

## THE DIRECT DETERMINATION OF AVAILABLE PHOSPHORIC ACID.

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THE direct determination of available phosphoric acid is not new, being official in several of the European countries. In this country, however, it has not met with favor, probably because the citrate method is not official here. The necessity of destroying the organic matter before precipitating with molybdate solution precludes the use of the molybdate method.

In 1893 Ross presented a method<sup>1</sup> for the direct determination of the reverted phosphoric acid. While the aim of this method met with hearty approval from the official chemists, the method itself did not, owing to some difficulties met with in the manipulation, and more particularly to the fact that it did not give results agreeing with the official method.<sup>2</sup> Agreement could hardly be expected seeing that the method did not account for that phosphoric acid removed in the water used in washing the citrate insoluble. Believing that this last-mentioned fact, *viz.*, that the Ross method did not account for the phosphoric acid contained in the wash-water of the official method, is the principal cause of the difference in the results by the two methods, in 1895, the writer did some work with the view of proving his hypothesis. This work consisted of the determination of the water-soluble phosphoric acid by the volumetric method, as modified and carried out by the writer;<sup>3</sup> the direct determination of the citrate-soluble by the citrate method, in fifty cc. of the citrate filtrate, and the determination of that removed by washing the citrate-insoluble residue, using the modified volumetric method. The sum of these three results should equal the available phosphoric acid by the official method.

It is perhaps sufficient to say that the citrate method at that time and later<sup>4</sup> gave satisfactory results on sixty or seventy samples. The results of the comparison are given in the table.

<sup>1</sup> U. S. Department of Agriculture, Division of Chemistry, Bulletin 38, p. 17.

<sup>2</sup> U. S. Department of Agriculture, Division of Chemistry, Bulletin 43, p. 72; and Bulletin 47, p. 81.

<sup>3</sup> This Journal, 18, 389, and U. S. Department of Agriculture, Division of Chemistry, Bulletin 49, p. 61.

<sup>4</sup> U. S. Department of Agriculture, Division of Chemistry, Bulletin 49, pp. 61, et seq.

	Direct method.					Official method.	
	Soluble. Per cent.	Reverted. Per cent.	Wash. Per cent.	Available. Per cent.	Total. Per cent.	Available. Per cent.	Total. Per cent.
1	10.13	3.60	0.24	13.97	16.15	14.00	16.18
2	12.46	2.96	0.17	15.59	16.09	15.49	15.99
3	10.88	3.68	0.21	14.77	16.10	14.79	16.12
4	4.80	5.13	0.29	10.22	11.70	10.14	11.62
5	8.25	2.65	0.47	11.37	12.17	11.24	11.97
6	7.56	3.61	0.26	11.45	14.48	11.58	14.64
7	8.08	2.24	0.25	10.57	12.79	10.64	12.75
8	7.00	4.76	0.37	12.08	16.48	12.21	16.54
9	9.03	3.12	0.28	12.43	13.86	12.31	13.74
10	1.18	6.22	0.68	8.08	12.74	8.03	12.69
11	1.08	6.35	0.99	8.42	12.96	8.32	12.86
12	3.10	4.88	1.48	9.46	15.41	9.50	15.45
13	5.10	1.73	0.21	7.04	8.16	7.03	8.35
14	8.87	2.10	0.09	11.06	11.39	10.86	11.19
15	4.75	2.30	0.39	7.44	8.84	7.45	8.85
16	4.97	2.98	0.38	8.33	10.72	8.44	10.83
17	4.27	2.34	0.19	11.80	12.53	11.82	12.55
18	7.47	3.34	0.30	11.11	13.28	11.23	13.40
19	5.55	3.59	0.40	9.54	14.48	9.70	14.64
20	7.50	2.06	0.16	9.72	11.92	9.70	11.90

Nos. 1, 2, and 3 were dissolved S. C. rock.

Nos. 4, 5, and 6 were dissolved S. C. rock and potash.

Nos. 7, 8, and 9 were dissolved animal bone.

Nos. 10, 11, and 12 were raw bone.

Nos. 13, 14, 15, 16, 17, 18, 19 and 20 were compounded for this work and were complete fertilizers.

The two methods gave practically the same results on availables and on totals. The work also shows very plainly why the Ross method differs from the official, from 0.09 per cent. to 1.48 per cent. being removed and accounted for in the wash-water of the official method that could not be accounted for by the Ross method. Of course the amount removed by the wash-water will vary somewhat in the hands of different analysts, according as they wash the citrate-insoluble much or little. It is the practice of the writer to wash until the filtrate and washings amount to about 250 cc.

At this point pressure of other work necessitated the dropping of this, and nothing more was done until the present summer, when it was determined to extend the work somewhat.

A comparison of the official method with the citrate and the molybdate methods, precipitating with magnesia mixture and

with molybdate solution, respectively, in the mixed filtrates, containing the water-soluble and the citrate-soluble, was undertaken.

The method pursued was as follows: the water-soluble, extracted as usual, was received in a 500 cc. flask, graduated roughly at 250 cc. and containing five to ten cc. nitric acid. The citrate-soluble was then extracted as usual, the filtrate and washings received in the flasks with the water-soluble. After cooling, the volume was completed, shaken, filtered, and in aliquots of 100 cc. the phosphoric acid was determined by each method, the molybdate solution being added directly to the solution without destroying the organic matter, but the precipitates were allowed to stand over night before filtering. The determinations were completed as usual. The samples were carefully selected to represent most classes of goods found on our markets. Most of them contained organic matter, some in considerable quantities.

	Available official method. Per cent.	Available Molybdate method. Per cent.	Available direct Citrate method. Per cent.
21 Dissolved S. C. rock	15.87	15.84	15.40
22 " " " "	14.40	14.51	14.50
23 " " " " and potash	13.45	13.45	13.24
24 " " " "	14.82	15.04	14.53
25 " " " "	15.60	15.66	15.47
26 " " " " and potash	11.78	11.90	11.76
27 " " " " " "	14.11	13.95	13.94
28 " " " " " "	11.96	11.80	11.60
29 " " " " " "	9.09	9.06	8.90
30 " " " " " "	10.44	10.36	10.24
31 " " " " " "	13.09	13.08	12.63
32 " " " " " "	9.02	8.87	....
33 " " " " " "	9.58	9.60	....
34 " " " " " "	10.01	10.13	....
35 Dissolved animal bone	10.58	10.65	10.35
36 " " " "	12.31	12.50	12.14
37 " " " "	14.27	14.10	13.86
38 Complete	7.71	7.67	7.13
39 " "	11.49	11.54	11.32
40 " "	9.61	9.71	9.86
41 " "	7.39	7.27	7.05
42 " "	9.08	9.03	8.90
43 " "	10.14	9.96	9.84
44 " "	9.70	9.87	....

	Available official method. Per cent.	Available direct. Molybdate method. Per cent.	Citrate method. Per cent.
45 Complete, contains great deal tankage	5.27	5.31	....
46 " "	8.51	8.39	....
47 " contains bone-black	6.46	6.64	....
48 " " blood	5.09	4.99	....
49 " "	8.18	8.18	....
50 " "	7.91	7.75	....
51 " "	7.37	7.35	....
52 " contains great deal fish	7.44	7.59	....
53 " "	9.38	9.36	....

The results by the citrate method were unexpectedly low. In the writer's hands this method had always given satisfactory results, even on low percentages. It is probable the low results were due to an excess of citrate, twenty to thirty cc. more having been added to each sample. This addition was unnecessary, and better results when more citrate was not added, leads to the belief that this additional citrate was the cause of the low results: No time remained, however, to confirm this opinion.

The results by the molybdate method were good. It was feared that the organic matter present would prevent the complete precipitation of the ammonium phosphomolybdate. To insure complete precipitation the samples were allowed to stand over night before filtering. In view of the results it is to be regretted that there was no opportunity for the determination of the time required for the complete precipitation of this salt under these conditions. It is probably not over two hours at 65° C.

Notwithstanding the oft-repeated statement that salts of organic acids and organic matter generally prevent the complete precipitation of ammonium phosphomolybdate, the molybdate method is used to determine soluble phosphoric acid in the presence of what organic matter may be dissolved by the water used in the extraction. In the Wagner method<sup>1</sup> for basic slag, we precipitate with molybdate solution in the presence of three grams of citric acid. Lorenz<sup>2</sup> precipitates in the presence of two per cent. of citric acid to prevent contamination with magnesia. Jüptner<sup>3</sup> uses as much as 100 grams of tartaric acid per liter of

<sup>1</sup> Principles and Practice of Agricultural Analysis, 2, 78.

<sup>2</sup> *Ibid.*, 2, 54.

<sup>3</sup> Abstract Experiment Station Record, 6, 610.

molybdate solution to prevent the precipitation of iron and the separation of molybdic acid. The successful use of the molybdate method in these cases seems to warrant the conclusion that we are needlessly alarmed at the presence of, at least, some forms of organic matter in phosphate solutions.

The direct determination of the available phosphoric acid possesses several advantages. Only one determination is required instead of two as by the present method. The probable error is reduced one-half. We can also determine the soluble, reverted, insoluble, and total phosphoric acid in one sample and with one weighing where it now takes two samples and two weighings.

The saving of time effected by this method is of considerable importance in control and in factory laboratories. whether we use the citrate or the molybdate method, and it is hoped that the subject will receive further attention.

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### NOTE UPON THE DETERMINATION OF NITROGEN IN FERTILIZERS CONTAINING NITRATES.

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JOHN FIELDS<sup>1</sup> describes a modification of the Gunning method<sup>2</sup>. In this modification potassium sulphide alone is used in the place of potassium sulphate and sodium thiosulphate.

In Fields' hands the average difference between the methods is 0.02 per cent., the modification giving the higher average.

The writer has used this modification, carried out in a slightly different manner, with very satisfactory results. To the nitrate in the digesting flask are added thirty-five to forty cc. sulphuric acid containing thirty-four grams salicylic acid per liter. Allow to stand in the cold until the nitrate is dissolved. Add six or seven grams of finely broken potassium sulphide, heat over a low flame for fifteen minutes, then over the full flame until clear. Cool and distil as usual. The following are all the results I have obtained by this method.

<sup>1</sup> This Journal, 18, 1102.

<sup>2</sup> U. S. Department of Agriculture, Division of Chemistry, Bulletin 46.