

A NEW METHOD FOR THE ESTIMATION OF NITROGEN IN
CELLULOSE NITRATE

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THE two methods commonly employed for the estimation of nitrogen in cellulose nitrate are: (i) The Lunge Nitrometer method¹ and (ii) The alkaline peroxide digestion or the modified De Varda's method.² In the former method the nitrate groups are reduced to nitric oxide (NO) by the Hg-H₂SO₄ system which is then measured. In the latter method the cellulose nitrate is dissolved by digestion with alkaline hydrogen peroxide followed by reduction with De Varda's alloy. The ammonia formed is estimated as usual. The De Varda's method has been used by Davidson,³ and Kenyon and co-workers.⁴ However, it is well known that during the saponification of cellulose nitrate by alkali the nitrogen is partly converted into nitrite,⁵ cyanide,⁶ nitrogen⁷ and ammonia.⁸ Therefore it is likely that some loss of nitrogen may occur during the digestion in the second method even though the losses may be minimised on account of the presence of the hydrogen peroxide. With a view to overcome this difficulty, the method has been modified as follows: The sample is dissolved in concentrated sulphuric acid. This solution is slowly added to a strong solution of caustic soda in the distillation flask of the ammonia estimation apparatus. The mixture is then treated with De Varda's alloy and the ammonia formed estimated as usual. A number of samples of cellulose nitrate have been prepared and analysed for their nitrogen content by (i) Lunge's method, (ii) the modified De Varda's method, and (iii) the new method.

EXPERIMENTAL

Preparation of Cellulose Nitrate.—Carefully purified cotton yarn (2 g.) cut to small bits (< 1/16") is immersed⁹ in a mixture (100 ml.) obtained by mixing 1 vol. nitric acid (sp. gr. = 1.52) and 2 vol. sulphuric acid (sp. gr. = 1.84) maintained at 0° C. At the end of the requisite period the cellulose nitrate is freed from the spent acid by filtration through a sintered glass filter. The nitrated sample is then plunged into a large volume of ice-cold water. The product is washed free from acid by repeated changes of water. The samples are dried by exposure to air and stored carefully.

ANALYSIS OF CELLULOSE NITRATE SAMPLES

1. *Lunge's Nitrometer Method.*—A Lunge Nitrometer calibrated to 50 ml. in 1/10 ml. is used. The nitrometer is filled with clean mercury. About 100 mg. of the sample is accurately weighed out into the cup of the nitrometer. It is then dissolved by the addition of 10 ml. of pure nitrogen-free concentrated sulphuric acid. The solution is then carefully drawn into the nitrometer without drawing in any air. The cup is then rinsed with two or three 2 ml. portions of pure sulphuric acid. Each lot of the acid is drawn into the nitrometer before the next lot is added. The apparatus is then vigorously shaken so that the mercury and the acid are mixed thoroughly. After allowing the apparatus to come to room temperature the pressure of the gas in the nitrometer is brought to atmospheric by raising or lowering the levelling tube. After the volume is measured the nitrometer is vigorously shaken again and the volume of gas at room temperature and pressure measured. Usually there is no change in volume.

2. *Modified De Varda's Method.*—100 mg. of the sample is accurately weighed into a Kjeldahl flask. Then 2-3 ml. of ethyl alcohol, 20 ml. ammonia-free distilled water, 5 ml. 25-30% H₂O₂ and 4 ml. of 40% caustic soda solution are added. The flask is then heated on a steam-bath till the sample is dissolved. It has been noticed during the course of the present investigation that lower the nitrogen content of the sample the longer is the time required for digestion. The excess of hydrogen peroxide is destroyed by heating on a steam-bath till effervescence ceases. The flask is then cooled to room temperature and 15 ml. of 40% caustic soda solution and 100 ml. of ammonia-free distilled-water added. 1.5 g. (60 mesh) De Varda's alloy is then added to the mixture and the flask immediately connected to the ammonia distillation train. When the hydrogen evolution has ceased (30 min.) the contents are boiled and the ammonia evolved is estimated by absorption in standard hydrochloric acid (50 ml. of 0.04 N) containing 10 drops of the mixed indicator¹⁰ and backtitrating the excess acid with carbonate-free 0.04 N sodium hydroxide from an automatic burette fitted with soda line traps. A blank is carried out with the reagents used. The mixed indicator¹⁰ is prepared by mixing

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2 ml. of aqueous methylene blue solution (1%) with 100 ml. of 0.04% solution of methyl red in 50% alcohol. The change at the end point is from pink through grey to green and is quite sharp. A blank is also carried out with the reagents used.

3. *The Proposed Method.*—100 mg. of the sample is accurately weighed and dissolved in 5 ml. of pure nitrogen-free sulphuric acid. The solution is neutralised by slow addition through a dropping funnel to a mixture of 30 ml. of 1:1 caustic soda solution and 100 ml. of ammonia-free distilled-water in the distillation flask which is connected to the ammonia distillation train. The funnel is then washed down with two or three 2 ml. portions of pure sulphuric acid, two 50 ml. portions of ammonia-free distilled-water and 5 ml. of ANALAR ethyl

alcohol. The solution in the flask is pale yellow or practically colourless. De Varda's alloy (1.5 g., 60 mesh) is introduced into the distillation flask through a side tube which is immediately stoppered. The evolution of hydrogen is complete in about half-an-hour. The solution is then raised to boil and the distillation continued for half-an-hour. All the ammonia distils were over within this time. The ammonia that distils over is estimated as described previously. A blank is also carried out with the reagents used.

The results are given in Table I. From the results it can be seen that the proposed method gives values in close agreement with those obtained by the Lunge's method. It is also evident that the modified De Varda's or the alkaline peroxide digestion method gives consistently lower values.

TABLE I

Estimation of nitrogen in cellulose nitrate. The numbers given are the percentage of N, found as an average of three measurements in each case

Sample number	Lunge's method	Modified De Varda's method	Proposed method
1	8.71	8.23	8.76
2	10.5	9.85	10.46
3	11.23	10.16	11.2
4	12.46	11.56	12.43
5	12.86	12.43	12.93

1. *The Methods of Cellulose Chemistry*. C. Dorée, 1947 edn., Chapman and Hall, p. 244.
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