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 method [1] 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 $Hg\text{-}H_2SO_4$ 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] nitrogen[7] 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 immersed[9] 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% H_2O_2 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 indicator[10] and backtitrating the excess acid with carbonate-free 0·04 N sodium hydroxide from an automatic burette fitted with soda lime traps. A blank is carried out with the reagents used. The mixed indicator[10] 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.

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

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.

1. *The Methods of Cellulose Chemistry*. C. Dorée, 1947 edn., Chapman and Hall, p. 244.
2. —, *Ibid*, pp. 247–48.
3. G. F. Davidson, *J. Text Inst.*, 1938, **29**, 198T.
4. W. O. Kenyon and Co-workers, *J. Amer. Chem. Soc.*, 1947, **69**, 342.
5. W. O. Kenyon and H. LeB. Gray *Ibid.*, 1936, **58**, 1422.
6. W. Will, *Ber.*, 1891, **24**, 400.
7. C. Hausserman, *Chem Ztg.*, 1905, **29**, 421.
8. A. Bechamp, *Compte Rendus* 1855, **41**, 817.
9. I. Sakurada, *Celluloschem*, 1934, **15**, 18; see also *Cellulose Chemistry*, E. Heuser, 1944 edn., p. 184, John Wiley.
10. A. C. Andersen and B. N. Jensen, *Z. Anal. Chem.*, 1931, **83**, 114.

ATOMIC WASTE PRODUCTS

THE probable increase in the number of atomic power plants within the next few years poses a serious problem to the industry. That is the disposal of the radioactive materials which are produced in the reactors.

One proposed method is to enclose it in large concrete blocks and drop it into the ooze at the bottom of the deepest part of the ocean. By the time the concrete is worn away, thousands of years would elapse and the radioactivity would have decreased to almost zero. But some experts feel that there may be strong currents in the sea at great depths, so the concrete would be worn away more rapidly and the radioactivity would be released; it would thus find its way into plants and fish and become dangerous as human food. On the other hand, even if this happened, the radioactivity would concentrate only in the bones and scales of the fish, which are not used as food.

Another suggested method of disposal is to bury these materials under heavy concrete in deep abandoned mines or even in deep natural caves. This would be safe enough except that explorers and archæologists centuries into the future might unsuspectingly encounter their rays. The strangest suggestion was made by an American professor who proposed that these materials should be loaded into a space rocket and sent permanently far from the earth, cruising through the remote regions of the universe like a lost star!

It was agreed at the United Nations Conference on the Peaceful Uses of Atomic Energy in Geneva that the problem *must* be solved, and that meanwhile scientists and governments should make certain, probably by international action, that proper precautions are always taken for the disposal of radioactive waste.