compounds diminishes with increasing complexity of structure then in such difficultly volatile metals as tungsten, chromium, platinum, and other metals fusing at high temperatures, and in their alloys, the molecule (in the solid state) must be possessed of large molecular weight and corresponding inertness toward chemical action.[1]

I am indebted to Dr. Wahl, of Philadelphia, through Mr. Garrison, for the material on which these analyses were made.

THE DIRECT ESTIMATION OF CITRATE SOLUBLE PHOSPHORIC ACID.

BY B. B. ROSS.

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THE direct determination of citrate soluble phosphoric acid, as is well known, is effected in many European laboratories by precipitating it, as magnesium ammonium phosphate in the presence of the ammonium citrate employed in effecting its solution.

The lack of general applicability, together with other objections, which have been urged against this method, however, has caused its employment to be somewhat restricted and the process has met with little favor in this country.

The presence of the citric acid in the solution has, of course, prevented the direct application of the molybdate method, and several processes have been proposed for the elimination of the citric acid preparatory to the precipitation of the phosphoric acid by the molybdate solution. The writer some years since (Proceedings Association Official Agricultural Chemists, 1885,) proposed the removal of the citric acid by precipitation in the hot solution by means of calcium chloride.

A number of results reported at that time showed quite a close agreement with the figures obtained by the regular official method, but some later tests indicated a loss resulting from the retention of small quantities of calcium phosphate in the precipitate of calcium citrate.

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[1] "Modern Theories of Chemistry," pp. 131, 287. Ostwald "Outlines of General Chemistry," pp. 190, 191; in reference to potassium as solid p. 275.

Kuntze (*Ztschr. f. Rübenzucker*, *1892*, 860,) recommends for the destruction of citric acid and other organic matters, evaporation of the solution and treatment with sulphuric and nitric acids, followed by thorough ignition. During the past year a number of experiments were made in the laboratory of the Louisiana State University with a view to the elimination of citric acid by means of oxidizing agents by the wet way.

After testing a number of different methods of oxidation it was found that the best and most satisfactory results were to be secured by the employment of the Kjeldahl digestion process. The mode of procedure finally adopted is essentially as follows:

After the completion of the thirty minutes' digestion of the sample with 100 cc. of citrate solution, twenty-five cc. of the liquid are at once filtered out into a dry vessel, preferably into a burette, as the solution can, after cooling, be transferred to another vessel without the dilution attendant upon rinsing the measuring vessel.

Bring the aliquot, thus measured, into a digestion flask of 250 to 300 cc. capacity, add about fifteen cc. concentrated sulphuric acid and place the flask on a piece of gauze over a moderately brisk flame.

Within about eight minutes the liquid will have become quite concentrated and will begin to darken appreciably and at the same time foaming will commence, but will occasion no trouble if an extremely high, or a very low flame be avoided.

After a further lapse of three or four minutes the foaming ceases and the contents of the flask appear quite black; about one gram of mercuric oxide or metallic mercury is now added and the digestion continued over a high flame.

The operation can be readily completed within less than half an hour, and, in many cases, within twenty-five minutes, a clear and almost colorless liquid being obtained.

After cooling, the solution is washed into a beaker, ammonia is added in slight excess, the solution acidified with nitric acid and the regular molybdate method followed, after addition of ammonium nitrate.

In case as large an amount as fifty cc. (corresponding to one gram of the sample) of the filtrate from the citrate treatment is employed, ten cc. of strong sulphuric acid are at first added and the digestion conducted in a flask of 350 to 500 cc. capacity; after the contents of the flask have blackened and the foaming has progressed considerably, the flask is removed from the flame and fifteen cc. more of sulphuric acid are added and the flask and contents heated with a low flame for two or three minutes; mercuric oxide is next added and the digestion is completed as before described.

Among the chief advantages of this process for the determination of citrate soluble phosphoric acid may be enumerated the following:

1st.—It affords a quick and direct method for the estimation of that form of phosphoric acid which, together with the water soluble, constitutes what is termed "available" phosphoric acid, and the amount of this available phosphoric acid is thus reached by two determinations instead of three according to the ordinary method.

2nd.—The economy of time and labor attendant upon this process gives it an advantage over the indirect method, since by the direct method it is only necessary to filter out twenty-five cc. (or possibly fifty cc.) of the citrate solution, thus obviating the frequently tedious task of filtering the whole liquid and bringing upon the filter and washing with water of a definite temperature the insoluble residue; in addition, the ignition of this residue, the subsequent digestion with acid, dilution to a definite volume and measurement of an aliquot, are operations which are either tedious or time-consuming and can to a large extent be avoided by the use of the direct process.

3rd.—If it is desired, this method can be used as a check or control process in connection with the regular method, the check determination being readily executed without the necessity of weighing a fresh quantity of the sample under examination.

The results of a number of comparative tests of this process and the regular official method are herewith inserted, the principal portions of the work reported having been performed by Mr. R. E. Blouin, assistant chemist, during the past fertilizer season.

The samples tested were ordinary commercial fertilizers and it will be observed that the agreement in the figures obtained by the two processes is, in the main, quite close.

RESULTS OF CITRATE-SOLUBLE DETERMINATIONS.

	By the direct method.	By difference. (Official method).
Sample No. 1	2.16	2.16
" " 2	5.63	5.67
" " 3	5.37	5.39
" " 4	2.44	2.64
" " 5	2.00	1.86
" " 6	5.40	5.33
" " 7	6.90	6.78
" " 8	4.55	4.51
" " 9	2.75	2.73
" " 10	2.04	1.98
" " 11	2.07	2.09
" " 12	6.46	6.48
" " 13	5.24	5.11
" " 14	5.12	5.06
" " 15	2.87	2.91
" " 16	1.61	1.53
" " 17	0.37	0.33
" " 18	0.94	0.90
" " 19	0.33	0.36

In order to further test the reliability of the method, a solution containing phosphoric acid derived from a chemically pure phosphate was employed and phosphoric acid in the aqueous solution was determined by the regular molybdate method; a given quantity of the same solution was next mixed with twenty-five cc. of ammonium citrate solution and after addition of fifteen cc. sulphuric acid, the digestion was conducted as before described and the phosphoric acid determined in the manner previously stated. The results were:

By first method (direct molybdate process) 8.06 per cent.
By second method (addition of citrate solution, etc.) 8.13 per cent.

Other tests with chemically pure salts showed differences which were well within the limits of variation permissible in ordinary analytical work.

Experiments were also made with employment of potassium nitrate in the place of mercuric oxide, but it was found that a number of additions of this substance was required and the time needed for the completion of the digestion was considerably lengthened.

The Gunning modification of the Kjeldahl digestion process was also tested but the foaming resulting from the employment of the large quantities of potassium sulphate rendered the use of this modification impracticable.

By the employment of either mercuric oxide or metallic mercury, however, the oxidation is effected rapidly and completely and the subsequent precipitation of the phosphoric acid is easily accomplished.

NOTES ON THE ESTIMATION OF CRUDE FIBER IN SUGAR CANE.

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THERE is no part of the analytical work connected with the chemical control of diffusion process sugar house so unsatisfactory as that of the estimation of the so-called "crude fiber" in the cane, or that portion of the stalk which is insoluble in water. Duplicate analyses, manipulated with great care, show wide variations. The average of such variations for 100 samples taken consecutively was 0.736 per cent. Since the percentage of fiber is used as a factor in calculating the percentage of sucrose on the weight of the cane it becomes highly desirable that either a better method of fiber estimation be devised, or a more accurate and quick method of estimating the percentage of the sucrose directly on the weight of the cane. After a systematic and thorough investigation of the subject I have come to the conclusion that a very accurate method of fiber estimation for technical purposes is not feasible, on account of the wide variation in fiber content in different parts of the cane stalk.

Extraction of the Soluble Bodies from the Chips.—A study was first made of the extraction of the sugars and other soluble bodies in the chips as follows: Twenty grams of chips taken from the comminuter were placed in a beaker, and nine volumes of water of varying temperatures added. The diffusates were polarized every fifteen minutes until the last two readings were the same.