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NOTE ON THE TER MEULEN-HESLINGA METHODS FOR THE ESTIMATION OF NITROGEN, CARBON AND HYDROGEN IN ORGANIC MATERIAL¹

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The purpose of this note is to make the excellent methods of Ter Meulen and Heslinga for the estimation of carbon, hydrogen and nitrogen more generally known in America, and to suggest some slight modifications based on two years' experience in their use. Both methods employ much less material than the customary macro methods without requiring the special equipment or unusual technique of the micro methods in general use.

The Carbon-Hydrogen Method.—This depends upon catalytic oxidation with manganese dioxide. A micro-balance is not necessary, though one with a sensitivity of 0.05 mg. is desirable. If such a balance is not available, the sample to be taken must be larger. With an ordinary analytical balance sensitive to 0.1 mg., the carbon-hydrogen estimation requires fifty to one hundred milligrams and takes one hour.

Several changes in the apparatus set-up recommended by Ter Meulen and Heslinga are suggested. We used compressed commercial oxygen, regulating the velocity of the gas flow by a double-head reduction valve, and introduced a manometer in the line next to the oxygen cylinder to register any resistance to the passage of the products of combustion or to the flow of oxygen that might arise. The oxygen was passed through a purifying train consisting first of sulfuric acid, then of ascarite to absorb carbon dioxide and lastly of dessicite to absorb moisture.

We used a much larger quartz combustion tube than that specified by Ter Meulen and Heslinga, namely 35 cm. long and 10 mm. bore. The additional length permits the use of a copper wire coil between the combustion boat and the end of the tube through which the boat is introduced. Heating this coil to a high temperature by a separate micro-burner during combustion helps to prevent back flow of gases, should there be a sudden increase in pressure. The larger diameter permits the use of more catalyst per unit length, so that it need not be renewed so frequently. A copper wire coil extending the length of the catalyst was found advantageous to prevent the catalyst from becoming too densely packed due to sudden increase in pressure, if combustion was too fast.

Much difficulty was encountered at first in preparing active catalyst.

¹ H. Ter Meulen and H. Heslinga, Leipzig, 1927; H. Ter Meulen, *Rec. trav. chim.*, **43**, 643 (1924); H. Ter Meulen, *ibid.*, **44**, 271 (1925).

We adopted the method of Rogers, Piggot, Bahlke and Jennings² for preparing manganese dioxide from calcium permanganate. We have found it advantageous in order to increase its density to subject the wet precipitate of manganese dioxide to great pressure in a hand-press before drying on a sand-bath. Catalyst thus prepared is very active and has a very long life. As it becomes exhausted, it changes in color from intense black to rusty black.

In analyzing nitrogenous substances Ter Meulen and Heslinga employ a layer of lead peroxide behind the manganese dioxide to hold back the nitrous oxide. Since the lead peroxide in the powdered form has a tendency to pack in the tube, we used it in granulated form of a 12–20 mesh size.

For absorption of the combustion products very light weight U-tubes were used, so that their loaded weight did not exceed 25 g. Water was absorbed by dessicite, carbon dioxide by ascarite. Behind the ascarite in the carbon dioxide absorption tube a short length of dessicite was used to prevent loss of moisture from this tube. Following the absorption train we found it most advantageous to use a Marriotte flask (aspirator bottle) in order to maintain a uniform, slightly reduced pressure in the absorption train. This can be attained by having the opening of the inlet tube dipping into the water in the bottle 20 mm. above the orifice of the outlet tube.

The method itself is very accurate; the limiting factor is the accuracy of weighing. Therefore, results obtained with an ordinary analytical balance and small samples will prove of interest. Thirteen analyses of sucrose, the average weight of sample being 40 mg., gave an average carbon content of 42.31% as against 42.1% theoretical. The sensitivity of the balance used was such that the variability due to lack of sensitivity of the balance might amount to 0.21% carbon for a 40-mg. sample. Six determinations of the carbon content of oxalic acid, the average weight of sample being 28 mg., gave 19.21% as against 19.05% theoretical. The experimental error that might be due to the weighing was 0.25% carbon. It is obvious, therefore, that if only an ordinary analytical balance is available, somewhat larger samples should be used.

The Nitrogen Method.—This depends upon hydrogenation with a nickel catalyst and titration of the resulting ammonia. Using an ordinary analytical balance we have obtained satisfactory results with as little as 20 mg. of sample. The time required is only thirty minutes.

The following modifications in set-up of apparatus are suggested: instead of heating the catalyst by a gas-burner under an asbestos box, we used an electric furnace for that portion of the quartz tube containing the

² T. H. Rogers, C. S. Piggot, W. H. Bahlke, and J. M. Jennings, *THIS JOURNAL*, **43**, 1973 (1921), Method 5.

catalyst. It is not then necessary to cool down during the day, even when changing the boats; a constant temperature may be maintained. Instead of collecting the ammonia in a solution kept just on the acid side of neutrality by addition from time to time of standard acid from a buret supported over the flask, we found it advantageous to collect it in an excess of acid and to titrate the excess at the end of the combustion, after having boiled the contents to remove carbon dioxide. We also found a 1% solution of alizarin sulfonate to be superior to methyl orange for the titration of the seventieth normal acid which we used. Micro-burets of 5 cc. capacity, with scale divisions of 0.02 cc. which could be estimated to 0.002 cc., were used for the titration.

By this technique we were able to determine total nitrogen in such plant materials as wheat leaves and straw in about 250 samples with an accuracy such that duplicate analyses varied by less than 0.1% of nitrogen and very often by only one or two hundredths per cent. When one considers that it is extremely difficult to secure homogeneity in such small samples of this type of material, the method may well be regarded as extremely satisfactory. The results are more accurate than those we could obtain upon the same material with the customary macro Kjeldahl method.

We regard the method as preferable to the Kjeldahl method wherever only a few determinations a day are to be made, for it is not much more time consuming. It is more accurate and does not require a separate digestion room with special hood to remove the gases of boiling sulfuric acid. If, as is the case in fertilizer and feeding stuffs control laboratories, hundreds of analyses have to be made daily, the Kjeldahl method is more expeditious. Moreover, since the Kjeldahl method employs a very much larger sample, it is to be preferred for inhomogeneous materials like fertilizers and feeding stuffs that are difficult to sample.

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