SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

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Modified starch products

Organic nitrogen

Using the Kjeldahl method

1 Scope

This SCAN-test Method specifies a procedure for the determination of organically bound nitrogen in starch and its derivatives used in the manufacture of papers or boards. The results may be used to calculate of the degree of substitution in starch derivatives, provided that the chemical structure of the nitrogen-containing substituent is known. The Method, as described, is not applicable to water-soluble starches. For these, total Kjeldahl nitrogen is determined without washing.

Neither inorganic nitrogen, which is water-soluble, nor the nitrogen contained in nitro, nitroso and azo groups is included in the value yielded by this determination.

2 Principle

The sample is suspended in cold water, filtered and washed with water and ethanol to remove water-soluble material, including nitrogen-containing residual chemicals from the manufacturing process. The insoluble fraction is dried and its nitrogen content is determined by the Kjeldahl method.

Note – If the washing is omitted and the procedure is carried out with an untreated sample, the values obtained for the nitrogen content will include some water-soluble nitrogen compounds, such as ammonium ions and amines.

3 Apparatus

Ordinary laboratory equipment, including:

3.1 *Kjeldahl digestion flasks*, preferably of 100 ml nominal capacity.

3.2 *Digestion stand*, including an electrically heated metal block, in which the digestion flask can be heated in a slightly tilted position. Heat should be applied only to that part of the flask containing liquid during the digestion.

3.3 *Distillation apparatus* for Kjeldahl distillations.

Note – Commercially available apparatus designed for Kjeldahl nitrogen determination can normally be used for the purpose of this Method.

4 Reagents

All reagents shall be of analytical grade. Ammonia-free distilled water shall be used. Water that has been treated with ion-exchange resins may contain nitrogen compounds and shall not be used.

4.1 *Washing solution*. Mix equal volumes of water and ethanol, C_2H_5OH.

4.2 *Ethanol*, C_2H_5OH, 95 %.

4.3 *Sulphuric acid*, concentrated, density 1840 kg/m^3.

4.4 *Sodium hydroxide solution*, 7,5 mol/1. Dissolve 300 g of sodium hydroxide, NaOH, by adding it, cautiously and in small portions, to about 600 ml of distilled water. Allow to cool and then make up to 1 litre with distilled water.

4.5 *Boric acid solution*, 20 g/l. Dissolve 20 g of boric acid, H_3BO_3, in distilled water and make up to 1 litre.

4.6 *Catalyst*. Mix 97 g of potassium sulphate, K_2SO_4, and 3 g of anhydrous copper sulphate, $CuSO_4$, to get a homogeneous mixture.

4.7 *Hydrochloric acid*, 100 mmol/1 HCl, the concentration being known to the nearest 0,1 mmol/l.

4.8 *Indicator solution.* Mix 2 volumes of a cold, saturated solution of neutral methyl red in 50 % (volume/volume) ethanol and 1 volume of a 0,25 g/1 solution of methylene blue in 50 % (volume/volume) ethanol. Store the solution in a bottle of brown glass.

5 Preparation of sample

Mix the sample thoroughly. If the sample contains lumps or other coarse particles, grind it until it all passes through a sieve with a nominal aperture of not more than 0,6 mm.

6 Procedure

This procedure should be performed in duplicate. In addition carry a blank test through the digestion and distillation steps.

Weigh about 10 g of the sample and disperse it in about 100 ml of distilled water. Filter the suspension through a dense filter paper in a Büchner funnel. Wash the starch on the filter 3 times with 100 ml of the washing solution (4.1). Finally, wash with 50 ml of ethanol (4.2).

Remove the filter paper with the starch from the funnel and dry it in a drying oven at 130 °C. Allow to cool in a desiccator.

Weigh, to the nearest 0,1 mg, about 1 g of the dried starch and transfer it to a dry Kjeldahl digestion flask (3.1). Add 4 g of the catalyst (4.6). Then add 25 ml of the sulphuric acid (4.3) in such a way that it rinses the inner wall of the neck of the flask. Mix the contents of the flask until the test portion is completely wetted. Add a glass bead to avoid bumping during the digestion.

Place the flask in the digestion stand (3.2) and heat carefully until the liquid boils gently. Continue heating until the liquid becomes clear and then for a further 1 h.

Allow the flask to cool. Carefully rinse the inner neck of the flask with a few millilitres of distilled water, allowing the rinsings to collect in the flask. Add slowly about 50 ml of distilled water. (This volume may be varied according to the distillation apparatus used.) Cool to room temperature.

The procedure for the distillation step depends on the design of the distillation apparatus. The receiver shall contain a suitable volume of the boric acid solution (4.5) and the lower end of the condenser shall be below the surface of the solution. Transfer quantitatively the liquid in the digestion flask to the distillation flask. Rinse the digestion flask with a few millilitres of water and add the rinsings to the distillation flask. Connect the distillation flask to the distillation apparatus. Add slowly and with caution at least 150 ml of the sodium hydroxide solution (4.4). The distillation apparatus must be designed so that this can be done without any loss of the released ammonia.

Heat the distillation flask and distil its contents until all the ammonia has been collected in the receiver. The heating rate and the time required for distillation depend on the design of the apparatus. If the distillation flask is heated internally with steam, distillation is normally completed after 20 min to 30 min, by which time about 200 ml of distillate has been collected.

Add 3–5 drops of the indicator solution (4.8) to the distillate. Titrate with the hydrochloric acid (4.7), using a 10 ml or 25 ml burette, as appropriate, until the colour of the distillate turns reddish violet.

7 Calculation

Calculate the nitrogen content of the starch to the nearest 0,001 % from the expression:

$$X = \frac{1{,}401\, c(V_1 - V_0)}{m} \qquad [1]$$

where

X is the nitrogen content, expressed as a percentage;
C is the concentration of the hydrochloric acid, in millimoles per litre;
V_0 is the volume of the hydrochloric acid used in the blank test, in millilitres;
V_1 is the volume of the hydrochloric acid used in the determination, in millilitre;
m is the mass of the washed and dried sample taken, in milligram;

1,401 = factor containing the molecular mass of nitrogen, 14,01, and the factor 0,1 required for the conversion of the result to a percentage.

8 Precision

Two samples of starch were analyzed by 4 laboratories. Each laboratory carried out the procedure in duplicate. The mean values ranged from 0,121 % to 0,128 % for one sample and from 0,287 % to 0,292 % for the other sample.

9 Report

The test report shall contain reference to this SCAN-test Method and the following particulars:

(a) date and place of testing;
(b) identification mark of the sample;
(c) the result as the arithmetic mean of the two determinations, to the nearest 0,01 per cent;
(d) any departure from the procedure described in this Method or any other circumstances that may have affected the result.

10 Additional information

The principle employed in this Method is the same as that in ISO 3188, *Starch and derived products – Determination of nitrogen by the Kjeldahl method – Titrimetric method*. In the ISO Standard, however, the washing step is not included and the titration is carried out with sulphuric acid. The test portion, and consequently the amounts of reagents, is larger in the ISO standard.

SCAN-test Methods are issued and recommended by KCL, PFI and STFI-Packforsk for the pulp, paper and board industries in Finland, Norway and Sweden.
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