XIX.—ON THE ESTIMATION OF PHOSPHORIC ACID AS MAGNESIC PYROPHOSPHATE.

BY THOMAS S. GLADDING.

In a valuable paper on the determination of phosphoric acid as magnesic pyrophosphate (*Amer. Chem. Journal*, vol. 1, 391) Gooch has demonstrated that this method, far from being as accurate as is generally supposed, is peculiarly liable to sources of error, which cause a considerable overestimation of the phosphoric acid actually present.

The great importance of this analytical determination from a commercial point of view, gives enhanced interest to any inquiry as to its accurate execution. In view of the vast capital at present engaged in the conversion of phosphatic materials into artificial fertilizers, and in view of the fact that chemists frequently differ so widely in this important determination, the necessity, both for the interests of commerce and the credit of science, of an accurate and rigid method can be clearly understood. In the case of large and valuable cargoes sold upon chemical analysis, the slight error of even $\frac{1}{10}$ of a per cent. in the estimation of phosphoric acid causes a difference in value ranging from twenty-five up to two hundred dollars.

I have been led by these considerations to a careful examination of the modes of procedure at present recommended by the best authorities and which are in common use among chemists.

In the latest American edition of *Fresenius' Quant. Analysis* the directions are, to add to the neutral or moderately ammonical solution of the phosphate, magnesia mixture in slight excess, and after letting stand for some time, $\frac{1}{3}$ its volume of strong ammonia solution. In the case of a previous precipitation as phospho-molybdate of ammonia, this precipitate is dissolved in weak ammonia and the neutral or slightly ammoniacal solution, treated as above.

The method recommended by the convention of chemists of the different experimental stations of Germany (held in Dec. 1881) is translated as follows: (Zeit. fur. Anal. Chem. 21, p. 290) "The beaker glass is now placed under the funnel, the filter pierced with a platinum wire, the precipitate washed into the beaker glass with $2\frac{1}{2}$ per cent. ammonia liquor, and dissolved by stirring with a glass rod, and then enough of the $2\frac{1}{2}$ per cent. ammonia liquor added, to bring the volume of the liquid up to about 75 cc. To 0.1 gram phosphoric acid, 10 cc. magnesia mixture are now dropped in accompanied by a constant stirring up." In a foot note is added "a gradual addition of the magnesia mixture is advisable under all circumstances even when the ammoniacal solution of the molybdate precipitate is previously nearly neutralized by addition of hydro chloric acid." This mode of procedure differs from that given in "Fresenius" principally in the one point of *insisting on a gradual* addition of the magnesia mixture. In both methods a strongly ammoniacal magnesia mixture is employed and this is added to a more or less strongly ammoniacal solution of the phosphate.

On the other hand the method giving the best results in the hands of Gooch, consisted in the addition of a *neutral* magnesia mixture to a *neutral* solution of the phosphate or still better, especially in the case of a previous precipitation as molybdic salt, in a double precipitation of the ammonia-magnesia-phosphate.

In testing the above methods great care was exercised in the preparation of the standard solutions. These were made by the use of chemically pure microcosmic salt. Upon careful ignition of this salt in a covered platinum capsule 5.1415 grams gave 2.5110 grams of phosphate of soda as residue or 34.00 per cent. of phosphoric acid against 33.98 per cent. required by theory. With this salt, two solutions were prepared, the one containing 4.121 grams of the salt in a liter or 0.035 grams $P^2 O^5$ in every 25 cc., the other 20.605 grams to a liter or 0.175 grams of $P_2 O^5$ in every 25 cc. 25 cc. were measured off with great accuracy by means of a pipette holding exactly 25 cc. by careful weight test, when filled to the mark. This was then carefully rinsed out. The small neck of the pipette, makes it easy to measure a liquid to within $\frac{1}{100}$ cc by this method. In addition to the experiments made with these solutions, others were made by direct weighings of the microcosmic salt.

METHOD I.

To the solution of the phosphate, diluted to 50 cc. and made slightly *alkaline* by the addition of $\frac{1}{2}$ cc. of ammonia liquor, the regular ammoniacal magnesium chloride mixture was added, 4 cc. to every 25 cc. of solution I. and 18 cc. to every 25 cc. of solution II. After letting stand for 15 minutes, 25 cc. of strong ammonia solution were added, and the liquid filtered off after about 30 miutes. The washing was performed with strong ammonia solution and was continued until 10 drops of the washings gave no precipitate with acid of silver nitrate when acidified. In these and all subsequent experiments the filter papers were each weighed, that an accurate weight allowance might be made for filter ash, and the precipitate was strongly ignited over a blast lamp for several minutes, until white. Two series of experiments were made, the one without a previous precipitation as phospho-molybdate of ammonia, the other with such previous precipitation.

A. Without previous precip. as molybdate salt.

Amount taken.	$Mg_2P_2O_7$ found.	P_2O_5 found.	P_2O_5 found.	Error.
1 25 cc. sol. I.	0.0559	0.0350	0.03575	2.14 p. c.
2 "	0.0557	"	0.03563	1.80 "
3 "	0.0559	"	0.03575	2.14 "
4 "	0.0557	"	0.03563	1.80 "
5 25 cc. sol. II.	0.2770	0.1750	0.17718	1.25 "
6 "	0.2763	"	0.17673	0.99 "
7 "	0.2760	"	0.17654	0.88 "
8 "	0.2762	"	0.17666	1.95 "

Average error 1.50 per cent.

B. With previous precip. as molyb. salt.

Amount taken.	$Mg_2P_2O_7$ found.	P_2O_5 required.	P_2O_5 found.	Error.
1 25 cc. sol. I.	0.0559	0.0350	0.03575	2.14 p. c.
2 "	0.0559	"	0.03575	2 14 "
3 "	0.0558	"	0.03569	1.97 "
4 "	0.0556	"	0.03555	1.57 "
5 25 cc. sol II.	0.2768	0.1750	0.17705	1.17 "
6 "	0.2780	"	0.17782	1.61 "
7 "	0.2774	"	0.17744	1.40 "
8 "	0.2776	"	0.17756	1.46 "

Average error 1.68 per cent.

METHOD II.

The same course was followed as in method I, excepting that the solution of phosphate was exactly NEUTRALIZED before the addition of the magnesia mixture.

A. Without previous precip. as molyb. salt.

Amount taken.	$Mg_2P_2O_7$ found.	P_2O_5 required.	P_2O_5 found.	Error.
1 25 cc. sol. I.	0.05570	0.0350	0.03563	1.80 p. c.
2 "	0.05570	0.0350	0.03563	1.80 "
3 25 cc. sol. II.	0.2758	0.1750	0.17641	0.81 "
4 "	0.2757	0.1750	0.17635	0.77 "
5 "	0.2753	0.1750	0.17609	0.62 "

Average error 1.16 per cent.

B. With previous precip. as molyb. salt.

Amount taken.	$Mg_2P_2O_1$ found.	P_2O_5 required.	P_2O_5 found.	Error.
1 25 cc. sol. I.	0.0556	0.0350	0.03555	1.57 p. c.
2 "	0.0556	0.0350	0.03555	1.57 "
3 25 cc. sol. II.	0.2770	0.1750	0.17718	1.25 "
4 "	0.2772	0.1750	0.17731	1.32 "

Average error 1.43 per cent.

METHOD III.

To the solution of phosphate, 75 cc. in volume and quite strongly ammoniacal, the magnesia mixture was added at the rate of one drop a second, the contents of the beaker being kept in constant rotation. The magnesia mixture was added from a burette, the rapidity of flow being regulated by a glass cock, or still better from an ordinary Mohr burette, the flow being regulated by a screw-clamp. The beaker was slightly inclined, so as to receive the drops on its side. The magnesia mixture by this arrangement flowed down the side of the beaker in a thin stream and an exceedingly gradual admixture with the phosphate solution was thereby secured. After the addition of the magnesia mixture, 25 cc. of strong ammonia were added and the whole allowed to stand for two or three hours. Very strong ammonia water was used in the washing as in several cases a tendency to run through the filter paper was observed, when a weaker ammonia solution happened to be employed. One part conc. ammonia water to three parts water was employed.

A. Without previous precip. as molybdate salt.

	Am't. taken.	$Mg_2P_2O_7$ found.	P_2O_5 required.	P_2O_5 found.	Error.
1.	25 cc. sol. I.	0.0547 g.	0.0350 g.	0.03499 g.	0.00 p.c.
2.	"	0.0547	0.0350	0.03499	0.00 p.c.
3.	25 cc. sol. II.	0.2736	0.1750	0.17500	0.00 p.c.
4.	"	0.2735	0.1750	0.17494	0.03 p.c.
5.	"	0.2738	0.1750	0.17513	0.07 p.c.
6.	0.5231 g. micro. salt	0.2775	0.17775	0.17750	—0.14 p.c.
7.	0.5120	0.2717	0.17397	0.17379	—0.10 p.c.

Average error. 0.05 p. c.

B. With previous precip. as molybdate salt.

	Am't. taken.	$Mg_2P_2O_7$ found,	P_2O_5 required.	P_2O_5 found.	Error.
1.	25 cc. sol. I.	0.0548 g.	0.0350 g.	0.03505	0.14 p.c.
2.	"	0.0548	0.0350	0.03505	0.14 p.c.
3.	25 cc. sol. II.	0.2736	0.1750	0.17500	0.00 p.c.
4.	"	0.2734	0.1750	0.17488	—0.07 p.c.
5.	"	0.2732	0.1750	0.17475	—0.14 p.c.
6.	"	0.2733	0.1750	0.17481	—0.11 p.c.

Average error. 0.10 c.

METHOD IV.

To the solution containing the phosphate, either neutral or ammoniacal, the magnesia mixture was added, and then 25 cc. of conc. ammonia water. After letting stand for thirty minutes, the liquid was filtered off and the precipitate thoroughly washed on the paper. The precipitate was then dissolved on the paper with dilute HCl, and washed into the original beaker. 25 cc. of conc. ammonia solution were now added to the filtrate, no care being taken to add it gradually. After the flocculent precipitate had settled, 5 cc. magnesia mixture were added and the whole allowed to stand several hours. The second precipitation was found to be incomplete without the addition of this extra magnesia mixture.

A. Without previous precip. as molybdate salt.

	Am't. taken.	$Mg_2P_2O_7$ found,	P_2O_5 required.	P_2O_5 found.	Error.
1.	25 cc. sol. II.	0.2736 g.	0.1750 g.	0.1750 g.	0.00 p.c.
2.	"	0.2735	0.1750	0.17494	0.03 p.c.
3.	"	0.2736	0.1750	0.17500	0.00 p.c
4.	0.5095 g. micro salt.	0.2712	0.17313	0.17336	0.13 p.c.
5.	0 5703 "	0.3030	0.19379	0.19380	0.00 p.c.
6.	1.0108 "	0.5372	0.34347	0.34361	0.04 p.c.

Average error. 0.03 p. c.

B. With previous precip. as molybdate salt.

	Am't. taken.	$Mg_2P_2O_7$ found.	P_2O_5 required,	P_2O_5 found,	Error.
1.	25 cc. sol. II.	0.2738 g.	0.1750 g.	0.17512 g.	0.00 p.c.
2.	"	0.2736 g.	0.1750 g.	0.1750 g.	0.07 p.c.

Average error. 0.035 p. c.

Still another method was investigated as follows: To the *neutral* solution of phosphate was added a *neutral* magnesia mixture in slight excess. No precipitate appeared except in the case of very conc. solutions. An extremely weak ammonia water was then added, drop by drop, to the liquid, to which was imparted at the same time a constant rotary motion. An exceedingly granular, pure precipitate was thus produced. The results obtained were perfectly accurate, but as the precipitate was very light and apt to fly, when removed from the paper into the capsule, for ignition, and as the method involved the extra labor over Method III, of first neutralizing the solution, it was not carried out in full.

A series of determinations by these several methods, on different fertilizers received in the course of business, was also carried out. The average error is calculated from the results obtained by Method IV, regarded as correct.

Fertilizer	Method I. P_2O_5 p. c.	Method II. $P._2O_5$ p. c.	Method III. P_2O_5 p. c.	Method IV. P_2O_5 p. c.
Superphosphate	10.88			10.50
"		9.49	9.38	9.37
Acid phosphate	14.65			14.20
"	15.20			14.75
Tankage	16.96			16.06
"		16.86		16.44
Bonemeal	22.20			21.60
"		21.83		21.51
Rock phosphate	25.15	24.96		24.45
"		28.93	28.32	28.39
Bone-ash	30.25		29.76	29 80
Bone-black			34.39	34.33
	Av. error 0.56 p. c.	Av. error 0.36 p. c.	Av. error 0.04 p. c.	

A study of these results demonstrates that the common method of precipitation as carried out under Methods I and II will invariably give results too high. In fertilizer work the error thus introduced will vary all the way from one or two-tenths of a per cent. when the solution is carefully neutralized and when it chances to be very dilute, up to six-tenths per cent. or even higher when the solution is more concentrated, or when molybdate of ammonia is present, or where the solution is strongly or even moderately ammoniacal when the magnesia mixture is added. This great variation of error undoubtedly explains many of the differences that have occurred in the analyses of different chemists. The errors thus obtained clearly arise from the too sudden formation of the ammonia-magnesia phosphate precipitate, the precipitate carrying down with it extraneous matter, the error increasing, of course, when a large amount of molybdate of ammonia is present. When no foreign matter is present and the exact theoretical amount of magnesium chloride is contained in the solution, this sudden precipitation is not injurious, as is seen in Method IV. Method III when carried out as here described gives accurate results even in the presence of molybdate of ammonia. This method, as it does not necessitate any previous neutralization of the solution with hydrochloric acid, and requires but one precipitation is the one to be most highly recommended. Strong ammonia water should be added in liberal amount to the solution, and also employed in the washing.

The breaking of the filter paper and washing of the molybdate salt into the beaker, without filtering the solution cannot be recommended. However thoroughly the yellow salt may be washed, there is always a slight residue insoluble in ammonia water. A solution and filtration of the molybdic precipitate is therefore necessary in accurate work.

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ABSTRACTS.

Abstracts from *Journal of the Chemical Society*, London, by Arthur H. Elliott, Ph. B., F.C.S.

On the Volumetric Estimation of Bismuth in the Form of Oxalate. By M. M. Pattison Muir, M. A., F. R. S. E. and C. E. Robbs, B. A. B. Sc. (Vol. XL., p. 1.)—Authors describe a process which depends upon the fact that potassium oxalate precipitates Bismuth as $Bi_2(C_2O_4)_3K_2C_2O_4$. The method of procedure is as follows:—

A solution of the bismuth in the minimum quantity of nitric acid is evaporated till only enough acid remains to give a solution when hot; a large excess of glacial acetic acid is added and the whole transferred to a measuring flask, washing with acetic acid (1:1). Standard potassium oxalate is now added till there is twice as much of this salt present as there is bismuth oxide; the flask is filled to the mark with acetic acid (1:1) and after shaking and allowing to