

The table on the preceding page shows the effect of the peaty matter and also a comparison of the methods, together with that of the *m*-phenylene diamine.

In some cases a pink color was obtained and no blue, due probably to the greater delicacy of the naphthylamine test, it being competent to detect 0.0001 part of nitrogen as N_2O_3 in 100,000. This we think is the extreme limit of the test, as different *shades*, not *depths* of color are obtained upon adding different quantities of the reagents, as Dr. J. T. Tanner¹ found. The iodo-zinc starch method is incapable of detecting less than 0.0002 part of nitrogen as N_2O_3 per 100,000.

In a few cases a blue color appeared, but no pink, but upon passing carbon dioxide through the water no blue was obtained. This may possibly have been due to hydrogen peroxide. Where large quantities of nitrites are present, a purple color instead of a blue is obtained, which is difficult to estimate; in such cases the water should be diluted before applying the test.

In conducting the Griess test, the directions given by Dr. Tanner² were followed with the additional precaution of using water free from nitrites in the preparation of the reagents. This was prepared by distilling the middle portion of ordinary distilled water with an excess of alkaline permanganate, collecting the middle portion of the distillate thus obtained. Water prepared in this way gives no test upon eighteen hours' standing, even when tightly stoppered.

A GRAVIMETRIC METHOD OF ESTIMATING PHOSPHORIC ACID AS AMMONIUM PHOSPHOMOLYBDATE.*

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THE estimation of phosphoric acid by weighing the yellow precipitate of ammonium phosphomolybdate has often been attempted, but, except in iron analysis, where the amount of phosphorus is very small, such a method has never yet been successful. The reason of such failure is evident when we consider the analyses that have been made of the yellow precipitate. A few only need be presented.

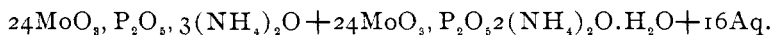
¹ Report National Board of Health, 1882, 280.

² *Loc. cit.*

* Read before the New York Section of the American Chemical Society, Nov. 8, 1895.

	Rammels- berg.	Struve and Svanberg.	Sonnen- schein.	Gibbs.
H ₂ O.....	5.77	9.49	11.23	3.94
NH ₄ OH.....	3.25	9.49	11.23	3.35
P ₂ O ₅	3.90	3.63	3.03	3.66
MoO ₃	86.45	86.88	86.87	89.05

Gibbs gives the following formula for the salt:



He prepared the salt by mixing solutions of ammonium molybdate (seven parts of water to three of the salt) and phosphate, adding nitric acid in excess to the solution and boiling. Such a method would give more or less occluded molybdic oxide. His analyses gave 3.70 per cent. and 3.83 per cent. of phosphorus pentoxide against the theoretical percentage of 3.66. Such results were sufficiently accurate for his purposes, but would discourage any suggestion of using the yellow salt as the basis of a gravimetric method. His formula is, however, without any doubt, the correct one, with the exception of the water of crystallization.

My own analysis of the salt precipitated in the manner described later on, and dried at a temperature of 105° C. to a constant weight, gives me the following composition:

	Theoretical.	By analysis.
48MoO ₃	91.38	91.36
2P ₂ O ₅	3.76	3.76
10NH ₃	2.25	2.31
11H ₂ O.....	2.61	2.57

For ammonia 1.015 grams gave 0.0234 gram NH₃ = 2.30 per cent.

For ammonia 20.193 grams gave 0.4690 gram NH₃ = 2.32 per cent.

For moisture 7.25 grams gave ——— = 2.53 per cent.

“ “ 10.30 “ “ “ = 2.61 “ “

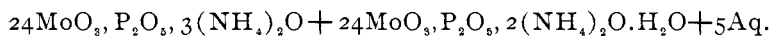
The water was determined by estimating total hydrogen by combustion with copper oxide.

For phosphoric acid, repeated analyses and syntheses gave almost exactly 3.76 per cent.

The molybdic acid was found by difference.

The fact that drying at 105° C. expels all the water except

eleven molecules, and that the yellow salt when dried over sulphuric acid in a close desiccator comes to the same weight as when dried at 105° C. would indicate that this salt contains no other water of crystallization. Any excess of water is apparently hygroscopic water and not water of crystallization. I therefore find the following as the correct formula for the crystallized yellow salt :



The following method of procedure has given me a precipitate of a very uniform composition and would seem to afford the simplest and easiest method yet presented for estimating phosphoric acid.

To the solution of phosphoric acid, (twenty-five cc. to fifty cc. in bulk, are added) twenty-five cc. of strong ammonia 0.900 sp. gr. : nitric acid, 1.42 sp. gr., is now added to acidity. The beaker containing the solution, is placed in a water-bath maintained at a constant temperature of 50° C. The ordinary ten per cent. acid molybdate solution is now added from a burette at the rate of about three drops per second, with constant stirring, (fifty cc. may be added in five minutes). When the molybdate solution to an excess of about ten cc. has been added, the beaker is allowed to remain for ten minutes in the bath. The contents are then filtered through a weighed filter paper.

The filtrate, without the washings, and after the addition of five cc. molybdate solution, is replaced in the bath for ten minutes. The liquid should remain clear or at most show only a faint opalescence.

For washing the precipitate, a wash water of dilute nitric acid 100:1 is employed. Three generous washings by decantation and three washings on the paper followed by one final washing with distilled water are sufficient. The paper and contents are now drained for a few minutes on some waste filter or blotting paper and then dried to a constant weight at a temperature of 105° C.

In this method, the formation of a pure granular precipitate of uniform composition and free from occluded salts, is secured by the gradual addition drop by drop of the molybdate solution

with constant stirring. The completeness of precipitation of the phosphoric acid is attained by the presence of a large amount of ammonium nitrate. The separation of molybdic oxide or iron salt is avoided by the low temperature employed.

For the final drying at 105° C. an air-bath was tried and decisively abandoned. The use of a liquid boiling at 108° C. to 110° C. is the only safe course. A water-oven consisting of several distinct divisions or floors, one above the other, and surrounded with dilute glycerol 1.160 sp. gr. boiling at 110° C. was found to work admirably. The lower bath or division is reserved for the final drying. None but dry or almost dry precipitates must be allowed in this lower division. The precipitate may be dried in an ordinary water-oven almost to a constant weight and then dried for one hour longer in a glycerol oven at 105° C. The filter papers used are dried at 105° C. and weighed between large, closely fitting ground watch-glasses. The final weighings of papers and contents are made in the same manner.

The following investigation serves to show the results that are secured by this method of analysis.

A chemically pure microcosmic salt was finely pulverized. Careful ignition of ten grams in a covered platinum dish gave 4.8955 grams of sodium phosphate, giving a percentage by calculation of 34.07 per cent. phosphorus pentoxide. Ten grams of the salt were now dissolved in one liter of water and aliquots taken. Twenty-five cc. containing 0.250 gram of microcosmic salt were treated exactly as above. Fifty cc. containing 0.500 gram microcosmic salt were treated by the official magnesia method. The following results were obtained :

	Taken.	Gladding method. Per cent.	Taken.	Magnesia method. Per cent.
1.....	0.250	34.07	0.500	34.07
2.....	0.250	34.08	0.500	34.05
3.....	0.250	34.06	0.500	34.09
4.....	0.250	34.10	0.500	34.08

A solution of one-tenth of the above strength was obtained by dilution. Of this the following quantities were used and the phosphoric acid therein obtained by the new method :

	Taken. cc.	Yellow salt obtained.	Phosphorus pentoxide obtained.	Theoretical phosphorus pentoxide.
1 10	0.091	0.00342	0.003407
2 1	0.010	0.00037	0.00034

These last experiments demonstrate the insolubility of the yellow salt and the applicability of the new method to very small amounts of phosphoric acid.

A number of comparative tests of fertilizers gave closely agreeing results, as follows :

	Official method. per cent.	New method. per cent.
Phosphoric acid.....	28.80	28.87
“ “	2.63	2.70
“ “	12.03	12.00
“ “	28.30	28.33
“ “	15.64	15.70
“ “	15.04	15.00
“ “	15.19	15.23
“ “	29.16	29.23

In all fertilizer work 0.250 gram were used for precipitation, and molybdate solution to an excess of about ten cc. was added. No more than ten cc. in excess should be used.

Tankages and fertilizers containing a notable amount of organic matter should be ignited before solution.

An application of this method to the direct determination of reverted or citrate soluble phosphoric acid promises good results. The method of procedure is as follows : The citrate filtrate and washings are made up to 200 cc. Twenty-five cc., equivalent to 0.250 gram of the fertilizer are treated as follows: Fifty cc. ammonia 0.900 sp. gr., are added and then nitric acid to acidity. The liquid is now diluted to half a liter to overcome the solvent action of the ammonium citrate, and heated in a bath to 65° C. Fifty cc. of molybdate solution are added in a thin stream with stirring and the whole digested for thirty minutes. The rest of the analysis is conducted precisely as in ordinary work, except that the filtrate is heated for thirty minutes longer at 65° C. The liquid should remain clear.