XXVII.—*The Pyrophosphate Method for the Determination of Magnesium.*

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It is known that in the determination of magnesium as pyrophosphate great care is necessary to obtain a precipitate of the composition $MgNH_4PO_4$ (Epperson, *J. Amer. Chem. Soc.*, 1928, **50**, 321) and that it is necessary to ensure that ignition yields pure magnesium pyrophosphate free from organic matter. Various devices for obtaining the product white have been suggested (McNabb, *ibid.*, p. 301; Hillebrand, *Bull. Geol. Survey, U.S.A.*, 1919, **700**, 151), but Epperson has shown that these expedients are of little value. Since platinum crucibles are expensive and may be damaged, it is desirable to utilise porcelain or sintered-glass crucibles. In this case, however, lower temperatures of ignition must be used. Theoretical considerations lead to the conclusion that the temperature necessary for a complete dissociation of $MgNH_4PO_4$ cannot be so high as hitherto used, *viz.*, 900—1200°. Most ammonium salts dissociate below 500°, and ortho- is transformed into pyro-phosphoric acid at or below 250°. Moreover, it is a common experience that the charring of organic material is the more complete, and the ash the whiter, the lower the temperature used. Further, McNabb (*J. Amer. Chem. Soc.*, 1927, **49**, 1451) has shown that the analogous dissociation of magnesium ammonium arsenate is complete at 500—600°. An attempt was therefore made to ignite magnesium ammonium phosphate at as low a temperature as possible, and 480° was chosen as being probably the most suitable.

EXPERIMENTAL.

For filtration, the sintered Jena-glass crucibles used (No. 3, with an average pore diameter of 20—30 μ) were very satisfactory : one of them was used 50 times, and is still in use, showing only a slight corrosion and having lost only 0·021 g. owing to repeated cleaning with concentrated hydrochloric acid.

The tests were made with $N/20$-solutions of magnesium chloride or sulphate as standard. The magnesium content of the former was checked by evaporation with yellow mercuric oxide, ignition, and weighing as magnesium oxide, or by evaporation with sulphuric acid and weighing as magnesium sulphate; for the latter standard, only the second method was used, the other method being impracticable. As the magnesium sulphate solution was slightly too concentrated, corrected values for the calculated amount of pyrophosphate were substituted in Tables II and III.

The details of the estimation were as follows. To a measured amount of the solution, diluted with 200 c.c. of water, were added 3 drops of concentrated hydrochloric acid and then a filtered solution of 0·5 g. of ammonium chloride and 1 g. of ammonium phosphate in 20 c.c. of water containing 2 or 3 drops of a 1% alcoholic solution of phenolphthalein. The mixture was heated to boiling, and aqueous ammonia was added slowly drop by drop until the colour remained pink after prolonged stirring, followed by 50 c.c. of ammonia solution (*d* 0·96) while the mixture was still hot. After standing over-night, the liquid was filtered through a sintered-glass crucible, the precipitate washed with about 50 c.c. of 2½% ammonium hydroxide solution, heated in an electric oven at 480° for 2 hours, and weighed. Subsequent heatings at the same temperature and weighings showed that the precipitate had attained constant weight in the first heating : it was a light snow-white powder. The results are in Tables I, II, and III.

TABLE I.

N/20-Solution of $MgCl_2,6H_2O$ used. Single precipitation.

Amount of solution taken,

10 c.c. $Mg_2P_2O_7$ calc., 0·0557 g.		20 c.c. $Mg_2P_2O_7$ calc., 0·1114 g.		50 c.c. $Mg_2P_2O_7$ calc., 0·2785 g.	
$Mg_2P_2O_7$ found, g.	Diff., g.	$Mg_2P_2O_7$ found, g.	Diff., g.	$Mg_2P_2O_7$ found, g.	Diff., g.
0·0545	−0·0012	0·1100	−0·0014	0·2770	−0·0015
0·0541	−0·0016	0·1098	−0·0016	0·2770	−0·0015
0·0551	−0·0006	0·1117	+0·0003	0·2775	−0·0010
0·0556	−0·0001	0·1107	−0·0007	0·2770	−0·0015
0·0556	−0·0001	0·1102	−0·0012	0·2778	−0·0007
0·0551	−0·0006	0·1105	−0·0009	0·2783	−0·0002
0·0550*	−0·0007*	0·1105*	−0·0009*	0·2774*	−0·0011*
Average error, −1·26%.		Average error, −0·81%.		Average error, −0·39%.	

* Mean.

TABLE II.

N/20-Solution of $MgSO_4,7H_2O$ used. Single precipitation.

Amount of solution taken,

5 c.c. $Mg_2P_2O_7$ calc., 0·0284 g.		25 c.c. $Mg_2P_2O_7$ calc., 0·1420 g.		50 c.c. $Mg_2P_2O_7$ calc., 0·2839 g.	
$Mg_2P_2O_7$ found, g.	Diff., g.	$Mg_2P_2O_7$ found, g.	Diff., g.	$Mg_2P_2O_7$ found, g.	Diff., g.
0·0293	+0·0009	0·1415	−0·0005	0·2845	+0·0006
0·0297	+0·0013	0·1404	−0·0016	0·2852	+0·0013
0·0286	+0·0002	0·1408	−0·0012	0·2838	−0·0001
0·0284	±0·0000	0·1409	−0·0011	0·2848	+0·0009
0·0283	−0·0001	0·1404	−0·0016	0·2850	+0·0011
0·0281	−0·0003	0·1406	−0·0014	0·2848	+0·0009
0·0287*	+0·0003*	0·1408*	−0·0012*	0·2850*	+0·0011*
Average error, +1·06%.		Average error, −0·85%.		Average error, +0·39%.	

* Mean.

TABLE III.

$N/20$-Solution of $MgSO_4,7H_2O$ used. Double precipitation.

Amount of solution taken, 50 c.c. $Mg_2P_2O_7$ calc., 0·2839 g.

$Mg_2P_2O_7$ found, g.	Diff., g.	$Mg_2P_2O_7$ found, g.	Diff., g.
0·2841	+0·0002	0·2848	+0·0009
0·2843	+0·0004	0·2848	+0·0009
0·2843	+0·0004	0·2847	+0·0008
		Mean 0·2845	+0·0006

Average error, +0·21%.

Tables II and III show that scarcely any alteration is effected by reprecipitation of the double phosphate.

In order to ascertain whether the conversion into pyrophosphate was complete at 480°, 0·2 g. samples of the pyrophosphate obtained were heated for ½ hour in a platinum crucible by a blast burner; the powder sintered to a hard crumbly mass, but the losses in four cases were 1·7, 1·7, 1·3 and 1·4 mg., giving an average of 1·5 mg. or 0·75%.

The method described above proved satisfactory in a long series of determinations of magnesium in mineral waters.

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