

normally closed by the spring, *a*, thus securing the rider. When, by turning the rod, *c*, the rider is lowered, just before it rests upon the beam, contact between *m* and *e* checks the corresponding motion of the sleeve, thus opening the forceps; continuing

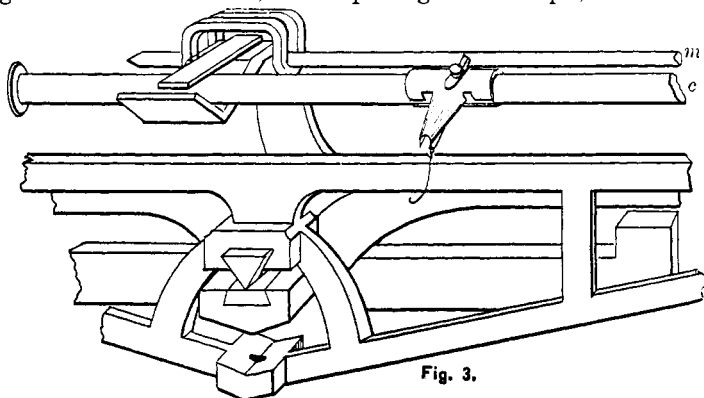


Fig. 3.

the movement, the rider is left hanging free upon the beam. Upon releasing the rod, *c*, the tension of the spring should be sufficient to close the forceps. When, however, it is often desirable to leave the rider upon the beam, by bending its loop, as shown in the side sketch, Fig. 2, this is easily effected.

Not the least advantage of this device is the readiness with which it can be extemporized.

ON THE ESTIMATION OF PHOSPHORIC ACID BY TITRATION OF THE YELLOW PRECIPITATE.

By B. W. KILGORE.

Received September 15, 1894.

METHODS based upon the principle of titrating the yellow precipitate with standard alkali have been described by a number of chemists, especially for the estimation of phosphorus in iron and steel and their ores, where it is present in very small quantities. Among them may be mentioned by abstract:

E. Thilo (abstract *J. Anal. Chem.*, 1, part 2, 219, 1887) in the estimation of P_2O_5 in Thomas Slag, precipitates at $70^\circ C$. with molybdic solution containing one part molybdic acid, three parts ammonium nitrate, and fifteen parts nitric acid, allows to stand five minutes, filters, washes with twenty per cent.

ammonium nitrate solution, and titrates with ammonium hydroxide and back with sulphuric acid.

C. E. Manby (*J. Anal. Appl. Chem.*, **6**, 82) precipitates near boiling, washes with three per cent. each nitric acid and potassium nitrate, dissolves in fifteen per cent. ammonium hydroxide, boils off the excess of ammonia, adds two cc. of nitric acid of 1.20 sp. gr., evaporates to dryness, heats sufficiently to expel nitric acid and ammonium nitrate, titrates with sodium hydroxide, and back with nitric acid.

J. O. Handy (*J. Anal. Appl. Chem.*, **6**, 204) precipitates at 85° C., shakes for five minutes, filters, washes five times with one per cent. nitric acid, five times with one per cent. potassium nitrate, and titrates.

M. Rothberg and W. A. Auchinvole (*J. Anal. Appl. Chem.*, **6**, 243) precipitates at 40° C., shakes for one minute, allows to stand in a warm place five more, filters, washes five times with one per cent. nitric acid, five times with three-tenths per cent. potassium nitrate, titrates with sodium hydroxide, and back with nitric acid.

Dr. Franz Hundeshagen (*Chem. News*, **60**, 168, 177, 188, 201, 215) in his analytical studies of ammonium phosphomolybdate, shows its composition under all conditions, when free of molybdic acid and other impurities, to be $12\text{MoO}_3 \cdot \text{PO}_4 \cdot 3\text{NH}_4$.

He washes the precipitate with five per cent. solution of ammonium nitrate, titrates with sodium hydroxide, and back with nitric acid. He found that it required twenty-three molecules of alkali to neutralize one molecule of ammonium phosphomolybdate.

And H. Pemberton, Jr., (*J. Am. Chem. Soc.*, **15**, 382) has published the description of a method on this principle, which he applied to the determination of phosphoric acid in high-grade phosphates. He uses one-tenth gram substance for analysis, precipitates at boiling with aqueous ammonium molybdate, washes with water, titrates with potassium hydroxide, free from carbonates, and back with hydrochloric acid. In his first work, he found that it required 23.2 molecules alkali to neutralize one molecule ammonium phosphomolybdate, but in his later work he has obtained twenty-three molecules.

The writer has made quite a good many determinations of phosphoric acid in materials of varying percentages by this method, with fairly good results generally but with very wide variations at times, the tendency of the method being to give high results, although the yellow precipitate was washed liberally to remove free acid. It was believed that molybdic acid was the cause of the variations, as it was known that molybdic acid would deposit from other molybdic solutions very quickly at the temperature of precipitation used in the Pemberton method. To see if the aqueous molybdate was an exception to this rule, and also to see if the official molybdate of the Association of Official Agricultural Chemists would take the place of the aqueous solution, the official molybdate was used for precipitating at boiling temperature, the method as described by Pemberton being carried out otherwise, except that two-tenths gram of substance was used.

Results obtained in this way were less subject to variations than when the aqueous molybdate was employed, though high percentages would still often be obtained. Both molybdates were then tried side by side in the water-bath at temperatures of 70° , 65° , and 60° C., (this means practically 5° lower temperature in the beaker), allowing five minutes for precipitation, which was found in all cases to be complete. The results thus obtained were favorable to the lower temperature of 60° C. in bath and to the official molybdate, there being very few variations from the gravimetric method when precipitation was made at 60° C. and by official molybdate. A great many results were obtained in testing these and other points, but most of the early ones were not kept. In the following table are brought together some of the earlier results and all of the later ones by the volumetric method, either as carried out by Pemberton or myself or both, in the order in which they were obtained, and also results by the gravimetric method on the same samples for comparison. The gravimetric results were not duplicated. Among the earlier results by the volumetric method, there are quite a number of wide variations from the gravimetric results, but the later ones by the volumetric method as carried out by myself, nearly all show close agreement with gravimetric results.

DETERMINATION OF PHOSPHORIC ACID IN VARIOUS FERTILIZERS BY
THE GRAVIMETRIC METHOD AND BY THE VOLUMETRIC
METHOD AS CARRIED OUT BY PEMBERTON
AND AS CARRIED OUT BY KILGORE.

No.	Official.	Pember- ton.	Kilgore.	No.	Official.	Pember- ton.	Kilgore.
1.....	10.40	10.34 ¹	35.....	10.41	10.26 ⁴
2.....	9.48	9.40 ¹	36.....	10.43	9.46 ³
3.....	10.52 ¹	37.....	12.26	9.94 ⁵
4.....	2.44	2.53 ¹	38.....	8.83	8.84 ¹
5.....	2.85	2.78 ¹	39.....	8.11	8.08 ⁴
6.....	3.90	3.83 ¹	40.....	13.36	8.87 ⁵
7.....	3.80 ¹	41.....	10.59	10.34 ¹
8.....	0.08	0.30 ¹	42.....	8.83	8.56 ⁴
9.....	2.17	2.18	43.....	9.17	9.26 ⁴
10.....	2.72	2.62 ¹	44.....	9.12	9.17 ²
11.....	3.76	3.76	45.....	10.20	10.33 ²
12.....	15.58	15.48 ¹	46.....	13.70	13.62 ²
13.....	15.40 ¹	47.....	13.92	13.92 ²
14.....	14.09	13.96 ²	48.....	15.75	15.50 ⁴
15.....	13.61	13.36 ²	49.....	8.14	8.40 ²
16.....	13.60 ²	50.....	8.40	8.22 ²
17.....	12.98	13.06 ¹	51.....	10.73	10.80 ²
18.....	9.79	10.60	9.60 ²	52.....	9.63	9.67 ²
19.....	9.70 ²	53.....	10.50	10.48 ²
20.....	9.95	10.25	9.90 ²	54.....	10.53	10.58 ²
21.....	10.20	9.83 ²	55.....	11.13	11.10 ⁴
22.....	1.25	1.14 ²	56.....	8.96	8.87 ¹
23.....	2.64	2.56 ²	57.....	10.75	10.72 ¹
24.....	1.68	1.58 ²	58.....	10.73	10.74 ⁴
25.....	4.06	4.05	59.....	11.63	11.53 ¹
26.....	2.07	2.10	60.....	9.59	9.64 ¹
27.....	1.37	1.31 ²	61.....	13.96	14.18 ³
28.....	2.14	2.19 ²	62.....	14.43	14.33 ⁶
29.....	1.30	1.23 ²	63.....	14.37	14.23 ⁶
30.....	3.93	3.93 ²	64.....	10.67	10.65 ¹
31.....	10.90	10.87	65.....	9.49	9.55 ¹
32.....	11.28	11.90 ²	66.....	10.61	10.77 ¹
33.....	8.89	10.55	9.00 ²	67.....	10.93	11.11 ¹
34.....	10.61	10.98	68.....	11.55	11.59 ¹
35.....	9.93	10.14	69.....	12.60	12.45 ⁶
36.....	9.72	9.98	70.....	10.16	10.45 ⁶
37.....	10.59	10.96	71.....	14.80	14.77 ⁶
38.....	9.04	9.10 ³	72.....	9.95	10.20 ⁴
39.....	8.72	8.72 ³	73.....	9.93	10.22 ²
40.....	10.07	10.00 ⁴	74.....	9.63	9.80 ²

No.	Official.	Pember- ton.	Kilgore.	No.	Official.	Pember- ton.	Kilgore.
75.....	10.52	10.49 ⁷	98.....	9.76	9.62 ⁷
76.....	11.00	10.98 ²	99.....	11.26	11.25 ³
77.....	10.68	10.71 ⁷	100.....	11.49	11.37 ⁷
78.....	13.42	13.26 ⁷	101.....	15.83	15.73 ⁷
79.....	12.63	12.60 ⁷	102.....	15.71	15.71 ⁷
80.....	15.06	14.89 ⁷	103.....	15.25	15.20 ⁷
81.....	14.79	14.84 ⁷	104.....	11.64	12.15	11.63 ³
82.....	14.87	14.84 ⁷	105.....	15.89	16.20	15.71 ³
83.....	12.22	12.17 ⁷	106.....	15.54	16.15	15.65 ⁷
84.....	12.75	12.72 ²	107.....	15.20	16.17	15.25 ³
85.....	12.46	12.34 ⁷	108.....	13.96	14.18 ⁷
86.....	11.23	11.09 ⁷	109.....	13.60	13.67 ⁷
87.....	9.03	9.12 ⁷	110.....	15.67	15.82 ⁷
88.....	10.49	10.40 ⁷	111.....	11.80	11.85 ⁷
89.....	15.43	15.30 ⁷	112.....	11.74	11.75 ⁷
90.....	16.27	15.86 ⁷	113 ⁸	19.93	20.35	19.85 ⁷
91.....	15.98	15.61 ⁷		19.83	20.15	19.95 ⁷
92.....	15.71	15.71 ⁷		19.91	20.15	19.90 ⁷
93.....	11.83	11.63 ⁷		19.85	20.10	19.80 ⁷
94.....	10.04	9.94 ⁷	114.....	17.17	17.20	17.15 ⁷
95.....	13.28	13.25 ⁷		17.12	17.40	17.10 ⁷
96.....	10.55	10.42 ⁷	115.....	2.42	2.47 ⁷
97.....	10.41	10.40 ⁷				

¹ Precipitated at boiling.

² Precipitated in bath at 70° C.

³ Precipitated in bath at 65° C.

⁴ Precipitated in bath at 65° C. with the addition of five cc. HNO₃ to fifty cc. molybdic solution (official).

⁵ Same as 4 with ten cc. HNO₃.

⁶ Same as 4 with three cc. HNO₃.

⁷ Precipitated in bath at 60° C.

⁸ C. P. Na₂HPO₄ + 12H₂O = 19.826 per cent. P₂O₅.

There are two main differences in the volumetric method as carried out by Pemberton and as carried out by myself. First, the temperature of precipitation in the former is at boiling; in the latter 60° in bath or 55° C. in beaker. At the former temperature molybdic acid deposits very quickly, especially if any considerable excess of the precipitant is present. If we know how much phosphoric acid our samples contain and add just enough molybdate to do the work, or are willing to add little by little of the precipitating reagent till the proper amount has been added, this objection is largely overcome, but the former we do not know and the latter is tedious and time-consuming,

especially when large numbers of analyses are being carried on at once. At 55° C., the official molybdate does not deposit, at worst, for fifteen minutes or more; precipitation is always complete in four or five minutes from the time the molybdate is added, and precipitation and filtration can be finished in almost, if not in, as short a time by this method of procedure as by the regular Pemberton method, with the advantages of less danger of molybdic acid depositing, and of being able to handle a larger number of determinations at once.

The second difference is in the two molybdic solutions. The official molybdic solution contains practically sixty grams MoO_3 to the liter, and the Pemberton solution, sixty-six grams to the liter, so there is no very great difference in their precipitating powers. In the official molybdate the proportion of free nitric acid to molybdic acid is always the same, being equivalent to nearly fifteen cc. 1.42 sp. gr. acid to fifty cc. molybdic solution; while in Pemberton's molybdate the quantity is just five cc. 1.42 sp. gr. nitric acid, no matter whether twenty-five cc. or fifty cc. of the aqueous molybdate is added. It will be readily understood that should any considerable excess of this aqueous molybdate be added (and such a thing is liable to be done), and there being only five cc. nitric acid to hold it in solution, precipitation of molybdic acid would be sure and quick. To see which of the two molybdates was most liable to deposit molybdic acid under the same conditions, the conditions being as nearly as possible those of precipitation without the phosphate, the following experiments were made: Fifty cc. official molybdate, containing three grams MoO_3 and fifteen cc. nitric acid were diluted with fifty cc. water; and to forty-five cc. of Pemberton's molybdate, containing 2.97 grams MoO_3 , were added, ten cc. saturated solution of ammonium nitrate, five cc. nitric acid, and forty cc. water. Both mixtures, being of the same volume and containing the same amount of molybdic acid, were placed in a water-bath at 60° C. The mixture of official molybdate showed no deposit for over twenty minutes, but a considerable one in one hour; the other mixture deposited seemingly the whole content of molybdic acid in less than four minutes and in fact this mixture could not be made to stand in the cold over three

or four minutes without throwing down great volumes of molybdic acid; but forty-five cc. and fifty cc. of the two molybdates are too much to precipitate the phosphoric acid from two-tenths gram substance, but not much in excess of safe quantities for most materials where four-tenths gram substance is used. With two-tenths gram substance, one-half the above quantities are about the right amounts to use. Experiments with them similar to the foregoing, were made as follows: Twenty-five cc. of official molybdate, containing one and five-tenths grams MoO_3 , and seven and five-tenths cc. nitric acid were diluted with five cc. water; and to 22.5 cc. of Pemberton's molybdate, containing 1.48 grams MoO_3 , were added five cc. nitric acid, ten cc. ammonium nitrate solution, and 12.5 cc. water. Both mixtures, being of the same volume and containing the same amount of molybdic acid, were allowed to stand as before. The mixture of official molybdate deposited about as in the first experiment; the Pemberton one remained clear for ten or fifteen minutes, when it commenced to get cloudy and in twenty minutes it was milky and a heavy deposit had formed. Seventeen cc. of the official molybdate and fifteen cc. of the Pemberton one contain the same amounts of MoO_3 , and when these quantities are used for precipitating equal amounts of nitric acid, five cc., are present in each case. When these amounts were diluted to fifty cc. and allowed to stand at 60°C . the deposits were the same as in the official molybdate in the two preceding experiments, which argues that the official molybdate contains about the right amount of nitric acid to prevent deposit of molybdic acid, and at the same time allow quick precipitation of phosphoric acid.

The aqueous molybdate as used in the Pemberton method works well when added in just the proper quantities, but there is not enough free nitric acid present to allow of much marginal excess. The official molybdate seems to contain a very large amount of free nitric acid. To test the effect of still larger quantities of free acid, the results in the table, as designated by the foot-notes, show that ten cc. additional nitric acid of 1.42 sp. gr. to fifty cc. molybdate hindered precipitation greatly; five cc. prevented its being complete in five minutes; while three cc. additional did not seem to interfere. The more free nitric acid

present, not to interfere with precipitation, the less liability there is of molybdic acid depositing. Just here I would add that the deposit from the official molybdic solution, at least, is not molybdic acid alone but a mixture of molybdic acid and ammonium molybdate. I found one deposit to contain 1.21 per cent. NH_3 .

The volumetric method as it has given me best results is as follows: Make solution as per the official nitric and hydrochloric acid method for total phosphoric acid, redissolve two grams substance in thirty cc. strong nitric acid and five to ten cc. hydrochloric acid, measure out twenty cc. for total or forty cc. for insoluble, corresponding to two-tenths and four-tenths gram substance respectively, into a four-ounce beaker, add ammonia till precipitate just begins to form, and dilute to seventy-five cc. If much of the nitric acid was driven off in making the solution add ten to fifteen grams ammonium nitrate, otherwise this is not necessary. Digest in water-bath at $60^\circ \text{C}.$ and after filtering the molybdate¹ used in the official method, precipitate in the usual way, allow to stand four or five minutes from the time the molybdate is added, filter as quickly as possible upon either a filter made by putting a platinum cone or disk, well filled with holes, into a three-inch funnel and covering with coarse asbestos, or upon the Hirsch funnel, or preferably upon a porcelain disk (the disk to be covered with filter paper) with rubber rim in three-inch glass funnel, using the pump in all cases. Wash the precipitate three to five times by decantation, using fifty to seventy-five cc. water each time and agitating thoroughly, then onto the filter and till no longer acid, titrate with potassium hydroxide and back with nitric acid.

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THE QUALITY OF WATER SUPPLIES.²

By WM. P. MASON.

A PAPER of some length, bearing the title "The Quality of Water Supplies," has just been presented before the American Society of Civil Engineers, at their Niagara meeting, which contains considerable matter provoking comment. The

¹ This solution is made by dissolving 100 grams molybdic acid in 417 cc. 0.96 sp. gr. ammonia, and pouring this into 1,250 cc. 1.20 sp. gr. nitric acid.

² Read at the Brooklyn meeting August 16, 1894.