Quantitative Analysis of Phosphoric Acid, Part VI. Determination of Phosphoric Acid in a Phosphate Fertilizer

By

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Phosphoric acid in a phosphate fertilizer is generally precipitated as ammonium phosphomolybdate from its nitric acid solution and determined as magnesium pyrophosphate. Shortly before[1], I published the results of investigation on the quantitative analysis of phosphoric acid and proposed many important improvements which are to be added to the old methods hitherto in use, together with my own method newly contrived. Now applying these new and improved methods to the analysis of a phosphate fertilizer, a critical study was carried out, and as the consequence it was made clear that, though the magnesium pyrophosphate method gave the best result, the ammonium phosphomolybdate method may also be employed with very satisfactory result both gravimetrically and volumetrically, and that especially the volumetric method may be regarded as the most convenient one for practical purpose.

I. Determination of total phosphate as magnesium pyrophosphate

The method adopted by the Department of Commerce and Industry is somewhat different from my own method, and according to my previous investigation such a method can not be expected to give an accurate result as it contains many sources of error[2]. To

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1. These Memoirs, **12**, 23, 39, 49, 135 (1929)
2. These Memoirs, **12**, 23−32 (1929)

prove this experimentally the determination of phosphoric acid in Kahlbaum's ammonium phosphate " zur Analyse mit Garantieschein " was conducted, using the method of the Department of Commerce and Industry on the one hand and that proposed by me on the other. For each experiment 0.2500 gram of ammonium phosphate was taken.

From these figures it is clearly seen that the method improved by me gives far more exact and concordant results, when compared with that adopted by the Department of Commerce and Industry. As the consequence all experiments described below were always conducted according to my method.

A sample of a phosphate fertilizer obtained from the Dainippon Zin-

(a) The method of the Department of Commerce and Industry

$Mg_2P_2O_7$ grm.	P_2O_5 (53.77%) %	Diffce. %
0.2116	53.99	0.22
0.2126	54.23	0.49
0.2098	53.54	−0.23
0.2100	53.59	−0.18

(b) The writer's method

$Mg_2P_2O_7$ grm.	P_2O_5 (53.77%) %	Diffce. %
0.2106	53.74	−0.03
0.2105	53.71	−0.06
0.2105	53.71	−0.06

zohiryo Kabushiki Kwaisha was powdered and 5.4874 gms. of it were treated with warm aqua regia and the solution thus obtained was diluted to 500 ml. For each experiment 25 ml. of this solution were taken and the phosphoric acid was determined first by precipitating it as ammonium phosphomolybdate and then changing it into magnesium pyrophosphate.

As there exists some sulphate in a phosphate fertilizer it may sometimes be precipitated together with ammonium phosphomolybdate and finally may come out with magnesium ammonium phos-

$Mg_2P_2O_7$ grm.	P_2O_5	
	grm.	%
0.0774	0.04938	18.01
0.0775	0.04944	18.03
0.0778	0.04963	18.10

phate in the form of magnesium sulphate[1], becoming thus a cause of the positive error.   To see whether such disturbance really occurs the precipitation of phosphoric acid was repeated twice using the

1. These Memoirs, **12**, 34 (1929)

reprecipitation method. The result, however, did not alter, showing that there was no bad effect of sulphate ion on the analysis, thus :—

$Mg_2P_2O_7$ grm.	P_2O_5	
	grm.	·%
0.0777	0.04957	18.08
0.0772	0.04925	17.96
0.0774	0.04938	18.01

II. Determination of total phosphate as ammonium phosphomolybdate

For analysis 5.4824 grm. of a phosphate fertilizer dried at 105° were treated with warm aqua regia, and the solution thus obtained was diluted to one litre. 25 ml. of this solution were taken for each determination, and the phosphoric acid was weighed as ammonium phosphomolybdate according to the method[1] previously published by me. The results of analysis were as follows :—

In these experiments the double precipitation method was used in order to remove the bad effect of sulphate ion if any.

With the object of knowing how far these results agree with those obtained by the magnesium pyrophosphate method a series of experiments were carried out taking 50 ml. of the same sample solution for each determination, and the following results were obtained.

$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	P_2O_5	
	grm.	%
0.6687	0.02528	18.44
0.6715	0.02538	18.52
0.6717	0.02539	18.52
0.6740	0.02547	18.59
0.6642	0.02511	18.32

$Mg_2P_2O_7$ grm.	P_2O_5	
	grm.	%
0.0800	0.05103	18.62
0.0788	0.05027	18.34
0.0805	0.05135	18.73
0.0795	0.05072	18.50
0.0796	0.05078	18.52

1. These Memoirs, **12**, 135 (1929)

Both results were thus found quite concordant.

The volumetric ammonium phosphomolybdate method[1] improved by me was also found to give exact results when applied to analysis of a phosphate fertilizer.   As the concentration of sulphuric acid in the sample solution is very small, its influence on the exactness of the analysis may be regarded as negligible.   The results of analysis conducted by taking 7 ml. of the above-stated sample solution for each determination were as follows :

Nearly the same results were produced, when the determination was made with ammonium phosphomolybdate purified by double precipitation, thus—

In this analysis care must be taken not to use ammonium molybdate in quantities beyond a certain limit.   If the molar ratio of ammonium molybdate to phosphoric acid becomes greater than 4, a considerable positive error is introduced to the value of phosphoric acid, as is shown in the following table :

$\frac{N}{10}$—NaOH used ml.	P_2O_5	
	grm.	%
23.40	0.007090	18.48
23.38	0.007864	18.46
23.40	0.007090	18.48

$\frac{N}{10}$—NaOH used ml.	P_2O_5	
	grm.	%
23.38	0.007084	18.46
23.30	0.007060	18.40
23.32	0.007066	18.41

Am. Molybdate Molar ratio to H_3PO_4	$\frac{N}{10}$—NaOH ml.	P_2O_5	
		grm.	%
2	16.70	0.005060	18.46
,,	16.73	0.005069	18.49
,,	16.65	0.005045	18.40
3	16.72	0.005066	18.48
,,	16.72	0.005066	18.48
,,	16.75	0.005075	18.51
4	17.00	0.005151	18.79
,,	16.98	0.005145	18.77
,,	16.95	0.005136	28.73
6	17.30	0.005242	19.12
,,	17.33	0.005251	19.15
,,	17.27	0.005233	19.08

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1. These Memoirs, **12**, 148 (1929)

III. Determination of a water soluble phosphate

Sometimes the sample solution for determining a water soluble phosphate is carelessly prepared in such a way that water is poured to a measuring flask containing a known quantity of a phosphatic fertilizer to fill up a definite volume, and this volume is taken as the volume of the soluble phosphate solution. Theoretically speaking, such a procedure can not be regarded as defectless in any case, and the error thus brought about becomes more significant, when the quantity of solid fertilizer taken becomes greater, as is shown in the following experiments.

Experiment 1.—1.5817 grm. of a phosphate fertilizer dried at $105°$ were digested with 160 ml. of water for an hour and water was added to it to fill up to 500 ml. The solution was then filtered, and 25-ml. and 5-ml. portions of the filtrate were analysed, the former gravimetrically and the latter volumetrically, according to the ammonium phosphomolybdate method. The results were as follows:

$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	$\frac{N}{10}$ —NaOH ml.	P_2O_5	
		grm.	%
0.3540	—	0.01339	16.92
0.3541	—	0.01339	16.92
0.3530	—	0·01334	16.87
—	17.60	0.005333	16.86
—	17.64	0.005345	16.90
—	17.62	0.005339	16.88

Experiment 2—2.9456 grm. of the same phosphate fertilizer were treated just in the same manner as in experiment 1.

$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	$\frac{N}{10}$ —NaOH ml.	P_2O_5	
		grm	%
0.6703	—	0.02535	17.21
0.6700	—	0.02533	17.20
0.6718	—	0.02537	17.24
—	16.75	0.005075	17.23
—	16.70	0.005060	17.18
—	16.73	0.005069	17.21

Experiment 3.—3 9110 grm. of the same phosphate fertilizer were employed.

$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	$\dfrac{N}{10}$—NaOH ml.	P_2O_5	
		grm.	%
0.9035	—	0.03415	17.46
0.9032	—	0.03414	17.46
0.9021	—	0.03410	17.44
—	22.46	0.006805	17.40
—	22.50	0.006818	17.43
—	22.50	0.006818	17.43

There are several modes of extracting soluble phosphate from a phosphatic fertilizer. In order to know which method works most satisfactorily the agitation method, the stationary method and the boiling water method were compared. The extract solution was separated from solid matter by filtration and diluted to 500 ml, and it was analysed by the ammonium phosphomolybdate method taking 25 ml. of the solution for gravimetric and 10 ml. for volumetric analysis.

A. The agitation method

Experiment 1.—2.5521 grm. of a phosphate fertilizer dried at 105° were mixed with 130 ml. of water and the mixture was agitated for an hour, at the rate of 500 revolutions per minute. The results were as follows:

$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	$\dfrac{N}{10}$—NaOH ml.	P_2O_5	
		grm.	%
0.5677	—	0.02146	16.81
0.5680	—	0.02147	16.82
0.5689	—	0.02150	16.85
—	28.40	0.008606	16.85
—	28.44	0.008618	16.88
—	28.34	0.008588	16.82

Experiment 2.—2.3553 grm. of the fertilizer were agitated with 354 ml. of water in the manner analogous to experiment 1. The results of analysis were as follows:

$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	$\frac{N}{10}$ —NaOH ml.	P_2O_5 grm.	%
0.5242	—	0.01982	16.83
0.5250	—	0.01984	16.85
0.5250	—	0.01984	16.85
—	26.12	0.007914	16.80
—	26.20	0.007939	16.85
—	26.12	0.007914	16.80

B. The stationary method

Experiment 3.—2 6800 grm. of the sample fertilizer were treated with 268 ml. of water and the mixture was left to stand over night. The results of analysis were as follows:

$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	$\frac{N}{10}$ —NaOH ml.	P_2O_3 grm.	%
0.5973	—	0.02258	16.85
0.5985	—	0.02262	16.88
0.5985	—	0.02262	16.88
—	29.73	0.009014	16.82
—	29.77	0.009020	16.83
—	29.83	0.009038	16.86

C. The boiling water method

Experiment 4.—1.9912 grm. of the dried sample were boiled with 100 ml. of water for 30 minutes, and the dissolved phosphate was analysed with the following results:

$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	$\dfrac{N}{10}$ — NaOH ml.	P_2O_5	
		grm.	%
0.4473	—	0.01691	16.98
0.4468	—	0.01689	16.96
0.4456	—	0.01684	16.92
—	22.25	0.006742	16.93
—	22.27	0.006748	16.94
—	22.31	0.006760	16.97

Experiment 5.—2.1364 grm. of the dried sample were boiled with 427 ml. of water for 30 minutes and the phosphoric acid dissolved out was analysed as usual, with the following results:

$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	$\dfrac{N}{10}$ — NaOH ml.	P_2O_5	
		grm.	%
0.4818	—	0.01821	17.05
0.4799	—	0.01814	16.98
0.4786	—	0.01809	16.94
—	23.83	0.00722	16.90
—	23.83	0.00722	16.90
—	23.86	0.00723	16.92

From the above results it is seen that the values of P_2O_5 given by the methods A and B are quite concordant, while the method C gives a somewhat higher value. This is perhaps due to the partial dissolution of $CaHPO_4$ in hot water.

IV. Determination of free phosphoric acid

Though ether is generally used as the extracting agent for free phosphoric acid in a phosphatic fertilizer the amounts of phosphoric acid thus extracted are not concordant, making the result very unreliable. In my experiment here described alcohol and acetone were selected as the solvents with the object of comparing their action with that of ether. Soxhlet's extractor was used for extraction and

the extracted acid slightly coloured yellowish brown was dissolved in water and diluted to 250 ml., from which 50 ml. were taken for gravimetric and 25 ml. for volumetric determination.

1. *Ether extraction*

Though the extraction of phosphoric acid with ether was observed to have been completed in 2 hours, the extractor was kept in action for 2 hours more to ensure safety. The amounts of phosphoric acid were found to be as follows:

Sample taken grm.	$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	$\frac{N}{10}$—NaOH ml.	P_2O_5	
			grm.	%
4.5669	0.6018	—	0.02275	2.49
„	—	36.88	0.01117	2.45
3.1438	0.2375	—	0.008977	1.43
„	—	14.72	0.004460	1.42
2.6391	0.1425	—	0.005386	1.02
„	—	9.13	0.002760	1.05
3.0698	0.3710	—	0.01402	2.28
„	—	23.05	0.006984	2.28
3.3696	0.2802	—	0.01059	1.57
„	—	17.46	0.005290	1.57
3.9891	0.3578	—	0.01352	1.70
„	—	22.20	0.006727	1.69
3.1619	0.4078	—	0.01542	2.44
„	—	25.28	0.007660	2.42

In these experiments too no reliable results could be obtained.

2. *Alcohol extraction*

Extraction with 99.8% alcohol was continued for 2 hours and the following values were found for the phosphoric acid extracted.

Sample taken grm.	$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	$\frac{N}{10}$—NaOH ml.	P_2O_5	
			grm.	%
3.5434	0.9090	—	0.03436	4.85
,,	—	56.26	0.01705	4.81
3.6202	0.9208	—	0.03481	4.81
,,	—	56.75	0.01720	4.75
2.0263	0.3364	—	0.02028	5.00
,,	—	33.47 .	0.01014	5.00
1.6912	0.4200	—	0.01588	4.69
,,	—	26.05	0.07893	4.67
2.0250	0.5233	—	0.01978	4.88
,,	—	32.53	0.009857	4.87

The values of phosphoric acid thus found are very much greater than those found with ether, but they are fairly constant.

3. *Acetone extraction*

Extra pure acetone obtained from Merck was used for extraction which was continued for 2 hours.

Sample taken grm.	$(NH_4)_3PO_4 \cdot 12MoO_3$ grm.	$\frac{N}{10}$—NaOH ml.	P_2O_5	
			grm.	%
1.8462	0.3750	—	0.01417	3.84
,,	—	23.45	0.007105	3.85
1.8372	0.3737	—	0.01413	3.83
,,	—	23.32	0.007066	3.85
1.2046	0.2420	—	0.009148	3.80
,,	—	15.12	0.004581	3.80
1.6250	0.3144	—	0.01188	3.66
,,	—	19.60	0.005939	3.65
2.1135	0.4121	—	0.01558	3.69
,,	—	25.61	0.007760	3.67

It is seen from the table that the most constant value is obtained for phosphoric acid when acetone is used as the solvent. The reason why amounts of free phosphoric acid extracted with different solvents differ from each other so widely is to be investigated in future.

Summary

1. With the object of knowing how far the writer's improved methods for determination of phosphoric acid can be applied to practical purpose the determinations of total phosphate, water soluble phosphate and free phosphoric acid in a phosphate fertilizer were carried out, and some of the results were compared with those obtained by the standard method of the Department of Commerce and Industry.

2. It was confirmed that though the magnesium pyrophosphate method gave the most exact results the ammonium phosphomolybdate method could also be used with sufficient accuracy.

3. From the practical point of view the volumetric phosphomolybdate method excels all other methods, especially for determination of a small quantity of phosphoric acid.

4. A comparative study on the extraction of free phosphoric acid was made using ether, alcohol and acetone as the solvents. It was confirmed as the result that use of ether is, by no means, recommendable, for the value of the phosphoric acid extracted with that solvent always varies according to the circumstances and it never gives a constant and reliable result. Acetone gave the best result and alcohol came next.