹ a great number of investigations has been carried out by many authors with the object of finding the best condition under which a constant and exact result may be secured. It was soon found out that such is, however, no easy task. The thorough investigation critically carried out both by D. Balarew² and Z. Kalaoglanow³ showed that of all the methods hitherto proposed, only B. Schmitz's method⁴ of precipitating magnesium ammonium phosphate from an acidic solution with ammonia at high temperature gives a reliable result. At present Schmitz's method is generally regarded as the best analytical process for determining phosphoric acid and is described as such in many text-books. The method is still not without some defects: first it is not directly applicable for determination of phosphoric acid separated as ammonium phosphomolybdate; secondly, by this method the value of phosphoric acid is often found too high, unless strict attention be paid to the quantity of ammonium chloride which must always be in an excess but not more than a certain limit (see below); thirdly, as it is worked at high temperature some precipi-

¹ Zs. anal. Chem., **6**, 403 (1869).

² Zs. anorg. u. allg. Chem., **101**, 229 (1917); **102**, 241 (1917); **103**, 73 (1918); **104**, 53, (1918); **106**, 268 (1919); **117**, 91 (1921).

³ Zs. anal. Chem., **57**, 353, 497 (1918).

⁴ Ibid., **45**, 512 (1906); **65**, 46 (1924).

tates adhere to the wall of the vessel so firmly that they can by no means be rubbed off mechanically and should therefore be dissolved in hydrochloric acid and reprecipitated once again, thus making the process very tedious. Moreover, magnesium ammonium phosphate first separated out from an acidic solution by addition of ammonia has a tendency to become a colloidal precipitate. As it can not be transformed into the crystalline form by mere heating the precipitate must be redissolved in hydrochloric acid in order to renew the precipitation. Sometimes we have to repeat the process several times before the crystalline precipitate is obtained, and as the consequence of such repetition, more ammonium chloride accumulates in the solution than the allowable limit. The method of precipitating magnesium ammonium phosphate at ordinary temperature is accompanied by many sources of error, such as precipitating normal magnesium phosphate $Mg_3(PO_4)_2$ and magnesium tetra-ammonium diphosphate $Mg\{(NH_4)_2PO_4\}_2$ together with it.

The present writer thought that it would not be impossible to get rid of these sources of error by properly controlling the composition of the magnesia mixture on the one hand and by keeping the P_H at some appropriate value on the other, and after having carried out many experiments to see their influence upon the analytical results ultimately succeeded in obtaining a simple but a very trustworthy procedure.

Experimental

I. Critical Study

In order to test the various methods proposed by many authors such as B. Schmitz¹, K. K. Järvinen², G. Jørgensen³ and others, and to find out, if possible, the cause of errors in these methods, determination of phosphoric acid in ammonium phosphate was performed according to their directions, in each case 50 ml of a solution which contained 10.1167 grams of the phosphate in 1 litre being taken.

	Schmitz's method			
	$Mg_2P_2O_7$		P_2O_5	Error
	gram.	colour	%	%
Ordinary	0.4262	white	53.75	-0.02
temperature		0.4260	„	53.73

¹ Loc. cit.

² Zs. anal. Chem., **44**, 333 (1905).

³ Ibid., **45**, 278 (1906); **50**, 336 (1611); **66**, 209 (1926).

High	0.4629	,,	58.38	+4.61
temperature	0.4607	,,	58.10	+4.35

Järvinen's method

The fine crystalline precipitates were left to stand for one, two or fifteen hours.

Hours of standing	Ignited residue			Mg ₂ P ₂ O ₇	P ₂ O ₅	Error	
	gram.	colour	gram. of Mg(PO ₃) ₂ (insoluble in HCl)	gram.	%	%	
Ordinary temperature	1	0.4233	white	0.0053	0.4245	53.54	-0.23
	2	0.4241	,,	0.0044	0.4251	53.61	-0.16
	15	0.4259	,,	0	0.4259	53.71	-0.06
High temperature	1	0.4595	,,	0	0.4595	57.95	+4.18
	15	0.4586	,,	0	0.4586	57.84	+4.07

Jørgensen's method

Ordinary temperature	1	0.4235	,,	0.0062	0.4249	53.59	-0.18
	15	0.4260	,,	0	0.4260	53.73	-0.04
High temperature	1	0.4655	,,	0	0.4655	58.71	+4.94
	15	0.4630	,,	0	0.4630	58.39	+4.62

The only reliable ordinary temperature method is that of Schmitz, while those of other authors give satisfactory results only when the precipitates of magnesium ammonium phosphate are left to stand for a long time. At high temperatures all methods tend to yield a positive error, the cause of which may be attributed to the formation of normal magnesium phosphate. Kalaoglanow¹ assumes the formation of (MgCl)₄ P₂O₇, (MgCl₃PO₄) and Mg₃(PO₄)₂ as the cause of the positive error, but according to the writer's experiments though normal phosphoric acid was detected by Tollen's reaction, the presence of chlorine was in no case observed. The same author also assumes the decomposition of magnesium ammonium phosphate into the single phosphates at high temperatures and tries to explain why too high values of phosphoric acid are found in the high temperature method. To see if such really be the case the precipitate of magnesium ammonium phosphate was heated to about 75° in a water bath or to boiling temperature in a sand bath before filtration, but the formation of normal phosphate was never observed.

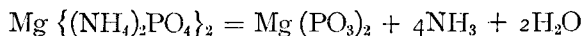
¹ Loc. cit.

Heated in a water bath	Mg ₂ P ₂ O ₇	P ₂ O ₅	Diff.
min.	grm.	%	%
30	0.4260	53.73	-0.04
60	0.4260	53.73	-0.04
Heated in a sand bath			
15	0.4264	53.78	+0.01
20	0.4263	53.76	-0.01

As is seen in the following table, it was found that the formation of the normal phosphate at high temperatures could be prevented by adding an excess of ammonium chloride; it gives the best result when the molar ratio of ammonium chloride to magnesium chloride is maintained at about 30. If more ammonium chloride than that is present it tends to dissolve magnesium ammonium phosphate and thus becomes a cause of negative error.

Mol. Ratio NH ₄ Cl : MgCl ₂	Mg ₂ P ₂ O ₇		P ₂ O ₅	Diff.
	grm.	Tollen's Reaction	%	%
22	0.4425	distinct	55.80	+2.03
26	0.4333	„	54.67	+0.90
29	0.4263	trace	53.76	-0.01
37	0.4226	none	53.30	-0.47
44	0.4194	none	52.88	-0.89

The ordinary temperature methods of Järvinen and Jörgensen are both accompanied by a negative error, as was stated before, and the contamination of magnesium ammonium phosphate with magnesium tetra-ammonium diphosphate is generally considered to be the cause. The latter phosphate when ignited changes not to magnesium pyrophosphate but to the metaphosphate and thus lowers the value of phosphoric acid:



The present writer thought that the formation of magnesium tetra-ammonium diphosphate is unavoidable unless magnesium is present in an excess far greater than to correspond to the ratio Mg : PO₄, and that it may gradually be transformed into magnesium ammonium phosphate when it is left to stand long with its mother liquor or heated. To confirm this view, pure magnesium ammonium phosphate was dissolved in dil. hydrochloric acid, and from this solution, to which some ammonium chloride had been added, magnesium ammonium phosphate was again precipitated with ammonia. The magnesium pyrophosphate from magnesium ammonium phosphate thus obtained was always observed to contain magnesium metaphosphate, the quantity of which, however,

became the less the longer the magnesium ammonium phosphate was left to stand with the mother liquor, as shown in the following table.

Hours of standing	Ignited residue			Mg ₃ P ₂ O ₇ gm.	H ₃ PO ₄ in the filtrate	P ₂ O ₅ %	Diff. %
	gram.	colour	Mg(PO ₃) ₂				
1	0.4186	white	0.0080	0.4204	+	53.02	-0.75
2	0.4227	„	0.0067	0.4242	+	53.50	-0.27
5	0.4250	„	0.0015	0.4253	+	53.64	-0.13
15	0.4262	„	0	0.4262	0	53.75	-0.02

When heated in a water bath for an hour and left to stand:

5	0.4259	„	0	0.4259	0	53.71	-0.06
5	0.4261	„	0	0.4261	0	53.74	-0.03

From this it was made clear how the precipitation reaction of magnesium ammonium phosphate should be conducted, how the precipitates should be treated before filtration, and also why Schmitz's method gave more accurate results than Jörvinen's and Jörgensen's.

The present writer was also able to confirm D. Balarew's opinion¹ that magnesium metaphosphate is formed by the interaction of magnesium pyrophosphate and phosphoric acid or ammonium phosphate, and also H. Neubauer's view² that magnesium metaphosphate gradually changes into the pyrophosphate when strongly ignited for a long time; 0.0405 gm. of magnesium metaphosphate lost 0.0159 gm. and became constant when ignited for 5 hours and a half (calculated loss = 0.0158 gm.).

II. Study of Magnesia Mixture

The magnesia mixture first used by B. Fresenius³ for determination of phosphoric acid was an ammoniacal solution containing magnesium sulphate and ammonium chloride in molecular proportion. This, however, never gave exact results though a great many trials were made by several authors⁴. In 1873 O. Abesser, W. Jani and M. Märcker⁵ succeeded in greatly improving the method by using a magnesia mixture in which magnesium chloride was substituted for magnesium sulphate

1 Loc. cit.

2 Zs. anal. Chem., **2**, 45 (1892).

3 Loc. cit.

4 Kubel: Zs. anal. Chem., **8**, 125 (1869).

Kissel: Ibid., **8**, 165 (1869); Heintz: Ibid., **9**, 16 (1870);

Schumann: Ibid., **11**, 382 (1872).

5 Ibid., **12**, 239 (1873).

with the following compositions: 110 gm. $MgCl_2 \cdot 6H_2O$ + 140 gm. NH_4Cl + 700 gm. conc. ammonia water + 1300 gm. water. The proportion of NH_4Cl to $MgCl_2$, adopted by different authors for preparation of the magnesia mixture is quite different; for example F. A. Gooch and Martha Austin¹ used 50 gm. of NH_4Cl to 110 gm. of $MgCl_2 \cdot 6H_2O$, while Järvinen² took 53 gm. of NH_4Cl and 102 gm. of $MgCl_2 \cdot 6H_2O$. The latter author first paid attention to the acidity of the phosphate solution used for analysis and also that of the magnesia mixture. He made the phosphate solution faintly alkaline and the magnesia mixture just neutral with ammonia, and after adding the former solution to the latter shaking it the while, finally added sufficient ammonia to make the precipitation of magnesium ammonium phosphate complete.

In all the investigations of these authors, the study of how the precipitation of magnesium ammonium phosphate is related to the composition and also to the acidity of the magnesia mixture seems still insufficient. The present writer therefore undertook an investigation of these two points using Kahlbaum's ammonium phosphate "Zur Analyse mit Garantieschein."

10.1167 gm. of the phosphate were dissolved in 1 litre and 50 ml of the solution were taken for each determination. A molar solution of magnesium chloride and about 5 molar solution of ammonium chloride with the acidity $P_H=5$ were taken, and these were added in different proportions to 50 ml of the above phosphate solution, when a minute crystalline precipitate of magnesium ammonium phosphate separated out. Then dilute ammonia water of 2.5 % concentration was slowly added, the mixture being well shaken all the while, till the phenolphthalein added beforehand became faintly coloured. About 10 ml of 20 % ammonia were now poured in, and after having been left to stand for an hour the solution was filtered, and the precipitate was washed with 2.5 % ammonia, dried and then ignited as usual. The results were as summarized in Table I.

It may be concluded from the table that the molecular ratio of ammonium chloride to magnesium chloride in the magnesia mixture should best be maintained between 5 and 15 (No. 1—No. 9), while that of magnesium chloride to phosphoric acid may be in the range between 1.3 and 10.5 (No. 10—No. 15). As to the reason why such an excess of ammonium chloride is needed, specially when worked at high temperature,

¹ Zs. anorg. Chem., **20**, 133 (1899).

² Zs. anal. Chem., **43**, 279 (1904).

Tbale I

No.	Water added	Magnesia Mixture						Mg ₂ P ₂ O ₇		P ₂ O ₅	Diff.
		MgCl ₂			NH ₄ Cl			g _m .	colour	%	%
		ml	g _m .	mol. ratio to (NH ₄) ₂ HPO ₄	ml	g _m .	mol. ratio to MgCl ₂				
1	10	7	0.67	1.8	7	1.88	5	0.4262	white	53.75	-0.02
2	10	"	"	"	10	2.68	7	0.4261	"	53.74	-0.03
3	10	"	"	"	14	3.75	10	0.4261	"	53.74	-0.03
4	10	"	"	"	14	3.75	10	0.4259	"	53.71	-0.06
5	5	"	"	"	21	5.65	15	0.4259	"	53.71	-0.06
6	5	"	"	"	21	5.65	15	0.4260	"	53.73	-0.04
7	5	"	"	"	28	7.50	20	0.4259	"	53.71	-0.06
8	—	"	"	"	35	9.38	25	0.4253	"	53.63	-0.14
9	—	"	"	"	35	9.38	25	0.4255	"	53.66	-0.11
10	—	5	0.48	1.3	7	1.88	7	0.4263	"	53.76	-0.01
11	—	10	0.95	2.6	14	3.75	7	0.4264	"	53.78	+0.01
12	—	15	1.43	3.9	21	5.65	7	0.4262	"	53.75	-0.02
13	—	20	1.90	5.2	28	7.50	7	0.4263	"	53.76	-0.01
14	—	30	2.86	7.8	42	11.28	7	0.4260	"	53.73	-0.04
15	—	40	3.81	10.5	56	15.04	7	0.4262	"	53.75	-0.02
16	50	7	0.67	1.8	10	2.68	7	0.4261	"	53.74	-0.03
17	100	7	0.67	1.8	10	2.68	7	0.4260	"	53.73	-0.04
18	200	7	0.67	1.8	10	2.68	7	0.4261	"	53.74	-0.03
19	300	7	0.67	1.8	10	2.68	7	0.4261	"	53.74	-0.03
20	400	7	0.67	1.8	10	2.68	7	0.4267	"	53.81	+0.04
21	500	7	0.67	1.8	10	2.68	7	0.4271	"	53.86	+0.09
22	600	7	0.67	1.8	10	2.68	7	0.4282	"	54.00	+0.23

and at the same time its amount must be kept under a certain limit has already been discussed in the part devoted to critical study. The experiments from No. 16 to No. 22 were conducted to find out the influence of dilution, which was found to give a marked positive error due to the formation of normal magnesium phosphate when the solution becomes too much diluted.

From the results thus studied it was found that the magnesia mixture which give the most exact result in the determination of phosphoric acid should be prepared in the following way: 50 grm. of crystalline magnesium chloride and 100 grm. of ammonium chloride (the molar ratio of the latter to the former is 7.6) are dissolved together in water, and to this solution conc. ammonia water is added till phenolphthalein added beforehand becomes distinctly red. After standing 2 or 3 days the solution is filtered, if necessary, and then dil. hydrochloric acid is added to it just to decolourize the phenolphthalein. The solution is now diluted with water to one litre and its acidity is so adjusted that the P_H value lies between 5 and 6. This is done without any difficulty by aid of methyl red ($P_H=4.4-6.3$) or p-nitrophenol ($P_H=5.0-7.9$).

III. On the Suitable Acidity of the Phosphate Solution

For the precipitation of magnesium ammonium phosphate, the phosphate solution made alkaline with ammonia was generally used. But it was soon found that the precipitates often become contaminated with magnesium tetra-ammonium diphosphate which changes into magnesium metaphosphate on ignition and becomes a cause of negative error.

B. Schmitz's modified method¹, in which phosphate solution previously acidified with hydrochloric acid is used, is not directly applicable for determination of phosphoric acid separated as ammonium phosphomolybdate. Moreover, when the acid is very concentrated, much ammonium chloride is produced on addition of ammonia and this tends to dissolve magnesium ammonium phosphate. The present writer, therefore, thought it necessary first to determine the P_H value of the phosphate solution from which the quantitative precipitation of magnesium ammonium phosphate is possible. 50 ml of the ammonium phosphate solution described in section I were taken for each experiment and the relation of the acidity to the accuracy of analysis was studied. The results are shown in Table II.

From the table it is clearly seen that the P_H value of the phosphate solution should be kept greater than 4.4 and less than 8.3, otherwise the value of phosphoric acid is found lower. For the sake of security the present writer always maintained it between 6.0 and 8.3, because the solution of such acidity may safely be used in the presence of molybdic acid too. The above safe range of acidity can conveniently be

¹ Loc. cit.

obtained by using methyl red ($P_H = 4.4 - 6.3$), p-nitrophenol ($P_H = 5.0 - 7.9$) bromthymolblue ($P_H = 6.0 - 7.6$) or neutral red ($P_H = 6.9 - 8.0$).

Table II

No.	P_H	Mag. mixture	$Mg_2P_2O_7$	P_2O_5	Diff.
		ml	gm.	%	%
1	1.3	25	0.4260	53.73	-0.04
2	1.3	"	0.4259	53.71	-0.06
3	4.4	"	0.4261	53.74	-0.03
4	4.4	"	0.4264	53.78	+0.01
5	4.4	"	0.4262	53.75	-0.02
6	6.0	"	0.4262	53.75	-0.02
7	6.0	"	0.4261	53.74	-0.03
8	6.0	"	0.4263	53.76	-0.01
9	7.5	"	0.4262	53.75	-0.02
10	7.5	"	0.4261	53.74	-0.03
11	7.5	"	0.4264	53.78	+0.01
12	8.3	"	0.4263	53.76	-0.01
13	8.3	"	0.4261	53.74	-0.03
14	8.3	"	0.4262	53.75	-0.02
15	9.3	"	0.4255	53.66	-0.11
16	9.3	"	0.4254	53.65	-0.12
17	11.0	"	0.4245	53.54	-0.23
18	11.0	"	0.4249	53.59	-0.18

IV. Influence of Temperature on the Precipitation of Magnesium Ammonium Phosphate

As was stated in the previous section the composition and acidity of the magnesia mixture and also the acidity of the phosphate solution which are most suitable for quantitative determination of phosphoric acid were determined. By using solutions having such composition and acidity, quantitative analyses were carried out at different temperatures in order to ascertain which temperature is most preferable. It is generally known, as was stated in section I, that at higher temperatures a somewhat higher

value is often obtained for phosphoric acid and the form of magnesium ammonium phosphate is very liable to become colloidal. Such a result was also found in these experiments, as may be observed in Table III (No. 1—No. 2).

Table III

For each determination, 50 ml of a solution containing 10.1167 gm. of $(\text{NH}_4)_2\text{HPO}_4$ in 1 litre were taken.

No.	Temp.	Mag. mixture	$\text{Mg}_3\text{P}_2\text{O}_7$		P_2O_5	Diff.
		ml	gm.	colour	%	%
1	70°—75°	25	0.4520	slightly gray	57.00	+3.23
2	70°—75°	25	0.4470	slightly gray	56.37	+2.60
3	18°→50°	25	0.4266	slightly gray	53.80	+0.03
4	18°→90°	25	0.4260	slightly gray	53.73	-0.04
5	22°—25°	25	0.4264	white	53.78	+0.01
6	22°—25°	25	0.4262	white	53.75	-0.02
7	13°—15°	25	0.4261	white	53.74	-0.03
8	13°—15°	25	0.4263	white	53.76	-0.01

At temperatures down to 35° the precipitates of magnesium ammonium phosphate were seen to be partly colloidal and became crystalline only after standing a long time. When worked at temperatures lower than 35° the precipitates were always obtained in crystalline form, and exact results were obtained (No. 5—No. 8). It is very interesting to note that analysis of phosphoric acid may also be conducted at high temperatures without any hindrance in the following way: The phosphate solution is first mixed with the magnesia mixture at ordinary temperatures, say 18°, and the solution in which some crystalline precipitates are formed is then heated to a high temperature, say 90°, and then treated with ammonia (No. 3—No. 4).

V. Time of Precipitation and of Standing

The time required for precipitation of magnesium ammonium phosphate and also the time allowed for the precipitates to stand influence the results of analysis in no small degree. A series of experiments was carried out in the following way: 50 ml of the solution containing 10.1167 gm. of ammonium phosphate in 1 litre were mixed with 25 ml

of the magnesia mixture as usual, when a small quantity of a fine crystalline precipitate of magnesium ammonium phosphate separated out. Now 2.5 % ammonia water was added to it at different intervals varying from one to five minutes, till the phenolphthalein added beforehand became distinctly red, and the solution was left to stand for certain times after addition of 10 ml of 20 % ammonia. It is seen from Table IV that as the time required for precipitation, that is, the time of adding the 2.5 % ammonia water, 3-5 minutes is sufficient and 30 minutes for the time the precipitates are left to stand.

Table IV

No.	Mag. mixture	Time required for precipitation	Time of standing	Mg ₂ P ₂ O ₇	P ₂ O ₅	Diff.
	ml	min.	min.	gram.	%	%
1	25	3-5	5	0.4256	53.67	-0.10
2	25	3-5	10	0.4260	53.73	-0.04
3	25	3-5	20	0.4262	53.75	-0.02
4	25	3-5	30	0.4263	53.76	-0.01
5	25	3-5	60	0.4263	53.76	-0.01
6	25	1-2	60	0.4259	53.71	-0.06

VI. Procedure for Precipitating Magnesium Ammonium Phosphate and Composition of the Precipitates

From what has been described so far we can deduce the following procedure for determining phosphoric acid as the best of all methods hitherto known.

The acidity of the phosphate solution whose concentration may be $\frac{1}{10} - \frac{1}{100}$ molar is so regulated that one or two drops of p-nitrophenol added to it show a slightly yellow colour, and to this solution the magnesia mixture prepared according to the manner described in section II is added in an excess and well agitated, whereupon a fine crystalline precipitate begins to separate out. Now 2.5 % ammonia water is added, the mixture being well shaken all the while, at such a rate as to complete the precipitation in 3-5 minutes, till the phenolphthalein added beforehand becomes distinctly red. About one-seventh volume of 20 % ammonia is now added and the solution left to stand for about 30 minutes. After

filtration, the precipitates are washed with 2.5 % ammonia water till they become free from chloride, and dried, ignited and finally weighed as usual.

To know whether the precipitate is really of the composition $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, it was analysed, with the following results :

The ppte taken	$\frac{\text{N}}{10}$ —HCl required to neutralize ammonia evolved	NH_3 (%)	
		found	calc.
0.4828 gm.	19.50 ml	6.88	6.94
0.5100 ,,	20.72 ,,	6.92	

The quantity of water of crystallization was calculated from that of magnesium pyrophosphate produced from a known quantity of the sample :

The ppte taken	$\text{Mg}_2\text{P}_2\text{O}_7$	$\text{MgNH}_4\text{PO}_4 = a$	$x\text{H}_2\text{O} = b$	$x \left(= \frac{b \times 137.46}{a \times 18.016} \right)$
0.6370 gm.	0.2886 gm.	0.3563 gm.	0.2807 gm.	6.0110
0.6370 ,,	0.2888 ,,	0.3565 ,,	0.2805 ,,	6.0036
1.3730 ,,	0.6228 ,,	0.7688 ,,	0.6042 ,,	5.9966

VII. Influence of Other Salts present

As to the influence of various substances on the precipitation of magnesium ammonium phosphate much is not yet known except that potassium ion and sulphation become the cause of positive error, while acetation and too large an excess of ammonium chloride cause negative error. The present writer quantitatively studied the influence of sodium chloride, potassium chloride, sodium nitrate, sodium sulphate, ammonium sulphate, sodium acetate, formic acid, oxalic acid, citric acid, tartaric acid, ammonium molybdate and ammonium chloride upon the reaction, using 50 ml of the ammonium phosphate solution and 25 ml of the magnesia mixture for each determination. The results of the experiments are given in Table V.

NaCl—Sodium chloride seems to retard the precipitation of magnesium ammonium phosphate, but this has no bad effect if the precipitate is left to stand for a long time with the mother liquor (No. 1—No. 6).

KCl—This affects the result of analysis in no small degree, giving a higher value for phosphoric acid (No. 7—No. 13). From the fact that the precipitate of magnesium ammonium phosphate contains potassium but not chlorine it appears very probable that some magnesium potassium phosphate is formed together with the corresponding ammonium salt so as to form a mixed crystal. When once crystallized in the form of

Table V

No.	Salt mixed		Time of standing	Mg ₂ P ₂ O ₇		P ₂ O ₅	Diff.
	Name	gram.	min.	gram.	colour	%	%
1	NaCl	3.0	30	0.4258	white	53.70	-0.07
2	"	3.0	120	0.4264	"	53.78	+0.01
3	"	6.0	30	0.4249	"	53.59	-0.18
4	"	6.0	150	0.4263	"	53.76	-0.01
5	"	9.0	50	0.4256	"	53.67	-0.10
6	"	9.0	150	0.4262	"	53.75	-0.02
7	KCl	6.0	120	0.4372	"	55.14	+1.37
8	"	4.0	120	0.4344	"	54.78	+1.01
9	"	2.0	120	0.4306	"	54.30	+0.53
10	"	1.0	60	0.4282	"	54.00	+0.23
11	"	0.6	60	0.4273	"	53.89	+0.12
12	"	0.2	60	0.4264	"	53.78	+0.01
13	"	0.1	60	0.4261	"	53.74	-0.03
14	NaNO ₃	6.0	30	0.4262	"	53.75	-0.02
15	"	6.0	120	0.4262	"	53.75	-0.02
16	"	9.0	120	0.4263	"	53.76	-0.01
17	Na ₂ SO ₄	6.0	600	0.4316	"	54.43	+0.66
18	"	6.0	120	0.4318	"	54.46	+0.69
19	"	4.0	120	0.4317	"	54.44	+0.67
20	"	2.0	60	0.4308	"	54.33	+0.56
21	"	1.0	60	0.4279	"	53.97	+0.20
22	"	0.6	60	0.4273	"	53.89	+0.12
23	"	0.2	60	0.4264	"	53.78	+0.01
24	(NH ₄) ₂ SO ₄	6.0	120	0.4348	"	54.83	+1.06
25	C ₂ H ₃ O ₂ Na	6.0	120	0.4218	"	53.20	-0.57
26	"	2.0	120	0.4235	"	53.41	-0.36
27	"	0.6	120	0.4248	"	53.57	-0.20
28	"	0.2	120	0.4250	"	53.60	-0.17
29	"	0.1	120	0.4255	"	53.66	-0.11
30	"	0.06	120	0.4258	"	53.70	-0.07
31	"	0.02	120	0.4262	"	53.75	-0.02
32	H ₂ CO ₃	6.10	120	0.4263	"	53.76	-0.01
33	"	3.66	120	0.4262	"	53.75	-0.02
34	H ₂ C ₂ O ₄	1.5	60	0.4261	"	53.74	-0.03
35	H ₈ C ₈ O ₇	2.5	120	0.4283	grayish black	54.02	+0.25
	after ignition again with HCl			0.4265	white	53.79	+0.02
36	"	0.5	120	0.4272	grayish black	53.88	+0.11
	after ignition again with HCl			0.4266	white	53.80	+0.03

No.	Salt mixed		Time of standing	Mg ₂ P ₂ O ₇		P ₂ O ₅	Diff.
	Name	gram.	min.	gram.	colour	%	%
37	"	0.15	120	0.4274	grayish black	53.90	+0.13
	after ignition again with HCl			0.4265	white	53.79	+0.02
38	"	0.08	120	0.4273	grayish black	53.89	+0.12
	after ignition again with HCl			0.4266	white	53.80	+0.03
39	"	0.05	120	0.4274	grayish black	53.90	+0.13
	after ignition again with HCl			0.4265	white	53.79	+0.02
40	H ₆ C ₄ O ₆	2.5	120	0.4338	grayish black	54.71	+0.94
	after ignition again with HCl			0.4310	grayish black	54.36	+0.59
	after ignition twice with HCl			0.4265	white	53.79	+0.02
41	"	0.15	120	0.4275	grayish black	53.92	+0.15
	after ignition again with HCl			0.4265	white	53.79	+0.02
42	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	2.40	30	0.4254	white	53.65	-0.12
43	"	2.40	120	0.4262	"	53.75	-0.02
44	"	4.80	120	0.4265	"	53.79	+0.02
45	NH ₄ Cl	5.36	120	0.4259	"	53.71	-0.06
46	"	10.72	120	0.4235	"	53.41	-0.36

MgNH₄PO₄·6H₂O it undergoes no change even when left to stand long in a solution containing KCl.

KCl	Mg ₂ P ₂ O ₇	P ₂ O ₅	Diff.
4.0 gram.	0.4262 gram.	0.2719 gram.	-0.02 %
6.0 "	0.4260 "	0.2718 "	-0.04 "

NaNO₃—No influence (No. 14—No. 16).

Na₂SO₄ and (NH₄)₂SO₄—Both give rise to positive error, and the precipitate of magnesium ammonium phosphate was always found to contain sulphuric acid, as, for example, from magnesium pyrophosphate obtained in the experiment shown in No. 24 0.0118 gram. of BaSO₄ was produced. No bad influence was observed if these sulphates were added after the precipitation of magnesium ammonium phosphate had been completed.

Na ₂ SO ₄	Mg ₂ P ₂ O ₇	P ₂ O ₅	Diff.
6.0 gram.	0.4363 gram.	0.2720 gram.	-0.01 %

The reason why Fresenius¹ and Winkler's² methods of using magnesium sulphate in the preparation of the magnesia mixture do not give satisfactory results will now be clear.

NaO₂C₂H₃—Though sodium acetate does not dissolve magnesium

1 Loc cit.

2 J. Soc. chem. Ind., 391 A. (1919).

ammonium phosphate, it makes the precipitation of the latter incomplete (No. 25—No. 31). This incompleteness could never be improved by allowing the precipitate to stand even for 20 hours.

$(\text{NH}_4)_2\text{HPO}_4$	$\text{Mg}_2\text{P}_2\text{O}_7$	P_2O_5	Diff.
0.5058 gm.	0.4217 gm.	53.18 %	-0.59 %

H_2CO_2 and $\text{H}_2\text{C}_2\text{O}_4$ —Both were found to have no effect (No. 32—No. 34).

$\text{H}_3\text{C}_6\text{O}_7$ —When citric acid exists in the solution it is adsorbed in the precipitate of magnesium ammonium phosphate and consequently magnesium pyrophosphate is found higher in its value and coloured grayish black (No. 35—No. 39). This hindrance may, however, be easily removed either by igniting the pyrophosphate with a few drops of conc. hydrochloric acid or nitric acid or by dissolving the precipitate of magnesium ammonium phosphate in dil. hydrochloric acid and again precipitating.

	$(\text{NH}_4)_2\text{HPO}_4$	$\text{Mg}_2\text{P}_2\text{O}_7$	P_2O_5	Diff.
1 st precipitation	0.5058 gm.	0.4266 gm.	53.80 %	+0.03 %
2 nd ,,	" "	0.4263 ,,	53.76 %	-0.01 %

$\text{H}_6\text{C}_4\text{O}_6$ —The effect of tartaric acid on the analysis of phosphoric acid was observed to be analogous with that of citric acid (No. 40—No. 41).

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{21}\cdot 4\text{H}_2\text{O}$ —Though its action is to retard the precipitation of magnesium ammonium phosphate, the complete precipitation may be brought about by simply keeping the precipitate with the mother liquor for 2 hours (No. 42—No. 44).

NH_4Cl —This becomes a cause of negative error only when it exists in too large an excess as was stated before (No. 45—No. 46).

Summary

1. With the object of finding a trustworthy procedure for analysis of phosphoric acid a critical study of various methods for precipitating magnesium ammonium phosphate hitherto proposed was carried out and the sources of error were experimentally sought.

2. The relation of the composition and acidity of the magnesia mixture to the accuracy of the analytical result was examined, and the magnesia mixture giving the most satisfactory result was prepared.

3. The dilution and acidity of the phosphate solution to be taken for analysis were determined.

4. Influence of various substances such as NaCl, KCl, NaNO₃, Na₂SO₄, (NH₄)₂SO₄, NaO₂C₂H₃, H₂CO₂, H₂C₂O₄, H₅C₆O₇, H₆C₄O₆, (NH₄)MoO₄ and NH₄Cl on the precipitation of magnesium ammonium phosphate were investigated.

5. As the result of this investigation a simple and exact procedure for precipitating phosphoric acid as magnesium ammonium phosphate was found out.

The writer wishes here to express his sincere thanks to Professor M. Matsui, at whose suggestion the work was carried out.
