containing lead from 49.06 per cent. to the normal sulphide, and iodine in a similar manner from 50.84 per cent. to a sulphide entirely free from it. All of these but the one approximating, $PbS,4PbI_2$, were inconstant in composition and more or less rapidly decomposed into lead sulphide and lead iodide, as might be expected from the knowledge of the chlor- and bromsulphides; the iodosulphide is readily decomposed by heat, acids, and alkalies; and even long exposure to light decomposes it.

ON THE DETERMINATION OF SMALL QUANTITIES OF PHOSPHORIC ACID BY THE CITRATE METHOD.[1]

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THE results obtained by analysts in different parts of the world in precipitating phosphoric acid directly by magnesia mixture, in presence of citric acid or its salts, show that this process may safely take the place of the molybdenum method with all standard tricalcium phosphates or their preparations. We have observed in our work the most satisfactory agreement between this method and the molybdenum method of the Association of Official Agricultural Chemists. This statement, however, holds true only when the phosphoric acid is present in considerable quantities, at least in excess of five per cent. With smaller quantities of phosphoric acid we have observed that the citrate method leads to results which are decidedly inferior to those obtained by the molybdenum process.

The principle of the citrate method may be stated as follows: In the presence of a considerable excess of ammonium citrate a solution of a magnesium salt, made alkaline by ammonia, will precipitate the phosphoric acid as ammonium magnesium phosphate. The iron and alumina which may be present in the solution will not be precipitated under the above circumstances either as hydroxides or as phosphates. The ammonium magnesium phosphate can be subsequently separated by filtration, converted into magnesium pyrophosphate and weighed. An examination of the

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[1] Read before the Washington Section, April 11, 1895.

pyrophosphate obtained as above will disclose the presence of iron and alumina, but experience has shown that an equivalent amount of phosphoric acid will be found in the filtrate after the separation of the ammonium magnesium phosphate. The errors are, therefore, mutually compensatory and results obtained agree within the ordinary errors of analysis with those of the molybdenum method.

Our experience having shown us that the above principles could not be applied in the presence of small quantities of phosphoric acid we were led to try the following simple expedient: Whenever we had to deal with a small percentage of phosphoric acid, for instance, anything below ten per cent., we added to the solution, before the precipitation, a sufficient quantity of a solution of a phosphate of known strength to bring the total percentage of phosphoric acid in the mixture up to that of a natural tricalcium phosphate of good quality; *viz.*, from fifteen to thirty per cent. In these circumstances we were able to obtain perfectly accurate results, even in cases where less than one per cent. of phosphoric acid was present. The following analytical data will illustrate the character of the work:

Solutions Employed.—No. 1. This is a solution of cottonseed-meal and castor pomace. It is part of a sample sent out last year, by the reporter on phosphoric acid, to the members of the Association of Official Agricultural Chemists.

Nos. 2 to 5 inclusive. These are solutions of natural phosphates containing very small percentages of phosphoric acid, some of them less than one per cent.

Nos. 6 to 10 inclusive. These are preparations made by diluting a standard solution of a superphosphate with water. This superphosphate was a part of a sample sent out by the official reporter for 1894.

Nos. 11 to 17 inclusive. These are natural rock phosphates containing large percentages of phosphoric acid, and the data show the agreement between the direct citrate and the official molybdenum method.

The above solutions for the citrate method were made by treating two grams of the material with fifty cc. of sulphuric acid and twenty cc. of nitric acid, and boiling until fumes of sulphuric acid began to escape.

CITRATE METHOD.

Solution No.	Citrate Method. Direct. Per cent. P_2O_5.	Citrate Method. After adding 25 cc. of known phosphate solution. Per cent. P_2O_5.	Citrate Method. Calculated for original solution. Per cent. P_2O_5.	Official molybdenum method. Per cent. P_2O_5
1.	1.08	8.93	2.51	2.46
	2.17[1]	8.97	2.55	2.50
	1.53	15.92	2.61	2.49
	2.30[1]	15.76	2.45	2.48
2.	0.76	10.91	0.89	1.02
	0.64	11.10	1.08	1.02
3.	3.76	14.10	4.08	4.08
	3.64	14.16	4.14	3.99
4.	0.32	10.78	0.76	0.77
	0.19	10.91	0.89	0.76
5.	0.25	10.82	0.80	0.88
6.	0.76	11.16	1.14	1.15
	0.96	11.16	1.14	1.15
7.	2.17	12.38	2.36	2.30
	2.36	12.31	2.29	2.31
8.	3.25	13.46	3.44	3.44
	3.25	13.46	3.44	3.46
9.	4.40	14.67	4.65	4.62
	4.47	14.48	4.46	4.59
10.	5.68	15.69	5.67	5.74
	5.29	15.63	5.61	5.77
11.	17.23	....	....	17.29
12.	37.77	....	....	37.77
13.	15.37	....	....	15.44
14.	29.16	....	....	29.22
15.	29.49	....	....	29.47
16.	31.64	....	....	31.64
17.	32.22	....	....	32.15

Explanatory Notes.—With solution No. 1 four determinations were made. In the first and third instances the mixture was allowed to stand twenty-four hours before filtering, while in the third and fourth instances it was allowed to remain for three days. The results clearly show the progressive separation of the crystalline precipitate, almost the full quantity being secured after the lapse of three days. In the first and second instances there was added enough of a solution of rock phosphate to bring the total phosphoric acid up to about nine per cent., while in the third and fourth determinations a solution of a richer rock was added, bringing the total phosphoric acid in the mixture up to about sixteen per cent. There was little difference noted in the

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[1] Stood 72 hours.

results. Beginning with solution No. 2, the increase in the content of phosphoric acid was secured by adding measured quantities of a solution of ammonium phosphate of known stength The results show that a chemically pure phosphate can be used with equal satety in place of solutions of rock phosphate. By a study of the results obtained with solution 10, it is seen that when the content of phosphoric acid reaches about six per cent. the direct method with magnesium citrate gives approximately correct results. It is to be recommended, however, in all cases where the sample contains less than ten per cent., that fortification with a solution of a phosphate of known strength be practiced.

Solutions 11 to 17 inclusive were made from samples of rock phosphate quite rich in phosphoric acid and, therefore, required no fortification. It is seen in all cases that the data obtained by the direct citrate method are almost identical with those secured by the official molybdenum process.

Conclusions.—(1) In all cases of samples of tricalcium phosphate, or acid phosphates made therefrom, containing the usual accompanying substances, the phosphoric acid may be correctly estimated by direct precipitation with magnesium citrate.

(2) In all cases of the analysis of natural rock phosphates containing less than five per cent. of phosphoric acid it is necessary to fortify the solution before precipitation by adding a measured quantity of a solution of phosphoric acid of known strength.

(3) The fortifying solutions employed may be made either from natural tricalcium phosphates or from chemically pure phosphate salts.

(4) The direct precipitation of the phosphoric acid in the presence of ammonium citrate by ammoniacal magnesia mixture is a quicker and less expensive process than the official molybdenum method and leads to results equally accurate.

(5) We have not applied the direct citrate method to the natural iron and aluminum phosphates, and therefore can make no statement in regard to its accuracy in the treatment of such samples.