ON THE ESTIMATION OF PHOSPHORIC ACID BY TITRATION OF THE AMMONIUM PHOSPHOMOLYBDATE PRECIPITATE WITH STANDARD ALKALI.[1]

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IN November, 1894. the writer published[2] some results of an investigation of the method on this principle as originally described[3] by Mr. H. Pemberton, Jr., and as modified by the writer, together with an account of some work upon molybdic solutions and temperatures of precipitation best suited for obtaining ammonium phosphomolybdate uncontaminated with molybdic acid.

These investigations were undertaken in part by the writer as reporter of the Association of Official Agricultural Chemists on methods for determining phosphoric acid for 1893–94, to see if the volumetric method was sufficiently accurate and trustworthy, or if it could be developed into a sufficiently reliable method to be used by these chemists in their official work.

The present official gravimetric method is rather long and often gives quite varying results in the hands of different analysts and not always the most concordant ones in the hands of the same analyst. These two objections to the molybdate method, together with the immense volume of phosphoric acid work which has to be done in connection with "Fertilizer Control Stations" and fertilizer factories makes it doubly important that a quick and accurate method for phosphoric acid estimation should, if possible, be found.

The volumetric method seemed to promise well, and it was accordingly sent out, both as originally described by Pemberton and as modified by the writer, to various official and other chemists interested in phosphoric acid work for trial. Three phosphate samples were prepared upon which to conduct the investigations.

No. 1 was a mixture of cottonseed meal and castor pomace, containing about two and a half per cent. phosphorus pentoxide.

No. 2 was an acid phosphate containing about seventeen per cent. phosphorus pentoxide.

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[1] This with some additional matter will appear in a bulletin from the North Carolina Experiment Station.

[2] This Journal, 16, 765.

[3] This Journal, 15, 382.

No. 3 was a solution of chemically pure disodium hydrogen phosphate ($Na_2HPO_4.12H_2O$), containing 19.826 per cent. phosphorus pentoxide.

The results obtained in this laboratory[1] on these samples by the different methods and presented to the association are shown in Table I.

These results, with a few exceptions, indicate well for the volumetric method, especially the method as described by the writer, there being only one result (20.10 per cent. on sample 3) by this method without the reasonable error of analysis. The larger percentage of the results however on samples 2 and 3 by the method as carried out by Pemberton are high.

The corresponding results on these samples by some sixteen other chemists were not as a whole nearly so encouraging as those presented above, which was likely due to the greater familiarity with the volumetric method in this laboratory.

Then, too, the very large amount of wash water (amounting in some cases to more than a liter) found necessary by a great many to remove free acid from the precipitate made the washing tedious and gave the method little or no advantage in most hands as regards time over the gravimetric method and no advantage in point of accuracy, the latter being especially true when it is made known that now and then unaccountably high results would be obtained by many in the midst of good ones. Notwithstanding these difficulties, most of the chemists who had tried the volumetric method in the different forms in which it was worked up to this time, considered their results on a whole as encouraging, but not such as to give them any considerable faith in the method, especially for high percentages.

At this point the writer again commenced studying further the volumetric method in its various phases and trying numerous modifications to it.

The results obtained last year[2] by the writer's modification of the Pemberton method, consisting of a different molybdic solution and temperature of precipitation, were much more uniform and satisfactory than those obtained by the original Pemberton method on the same samples.

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[1] The results of other chemists on these samples will be found in Bul. 43. Div. Chem. U. S. Dept. Agr., page 81.

[2] This Journal. 16, 767.

TABLE I. TOTAL PHOSPHORIC ACID IN ABOVE SAMPLES 1, 2, AND 3.

Analyst.	No. 3.					No. 2.					No. 1.				
	Methods and washings.					Methods and washings.					Methods and washings.				
	Official gravimetric.	Volumetric as carried out by Pemberton.	Washings.	Volumetric as carried out by Kilgore.	Washings.	Official gravimetric.	Volumetric as carried out by Pemberton.	Washings.	Volumetric as carried out by Kilgore.	Washings.	Official gravimetric.	Volumetric as carried out by Pemberton.	Washings.	Volumetric as carried out by Kilgore.	Washings.
	Per cent.	Per cent.	cc.	Per cent.	cc.	Per cent.	Per cent.	cc.	Per cent.	cc.	Per cent.	Per cent.	cc.	Per cent.	cc.
W. M. Allen...	....	....	....	....	....	17.13	...	....	17.15	650 to 800	2.52	....	....	2.50	350 to 400
	....	....	....	....	....	17.18	....	...	17.00		2.52	....	....	2.55	
	....	....	....	....	....	17.15	....	....	17.10		....	....	....	2.55	
F. B. Carpenter	19.93[3]	20.00	....	19.85	....	....	...	....	....	....	....	....	....	....	....
	19.94[3]	20.15	....	20.10	....	17.04	17.10	....	17.15	....	2.65	2.58	....	2.55	....
	19.93	....	....	....	....	17.12	17.15	....	17.15	....	2.61	2.63	....	2.58	....
	19.91	....	....	....	....	17.10	....	....	....	....	....	....	....	....	....
B. W. Kilgore.	20.06	20.35	650	19.85	....	17.17	17.20	500	17.15	450	2.42	....	....	2.50	250
	19.93	20.15	850	19.95	650	17.12	17.40	500	17.10	450	....	....	....	2.45	250
	19.83[4]	20.15	850	19.90	850	16.98[1]	....	....	16.97	450	....	....	....	....	....
	19.83[4]	20.10	1,000	19.90	800	16.98[1]	....	....	17.00	500	....	....	....	....	....
	19.91[3]	....	....	19.80	1,000	....	....	....	17.10	500	....	....	....	....	....
	19.85[3]	....	....	....	....	....	...	....	....	....	....	....	....	....	....
C. B. Williams.	20.03[3]	....	...	....	....	....	....	....	17.10	500	....	....	....	2.50	500
	20.05[3]	....	....	....	...	16.96[1]	....	....	17.10	500	....	....	....	2.50	....

[1] The "white" precipitate was dissolved and reprecipitated.

[3] Precipitated with magnesia mixture direct.

[4] One gram citric acid added before precipitating with magnesia mixture.

This modified method gave quite as good results in the writer's hands as did the official method. It was therefore decided to use this modified procedure, that is, precipitation at 60° C., and with the official molybdic solution as the starting-point for the investigation.

Knowing that the deposition of molybdic acid was the cause of the trouble in the volumetric method, various ways of getting rid of it were tried. One attempt was to dissolve the ammonium phosphomolybdate in the least possible quantity of concentrated ammonia, thus changing any molybdic acid to ammonium molybdate, acidifying with nitric acid, evaporating to dryness and heating to drive off all nitric acid. This was not practicable for other reasons than that molybdic acid was again formed from the ammonium molybdate on heating to a temperature that would drive off nitric acid. Distillation of the ammonia from the "yellow precipitate" and the calculation of the phosphoric acid from that would not do in that the deposit of molybdic acid carries ammonium molybdate with it. Finally it was determined to try to find wash solutions, which would dissolve molybdic acid, but not ammonium phosphomolybdate.

Using a chemically pure disodium hydrogen phosphate containing 19.826 per cent. phosphorus pentoxide, the following results were obtained with different strengths of nitric acid for washing, finishing with potassium nitrate solution and water to remove nitric acid.

WASH SOLUTIONS.

No. of times washed with water by decantation.	No. of times washed with dilute nitric acid by decantation.	No. of times washed with three per cent. potassium nitrate by decantation.	Washed on filter with water. cc.	5 cc. 1.42 sp. gr. nitric acid in 100 cc. water. per cent.	10 cc. 1.42 sp. gr. nitric acid in 100 cc. water. per cent.	20 cc. 1.42 sp. gr. nitric acid in 100 cc. water. per cent.	Washed with water only. per cent.
.	1	2	275	....	....	19.80	....
1	1	1	275	....	19.84	....	....
2	1	.	275	19.98	....	....	....
.	2	1	400	....	....	19.80	....
.	2	1	400	....	19.87	....	....
1	2	.	275	19.80	....	....	....
3	.	.	400	....	....	....	19.98
.	2	1	230	....	19.87	....	....
.	2	1	350	....	19.83	....	....
3	.	.	700	....	....	....	19.93
3	.	.	550	....	....	....	19.87

The washing with dilute nitric acid and three per cent. potassium nitrate solution was always by decantation, using fifty cc. to seventy-five cc., agitating thoroughly and allowing the precipitate to settle completely each time. When the washing was with water alone, the results are high, while washing twice by decantation with the wash containing ten cc. 1.42 sp. gr. nitric acid in 100 cc., once by decantation with three per cent. potassium nitrate solution, and then with about 300 cc. water on the filter, the results are close to theoretical ones.

Solubility of Molybdic Acid in Various Wash Solutions.—It now seems important to investigate the solubility of molybdic acid in various solutions which might be used for washing. The results of this work are contained in the table below and the solubility is expressed in terms of the number of cc. of the standard volumetric alkali neutralized by the molybdic acid dissolved. 100 cc. of this alkali equals 32.38 cc. normal alkali.

SOLUBILITY OF MoO_3 IN VARIOUS WASH SOLUTIONS.

No. MoO_3 used.	Amount of MoO_3. grams.	Amount of solution cc.	Time of standing, hours.	Water.	2 cc. 1.42 sp. gr. nitric acid in 100 cc. Water.	5 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	10 cc. 1.42 sp. gr. nitric acid in 100 cc water.	20 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	2.5 per cent. potassium nitrate.	5 per cent. potassium nitrate.	5 per cent. sodium nitrate.
1	2	100	1	1.4[1]	..	..	5.6	6.8	0.4[2]	0.5[2]	0.5[2]
2	1	100	2	..	7.4	8.1	8.8	..	..	7.5[2]	..
3	.	...	.	..	..	..	2.8[3]	..	3% KNO_3	..	..
	1	100	½	..	1.3[2]	1.5	2.0, 2.3	2.8	0.92	..	..
	1	100	1	0.45[2]	0.8	1.5	2.5	3.1	2.5	..	..
4	1	100	½	..	2.4[2]	3.55[2]	5.15	6.3	0.92[2]	..	..
	1	100	1	..	2.9[2]	4.7[2]	7.3	8.85	1.0[2]	..	..
5	1	100	.	..	..	..	2.2	..	0.8	..	..
			½	1.4[4]	..	..	2.2	..	0.7	..	..
	1	100		..	..	..	2.8	..	0.8	..	..
			1	..	..	..	2.8	..	0.8	..	..

[1] Stood eighteen hours and then filtered turbed, though double filter was used; result too high.

[2] Filtered turbid; results too high.

[3] Used as in washing the yellow precipitate. One portion of 100 cc. was added, stirred and allowed to stand fifteen minutes, and filtered off; then another 100 cc. portion was added and titrated in the same way.

[4] Stood twenty-four hours before a clear filtrate could be obtained.

These solubility determinations were made by allowing 100 cc. of the respective solutions to stand in a beaker with the molybdic acid for the time indicated in the table, stirring once or twice to keep the molybdic acid in contact with the liquid, but allowing sufficient time before filtration for most of it to settle to the bottom of the beaker. The washes were then filtered through double filters, evaporated to dryness (when nitric acid was present), heated in an air-bath until nitric acid was driven off, and titrated. It was found very difficult to prevent the molybdic acid from passing through the filter when water was used as the solvent. It would remain suspended in a very finely divided state in water for twenty-four hours and pass through the filter. The results for the water solubility are therefore generally too high. This is also true to a less extent of the solubility in two and a half, three, and five per cent. potassium nitrate solutions, and in the five per cent. sodium nitrate solution ; and to a still less extent of the solubility in two and five cc. nitric acid solutions.

The results are not all uniform but fairly so when the same molybdic acid was used. None of these molybdic acids were pure.

Numbers 1 and 2 contained considerable quantities of ammonium nitrate and ammonium molybdate, and perhaps some sodium molybdate. Numbers 3, 4, and 5 were washed by decantation for a day or more with large quantities of dilute nitric acid, and finally once or twice with water, and contained, so far as we ascertained, only ammonium molybdate as impurity. The impurities did not, we think, materially affect the solubility of these acids in the wash solutions. The results, at any rate, are of value in showing the comparative solvent action of the different washes for molybdic acid under conditions similar to those in which they are used in the method.

They show that water, and sodium and potassium nitrate solutions have very little solvent action upon molybdic acid ; while that of the stronger nitric acid solutions is quite considerable. After all, these results may represent more nearly what we want than they would, had pure molybdic acid been used; for in the volumetric method it is not a solvent for molybdic acid alone that is wanted, but for a mixture of molybdic acid and ammonium molybdate perhaps in quite variable quantities.

Of the dilute nitric acid washes, the one containing ten cc., 1.42 sp. gr., nitric acid in 100 cc. of the wash was adopted because it possesses good solvent power for molybdic acid and is of practically the same acidity as the solution in which the precipitation of ammonium phosphomolybdate is made in the official method. The official molybdic solution contains nearly fifteen cc., 1.42 sp. gr., nitric acid in fifty cc.; and a solution requiring fifty cc. of molybdic solution to precipitate the phosphoric acid in it usually has a volume near 100 cc.; the two would give a volume of 150 cc, containing about ten cc. nitric acid in the 100 cc.

We know that precipitation is complete in a solution of this acidity, and no solvent action takes place on long standing. It therefore seems reasonable to conclude that nitric acid of the same strength would exert little or no solvent action on the ammonium phosphomolybdate in the short time required to wash the precipitate.

SOLUBILITY OF AMMONIUM PHOSPHOMOLYBDATE IN THE FOREGOING WASH SOLUTIONS.

It now appeared desirable to investigate the solubility of ammonium phosphomolybdate in these same wash solutions. This was done by preparing a pure phosphomolybdate from sodium phosphate by precipitating with a deficient quantity of molybdic solution, pouring off the filtrate, washing by decantation with dilute nitric acid, and finally with water to remove most of the nitric acid, and drying to constant weight at 130° to 150° C. This phosphomolybdate contained 3.789 per cent. phosphorus pentoxide, the theory being 3.783, showing that it was practically pure. The solubility is expressed in terms of the number of cc. of standard volumetric alkali required to neutralize the phosphomolybdate dissolved. One cc. of this alkali equals one milligram phosphorus pentoxide.

SOLUBILITY OF AMMONIUM PHOSPHOMOLYBDATE IN WASH SOLUTIONS.

	Amount of solution.	Time of standing —hours.	Water at 65° C.	Water at laboratory temperature, about 27° C.	2 cc. HNO_3 in 100 cc. wash.	5 cc. HNO_3 in 100 cc. wash.	10 cc. HNO_3 in 100 cc. wash at 65° C.	10 cc. HNO_3 in 100 cc. wash at laboratory temperature.	20 cc. HNO_3 in 100 cc. wash.	3 per cent. KNO_3 solution.
0.75 to 1.4 grams substance stood in 500 cc. of the solution for the time indicated, and 200 cc. was taken each time for the test.	200	24	5.2[1]	0.85[1]	0.2	0.25	20.1	0.6	0.75	0.5
	200	106	6.0[2]	3.0[3]	2.05	5.5	16.75[2]	6.75	11.45	4.35
Results from allowing precipitates from 20 per cent. phosphate to stand in these solutions.	200	½	..	none	..	none	..	none	none	none
	200	1	..	trace	..	trace	..	trace	trace	trace

From 0.75 to one and four-tenths grams of the prepared phosphomolybdate was shaken up in flasks with 500 cc. of the wash solutions. Two hundred cc. of this was filtered off at the end of twenty-four hours and 106 hours respectively, evaporated to dryness (when nitric acid was present), the nitric acid driven off, and the residue titrated. The phosphomolybdate settled in only two or three of these washes in less time than twenty-four hours, and even then the very fine particles remained suspended in the water solutions, and it was found impossible to get clear filtrates from them. The results for water-solubility are therefore too high. For the reason just stated the solubility of ammonium phosphomolybdate in the washes could not be determined for the times they would ordinarily stand in contact with the precipitate in washing by the use of the pure molybdate. If, however, the solubility of even this pure phosphomolybdate was proportional to the time of standing in the washes, the amount that would have been dissolved by all the washes (dilute nitric acid, potassium nitrate, and water) used in washing a precipitate in the ordinary thirty minutes required for washing could hardly have been found. I calculated that on this basis a plus correction of

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[1] These filtered very turbid; they had not settled in twenty-four hours.

[2] These stood at laboratory temperature (about 27° C.) after first twenty-four hours.

[3] Filtered turbid; results too high.

about 0.016 per cent. would be necessary on basis of two-tenths gram substance.

The solubility of the "yellow precipitate" just as it is precipitated in ordinary work along with the salts carried down with it was also determined in the wash solution by allowing 200 cc. of them to stand in contact with the precipitate for one-half and one hour, respectively, after stirring thoroughly. The precipitates settled completely and quickly in this way. In none of these washes could more than a trace of phosphoric acid be found. Again all the washings (3600 cc.) from six determinations of phosphoric acid in two phosphate solutions (a 3.30 per cent. and a 19.83 per cent.) were combined, evaporated down and the phosphoric acid in them determined by the gravimetric method, when 0.38 milligrams phosphorus pentoxide was found, corresponding to a plus correction of 0.03 per cent. on basis of two-tenths gram substance. A similar result was obtained from the washings from eight determinations on the same samples.

These results indicate that while the wash solutions used in the volumetric method have marked solvent power for molybdic acid, they have practically no solvent action on ammonium phosphomolybdate, and that a correction for ordinary work at least is not necessary. There is danger, however, of mechanical loss. The precipitate is first washed by decantation with dilute nitric acid and potassium nitrate, and afterwards with water to remove nitric acid. In this after washing, when all the salts have been removed from the precipitate and as much as 600 or 700 cc. has been used, the precipitate begins to pass through the filter mechanically and settle to the bottom of the receptacle. We have not, however, found it necessary to wash with more than 300 cc. of water in our present manipulation of the method. We consider that 500 or 600 cc. of water may be used without this loss, but the filtrate should be closely observed when the washing goes beyond this amount.

INVESTIGATION OF MOLYBDIC SOLUTIONS.

Besides the comparison of the aqueous molybdate of Pemberton with the official molybdic solution recorded in my last year's work,[1] nine other molybdic solutions of different formulas, in-

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[1] This Journal, 16, 769.

cluding five or six of those most highly recommended by different analysts, and the remainder of our own making, have been tried. The formulas of these solutions need not be given. They varied quite widely in the proportions of molybdic acid to free nitric acid and ammonium nitrate as well as in degrees of concentration.

Without going into a detailed discussion of the results and the advantages possessed by the different molybdic solutions for different purposes, we will merely state that we found the official molybdic solution of the following formula and made by dissolving 100 grams of molybdic acid in 400 grams, or 417 cc., of ammonia of 0.96 sp. gr., and pouring this into 1250 cc., or 1500 grams nitric acid of 1.20 sp. gr. to be the one best suited to the volumetric method for very small quantities of phosphoric acid, one per cent or less. For percentages larger than one, the foregoing solution with the addition of eighty extra cc. of 1.42 sp. gr. nitric acid, or five cc. to each 100 cc. of official molybdic solution was found to be the best. 100 cc. of this latter solution contains practically six grams of molybdic acid, four and six-tenths grams ammonium nitrate, and thirty-five cc. free nitric acid of 1.42 sp. gr., which is about the largest quantity of free nitric acid in proportion to molybdic acid that can be used in a molybdic solution not to interfere with quick and ready precipitation of phosphoric acid. When a larger proportion of free nitric acid is in the solution, precipitation of phosphoric acid is either incomplete or is very materially retarded. This modified official molybdic solution, containing the large amount of nitric acid, can be readily used for all percentages of phosphoric acid, but it contains rather too much free nitric acid to allow of the quickest precipitation of very small quantities, but by extending the time of precipitation to eight to ten minutes it will be found to be complete even when very small amounts are present. The judgment and manipulation of the analyst will, however, be the best guide as to whether he will employ the solution containing the larger amount of nitric acid for all percentages, or whether he will only use it for those above one or so, and use the regular official solution for less amounts.

EFFECT OF ORGANIC ACIDS IN PREVENTING DEPOSITION OF MOLYBDIC ACID.

Jüptner[1] has successfully used two-tenths to six grams of tartaric acid per 100 cc. of molybdic solution for preventing the deposition of molybdic acid in the determination of phosphorus in steel. One to four grams of citric acid to 100 cc. of the two foregoing molybdic solutions were employed in the hope of accomplishing the same object. When three and four grams of citric acid were used precipitation was not complete in fifteen or twenty minutes, and with smaller quantities (one, one and five-tenths, and two grams) precipitation was complete in a reasonable length of time (seven to fifteen minutes), but the results at best showed no advantage over those obtained on the same samples with molybdic solutions without the presence of citric acid.

ACIDITY OF AMMONIUM PHOSPHOMOLYBDATE.

Hundeshagen[2] has stated that it required twenty-three molecules of Na_2CO_3 (or of Na_2O) to neutralize the ammonium phosphomolybdate containing one molecule of phosphorus pentoxide.

H. Pemberton, Jr.,[3] working upon a solution of chemically pure disodium hydrogen phosphate, found that 23.2 molecules of sodium carbonate were necessary to neutralize the ammonium phosphomolybdate containing one phosphorus pentoxide molecule; a second determination,[4] however, working in the same way, gave him 22.99 molecules.

In the course of my work upon the volumetric method, I have determined the acidity of ammonium phosphomolybdate in two ways. First, by finding the amount of alkali necessary to neutralize the ammonium phosphomolybdate formed from a given amount of phosphate. This was done by dissolving ten grams of chemically pure disodium hydrogen phosphate in a liter of water, carefully measuring out twenty cc. portions, precipitating with molybdic solution, washing thoroughly according to our practice in the volumetric method, and titrating with alkali.

The results obtained are as follows:

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[1] Abs. Expt. Sta. Record, **6**, 610.

[2] *Ztschr. anal. Chem.*, **28**, 141-172.

[3] This Journal, **15**, 382.

[4] *Ibid*, **16**, 278.

	Cc. of phosphate solution used.	Equaling grams $Na_2HPO_4.12H_2O$.	Equaling grams P_2O_5.	Cc. KOH solution required to neutralize phosphomolybdate formed.
1	20	0.20000	0.039652	39.80
2	20	0.20000	0.039652	39.80
3	20	0.20000	0.039652	39.80

Dividing the weight of phosphorus pentoxide by the number of cc. alkali required to neutralize the phosphomolybdate formed, we find that 100 cc. alkali has neutralized an amount of ammonium phosphomolybdate containing 99.628 milligrams phosphorus pentoxide.

The alkali was now titrated against semi-normal hydrochloric acid, carefully standardized by silver nitrate to contain 18.2285 grams hydrochloric acid per liter. 100 cc. of the alkali equaled 64.5 cc. of the semi-normal acid, which contained 1175.74 milligrams hydrochloric acid, which in turn equals 1519.3 milligrams potash, or 2228.6 milligrams potassium carbonate. Therefore, 1519.3 milligrams potash equals 99.628 milligrams phosphorus pentoxide in the yellow precipitate. Dividing each of these by its molecular weight, we obtain

for phosphorus pentoxide $\frac{99.628}{142.06} = 0.7013.$

for potash $\frac{1519.3}{94.22} = 16.125.$

Then, $P_2O_5 : K_2O = 0.7013 : 16.125 = 1 : 22.993.$

The relation between standard alkali and phosphorus pentoxide in the "yellow precipitate" was now determined by preparing pure phosphomolybdates by precipitating sodium phosphate with a deficient quantity of molybdic solution, pouring off the filtrate, washing by decantation, first with dilute nitric acid and then with water, and drying at 130° to 150° C. to constant weight. These phosphomolybdates contained 2.232 per cent. nitrogen (average of seven analyses), the theory being 2.238; and 1.645 per cent. phosphorus, the theory being 1.651. The following results were obtained by titrating a portion of three of these:

	Grams ammonium phosphomolybdate used.	Cc. standard alkali required to neutralize.
1	1.2322	46.55
2	0.8050	30.45
3	0.7955	30.10
Total	2.8327	107.10

One hundred cc. of alkali has, therefore, neutralized 2.6449 grams of ammonium phosphomolybdate, which multiplied by 3.783, (the per cent. of phosphorus pentoxide in the "yellow precipitate") gives 100.05 milligrams phosphorus pentoxide in 2.6449 grams of this salt, and which corresponds to 100 cc. of the alkali used.

One hundred cc. of this alkali was found as before to equal 64.74 cc. semi-normal hydrochloric acid, which contains 1180.14 milligrams hydrochloric acid, and which in turn equals 2237.08 milligrams of potassium carbonate. Therefore 2237.08 milligrams potassium carbonate equals the 100.05 milligrams of phosphorus pentoxide contained in the 2.6449 grams of "yellow precipitate."

Dividing by molecular weights, there is found

for phosphorus pentoxide $\frac{100.05}{142.06} = 0.7042.$

for potassium carbonate $\frac{2237.08}{138.22} = 16.185.$

Therefore, $P_2O_5 : K_2CO_3 = 0.7042 : 16.185 = 1 : 22.983.$

It has, therefore, required practically twenty-three molecules of potassium carbonate (or of potash) to neutralize an amount of ammonium phosphomolybdate ($6NH_4.P_2O_5.24MoO_3$) containing one molecule of phosphorus pentoxide. On this basis, one cc. of a standard alkali containing 18.17106 grams of potassium hydroxide to the liter would equal one milligram phosphorus pentoxide. 100 cc. of this solution will neutralize 32.38 cc. of normal acid; and either the acid or alkali to be used in the volumetric method can be made by diluting 323.8 cc. of corresponding normal solution to one liter.

The above calculations are based upon the following atomic weights:

Sodium	23.05	Oxygen	16.	Chlorine	35.45
Hydrogen	1.007	Potassium	39.11	Molybdenum	96.
Phosphorus	31.03	Carbon	12.	Nitrogen	14.03

RESULTS BY VOLUMETRIC METHOD AS NOW WORKED IN THIS LABORATORY COMPARED WITH GRAVIMETRIC RESULTS.

The writer was again reporter of the Association of Official Agricultural Chemists on methods for determining phosphoric acid for 1894–95, and the foregoing investigation was made with a view of setting the method in better shape for trial by this association and for perfecting it, if possible, for use in this laboratory. The method was accordingly changed quite materially, redescribed to accord with results of the preceding work, and sent out to various official and other chemists for trial with three samples upon which to conduct the work. These samples were:

No. 1 was a chemically pure disodium hydrogen phosphate solution containing ten grams of the salt per liter, the theoretical percentage of phosphorus pentoxide in it being 19.826.

No. 2 was solution No. 1 diluted with five parts of water, and therefore contained the equivalent of 3.304 per cent. phosphorus pentoxide in fifty cc.

No. 3 was a mixed fertilizer.

The results obtained in this laboratory on these samples by gravimetric and volumetric methods and presented to the association are brought together in Table II.

These results are what, I deem, may be termed *most excellent.*

It may not be out of place here to state also that the results of nine other chemists on these same samples, including thirty-one determinations on No. 1 and thirty-three on No. 2, excluding three results, are as good as those in the table. Seventy-three per cent. of all the results of thirteen chemists on sample No. 1 are within 0.05 per cent. of the theory, and ninety-three per cent. within one-tenth per cent., there being only three results varying more than one-tenth. On sample No. 2 eighty-five per cent. of all results are within 0.05 per cent. of the theory and all are within one-tenth.

This summary of results of members of the Association of Official Agricultural Chemists by the volumetric method are in rather marked contrast to the results of this and all previous years by the official gravimetric method, and also to the results by the volumetric method as worked last year. The results last year by the volumetric method were considered on the whole as encouraging, while the method as worked this year has given extremely good results in all hands.

The volumetric and gravimetric methods have been compared in this laboratory upon quite a variety of phosphates and fertilizer materials of varying percentages. The results follow in Table III.

TABLE II. TOTAL PHOSPHORIC ACID BY GRAVIMETRIC AND VOLUMETRIC METHODS.

Analyst.	Sample No. 1. Methods and washings.				Sample No. 2. Methods and washings.				Sample No. 3. Methods and washings.			
	Official gravimetric.	Volumetric.	Washing water.	Difference + greater — less than gravimetric.	Official gravimetric.	Volumetric.	Washing water.	Difference + greater — less than gravimetric.	Official gravimetric.	Volumetric.	Washing water.	Difference + greater — less than gravimetric.
	Per cent.	Per cent.	cc.	Per cent.	Per cent.	Per cent.	cc.	Per cent.	Per cent.	Per cent.	cc.	Per cent.
W. M. Allen	19.93	19.81	275		3.38	3.28	265		12.50	12.32	275	
	19.97	19.84	250	—.11	3.39	3.27	300		12.59	12.39	300	—.17
	19.96	19.88	285		....	3.27	275	—.109	....	12.39	350	
	....	....	....		....	3.29	275		....	....	....	
	....	....	....		....	3.28	300		....	....	....	
	....	....	....		....	3.27	275		....	....	....	
C. B. Williams	19.91	19.80	220		....	3.32	210		....	12.32	240	
	....	19.85	230	—.073	....	3.32	220		....	12.32	270	
	....	19.85	250		....	3.32	205		...	12.32	235	
	....	19.85	250		....	3.32	220		....	12.42	220	
F. B. Carpenter	19.83	19.85	275	+.03	3.38	3.32	250	—.006	12.43	12.39	250	+.0
	....	19.87	275		3.33	3.34	250		12.37	12.43	250	
B. W. Kilgore	19.96	19.83	280		3.38	3.32	300		....	12.40	225	
	19.89	19.83	280	—.12	3.39	3.31	200	—.083	....	12.40	190	
	20.00	19.83	250		3.40	3.30	200		....	12.37	200	
	....	....	....		....	3.30	210		....	12.37	250	
Average	19.93	19.84	....	....	3.38	3.302	....	....	12.475	12.37	....	....
Theory	19.826	19.826	....	....	3.304	3.304	....	....	....	....	....	....
Variation of lowest result from theory	0.004	0.026	....	....	0.026	0.034	....	....	....	....	....	...
Variation of highest result from theory	0.174	0.054	....	....	0.096	0.034	....	....	....	....	....	....

TABLE III. DETERMINATIONS OF PHOSPHORIC ACID IN VARIOUS MATERIALS BY VOLUMETRIC AND GRAVIMETRIC METHODS.

Material.	Number.	Gravimetric Method.	Volumetric method.	Washing water.	Difference greater + less − than gravimetric method.	Material.	Number.	Gravimetric method.	Volumetric method.	Washing water.	Difference greater + less − than gravimetric method.
C. B. Williams, Analyst…….		Per cent.	Per cent.	cc.	Per cent.			Per cent.	Per cent.	cc.	Per cent.
Cottonseed meal	1	0.08	0.08	130	.00	Fertilizers and fertilizing materials	16	9.54	9.45	260	—.09
Fertilizers and fertilizing materials	2	0.37	0.35	160	—.02		17	10.72	10.65	270	+.07
	3	1.32	1.28	100	—.04		18	6.46	6.40	230	—.06
	4	1.50	1.45	240	—.05		19	6.55	6.60	250	+.05
	5	0.88	0.79	215	—.09		20	5.45	5.50	290	+.05
	6	0.65	0.61	250	—.04		21	6.52	6.60	280	+.08
	7	0.64	0.61	250	—.03		22	7.47	7.44 7.44	250 230	+.03
	8	1.27	1.25	240	—.02		23	7.42	7.44 7.48	240 230	+.04
	9	1.29	1.25	250	—.04		24	17.55 17.55	17.52 17.52	260 260	—.03
	10	4.96	4.95	155	—.01	Florida phosphate	25	38.12	37.80 37.84	260 260	—.30
	11	4.98	4.92	180	—.06	Acid phosphate	26	15.49	15.35	290	—.14
	12	11.80	11.80	120	.00	" "	27	13.27	13.15	280	—.12
	13	11.58	11.45	250	—.13						
	14	9.77	9.80	240	+.03						
	15	10.04	10.05	220	+.01						
W. M. Allen, Analyst………											
Mixed fertilizer	1	11.58	11.45 11.48 11.53	250 260 280	—.09	Acid phosphate	3	15.49	15.47 15.43	250 275	—.04
" "	2	9.54	9.50 9.53	275 285	—.02	Mixed fertilizer	4	10.72	10.70 10.67	260 275	—.03
						" "	5		15.35		
B. W. Kilgore, Analyst…….											
Mixed fertilizer	1	9.77 9.75	9.76	275	.00	Mixed fertilizer	11	10.72	10.68	275	—.04
" "	2	9.03	8.96	210	—.07	Acid phosphate	12	13 27	13.21	275	—.06
	3	10.67	10.66	220	—.01	Mixed fertilizer	13	11.71	11.63	275	—.08
	4	11.58	11.60	275	+.02	" "	14	11.88	11.75	275	—.13
	5	9.77	9.76	275	—.01	" "	15	9.43	9.38	250	—.05
	6	10.04	10.01	275	—.03	" "	16	9.71	9.80	230	+.09
	7	9.54	9.48	275	—.06	Bone meal	17	10.38	10.30	250	—.08
Acid phosphate	8	15.49	15.42	275	—.07	Acid phosphate	18	20.53	20.48	210	—.05
Insoluble	9	2.57	2.60	230	+.03	" "	19	15.02	15.10	220	+.08
Reporter's sample No. 1[1]	10	19.96 19.89	19.88 19.88	260 260	—.05	Reporter's sample No. 2[2]	20	3.38 3.39	3.30 3.31	220 220	—.08
						Reporter's sample No. 3	21		12.43 12.43 12.45	260 260 260	

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[1] C. P. $Na_2HPO_4.12H_2O$ = 19.826 per cent. P_2O_5.

These volumetric results show close agreement with the gravimetric ones, though they are generally slightly lower than the latter. When we observe the close agreement of duplicate results by the volumetric method and remember the tendency of the molybdate method to give high results, we have ground for believing that the volumetric results are more nearly correct.

RESULTS ON A HIGH GRADE PHOSPHATE.

To see how the volumetric method would work on a very high percentage phosphate and to see how the results by the two methods would compare on it, a high grade Florida phosphate was submitted to analysis, with the following results :

	C. B. Williams, analyst. per cent.	B. W. Kilgore, analyst. per cent.
Gravimetric method	38.12	
Volumetric method	37.80 37.84	37.80 37.88
Less by volumetric method	0.30	

The foregoing results by the volumetric method, our work upon it, and experience with it generally lead us to consider it a more accurate and reliable method than the molybdate-magnesia method. Since the change of temperature of precipitation, precipitating reagent, wash solutions, and manner of washing from what they were in the Pemberton method, the difficulty of getting occasionally very high results in the midst of good ones, and which did so much to destroy faith in the method, seems not to occur under the new method of procedure. The accuracy, reliability and rapidity of the method, a man being able to make, we think, twice as many determinations by it as by the gravimetric method, causes us to feel that the large amount of time which we have put upon the method has been well spent and will soon repay us in the saving of time on this class of work in our own laboratory, to say nothing of the service it may be to others having, as we do, large amounts of phosphoric acid work to do.

I am indebted to Messrs. C. B. Williams and W. M. Allen for assistance in carrying out the foregoing work.

The method, as we have found it to give the best results, may be described as follows :

Weigh two grams of substance and make solution by one of the following methods: (1) Evaporate with five cc. of magnesium nitrate solution, ignite, and dissolve in hydrochloric acid. This is for organic materials. (2) Dissolve in thirty cc. concentrated nitric acid with a small quantity of hydrochloric acid. (3) Add thirty cc. concentrated hydrochloric acid, heat, and add cautiously in small quantities at a time about five-tenths gram of finely pulverized potassium chlorate. These (2 and 3) are for ordinary phosphates and fertilizers. (4) Dissolve in fifteen to thirty cc. of strong hydrochloric acid and five to ten cc. of nitric. This is for phosphates containing much iron and aluminum. Method 2 is preferred when these acids are a suitable solvent for the material. Make up to 200 cc. (or any other convenient volume), measure out twenty cc. for totals, or for percentages above five or six; and forty cc. for insolubles, or for percentages below five or six, corresponding to two-tenths and four-tenths gram substance respectively, add about five cc. concentrated nitric acid, when method 2 for solution has been used and about ten cc. when method 1, 3, or 4 has been used. Now add ammonia until precipitate just begins to form, dilute high percentage solutions to about 100 cc., and low percentage ones to from sixty to seventy-five cc., digest in water-bath at 60° to 65° C., and after filtering the molybdic solution to be used in this method, precipitate, not using any greater excess of molybdic solution than is necessary to insure complete precipitation; let stand in bath six minutes from the time the molybdate is added, and filter as quickly as possible upon a three-inch Hirsch funnel, whose perforations are covered with a disk of soft filter-paper, or in a Gooch crucible with one or two pieces of filter-paper slightly larger than the bottom of the crucible, tightly pressed against the bottom of the crucible, or upon a filter made by putting a platinum cone or disk, well filled with holes, into a three-inch funnel and covering with coarse asbestos, using the pump in all cases. Filter-paper may be used, but the other filters in the order named are much to be preferred.

It is *especially urged* that the three-inch Hirsch funnel be used where possible, as it permits of rapid filtration and easy and thorough washing. Wash the precipitate twice by decantation with dilute nitric acid, using fifty to seventy-five cc. each time and agitating thoroughly, once by decantation with the same amount of three per cent. potassium or ammonium nitrate solution, then on the filter and with 200 to 500 cc. water, (250 cc. is usually enough) or until no longer acid. Now wash the precipitate with filter back into the beaker, titrate with potassium hydroxide, and back with nitric acid, using phenolphthalein as indicator and adding acid until color disappears.

In washing by decantation, if the precipitate is allowed to settle completely each time, no trouble will be experienced in the after washing.

Where the phosphoric acid is below one per cent., the precipitation is not so rapid as in larger percentages and may require eight or even ten minutes to be complete.

REAGENTS TO BE USED IN THE VOLUMETRIC METHOD.

Molybdic Solution.—Dissolve 100 grams of molybdic acid in 400 grams, or 417 cc. of ammonia, sp. gr. 0.96, and pour the solution thus obtained into 1500 grams, or 1250 cc. of nitric acid, sp. gr. 1.20, and add eighty cc. nitric acid, sp. gr. 1.42. Or to each 100 cc. of the official molybdic solution (the above formula without the eighty cc. nitric acid), add five cc. 1.42 sp. gr. nitric acid. This solution should be filtered each time before using.

Dilute Nitric Acid Wash.—Dilute 100 cc. 1.42 sp. gr. nitric acid to one liter.

Potassium or Ammonium Nitrate Wash.—Dissolve three grams of either in 100 cc. of water.

Alcoholic Solution of Phenolphthalien.—100 cc. to one gram.

Standard Potassium Hydroxide.—This solution should contain 18.17106 grams potassium hydroxide to the liter. One cc. of this solution equals one milligram phosphorus pentoxide (one per cent. phosphorus pentoxide on basis of one-tenth gram substance) 100 cc. of it will neutralize 32.38 cc. normal acid, and can be made by diluting 323.81 cc. of normal potassium hydroxide, which has been freed from carbonates by barium hydroxide to one liter.

Standard Nitric Acid of same, or one-half, the strength of alkali. Hydrochloric or sulphuric acid will do.

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