GRAMS ANHYDROUS MATERIAL CONTAINED IN 100 GRAMS SOLUTION.

	From unsaturated solution.	From supersaturated solution.	Average.
10°	26.86	27.27	26.9
15°	27.87	28.00	27.9
20°	29.06	28.98	29.0
25°	30.13	30.13	30.1
30°	31.49	31.43	31.4

	Grams $Na_2SO_4Al_2(SO_4)_3$ per 100 g.		Grams $Na_2SO_4Al_2(SO_4)_3 24H_2O$ per 100 g.	
	Water.	Solution.	Water.	Solution.
10°	36.7	26.9	103.1	50.8
15°	38.7	27.9	111.3	52.7
20°	40.9	29.0	121.4	54.8
25°	43.1	30.1	131.8	56.9
30°	45.8	31.4	146.3	59.4

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THE COLORIMETRIC ESTIMATION OF PHOSPHATES IN SOLUTION WITH OTHER SALTS.

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In the course of experiments to determine the quantity of phosphorus in some samples of meat by the colorimetric method it soon became evident that the salts obtained in solution with the phosphates as the result of the oxidizing agents used interfered very seriously with the intensity of color. The influence of salts on the color was therefore given further study. Attention was given to those salts that are likely to be found present in practice, such as occur in soil extracts, plant extracts, and the salts resulting from the oxidation of organic matter, with sodium peroxide, magnesium nitrate, sodium carbonate and magnesium oxide, or a mixture of concentrated nitric and sulphuric acids. Altogether ten reagents were studied: namely, sodium nitrate, potassium nitrate, calcium nitrate, magnesium nitrate, sodium sulphate, potassium hydrogen sulphate, potassium ethyl sulphate, magnesium sulphate, sodium chloride, and nitric acid.

Solutions for comparison were prepared by diluting 2 or 4 cc. of a standard phosphate solution to 30 cc. A known quantity of a certain salt was then added and the solution left standing until the salt was completely dissolved. The color was then developed by adding 5 cc. each of nitric acid, sp. gr. 1.07, and ammonium molybdate solution and diluting to 50 cc. After twenty minutes the color thus developed was compared with that of a standard phosphate solution containing the same quantities of phosphorus, ammonium molybdate, and nitric acid, but none of the salt. The quantities of nitric acid and molybdate solution here used

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have been shown by Woodman and Cayvan[1] and by Veitch[2] to give the maximum coloration to the phosphate solutions. The concentrations of the salts were varied from zero to the maximum quantity the solution would dissolve, or until there was no color developed, or a precipitate formed before a reading could be taken. The color comparisons were all made by means of the Schreiner colorimeter.[3] The instrument is simple in construction and operation and gives accurate results.

The reagents used in the work were prepared with the greatest of care to prevent contamination with silica. The standard solutions of ammonium molybdate and sodium hydrogen phosphate were kept in bottles carefully paraffined on the inside. The standard phosphate solution used in preparing the colorimetric solutions was prepared by weighing out 3.771 grains of pure crystallized sodium phosphate, $Na_2HPO_4.12H_2O$, and dissolving it in silica-free water to make a liter of solution. Each cubic centimeter of this solution contains 1 mg. PO_4. The other reagents were of the same concentration as those used by Veitch[4] and Schreiner.[5] In all the determinations the standard colorimetric solution and the solutions of unknown intensity were brought to the same temperature before the colors were developed, for, as shown by Woodman and Cayvan, the intensity of color developed by the addition of nitric acid and molybdate solutions depends to some extent upon the temperature of the solutions.

The results obtained are given in the table following: The first column shows the number of cubic centimeters of standard phosphate solution in 50 cc. of solution containing the salt named in the second column. The quantities of salt present in the different determinations are represented by the numbers at the head of the columns that follow. The other numbers in the table give the percentage errors produced in the determination by the quantities of salt noted at the head of the columns. These values, except one, are negative, *i. e.*, the presence of these salt lessens the intensity of color. The effect of an excess of nitric acid on the color was also studied and it was found that an excess of 2, 5, 10, and 15 cc. of acid, sp. gr. 1.07, over the 5 cc. regularly used, respectively, caused a decrease of 21, 43, 60, and 76 per cent. in the coloration with 4 cc. of standard phosphate.

The tabular results show that sodium nitrate and probably potassium ethyl sulphate at first decrease the normal intensity of color in proportion to the quantity of salt present, but as the quantity of salt is increased a fixed value is reached, where further addition of salt has apparently

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[1] THIS JOURNAL, 23, 96 (1901).

[2] *Ibid.*, 25, 169 (1903).

[3] Bull. No. 31, Bureau of Soils, U. S. Dept. of Agr., 1906.

[4] Veitch, *Loc. cit.*

[5] Schreiner, *Loc. cit.*

no effect on the intensity of color. Sodium sulphate, potassium acid sulphate, magnesium sulphate, sodium chloride, and an excess of nitric acid all greatly reduce the color, and when present in large quantities only a trace of color appears, but the errors found are not directly proportional to the weight of salt added. The nitrates of calcium and magnesium exhibit a different effect. With 7 grams of the former, or 4 grams of the latter salt, in 50 cc. of a solution containing 4 cc. of standard phosphate solution, a minimum color results. The presence of still larger quantities of these salts tends to restore the normal color so that in very concentrated solutions the color is nearly normal. A graphic representation of the results, plotting grams of salt against percentage errors, makes these relations more apparent.

PERCENTAGE ERROR CAUSED BY FOREIGN SALTS IN THE COLORIMETRIC DETERMINATION OF PHOSPHATES.

Cubic centimeters of standard phosphate.	Grams of salt in 50 cc.	0.1	0.2	0.3	0.4	0.5	0.6	0.8
2	$NaCl$	..	9.4	..	..	16	..	..
4	$NaNO_3$	..	..	..	..	12	..	18
4	$Na_2SO_4.10H_2O$	14	20	26	31	34	37	..
4	$KHSO_4$	2	12	..	29	..	34	44
4	$KC_2H_5SO_4$	5	..	10	..	24	..	34
4	KNO_3	19	12	16	14	28	..	..
2	$MgSO_4.7H_2O$	12	18	..	20	18	..	..
2	$Mg(NO_3)_2.6H_2O$	..	..	..	..	16	..	..
4	$Mg(NO_3)_2.6H_2O$	7	10	12	13	..	15	13
2	$Ca(NO_3)_2.4H_2O$	..	..	..	..	18	..	..

PERCENTAGE ERROR CAUSED BY FOREIGN SALTS IN THE COLORIMETRIC DETERMINATION OF PHOSPHATES.

Cubic centimeters of standard phosphate.	Grams of salt in 50 cc.	1	1.5	1.75	2.5	3	4	6	7	8	10	12	15	20	30
2	$NaCl$	18	36	..	..	52	60	56	..	60	..	..	..	..	..
4	$NaNO_3$	24	36	38	38	..	40	..	..	..	..	..	..	..	..
4	$Na_2SO_4.10H_2O$	..	..	..	..	..	..	..	..	..	..	..	..	..	..
4	$KHSO_4$	..	72	..	86	..	..	..	..	..	..	..	..	..	..
4	$KC_2H_5SO_4$	..	50	47	47	49	52	..	..	..	..	..	..	..	..
4	KNO_3	40	..	..	60	66	74	..	..	..	..	..	..	..	..
2	$MgSO_4.7H_2O$	39	47	..	58	60	67	74	..	..	80	..	..	..	..
2	$Mg(NO_3)_2.6H_2O$	9	..	..	..	30	32	35	..	20	24	16	13	10	+12[1]
4	$Mg(NO_3)_2.6H_2O$	18	24	..	39	31	30	20	20	11	..	..	..	..	..
2	$Ca(NO_3)_2.4H_2O$	32	..	..	..	..	39	44	45	..	32	..	..	5	..

The quantity of the different salts that will introduce an error of approximately 5 per cent. in the readings, is given in the following table. The results were taken from curves and calculated to parts per million, and are only close approximations. The values will, however, serve to fix the limiting conditions for which the colorimetric method may be

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[1] The volume of the solutions containing the quantities of the salts given in the last six columns exceeded 50 cc.

safely used in the estimation of phosphates in the presence of the above salts.

Salt.	Parts per million.	Concentration, normal.
Sodium sulphate, decahydrate	500	0.003
Potassium nitrate	1000	0.01
Magnesium sulphate (hydrate)	1000	0.008
Potassium hydrogen sulphate	1500	0.02
Calcium nitrate	2000	0.025
Magnesium nitrate	2000	0.03
Sodium chloride	2000	0.035
Potassium ethyl sulphate	3000	0.035
Sodium nitrate	5000	0.06

The results here presented supplement the work of Veitch[1] who showed that ammonium salts, and certain chlorides influenced the color of phosphomolybdate solutions. The data make evident the limitations of this colorimetric method. The oxidation of organic matter with magnesium nitrate, the method recommended by Wiley,[2] introduces relatively small errors in the estimation of phosphates by this colorimetric method, for it will be noted, that a considerable quantity of this reagent may be present within certain limits without influencing appreciably the intensity of color. Some experiments have been conducted with meat samples in which the material was completely oxidized by electrolytic oxygen and oxides of nitrogen obtained in the electrolysis of concentrated nitric acid. These preliminary experiments indicate that the colorimetric method can then probably be applied with success, provided the final concentration of acid is made the same as in the solution of standard phosphate used in the comparisons. Work on the details of this operation are in progress.

This work was undertaken at the suggestion of Dr. Herman Schlundt. I here wish to express my sincere thanks for his kind interest and the assistance he has given me in my work.

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NOTES.

On the Procedure for the Oxidation of Chromic Acid to Perchromic Acid.—In the identification of chromium by the oxidation of chromic acid to perchromic acid many, if not all, authors state that the solution should *first* be acidified with some acid, preferably dilute sulphuric acid, then shaken with an excess of ether, and finally a little hydrogen peroxide added and the whole shaken again so that the perchromic acid formed may be dissolved in the ether to give a blue color. This method of procedure sometimes proves troublesome, except under certain con-

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[1] Veitch, *Loc. cit.*

[2] Wiley, "Agricultural Analysis" (1906), Vol. I, p. 587.