

The presence of calcium sulphate slightly increases the phosphoric acid dissolved from tricalcium phosphate, produces probably a slight increase with monocalcium phosphate, but a marked decrease with dicalcium phosphate.

The presence of calcium carbonate decreases the phosphoric acid dissolved from all three phosphates.

Carbon dioxide increases the phosphoric acid dissolved from tri- or dicalcium phosphate, but does not appear to affect the action of water upon monocalcium phosphate.

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## THE COLORIMETRIC ESTIMATION OF PHOSPHATES; SECOND METHOD.<sup>1</sup>

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THE estimation of small amounts of water-soluble phosphates has within the past few years become a matter of considerable interest in sanitary, physiological, and agricultural chemistry, as well as in physico-chemical studies on slightly soluble phosphates. The small amounts available for analysis in many cases led to the adoption of colorimetric instead of gravimetric methods. Quite a number of procedures have been devised during the past few years,<sup>2</sup> but all have as a basis the development of the yellow color of the phosphomolybdates in acid solution. This phosphomolybdate coloration is influenced somewhat by the presence of larger quantities of other salts, but the chief difficulty lies in the similar and even more intensive coloration produced by the silicomolybdates. The chief aim in the various proposed procedures has been the elimination of the color produced by these silicomolybdates, either by eliminating the silica itself or by means of a differential coloration of the solutions by varying the procedure. Another difficulty met with in dealing with the natural solutions is the disturbing influence of foreign organic coloring-matter. It has, therefore, always been necessary to completely decolorize the solution before proceeding with the colorimetric test.

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<sup>2</sup> See West-Knights: *Analyst*, **5**, 197 (1880); Lepierre: *Bull. Soc. Chim.* (3), **15**, 1213 (1896); Jolles and Neurath: *Monatsh. Chem.*, **19**, 5 (1898); Jolles: *Arch. f. Hygiene*, **34**, 22 (1899); Woodman and Cayvan: *This Journal*, **23**, 96 (1901); Woodman: *Ibid.*, **24**, 735 (1902); Veitch: *Ibid.*, **25**, 169 (1903); Schreiner: *Ibid.*, **25**, 1056 (1903); **26**, 808 (1904).

In a recent paper on the colorimetric estimation of magnesium<sup>1</sup> it was shown that very small quantities of magnesium could be precipitated as magnesium ammonium phosphate, washed with ammonia water and then dissolved in nitric acid and the phosphoric acid estimated by the well-known phosphomolybdate colorimetric methods referred to above. This work has been continued in the laboratory of soil chemistry, especially in its application to the estimation of phosphates. It was but natural to try the reverse of the magnesium procedure, that is, to add a magnesia reagent to a solution of a phosphate and thus precipitate the phosphate in the form of magnesium ammonium phosphate, and by washing get rid of all silica, organic coloring-matter, as well as perhaps other salts, the presence of which would influence the phosphomolybdate coloration. The results of this test is given in Table I. In the first two columns the actual amount of  $P_2O_5$  used in making the test is given, and in the last two columns the parts of  $P_2O_5$  per million of solution.

TABLE I.—PRELIMINARY TEST.

Milligrams $P_2O_5$ .		Parts $P_2O_5$ per million of solution.	
Present.	Found.	Present.	Found.
0.625	0.621	12.50	12.42
0.625	0.625	12.50	12.50
0.625	0.600	12.50	12.00
0.625	0.637	12.50	12.74

A more extended series of solutions of phosphates, as well as solutions containing the silicates, sulphates, chlorides and nitrates of sodium, potassium, calcium and magnesium, was then made with equally good results, as will be shown. In the colorimetric magnesium method the calcium was removed by precipitation with ammonium oxalate. It appeared to be safest to follow this same procedure in the present method, although the necessity is not so apparent.

#### METHOD FOR DETERMINING PHOSPHATES COLORIMETRICALLY.

The following reagents will be required:

(1) *Ammonium Molybdate Solution*.—Fifty grams of the pure salt in 1 liter of solution.

(2) *Nitric Acid*.—Specific gravity 1.07.

(3) *Standard Phosphate Solution*.—0.5045 gram of pure freshly crystallized sodium phosphate,  $Na_2HPO_4 \cdot 12H_2O$ , is dissolved in

<sup>1</sup> This Journal, 26, 961 (1904).

water, 100 cc. of nitric acid (sp. gr. 1.07) added, and the whole diluted to 1 liter. The nitric acid is added to lessen the contamination with silica from the glass. One cc. = 0.0001 gram  $P_2O_5$ .

(4) *Standard Colorimetric Solution*.—This is prepared by diluting 10 cc. of the standard phosphate solution (3) to about 80 cc. and then adding 9 cc. of nitric acid (2), 8 cc. of ammonium molybdate solution (1), and making up to 100 cc. After standing twenty minutes it is ready for use. Each cubic centimeter of this colorimetric solution is equal to 0.00001 gram  $P_2O_5$ .

(5) *Ammonium Hydroxide*.—Reagent.

(6) *Ammonium Hydroxide Wash Liquid*.—One part of strong ammonia water (sp. gr. 0.9) and 9 parts of water. This liquid should be practically free from silica, and for this reason is best prepared from redistilled ammonia water.

(7) *Ammonium Oxalate*.—Saturated solution.

(8) *Magnesia Reagent*.—Dissolve 13 grams of magnesium chloride,  $MgCl_2 \cdot 6H_2O$ , and 20 grams of ammonium chloride,  $NH_4Cl$ , in about 900 cc. of water, add 50 cc. of strong ammonia water (sp. gr. 0.9) and dilute to 1 liter. One cc. of this solution will precipitate 3.5 mg. of  $P_2O_5$ .

(9) *Filter-paper*.—This must be free from silica. Schleicher and Schüll's No. 589 or 590, 7 cm. has been found to be very satisfactory for this colorimetric work.

The colorimeter used in these tests was the same as the second instrument described briefly in the earlier paper on the colorimetric estimation of magnesium.

The procedure for the method is as follows: Measure out a convenient volume of the solution to be estimated, usually 50 cc., into an evaporating dish, add 1 drop of ammonia water (5), and 2 or 3 drops of the ammonium oxalate solution (7); evaporate to dryness on a water-bath. To the cooled dish add 1 cc. of the magnesia reagent (8) work up the residue well with a glass rod and then allow to stand about two hours. The precipitated magnesium ammonium phosphate is then washed as follows: Add about 5 cc. of the ammonium hydroxide wash-liquid (6) to the dish, washing down the sides, and then pour the liquid through a small filter (9). Repeat this operation five times, then wash down the filter and funnel until the filtrate measures approximately 50 cc.; then rinse the dish once with about 5 cc. of cold water,

and pour through the filter in such a way as to wash the filter; reject the washings and put a clean salt mouth bottle or other receptacle under the funnel. Add 5 cc. of nitric acid (2) to the dish, working this about with the glass rod and pour through the funnel in such a manner as to wet all the inside of the funnel; then wash the dish five times with hot water (about 5 cc. each) and continue washing the filter until about 45 cc. of the filtrate have been obtained. To the cooled liquid add 4 cc. of the ammonium molybdate solution (1) and, after twenty minutes, read against the standard colorimetric phosphate solution (4).

The remarks on the development of the color and handling of the solutions given in the earlier papers cited naturally apply also in the present instance. As mentioned above, the ammonia wash-liquid should be practically free from silica, which end is readily attained by distillation. If old ammonia water containing considerable silica is used, the single last washing with pure water will not, of course, remove all of the silica from the filter-paper, and the results will be erroneous.

In Table II a series of results obtained with solutions of varying concentrations of phosphates is given. The first two columns give the actual amounts worked with, the second two the parts per million of solution.

TABLE II.—TESTS ON SOLUTIONS OF PHOSPHATES.

Milligrams $P_2O_5$ .		Parts $P_2O_5$ per million of solution.	
Present.	Found.	Present.	Found.
1.250	1.245	25.00	24.90
1.250	1.235	25.00	24.70
1.250	1.250	25.00	25.00
1.000	1.010	20.00	20.20
1.000	1.010	20.00	20.20
0.750	0.775	15.00	15.50
0.750	0.755	15.00	15.10
0.625	0.620	12.50	12.40
0.625	0.624	12.50	12.48
0.625	0.618	12.50	12.36
0.625	0.621	12.50	12.42
0.500	0.507	10.00	10.14
0.500	0.514	10.00	10.28
0.500	0.508	10.00	10.16
0.500	0.500	10.00	10.00
0.375	0.373	7.50	7.46
0.375	0.387	7.50	7.74

TABLE II.—(Continued.)

Milligrams P <sub>2</sub> O <sub>5</sub> .		Parts P <sub>2</sub> O <sub>5</sub> per million of solution.	
Present.	Found.	Present.	Found.
0.313	0.311	6.26	6.22
0.313	0.312	6.26	6.24
0.250	0.250	5.00	5.00
0.250	(0.300)	5.00	(6.00)
0.250	0.250	5.00	5.00
0.250	0.248	5.00	4.96
0.250	0.248	5.00	4.96
0.250	0.256	5.00	5.12
0.250	0.252	5.00	5.04
0.200	0.203	4.00	4.06
0.200	0.198	4.00	3.96
0.150	0.155	3.00	3.10
0.150	0.153	3.00	3.06
0.125	0.124	2.50	2.48
0.125	0.132	2.50	2.64
0.125	0.131	2.50	2.62
0.100	0.105	2.00	2.10
0.100	0.108	2.00	2.16
0.063	0.064	1.26	1.28
0.050	0.055	1.00	1.10
0.050	0.054	1.00	1.08

An examination of the results shows them to be quite satisfactory for such small quantities. All the results are fully within one part per million of solution, except the twenty-first result, in parenthesis, where six parts per million were found when only five parts were present.

The influence of other salts, and more especially silicates, was tried by making solutions of varying amounts of phosphates and constant amounts of the silicates, sulphates, chlorides and nitrates of sodium, potassium, calcium and magnesium. The concentration of these substances in the solutions was approximately as follows :

Parts per million.		Parts per million.	
Mg.....	10.0	SO <sub>4</sub> .....	40.0
Ca.....	10.0	Cl.....	20.0
K.....	10.0	NO <sub>3</sub> ..	15.0
Na.....	5.0	SiO <sub>2</sub> .....	10.0
Total salts = 120 parts per million of solution.			

The results obtained with these solutions are given in Table III.

TABLE III.—TESTS ON SOLUTIONS OF PHOSPHATES CONTAINING ALSO SILICATES, SULPHATES, CHLORIDES, AND NITRATES OF SODIUM, POTASSIUM, CALCIUM, AND MAGNESIUM.

Milligrams $P_2O_5$ .		Parts $P_2O_5$ per million of solution.	
Present.	Found.	Present.	Found.
1.250	1.215	25.00	24.30
1.250	1.210	25.00	24.20
1.000	1.020	20.00	20.40
1.000	1.005	20.00	20.10
0.750	0.775	15.00	15.50
0.750	0.762	15.00	15.24
0.625	0.614	12.50	12.28
0.625	0.630	12.50	12.60
0.500	0.510	10.00	10.20
0.500	0.512	10.00	10.24
0.500	0.500	10.00	10.00
0.500	0.504	10.00	10.08
0.375	0.383	7.50	7.66
0.375	0.385	7.50	7.70
0.250	0.248	5.00	4.96
0.250	0.255	5.00	5.10
0.250	0.270	5.00	5.40
0.250	0.252	5.00	5.04
0.250	0.267	5.00	5.34
0.250	0.283	5.00	5.66
0.200	0.203	4.00	4.06
0.200	0.222	4.00	4.44
0.150	0.150	3.00	3.00
0.150	0.162	3.00	3.24
0.125	0.144	2.50	2.88
0.125	0.155	2.50	3.10
0.100	0.121	2.00	2.42
0.100	0.113	2.00	2.26
0.050	0.097	1.00	1.94
0.050	0.072	1.00	1.44

This method has several advantages: (1) It is based on the same procedure as that followed in gravimetric work; (2) all other salts, including silicates, are completely removed and the phosphomolybdate color is, therefore, developed in a solution free from disturbing factors; (3) the presence of coloring-matter in the original solution does not influence the result, as it is entirely removed or destroyed during the procedure. The method has shown itself to be quite rapid and, as with the magnesium method, proper attention to details will enable one man to make twenty to twenty-five determinations in a working day of seven hours.