5. The necessity for a more powerful light source for this type of investigation is emphasized.
6. The rate of precipitation of Bredig sols is not influenced by radiation.

NEW YORK CITY

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

THE PYROPHOSPHATE METHOD FOR THE DETERMINATION OF MAGNESIUM AND PHOSPHORIC ANHYDRIDE[1]

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RECEIVED SEPTEMBER 2, 1927 PUBLISHED FEBRUARY 4, 1928

Probably no determination in analytical chemistry has been the subject of a greater number of conflicting statements than that involving the precipitation of magnesium ammonium phosphate. It is the purpose of this paper to give the results of extensive tests of such statements, and to urge the establishment of a standard procedure which defines, so far as they are known, the most favorable conditions for obtaining a normal precipitate of $MgNH_4PO_4$, and the subsequent ignition of that precipitate to pyrophosphate, $Mg_2P_2O_7$.

In investigating the conditions most favorable for the precipitation of magnesium ammonium phosphate, methods recommended for the determination of magnesium and of phosphoric anhydride were studied. Various procedures suggested in publications on the subject since 1873 were tested, and the effects of those impurities most likely to occur in the regular course of analysis were determined. In most cases short (four hours) single precipitations were made to determine the maximum effect of any variation, and overnight (sixteen hours) single precipitations were made to determine whether standing would cause the precipitate to regain normal composition. Reprecipitation under the conditions to be recommended was tried in many cases.

Since the final treatment of the magnesium ammonium phosphate should be the same whether the precipitate is obtained in the determination of magnesium or of phosphoric anhydride, some commonly recommended methods for obtaining pure pyrophosphate were first investigated and the following observations were made. (1) Solution of the magnesium ammonium phosphate in nitric acid, followed by evaporation to dryness and igniton, has no apparent effect on the final pyrophosphate. (2) Moistening the ignited pyrophosphate with one or two drops of nitric acid, followed by re-ignition, has no effect, either good or harmful. (3) Solution of the ignited pyrophosphate in nitric acid and evaporation of the solution was found to be literally impossible, confirming the experience of Lundell and

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[1] Published by permission of the Director, National Bureau of Standards, U. S. Department of Commerce, Washington, D. C.

Hoffman.[2] Because of decrepitation and apparent breaking down of the compound accurate results cannot be obtained.[3] None of these expedients for obtaining a white residue is desirable or necessary if care is taken in the charring of the paper and ignition of the precipitate.

Tests were also carried out to determine the concentration of ammonia solution most desirable for use as wash water for the magnesium ammonium phosphate precipitate, that having been a matter of much dispute. Many authors have recommended solutions containing one-third ammonia water by volume. Such solutions are most inconvenient to use and were found to be unnecessary and undesirable. As shown in Table I, it was found that water containing from 2.5 to 10% of ammonia water (sp. gr. 0.90) by volume could be used for washing the precipitate with equally correct results, while no advantage was found in adding ammonium nitrate to the wash water.

TABLE I

DATA OBTAINED IN TESTS OF SOLUTIONS USED FOR WASHING $MgNH_4PO_4.6H_2O$

Figures reported are averages of two or more determinations

Wash soln.[a]	Time of pptn., hrs.	Solution A = $MgCl_2$ B = $NaNH_4HPO_4$	$Mg_2P_2O_7$ equiv. of soln. taken, g.	$Mg_2P_2O_7$ found, g.	Residue after 24 hours
2.5% NH_4OH	3	A	0.0982	0.0969	In all cases residues were barely visible in filtrates from phosphate solutions; residues were visible in filtrates from $MgCl_2$ solutions but averaged less than 0.0001 g.
	3	B	.0953	.0953	
	24	A	.0982	.0980	
	24	B	.0953	.0956	
5% NH_4OH	3	A	.0982	.0982	
	3	B	.0953	.0955	
	24	A	.0982	.0980	
	24	B	.0953	.0954	
10% NH_4OH	3	A	.0982	.0986	
	3	B	.0953	.0952	
	24	A	.0982	.0982	
	24	B	.0953	.0951	
2.5% NH_4OH +5% NH_4NO_3	3	A	.0982	.0981	
	3	B	.0953	.0950	
	24	A	.0982	.0982	
	24	B	.0953	.0953	

[a] Wash solutions made to specified percentage by volume with ammonia (sp. gr. 0.90) and distilled water.

The procedure called "Standard Procedure" in this paper has been found by a number of operators at the Bureau of Standards to avoid the usual errors, and it is believed to afford the most favorable conditions possible for the precipitation of magnesium ammonium phosphate and its subsequent ignition to magnesium pyrophosphate. Since it is evident that

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[2] Lundell and Hoffman, *Ind. Eng. Chem.*, **15**, 46 (1923).

[3] W. M. McNabb has stated [THIS JOURNAL, **49**, 891 (1927)] that this treatment succeeds if the nitric acid is neutralized with ammonia before evaporation and ignition.

correct results are largely dependent on the details of the operation, the procedure given has been followed as exactly as possible in all comparative tests, except for the variations stated.

Discussion of Procedures for the Determination of Magnesium

In the determination of magnesium, microcosmic salt ($NaNH_4HPO_4$) has been most often used as the precipitant. Since it has been stated that the presence of sodium in the reagent leads to precipitates of abnormal composition and high results, various reagents were tested. It was found that slightly higher results were obtained by the use of disodium phosphate or microcosmic salt as precipitants than by the use of diammonium phosphate, $(NH_4)_2HPO_4$. This is true only of single precipitations, however, because two precipitations give practically correct results in all cases, as shown in Table II. Apparently, any abnormality or occlusion in the precipitate is remedied by reprecipitation in the presence of a *slight* excess of the reagent.

TABLE II

DATA OBTAINED IN COMPARISON OF PRECIPITANTS FOR MAGNESIUM AS $MgNH_4PO_4.6H_2O$

Figures reported are averages of three or more determinations

Precipitant (sat. soln.), cc.		No. of pptns.	Time of standing (each pptn.), hrs.	$Mg_2P_2O_7$ found, g.	$Mg_2P_2O_7 \Bumpeq MgCl_2$ taken, g.	Residue after 24 hrs.[a]
A (Na_2HPO_4)	5	1	4	0.0287	0.0280	0.0002
B ($NaNH_4HPO_4$)	5	1	4	.0285	.0280	
C $(NH_4)_2HPO_4$	3	1	4	.0280	.0280	
A	10	1	4	.0712	.0692	.0003
B	10	1	4	.0699	.0692	
C	5	1	4	.0693	.0692	
A	5	1	12	.0278	.0280	.0001
B	5	1	12	.0280	.0280	
C	3	1	12	.0280	.0280	
A	10	1	12	.0709	.0692	.0001
B	10	1	12	.0694	.0692	
C	5	1	12	.0692	.0692	
A	5	2	12	.0277	.0280	0001
B	5	2	12	.0278	.0280	
C	3	2	12	.0278	.0280	
A	10	2	12	.0691	.0692	.0001
B	10	2	12	.0691	.0692	
C	5	2	12	.0691	.0692	
A	35	1	12	.6440	.6325	.0001
B	35	1	12	.6457	.6325	
C	25	1	12	.6327	.6325	
A	35	2	12	.6325	.6325	.0001
B	35	2	12	.6325	.6325	
C	25	2	12	.6325	.6325	

[a] Largest residue in each series filtered after standing 24 hours, ignited and weighed.

In tests of procedures for the determination of magnesium, solutions of magnesium chloride made from Kahlbaum's C. P. salt were used. The solutions were slightly acidified with hydrochloric acid to prevent action of the alkaline solution on glass, and were kept in glass-stoppered bottles made of Jena glass. The solutions were first analyzed for magnesium content by a number of determinations as pyrophosphate. However, since this method was itself being tested, it seemed desirable to standardize the solutions by a different method. Accordingly, varying amounts of the solution, measured from a buret, were treated with precipitated mercuric oxide in water suspension. The solution was carefully dried and ignited and the process repeated until all of the magnesium chloride present was converted into oxide. It was then weighed as such. It is believed that a very accurate measure of the real magnesium content of the solution was thus obtained.[4] For the sake of convenient comparison, the weight of magnesium pyrophosphate calculated from the amount of magnesium oxide or phosphoric anhydride in the sample of solution taken is given in all tables.

Standard Procedure for the Determination of Magnesium

To the neutral or weakly acid solution of magnesium chloride, containing not more than 0.1 g. of MgO, add 5 cc. of concentrated hydrochloric acid, and methyl red indicator. Dilute the solution to 150 cc. and add 10 cc. or a 5- to 10-fold excess, of the precipitant, preferably a saturated solution of $(NH_4)_2HPO_4$. Then add ammonia water (sp. gr. 0.90) slowly, while stirring, to neutralization. Stir for about five minutes, or until the precipitate of $MgNH_4PO_4$ is well formed, then add 5 cc. excess of ammonia water and stir for ten minutes. Let stand for at least four hours, preferably overnight, filter and wash with water containing from 3 to 5% by volume of ammonia water (sp. gr. 0.90). Dissolve the precipitate by washing on the filter with warm 1:9 hydrochloric acid (sp. gr. 1.02). Add methyl red indicator and about 1 cc. of $(NH_4)_2HPO_4$ solution and finish the precipitation as before, but in a volume of 100 to 150 cc. In this precipitation digestion for four hours is sufficient. In igniting the final precipitate, the wet filter paper and precipitate should be placed in a weighed platinum crucible, charred without flaming, then ignited at a low temperature (approximately 500°) and with the lid open enough for circulation of air, until the residue is white, and finally at approximately 1000° to constant weight.

Discussion of the Results Obtained in the Determination of Magnesium

A summary of results obtained in the tests of procedures for the determination of magnesium is given in Table III. As shown in Table III-A,

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[4] Fresenius-Cohn, "Quantitative Chemical Analysis," John Wiley and Sons, Inc., New York, **1904**, Vol. 1, p. 276.

a large excess of ammonium chloride was found to produce high results for single precipitations but on reprecipitating under standard conditions the true values were obtained. Absence of ammonium chloride was found not to affect the precipitate materially.

TABLE III

DATA OBTAINED IN THE DETERMINATION OF MAGNESIUM AS $Mg_2P_2O_7$

Figures reported are averages of three or more determinations

(All precipitations as specified in standard procedure, unless otherwise specified in table. Final volume approximately 170 cc.)

Variation in standard procedure	No. of pptns.	Wt. of $Mg_2P_2O_7 \Leftrightarrow MgCl_2$ taken, g.	Wt. of $Mg_2P_2O_7$ found, g.	Remarks[a]
		III-A		
Excess NH_4Cl, g.				
16	1 (4 hr.)	0.1367	0.1388	(1)
16	1 (16 hr.)	.1367	.1383	(1)
16	2 (16 hr.)	.1367	.1367	(2)
None	1 (16 hr.)	.1156	.1161	(1)
1	1 (16 hr.)	.1156	.1179	(1)
5	1 (16 hr.)	.1156	.1180	(1)
10	1 (16 hr.)	.1156	.1189	(1)
25	1 (16 hr.)	.1156	.1191	(1)
		III-B		
Excess NH_4OH, cc.				
25	1 (4 hr.)	.1367	.1395	(1)
25	1 (16 hr.)	.1367	.1395	(1)
25	2 (16 hr.)	.1367	.1367	(2)
40 ($^1/_4$ vol.)	1 (16 hr.)	.1367	.1366	(1)
55 ($^1/_3$ vol.)	1 (16 hr.)	.1637	.1369	(1)
85 ($^1/_2$ vol.)	1 (16 hr.)	.1367	.1397	(1)
		III-C		
Excess $(NH_4)_2HPO$				
150 cc. sat. soln.	1 (4 hr.)	.1367	.0960	(1)
"	1 (16 hr.)	.1367	.1038	(1)
"	2 (16 hr.)	.1367	.1370	(3) (1)
		III-D		
NaCl				
0.11 g. per cc.	1 (4 hr.)	.1367	.1571	Winkler procedure[5]
0.11 g. per cc.	1 (16 hr., hot)	.1384	.1427	Gibbs procedure
0.11 g. per cc.	1 (2 hr.)	.1367	.1575	Jarvinen procedure
0.11 g. per cc.	2 (16 hr.)	.1367	.1367	(2)
KCl				
0.11 g. per cc.	1 (4 hr.)	.1367	.1706	Winkler procedure
0.11 g. per cc.	1 (16 hr., hot)	.1384	.1427	Gibbs procedure
0.11 g. per cc.	1 (2 hr.)	.1367	.1692	Jarvinen procedure
0.11 g. per cc	2 (16 hr.)	.1367	.1378	3rd pptn. 0.1370

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[5] Winkler, *Z. angew. Chem.*, **32**, I, 99 (1919).

TABLE III (*Concluded*)

Variation in standard procedure	No. of pptns.	Wt. of $Mg_2P_2O_7 \Leftrightarrow MgCl_2$ taken, g.	Wt. of $Mg_2P_2O_7$ found, g.	Remarks[a]
		III-E		
Pptn. made in ammoniacal soln.				
Hot soln.	1 (4 hr.)	.1367	.1405	(1)
Cold soln.	1 (2 hr.)	.1367	.1390	(1)
Cold soln.	1 (16 hr.)	.1367	.1397	(1)
Cold soln.	2 (16 hr.)	.1156	.1150	(2)
		III-F		
Jarvinen procedure	1 (2 hr.)	.1367	.1370	Pptn. in neutral soln.
		III-G		
Gibbs procedure	2 (16 hr.)	.1367	.1367	Pptn. in hot soln.
		III-H		
$(NH_4)_2C_2O_4$				
1 g. added	1 (16 hr.)	.1384	.1391	(1)
1 g. added	2 (16 hr.)	.1367	.1368	(2)
		III-K		
$(NH_4)_2SO_4$				
(5 cc. H_2SO_4, no HCl)	1 (16 hr.)	.1367	.1367	(1)
		III-L		
Citric acid				
0.5 g. added	1 (16 hr.)	.1367	.1366	(1)
2.0 g. added	1 (16 hr.)	.1367	.1367	(1)

[a] (1) Standard procedure followed throughout except for variation noted.

(2) Reprecipitated under standard conditions.

(3) First precipitation incomplete; second precipitation made from combined precipitates recovered from the filtrate, added to first precipitate.

A large excess of ammonia was found, Table III-B, to have about the same effect as ammonium chloride. Reprecipitation, in this case also, produced a normal precipitate, with correct results. A concentration of ammonia water higher than one-third by volume was found to give high results.

As shown in Table III-C, a very large excess of the precipitant, $(NH_4)_2HPO_4$, was found to give very low results in single precipitations. Apparently, the precipitate is partially soluble in a strong solution of $(NH_4)_2HPO_4$, for further precipitation occurred when the filtrate was diluted and allowed to stand. When the complete precipitate, obtained by repeated dilution, standing and filtration, was dissolved and reprecipitated under proper conditions, the results were very nearly correct. There should be no reason, however, in the ordinary course of analysis, for the addition of such a large excess of the precipitant.

The presence of sodium chloride in the solution was found, Table III-D, to produce high results with single precipitations, but on reprecipitating true values were obtained. Equal amounts of potassium chloride gave higher and less uniform results with single precipitations than the sodium chloride. Reprecipitation under standard conditions improved the result but did not bring it within the usual limits of experimental error.

The addition of the precipitant to an ammoniacal solution has long been practiced, and even recommended. Precipitations in hot ammoniacal solution gave decidedly high results, Table III-E, as did all single precipitations in ammoniacal solutions. Reprecipitation under standard conditions of precipitates from runs made in hot ammoniacal solutions gave results which were consistently lower than the true values. Apparently reprecipitation does not remedy the error. However, there should be no reason, in the ordinary course of analysis, for the addition of the precipitant to an ammoniacal solution, since it is necessary only to acidify the solution. The danger of error in precipitations if the solution is not acid when the reagent is added, is to be emphasized.

Precipitation in a neutral solution by the method of Jarvinen[6] gave average results, Table III-F, which were only slightly high, but separate results of a series were not sufficiently uniform to be within a reasonable limit of experimental error. Since this method requires that there be no excess of ammonium salts, it would necessitate in the usual course of silicate analysis an additional time-consuming operation for evaporation to dryness and driving off ammonium salts. In the case of the presence of sodium or potassium chloride, Table III-D, the method did not lessen the error in single precipitations.

Double precipitations in hot solution, according to the method of Gibbs,[7] gave closely agreeing, true results, Table III-G. It is therefore evident that cooling the solution before precipitation is unnecessary. However, it has been found that the crystalline precipitate is formed in a slightly coarser and more easily filterable condition, with less tendency to adhere to the sides of the beaker, when precipitation is made in a cool solution. Precipitations made in hot solution in the presence of sodium or potassium chloride, Table III-D, did not seem to obviate the necessity of reprecipitating to obtain true results.

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[6] Jarvinen, *Z. anal. Chem.*, **44**, 333 (1905). In this method the solution, free from an excess of ammonium salts, is rendered neutral to lacmoid indicator and a normal solution of $(NH_4)_2HPO_4$ containing 40 cc. of 10% solution of ammonia per liter is added dropwise. When most of the precipitate has separated, a 1% solution of ammonia is added dropwise until the solution smells strongly of ammonia; then a 10% solution of ammonia to one-third the volume of the whole. The solution is filtered after two hours.

[7] Wolcott Gibbs, *Am. J. Sci.*, [3] **5**, 114 (1873). Precipitation is effected with microcosmic salt from a concentrated, neutral boiling solution containing NH_4Cl. After cooling, $^1/_3$ of the volume of a 10% ammonia solution is added. No details are given as to excess of precipitant or time of standing, in which cases standard procedure was followed.

Single precipitations in the presence of ammonium oxalate gave slightly high results, Table III-H, but on reprecipitating under standard conditions correct values were obtained.

The presence of ammonium sulfate, arising from the use of sulfuric acid instead of hydrochloric in the course of analysis, showed no effect, Table III-K.

The presence of citric acid in amounts varying from 0.5 to 2.0 g. was found to have no effect on the precipitate, Table III-L.

In precipitating $MgNH_4PO_4$ from phosphate solutions containing an excess of $MgCl_2$, the results of similar variations in procedure are not always comparable to those obtained when precipitating from magnesium solutions containing an excess of phosphate.

Discussion of Procedures for the Determination of Phosphoric Anhydride

In the tests of procedures for the determination of phosphoric anhydride, solutions of diammonium phosphate, made from Kahlbaum's C. P. salt, were used. The solutions were kept in glass-stoppered Jena glass bottles and were slightly acidified with nitric acid to prevent action of the alkaline solution on the glass. The solutions were analyzed for P_2O_5 content by a number of determinations as magnesium pyrophosphate. In these determinations, a standard method, directly comparable with that used in the determination of magnesium, was used.

The only method for the determination of phosphoric anhydride which appeared practicable as a check on the magnesia method was an adaptation of the silver phosphate method. The method as used was developed for this investigation and was based on the possibility of obtaining quantitatively a uniformly normal precipitate of silver phosphate, Ag_3PO_4, the silver in which can then be obtained by the Volhard method. Various authors[8] have confirmed the value of such a method in different forms and it is believed that as given the method will be found accurate for the determination of phosphoric anhydride in solutions containing no interfering substances. The procedure developed is as follows.

To the cool phosphate solution, very slightly acid with nitric acid, and containing not more than 0.1 g. of P_2O_5, add 5 cc. of a saturated solution of sodium acetate. Add an excess of 10% silver nitrate solution until no more precipitate appears. Heat on the steam-bath for about ten minutes, then filter through a Gooch crucible and wash thoroughly with hot water. Dissolve the precipitate by washing through the crucible with dilute nitric acid (1:4, sp. gr. 1.10) and titrate with a standard solution of potassium thiocyanate, by the Volhard method, using ferric ammonium sulfate as

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[8] (a) Kolthoff, *Pharm. Weekblad,* **59,** 205 (1922); (b) Clark, *J. Soc. Chem. Ind.,* **7,** 311 (1888); (c) Holleman, *Z. anal. Chem.,* **33,** 185 (1894); (d) Wilkie, *J. Soc. Chem. Ind.,* **29,** 794 (1910).

indicator. Comparative results showing the degree of uniformity and the very close agreement between this and the pyrophosphate method, are given in Table IV.

TABLE IV

DETERMINATION OF PHOSPHORIC ANHYDRIDE

Solution	Grams per cc.[a] P_2O_5 (weighed as $Mg_2P_2O_7$)	P_2O_5 (titrated as Ag_3PO_4)
$NaNH_4HPO_4$	0.00682	0.00686
$(NH_4)_2HPO_4$	.01045	.01045
$(NH_4)_2HPO_4$	.00930	.00930
$(NH_4)_2HPO_4$	.00956	.00956

[a] Each result is the average of at least three closely agreeing determinations.

Standard Procedure for the Determination of Phosphoric Anhydride

To the neutral or weakly acid solution of phosphate, containing not more than 0.1 g. of P_2O_5, add 5 cc. of concentrated hydrochloric acid, and methyl red indicator. Dilute the solution to 150 cc. and add 10 cc. or a 5- to 10-fold excess, of the precipitant, preferably magnesia mixture without ammonia (50 g. of $MgCl_2.6H_2O$, 100 g. of NH_4Cl and 5 cc. of concentrated HCl in 1 liter of H_2O). The solution should be acid after the addition of the precipitant. Then add ammonia water (sp. gr. 0.90) slowly, while stirring, to neutralization. Stir for about five minutes, or until the precipitate of magnesium ammonium phosphate is well formed, then add 5 cc. excess of ammonia water and stir for ten minutes. Let stand for at least four hours, preferably overnight, filter and wash with water containing from 3 to 5% by volume of ammonia water (sp. gr. 0.90). Dissolve the precipitate by washing on the filter with warm 1:9 hydrochloric acid (sp. gr. 1.02). Add methyl red indicator, 1 cc. of magnesia mixture and finish the precipitation as before but in a volume of 100 to 150 cc. In this precipitation digestion for four hours is sufficient. In igniting the precipitate, the wet filter paper with the precipitate should be placed in a weighed platinum crucible, charred without flaming, then ignited at a low temperature (approximately 500°) and with the lid open enough for circulation of air until the residue is white, and finally at approximately 1000° to constant weight.

Discussion of the Results Obtained in the Determination of Phosphoric Anhydride

As shown by figures given in Table V-A, an excess of ammonium chloride was found to give high results in single precipitations as in the case of magnesium. When the solutions were allowed to stand for sixteen hours the results, however, were better. On reprecipitating under "standard" conditions, the results were correct. Absence of added ammonium chloride did not affect the precipitate materially. It will be noted that in the case of large excess of ammonium chloride (25 g.) results were low, differing from the determination of magnesium. Apparently the same effect is noted later (Table V-C) where it is indicated that the presence of ammonium chloride has a tendency to compensate for high results due to large excess of magnesium chloride.

TABLE V

DATA OBTAINED IN DETERMINATION OF PHOSPHORIC ANHYDRIDE AS $Mg_2P_2O_7$

Figures reported are averages of three or more determinations

(All precipitations as specified in standard procedure, unless otherwise specified in table. Final volume approximately 170 cc.)

Variation from standard procedure	No. of pptns.	Wt. of $Mg_2P_2O_7 \Bumpeq P_2O_5$ taken, g.	Wt. of $Mg_2P_2O_7$ found, g.	Remarks[a]
		V-A		
Excess NH_4Cl, g.				
16	1 (4 hr.)	0.1458	0.1463	(1)
16	1 (16 hr.)	.1458	.1461	(1)
16	2 (16 hr.)	.1458	.1457	(2)
None	1 (16 hr.)	.1496	.1499	Results not uniform
1	1 (16 hr.)	.1496	.1500	Results not uniform
5	1 (16 hr.)	.1496	.1500	Results not uniform
10	1 (16 hr.)	.1496	.1499	(1)
25	1 (16 hr.)	.1496	.1473	(1)
		V-B		
Excess NH_4OH, cc.				
25	1 (4 hr.)	.1458	.1473	(1)
25	1 (16 hr.)	.1458	.1459	(1)
25	2 (16 hr.)	.1458	.1457	(2)
40 ($^1/_4$ vol.)	1 (16 hr.)	.1458	.1458	(1)
55 ($^1/_3$ vol.)	1 (16 hr.)	.1458	.1465	(1)
85 ($^1/_2$ vol.)	1 (16 hr.)	.1458	.1473	(1)
		V-C		
Excess Mg mixture, cc.				
100	1 (4 hr.)	.1458	.1520	(1)
100	1 (16 hr.)	.1458	.1487	(1)
100	2 (16 hr.)	.1458	.1457	(2)
150	1 (10 min.)	.1458	.1445	Schmitz method
100 cc. Mg mix.				
14 g. NH_4Cl added	1 (16 hr.)	.1458	.1485	Mahon method
25 g. NH_4Cl added	1 (16 hr.)	.1458	.1480	Mahon method
2 g. NH_4Cl added	1 (16 hr.)	.1458	.1430	Mahon method
No NH_4Cl added	1 (16 hr.)	.1458	.1216	Mahon method
		V-D		
Pptn. made in ammoniacal soln.				
4 cc. NH_4OH	1 (3 hr.)	.1458	.1462	Neubauer
(2.5% by vol.)	2 (16 hr.)	.1458	.1468	Neubauer
(2.5% by vol.)	2 (16 hr.)	.1496	.1505	(1) (2)

TABLE V (*Concluded*)

Variation from standard procedure	No. of pptns.	Wt. of $Mg_2P_2O_7 \Bumpeq P_2O_5$ taken, g.	Wt. of $Mg_2P_2O_7$ found, g.	Remarks[a]
		V-E		
Jarvinen procedure	1 (2 hr.)	.1458	.1464	Neutral soln.
		V-F		
Pptn. made in hot soln.	1 (16 hr.)	.1458	.1460	In comparison with Gibbs' method for Mg (1) (2)
	2 (16 hr.)	.1458	.1463	
		V-G		
$(NH_4)_2SO_4$ present	1 (16 hr.)	.1496	.1520	H_2SO_4 substituted for HCl in standard procedure (2)
$(NH_4)_2SO_4$ present	2 (16 hr.)	.1496	.1502	
		V-H		
Citric acid, g.				
2	1 (16 hr.)	.1458	.1443	(1)
0.5	1 (16 hr.)	.1458	.1450	
0.5	2 (16 hr.)	.1458	.1451	(1) (2)

[a] (1) Standard procedure followed except for variation noted.
(2) Reprecipitated under standard conditions.

Excess ammonium hydroxide was found, Table V-B, to have substantially the same effect as in the determination of magnesium. A concentration higher than $^1/_4$ volume was found to give high results, as in the determination of magnesium, while reprecipitation gave correct results.

A large excess of the precipitant ($MgCl_2.NH_4Cl$) was found, Table V-C, to give high results on single precipitation, correct results being obtained by reprecipitating under standard conditions. Precipitations by the method of Schmitz[9] gave low results, probably owing to the extremely short time allowed before filtering. Tests of Mahon's assertion[10] that excess of ammonium chloride compensates for the error due to excess of magnesia mixture, showed his statements to be incorrect. However, results were very low when no ammonium chloride, or very small amounts, were present, indicating that the presence of this salt has the tendency claimed, but does not wholly remedy the condition.

Precipitations made in ammoniacal solutions were found, Table V-D,

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[9] Schmitz, *Z. anal. Chem.*, **45,** 512 (1906); *ibid.*, **65,** 46 (1924). A large excess (150 cc.) of acidified magnesia mixture and 10–20 cc. of a saturated solution of NH_4Cl are added, the solution is heated to boiling and a 2.5% solution of ammonia added, with constant stirring, until the solution is alkaline to phenolphthalein. The solution is then cooled and one-fifth of its volume of ammonia is added. The solution is filtered after standing for ten minutes.

[10] Mahon, THIS JOURNAL, **20,** 445 (1898). The method is not described in detail. It is stated that when $MgCl_2$ is in large excess the error is reduced by the presence of NH_4Cl, but the ratio necessary for accurate results is not indicated.

to give high results, contrary to statements of Neubauer.[11] Reprecipitation under standard conditions did not remedy the error.

Precipitations in exactly neutral solution, according to the method of Jarvinen,[12] gave results, Table V-E, that were not uniform and averaged slightly higher than the true figure, as was the case in the determination of magnesium.

Precipitations in hot solution gave slightly high results, Table V-F, differing from the determination of magnesium, which was not affected by the temperature of precipitation.

The presence of ammonium sulfate, owing to the use of sulfuric acid instead of hydrochloric, gave high results, Table V-G. In the determination of magnesium it had no effect.

Precipitations in the presence of citric acid, Table V-H, gave low results which were not uniform. This was not entirely remedied by reprecipitation under standard conditions.

Conclusions

The most significant fact brought out by these studies is that a double precipitation, the second under exactly defined conditions, is necessary, to insure the quantitative precipitation of $MgNH_4PO_4$. Consequently this procedure should be followed in all accurate work. It is also demonstrated that in the determination of magnesium the errors due to (1) a very large excess of precipitant, (2) the presence of potassium chloride and (3) the addition of the precipitant to an ammoniacal solution, were not entirely remedied by reprecipitation. These conditions may easily be avoided, however, except that due to excess of potassium chloride. In this case it was found that a third precipitation usually gave a precipitate of the desired composition and a correct result.

In the determination of phosphoric anhydride the only errors not remedied by reprecipitation are those due to (1) addition of the precipitant to the solution while ammoniacal, (2) precipitation in hot solution (slight

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[11] Neubauer, *Z. anorg. Chem.*, **4**, 251 (1893); *Z. angew. Chem.*, **9**, 435 (1896). The phosphate is precipitated in 100 cc. of a cold solution containing 2.5% of ammonia by adding dropwise, with constant stirring, as many cc. of magnesia mixture as there are centigrams of P_2O_5 present. The solution is then stirred, allowed to stand for three hours, filtered, the precipitate washed with a 2.5% solution of ammonia and ignited to constant weight. A correction for loss on ignition is added by the author.

[12] Jarvinen, *Z. anal. Chem.*, **43**, 279 (1904). The phosphate solution is mixed with NH_4OH until the odor of ammonia is noted. The solution is poured slowly, with constant stirring, into a neutral mixture of $MgCl_2$ and NH_4Cl. Free ammonia should be absorbed by the formation of the precipitate. If the mixture smells of ammonia, trimagnesium phosphate may be formed. After precipitation is complete, a 0.5% solution of ammonia is added until a strong odor of ammonia is detected; finally, one-third of the volume of a 10% solution of ammonia. The mixture is allowed to stand for two hours and filtered.

error only), (3) the presence of ammonium sulfate and (4) the presence of citric acid. The first two can be avoided; while the error caused by sulfate is negligible in any but the most accurate work.

The general impression of great difficulty and inaccuracy that has surrounded the determination of magnesium and phosphoric anhydride as magnesium pyrophosphate, is largely the effect of the mass of conflicting publications on the subject. The standard procedures here recommended have been found to give accurate results with reasonable care and the data presented should answer many questions as to the value of recommendations to be found in the literature on the subject.

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THE EQUILIBRIUM PRESSURE OVER COEXISTING SALT HYDRATES AT TEMPERATURES BELOW 0°

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RECEIVED SEPTEMBER 6, 1927 PUBLISHED FEBRUARY 4, 1928

The phase relations for salt hydrates have been worked out fairly completely but there remain one or two minor points which appear not to have been specifically discussed. One of these is the question as to whether the vapor pressure curve of a system composed of two adjacent hydrates and vapor intersects the ice-vapor curve in the low temperature region.

The principle involved will be evident from a consideration of the P-T diagram as given in Fig. 1. The hydrates are denoted by S_1, S_2, S_3, etc.; the saturated solution by L, other solutions by L^{I}, L^{II}, etc.; ice by I and the vapor by V. The vapor pressure of all unsaturated solutions of the salt ranges between the water line and the line representing the vapor pressure of the system S_1-L-V; that of the system S_1-S_2-V is another line below the S_1-L-V line. Similarly, if other hydrates exist, there is a corresponding curve, for example, S_2-S_3-V for each pair of adjacent hydrates. Now the line for the unsaturated solution intersects the ice curve at the ordinary freezing temperature of the particular solution, the phases then present being I-L^{I}-V; that for the saturated solution S_1-L-V intersects the ice curve at the eutectic temperature, the four coëxisting phases being S_1-I-L-V. The question now arises as to whether the curve for systems composed of two hydrates and vapor will meet the ice-vapor curve if the temperature is sufficiently low; this point must, according to Blasdale, be considered.[1] Such an intersection would imply

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[1] Blasdale, "Equilibria in Saturated Salt Solutions," Chemical Catalog Company, New York, 1927, p. 39.