[CONTRIBUTION FROM THE OFFICE OF PLANT PHYSIOLOGICAL AND FERMENTATION INVESTIGATIONS, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE.]

ON THE FACTOR TO BE USED FOR THE CALCULATION OF THE PHOSPHORIC ACID IN NEUMANN'S METHOD.[1]

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Received February 15, 1915.

The method of Neumann[3] for the determination of phosphorus is now frequently used by physiological chemists. The method depends on the precipitation of the phosphorus as ammonium phosphomolybdate from an acid solution containing 10% of ammonium nitrate and the titration of the precipitate with 0.5 *N* sodium hydroxide. The precipitate is washed with cold water and is boiled with an excess of the standard alkali to expel the ammonia which it contains. Assuming that the precipitate has the composition $12MoO_3.(NH_4)_3PO_4.2HNO_3$, after the expulsion of the ammonia each mol should require 56 mol of 0.5 *N* sodium hydroxide and 1 cc. of the alkali should be equivalent to $31.04/56 = 0.554$ mg. P, which is the factor given by Neumann. Heubner[4] has recently shown that the factor is too low and proposes the factor 0.57. Wardlaw[5] also claims that the factor is too low and that it varies with the amount of phosphorus present. Having occasion to use the methods in connection with a biological investigation into the chestnut bark disease, we have made a careful redetermination of the factor and have obtained results essentially in agreement with those of Heubner.

Series A.—Twenty-four grams of disodium hydrogen phosphate, $Na_2HPO_4.12H_2O$, were dissolved in 4 l. of water. Portions of 100 cc. each were analyzed by the method of Fresenius[6] (*a*) and of Schmitz[7] (*b*) giving:

(*a*) 0.2064, 0.2058, 0.2068, 0.2074, 0.2071, 0.2068, 0.2070, 0.2068; mean 0.2068 g. $Mg_2P_2O_7$, equivalent to 0.5758 mg. P per cc.

(*b*) 0.2050, 0.2050, 0.2060, 0.2059, 0.2056; mean 0.2055 g. $Mg_2P_2O_7$, equivalent to 0.5723 mg. P per cc.

(*c*) Direct ignition of 50 cc. portions gave 0.1245, 0.1249, 0.1248, 0.1248, 0.1248 g. $Na_4P_2O_7$, equivalent to 29.09 mg. P. One cubic centimeter of the solution may, therefore, be assumed to contain 0.5766 mg. P.

Precipitation.—Ten, 20 or 40 cc. of the above solution were placed in a flask with 10 cc. of a mixture of equal volumes of concentrated sulfuric

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[1] Published by permission of the Secretary of Agriculture.

[2] The writer wishes to acknowledge his indebtedness to Mr. E. H. Kellogg for assistance in carrying out the analyses reported in this paper.

[3] *Z. physiol. Chem.*, **37**, 129 (1902–3).

[4] *Biochem. Z.*, **64**, 393 (1914).

[5] *C. A.*, **8**, 3540 (1914).

[6] "Quant. Anal.," 6th Ed., I, 402 (1903).

[7] *Z. anal. Chem.*, **43**, 279 (1904); **44**, 333 (1905); **45**, 512 (1906).

and nitric acids, 75 cc. of a 50% ammonium nitrate solution and enough water to make, with the 10% solution of ammonium molybdate (usually 40 cc.), a total volume of 250 cc. The solution was warmed to 80° before the addition of the molybdate solution. The stoppered flask was then vigorously shaken for a minute or two and after settling for 15 minutes the liquid was decanted through a $12^1/_2$ cm. folded filter. The precipitate was shaken with 150 cc. of ice water, then the liquid was decanted and this was repeated three or four times. The washed filter was placed in the flask containing the precipitate and reduced to pulp with 150 cc. of distilled water. An excess of 0.5 *N* NaOH was added, the solution boiled for 15 or 20 minutes to expel the ammonia and, after cooling, the excess of alkali was titrated back with 0.5 *N* H_2SO_4.

The following results were found: Using 40 cc. of the phosphate solution, the factors were 0.577, 0.572, 0.577, 0.571, 0.568. Using 20 cc., 0.578, 0.574, 0.574, 0.577, 0.576. Using 10 cc., 0.576, 0.579, 0.568, 0.582, 0.582. Mean, 0.575.

Series B. Primary Potassium Phosphate as Standard Substance.—A solution was employed which contained in each cc. 0.378 mg. of P, as found by determinations according to the Fresenius and the Schmitz gravimetric methods. Twelve portions of this solution of 25 cc. each were titrated according to the Neumann method and the following volumes of 0.5 *N* sodium hydroxide were required, corrected for the volume required in the titration of a blank solution containing no phosphate, but traces of carbonic acid and material resulting from the disintegration of the filter paper. The amount of this correction, which is applied in all cases, is 0.2 cc. of the alkali solution, leaving as the corrected volumes:

16.82, 16.95, 16.70, 16.95, 16.61, 16.80, 16.51, 16.48, 16.97, 16.45, 16.80 and 16.80 cc. of 0.5 *N* NaOH.

The mean factor calculated from these titration volumes is 0.568.

Series C. Secondary Ammonium Phosphate as Standard Substance.—An aqueous solution was used which contained in each cc. 0.31618 mg. P, as found by determination according to the method of Fresenius (*a*), or 0.31607 mg. P according to the method of Schmitz (*b*). Twelve 50-cc. portions of this solution were titrated according to the Neumann method. The volumes of standard sodium hydroxide required, corrected for the volume found in the titration of a blank analysis, were as follows:

27.80, 27.65, 27.65, 27.64, 27.60, 27.60, 27.60, 27.60, 27.42, 27.61, 27.53, 27.60 of 0.5 *N* NaOH.

The mean factor calculated from these figures is 0.573 (*a*), and 0.573 (*b*).

Series D. Phosphoric Acid as Standard Substance.—For this series a dilute solution was used which contained in each cc. 0.35254 mg. P as found by the gravimetric analysis according to the Fresenius method (*a*), or 0.35110 mg. P according to the Schmitz method. Eighteen portions of this solution of 50 cc. each were titrated according to Neumann's method. The volumes of 0.5 *N* sodium hydroxide required, corrected for the blank analysis, were as follows:

31.00, 31.15, 30.85, 31.12, 31.13, 30.95, 31.15, 31.00, 31.13, 30.98, 31.20, 30.95, 31.05, 30.95, 31.02, 31.00, 31.08, 31.15.

The average factor calculated from these data is 0.568 (*a*) or 0.566 (*b*).

Series E. Primary Potassium Phosphate as Standard Substance.—The solution used for this series contained in each cc. 1.51540 mg. P as found by the gravimetric analysis according to the method of Fresenius (*a*), or 1.50767 mg. P as found by the method of Schmitz (*b*). Twenty-four portions of this solution of 10 cc. each were titrated according to the Neumann method. The (corrected) volumes of 0.5 *N* sodium hydroxide required were as follows:

26.58, 26.54, 26.60, 26.51, 26.54, 26.50, 26.50, 26.42, 26.50, 26.51, 26.60, 26.55, 26.60, 26.52, 26.60, 26.60, 26.40, 26.42, 26.48, 26.45, 26.58, 26.50, 26.51, 26.45.

The mean factor calculated from these data is 0.572 (*a*), or 0.569 (*b*).

The average factor for all five series is 0.571, based on the Fresenius gravimetric method (*a*), or 0.570, based on the Schmitz gravimetric method (*b*).

Conclusions.

(1) While Neumann's method, as modified by Gregersen, is both accurate and reliable, the factor (0.554) used for calculating the phosphoric acid is too low.

(2) The results presented in this paper fully corroborate the factor 0.57 as being very nearly correct, under the conditions outlined in this paper.

(3) Gregersen's modification to overtitrate the dissolved yellow precipitate with 0.5 *N* H_2SO_4, with a view to remove the carbon dioxide present by boiling, and then titrate back with 0.5 *N* NaOH, while in principle correct, is inconvenient since it increases the time required for each individual analysis.

(4) Instead of Gregersen's modification, it is best to run a blank analysis—or better several blank analyses—which compensates the errors due (*a*) to impurities (phosphorus) present in the reagents employed, (*b*) to carbon dioxide contained in the liquids to be titrated, and (*c*) to the acidity caused by the action of the boiling standard alkali on the filter paper. The figure secured for the blank analysis is to be subtracted from the acidimetric analysis proper. With uniform work the same blank may be applied to one or even several series of phosphoric acid estimations.

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