

	Särnström.	Volhard.	Gravimetric.
A. Magnetic .....	0.07	0.10	0.07
Specular.....	...	0.08 <sup>1</sup>	...
B. Mixture of blue } ..	0.30	0.31	0.29
granular and red } ..	0.32	0.29	0.30
hematite. } ..	0.28	...	...
C. Limonite .....	1.03	1.02	1.09
.....	1.05	1.05	...
D. Silicious ore.....	2.98	3.08	2.93
.....	3.07	3.07	...
Cary Empire.....	3.93	T. V. Church	} 3.94
.....	3.88	Illinois Steel Co	
Dexter No. 2.....	6.04	...	} 6.01
	6.02	6.02	
	6.01	...	
Davis ore .....	8.78	8.62	8.86
Newark ore.....	1.48	A. G. McKenna,	} (Ford's)
No. 57 .....	5.39	Duquesne Steel Works,	
No. 218.....	5.59	5.59	1.50

In the determination of small amounts of manganese this method presents an advantage over Volhard's method in giving a more distinct end reaction.

The method can be used for iron and steel determinations if the usual precautions are taken to oxidize the carbon. But it is not so well adapted to these on account of the impracticability of taking large amounts for analysis.

LABORATORY OF MIXER AND DUBOIS,  
ISHPEMING, MICH.

## ON VARIOUS MODIFICATIONS OF THE PEMBERTON VOL- UMETRIC METHOD FOR DETERMINING PHOSPHORIC ACID IN COMMERCIAL FERTILIZERS.

By F. P. VEITCH.

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IF an excuse is needed for adding to the already voluminous literature on the method as proposed by Pemberton<sup>2</sup> and modified by Kilgore, it is found<sup>3</sup> in the action taken by the Association of Official Agricultural Chemists at their last meeting. The method, as modified by Kilgore, gave almost uniformly excellent results on known solutions, in a two years trial in the hands of a number of analysts, and only failed to become

<sup>1</sup> This was so low as to necessitate filtering through asbestos in order to see end reaction by Volhard's method.

<sup>2</sup> This Journal, 15, 382.

<sup>3</sup> Bul. 43, Div. Chem. U. S. Dept. Agr., 104.

an official method because many of the members had not worked with it.

During the past fall the writer has used the Kilgore modification as a check in quite a number of gravimetric determinations with very satisfactory results. While this modification may be considered as accurate as the molybdate for this class of work, at least on low percentages and in careful hands, it was felt that if the exact time and temperature elements could be gotten rid of, there would be a saving of both time and care where a large number of determinations were to be made. With this end in view, it was determined to study the following points :

1. The method of filtering and washing.
2. The time of standing after adding the molybdate solution.
3. The use of tartaric acid to prevent the precipitation of molybdic acid.

With regard to the first point it was found desirable to use simply the paper and funnel, doing away with the use of pressure and filtering twenty at a time. To simplify washing the dilute nitric acid and three per cent. potassium nitrate were omitted from the washings.

As the filter paper and funnel have been used with pressure with satisfactory results, there seems to be no objection to the use without pressure, so to condense the work as much as possible, the subjects were studied in pairs, as follows :

*A.* The method of filtering and washing and the time of standing after adding the molybdate solution.

*B.* The method of filtering and washing, and the use of tartaric acid to prevent the precipitation of molybdic acid.

*A.* THE EFFECTS OF THE METHOD OF FILTERING AND WASHING AND THE TIME OF STANDING AFTER ADDING THE MOLYBDIC SOLUTION.

After some preliminary work, during which the volumetric method, as carried out at the New Jersey Station,<sup>1</sup> was tried and found to work very satisfactorily, it was determined to try the effect of standing for one half hour and for one hour at from 40°-50°C. It was thought best to allow some range of tempera-

<sup>1</sup> Bul. 43, Div. Chem. U. S. Dept. Agr., 92.

ture, as the care required to maintain a constant temperature is considerable.

The molybdate used was the official solution, to which ten cc. 1.42 sp. gr. nitric acid per cubic centimeter had been added. After standing the required length of time, the solutions were filtered off without pressure, the precipitates washed three times by decantation, allowing the precipitate to settle each time before decanting, the precipitates then transferred to the filters, the beakers washed out thoroughly and the precipitates washed until the wash water was neutral to litmus paper, which required from 200 cc. to 300 cc.; this latter amount has been found to free the precipitate from adhering acid in every instance. To feel sure that no appreciable amount of acid was retained in the filter, the washing was continued in a number of cases after no reaction was given with litmus paper, the washing received in clean beakers and titrated with the standard solutions. Table I gives the amount of acid removed by this extra washing as expressed in percentages of  $P_2O_5$ .

TABLE I.—THE AMOUNT OF ACIDITY EXPRESSED AS  $P_2O_5$  RETAINED IN PRECIPITATES AFTER WASHINGS WERE NEUTRAL TO LITMUS PAPER.

Number.	Amount of washing until neutral to litmus paper. cc.	Amount of washing after neutral to litmus paper. cc.	Amount of acidity in last wash water, expressed as $P_2O_5$ . Per cent.	Per cent. $P_2O_5$ in precipitate on filter. Per cent.	Remarks.
1	140	50	0.00	2.14	
2	135	"	0.01	2.81	
3	140	"	0.01	1.88	
4	200	"	0.04	1.48	
5	150	"	0.00	2.52	
6	225	75	0.05	9.68	
7	"	"	0.025	12.93	
8	"	"	0.025	6.46	
9	"	"	0.025	15.35	
10	"	"	0.000	15.28	
11	"	"	0.000	10.10	
12	"	"	0.000	17.09	
13	"	"	0.000	17.65	
14	"	"	0.025	22.10	
15	"	"	0.015	20.77	
			Average.....	0.016 per cent.	

These results show that when the washings become neutral to litmus paper, the precipitates are practically free from acid. It may be well to call attention to the fact that a first-class grade of filter paper should be used, otherwise the precipitate may run through the filter.

In Table II the results obtained when the solutions stood one-half and one hour and were then treated as above mentioned are compared with the gravimetric.

TABLE II.—COMPARISON OF TIME OF STANDING.

Stood one-half hour at 40°-50.					Stood one hour at 40°-50.				
Number.	Washings.	Percent stand- ing one-half hour.	Percent grav- imetric.	Difference + or - from gravi- metric.	Number.	Washings.	Percent stand one hour.	Percent grav- imetric.	Difference + or - from gravi- metric.
1	200	0.50	0.57	-0.07	1	200	1.84	1.75	+0.09
2	"	2.58	2.42	+0.16	2	"	1.96	1.79	+0.17
3	"	2.86	2.74	+0.12	3	"	2.38	2.38	0.00
4	"	2.06	2.17	-0.11	4	"	2.14	2.03	+0.11
5	"	2.10	2.17	-0.07	5	"	1.58	1.48	+0.10
6	"	5.00	5.06	-0.06	6	"	2.56	2.74	-0.18
7	"	4.41	4.56	-0.15	7	"	4.87	4.78	+0.09
8	"	3.06	3.08	-0.02	8	"	1.39	1.39	0.00
9	"	1.89	1.88	+0.01	9	"	2.08	2.07	+0.01
10	"	0.59	0.61	-0.02	10	"	2.88	3.06	-0.18
11	"	3.42	3.32	+0.10	11	"	2.40	2.54	-0.14
77	"	1.69	1.56	+0.12	12	"	3.43	3.25	+0.18
				-----	13	"	3.18	3.33	-0.15
					14	"	1.42	1.39	+0.03
					15	"	1.01	0.91	+0.10
									-----
									Average difference . . . . . 0.102
									Difference of averages . . +0.015

From these results it appears that standing as long as one hour before filtering does not give results differing from the gravimetric more than the allowance for duplicates by that method. These results are not what was to have been expected from Kilgore's<sup>1</sup> experiments with various molybdates, as he found that both the official solution and that used by Pemberton gave deposits of

<sup>1</sup> Bul. 43, Div. Chem. U. S. Dept. Agr., 103.

molybdic acid in less than half an hour when heated to 60°. This difference is possibly explained by the fact that the ratio of nitric acid to the molybdic acid in solution was much greater than in his experiments, due to the precipitation of most of the molybdic acid by the phosphoric acid present.

*B.* THE EFFECT OF THE METHOD OF FILTERING AND WASHING  
AND THE USE OF TARTARIC ACID TO PREVENT THE  
PRECIPITATION OF MOLYBDIC ACID.

Jüpner's<sup>1</sup> experiments indicate that the precipitation of molybdic acid may be entirely prevented by the use of tartaric acid; also that the higher the temperature of precipitation the more tartaric acid required to keep the molybdic acid in solution.

Kilgore,<sup>2</sup> whose results are published since this work was done, comes to the conclusion that the use of citric acid for this same purpose possesses no advantage over the official molybdate solution, to which ten cc. of nitric acid per hundred has been added, and requires a much longer time for the complete precipitation of the ammonium phosphomolybdate.

In the work given below the official molybdate solution plus ten cc. nitric acid and one gram tartaric acid per 100 cc. was used. A very little work soon proved that adding the molybdate to the phosphate solution at 30°, and allowing to stand one hour at the temperature of the laboratory, will not give satisfactory results, and standing one hour at 30°, gave very little better results, the ammonium phosphomolybdate remaining in solution and precipitating some time after running through the filter. Standing over night in the cold, however, gave excellent results, on low percentages, upon which alone it was tried. It was next determined to try the plan of allowing solutions to stand at 40°-50° for one hour and for two hours; the results, which are in most instances, comparable with those obtained by the gravimetric method, are given, with the results by the method of allowing to stand over night, in Table III.

<sup>1</sup> Abs. Expt. Record, 5, 610.

<sup>2</sup> This Journal, 17, 960.

TABLE III.—COMPARISON OF TIME OF STANDING, USING MOLYBDIC SOLUTION CONTAINING TARTARIC ACID.

Stood one hour at 40°-50°.					Stood two hours at 40°-50°.					Stood over night in the cold.				
Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or - from volumetric.	Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or - from volumetric.	Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or - from volumetric.
1	250	4.76	6.35 6.20	-1.51	1	275	1.40	1.33	+0.07	1	200	0.99	0.92	+0.07
2	"	2.54	2.38	+0.16	2	"	0.94	1.20	-0.26	2	"	2.14	2.16	-0.02
3	"	1.48	1.64	-0.16	3	"	0.65	0.50	+0.15	3	"	0.76	0.79	-0.03
4	"	2.41	2.57	-0.16	4	"	3.15	3.26	-0.11	4	"	1.35	1.32	+0.03
5	"	4.79	6.75 6.82	-2.00	5	"	2.77	2.58	+0.19	5	"	0.42	0.44	-0.02
6	"	1.81	2.28	-0.47	6	"	1.58	1.50	+0.08	6	"	1.70	1.65	+0.05
7	"	1.91	1.96	-0.05	7	"	2.20	2.08	+0.12	7	"	2.81	2.88	-0.07
8	"	2.22	2.06	+0.06	8	"	2.49	2.42	+0.07	8	"	1.12	1.12	0.00
9	"	0.72	0.69	+0.03	9	"	2.48	2.32	+0.16	9	"	1.56	1.49	+0.07
10	"	0.90	1.35 1.32	-0.44	10	"	2.28	2.40	-0.12	10	"	1.68	1.65	+0.03
					11	"	2.18	2.39	-0.19	11	"	1.18	1.10	+0.08
										12	200	2.52	2.45	+0.07

From these results it would appear that standing at 40°-50° for one hour is not to be relied on, at least for low percentages, the results in all cases being too low. Standing at 40°-50° for two hours, however, tends to give results slightly higher than those obtained by the volumetric method, while standing in the cold over night gives results practically identical with it.

This work of determining the temperature and time of standing that would probably give the best results, was done with low percentage solutions, as they were the most convenient at the time.

The figures so far obtained indicated that for further study with the official molybdate solution containing ten cc. of nitric acid extra, standing one-half hour at 40°-50°, was to be preferred, as standing for one hour tends to slightly high results. It is believed, however, that standing for one hour will still give results comparable with results by the gravimetric method, but the precipitates require more washing, and longer time is required to complete the determinations.

For the further study of the use of tartaric acid, standing at 40°-50° for two hours was selected.

For this final comparison of the various modifications solutions of fertilizers in which the phosphoric acid had been carefully determined gravimetrically by Mr. W. W. Skinner, were used. The samples cover practically all grades of commercial fertilizers, and have quite a range in percentage of phosphoric acid. The solutions and precipitates in both modifications were treated alike in all cases, except the time of standing.

TABLE IV.—COMPARISON OF VARIOUS MODIFICATIONS WITH THE GRAVIMETRIC.

Number.	One gram tartaric acid per 100 cc. molybdate two hours at 40°-50°.	Official molybdate + ten cc. HNO <sub>3</sub> per 100 cc. one-half hour at 40°-50°.	Gravimetric. (Skinner).	Volumetric.	Difference + or - from gravimetric. Tartarated. Molybdate.	Difference + or - from gravimetric. Official molybdate + ten cc. HNO <sub>3</sub> per 100 cc.	
1	9.73	9.68	9.75	....	-0.02	-0.07	
2	15.65 15.42 (12.85) <sup>1</sup>	15.35	15.34	15.45	+0.16	-0.01	
3	13.05 13.15	12.93	13.06	....	+0.04	-0.13	
4	6.60 } 6.68 } <sup>2</sup>	6.48 <sup>2</sup> 6.43 <sup>3</sup>	6.30	....	+0.34	+0.16	
5	13.35 10.00	13.28	13.35	....	0.00	0.07	
6	9.95 (10.33) <sup>1</sup>	10.10 10.20	10.19	..	-0.21	-0.09	
7	17.10 17.20	17.03 17.15	17.40	16.93	-0.25	-0.31	
8	17.70 17.68	17.60 17.70	17.94	17.65	-0.25	-0.29	
9	22.08 22.08	22.10	22.29	22.15	-0.21	-0.19	
10	20.95	22.68 20.85	20.85	....	+0.10	-0.07	
Average	14.617	14.541	14.647		0.156	0.141	
					Difference of averages.....	-0.03	-0.10

In several instances where the modified methods gave decidedly lower results than the gravimetric method, the determinations were also made by the Kilgore modification, the results

<sup>1</sup> Omitted from averages.

<sup>2</sup> Fifteen cc. molybdate used.

<sup>3</sup> Ten cc. molybdate used.

agreeing in all cases with the results by the modified methods.

The results agree fairly well with the reported results by the Kilgore method, which averages slightly lower than the gravimetric results. The average difference by these modifications is 0.156 and 0.141 per cent., and the average of the plus and minus differences is 0.03 and 0.106 by the tartrated molybdate and by the Kilgore molybdate respectively.

Only two results are noticeably higher than the gravimetric, and only one of these differs by more than two-tenths per cent. This seems to be due to the presence of a great excess of molybdate, as it will be noticed that when less molybdate was used the result was nearer the gravimetric. From the observation of quite a number of results, the writer believes that the amount of molybdate added should not be more than enough to precipitate one and a half times the phosphoric acid found to be present, otherwise the results are too high.

From the figures presented the following conclusions may be drawn :

1. The molybdate solution, to which nitric acid has been added, standing one-half hour at 40°-50°, gives results comparing very favorably with the gravimetric.
2. While the use of tartaric acid in the molybdate solution gives good results, it possesses no advantage and the extra time of standing makes it not so desirable.

The official molybdate plus ten cc. nitric acid per 100 cc., using the funnel and paper without pressure in filtering, and only water for washing is preferred by the writer to the usual way of carrying out the volumetric method; this admits of a better distribution of the work, which makes it in his hands a more rapid method where a large number of determinations are to be made.