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Pulps — Determination of limiting viscosity number in cupri-ethylenediamine (CED) solution

Pâtes — Détermination de l'indice de viscosité limite en utilisant une solution de cupri-éthylènediamine (CED)

Reference number
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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 5351 was prepared by Technical Committee ISO/TC 6, *Paper, board and pulps*, Subcommittee SC 5, *Test methods and quality specifications for pulps*.

It cancels and replaces ISO 5351-1:1981, which has been technically revised.

Introduction

The viscosity (or dynamic viscosity), symbol η, of a fluid is defined by the Newtonian equation

$$\tau = \eta\dot{\gamma} \tag{1}$$

where

τ is the shear stress;

η is the viscosity;

$\dot{\gamma}$ is the velocity gradient dv/dz (v being the velocity of one plane relative to the other and z the co-ordinate perpendicular to the two planes).

In non-Newtonian behaviour, normally the case with high molecular mass polymer solutions such as cellulose, the ratio of the shear stress to the velocity gradient varies with the shear stress.

The data required for evaluation of the limiting viscosity number of pulp in dilute solutions (for terms and definitions, see Clause 3) are derived by means of a capillary-tube viscometer. The results of these measurements are seriously affected by the shear rate.

The concentration c of the pulp is therefore chosen so that, if multiplied by the limiting viscosity number $[\eta]$, it gives a product $[\eta] \times c$ equal to $3{,}0 \pm 0{,}4$, corresponding to a viscosity ratio η/η_0 equal to 6 to 10. The determination is then carried out at a reproducible shear rate G of $(200 \pm 30)\ s^{-1}$; this involves the employment of two viscometers, one for calibration and one for the measurement of the viscosity of the pulp.

The viscosity of a pulp in CED solution gives an indication of the average degree of polymerization (DP) of the cellulose (see Annex C). Such a measurement therefore gives a relative indication of the degree of degradation (decrease in cellulose molecular mass) resulting from the pulping and/or bleaching process.

Caution should be taken in drawing conclusions regarding strength properties of the pulp strictly from viscosity measurements unless previous investigation has identified the relationship. A direct relationship between pulp strength and viscosity has not been found.

Pulps — Determination of limiting viscosity number in cupri-ethylenediamine (CED) solution

1 Scope

This International Standard specifies a method which yields a number that is an estimate of the limiting viscosity number of pulp in a dilute cupri-ethylenediamine (CED) solution.

This method is primarily applicable to CED-soluble samples of bleached chemical pulps but can also be applied to any kind of pulp that dissolves completely in CED solution.

NOTE 1 The results can be used to estimate the extent of cellulose degradation caused by cooking or bleaching. Results obtained with samples containing appreciable amounts of substances other than cellulose must be interpreted with caution, however.

NOTE 2 In the strictest sense, viscosity measurement procedures are applicable only to the polysaccharide fraction of the sample. This notwithstanding, viscosity measurement can usually be used to obtain a result on unbleached pulps having lignin contents of up to 4 %, because most of these pulps can be successfully dissolved in CED. However, the simple fact that an unbleached pulp can be dissolved in CED does not mean the results are valid. In summary, viscosity results for pulps containing more than 0,5 % of lignin are not acceptable for technical specification purposes.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 638, *Pulps — Determination of dry matter content*

ISO 7213, *Pulps — Sampling for testing*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
shear rate
G
velocity gradient of a fluid layer, parallel to the direction of flow, at the periphery of the capillary, defined by the equation

$$G = \frac{4V}{\pi r^3 t_f} \tag{2}$$

where

V is the volume between two arbitrary calibration marks on the viscometer, in millilitres;

r is the radius of the capillary tube, in centimetres;

t_f is the efflux time of the fluid, in seconds.

3.2
viscosity ratio
(formerly called relative viscosity)
η_{ratio}
ratio of the viscosities η and η_0 of a polymer solution of stated concentration and of the solvent, respectively, at the same temperature, given by

$$\eta_{ratio} = \frac{\eta}{\eta_0} \tag{3}$$

NOTE It is dimensionless.

3.3
viscosity relative increment
viscosity ratio (3.2) minus one:

$$\frac{\eta}{\eta_0} - 1 = \frac{\eta - \eta_0}{\eta_0} \tag{4}$$

NOTE It is dimensionless.

3.4
viscosity number
VN
ratio of the viscosity relative increment (3.3) to the polymer concentration c, expressed in grams per millilitre, in the solution:

$$\mathrm{VN} = \frac{\eta - \eta_0}{\eta_0 \times c} \tag{5}$$

NOTE It is measured in millilitres per gram.

3.5
limiting viscosity number
$[\eta]$
limiting value of the viscosity number (3.4) at infinite dilution:

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta - \eta_0}{\eta_0 \times c} \right) \tag{6}$$

NOTE 1 It is measured in millilitres per gram.

NOTE 2 In the literature, the term intrinsic viscosity is often used and is equal to the limiting viscosity number. There is no general conversion factor between the limiting viscosity number in ml/g and other viscosities, determined by other methods and expressed in mPa·s (see [7]).

4 Principle

Measurement of the times of efflux of the diluted solvent and the pulp solution through a capillary-tube viscometer at a specified concentration at 25 °C. Calculation by Martin's formula (see [9]) of the limiting viscosity number from these measurements, and from the known concentration of the solution.

5 Reagents and materials

Use only chemicals of recognized analytical grade and only distilled or deionized water.

5.1 Cupri-ethylenediamine (CED) solution, c(CED) = (1,00 ± 0,02) mol/l, saturated with copper(II) hydroxide, for convenience referred to as CED solution.

The solution contains 1,0 mol of copper and 2,0 mol of ethylenediamine per litre. It is commercially available, or may be prepared and analysed as described in Annex A.

NOTE By reason of allergens, avoid contact of skin with CED and ethylenediamine solutions. Ethylenediamine is volatile, and repeated exposure may lead to severe respiratory allergic reactions with subsequent sensitization. Cupri-ethylenediamine solutions should not be pipetted by mouth. CED solution is also environmentally harmful, and it is recommended that a suitable destruction procedure be used before disposal.

5.2 Glycerol, solution in water, $c(C_3H_8O_3)$ = 65 % (by mass), having a viscosity of about 10 mPa·s.

5.3 Nitric acid (HNO_3), dilute solution for cleaning the pieces of copper wire (6.4).

5.4 Reagents for calibrating capillary-tube viscometers equipped with an automatic time-recording device.

As specified in the manufacturer's instructions.

6 Apparatus and materials

Ordinary laboratory apparatus and the following:

6.1 Capillary-tube viscometers (6.1.1 and 6.1.2), each with a water jacket connected to a constant-temperature bath (6.3). Two different viscometers are required because of the great difference between the viscosities of the test solution and the solvent. Suitable viscometers are shown in Figure 1.

NOTE Viscometers without a water jacket may be used if measurement is made while the viscometer is immersed in the constant-temperature bath.

Capillary-tube viscometers equipped with an automatic time-recording device may be used provided they comply with this International Standard and give similar results.

Clean the viscometers by rinsing with water and acetone. If any residual material remains after cleaning, clean again with a sulfuric acid based cleaning solution designed for use with laboratory glassware. Soak particularly dirty tubes overnight or longer in this cleaning solution to remove all traces of contaminants. After cleaning, drain all cleaning solution from the tube, rinse well with water and acetone and dry.

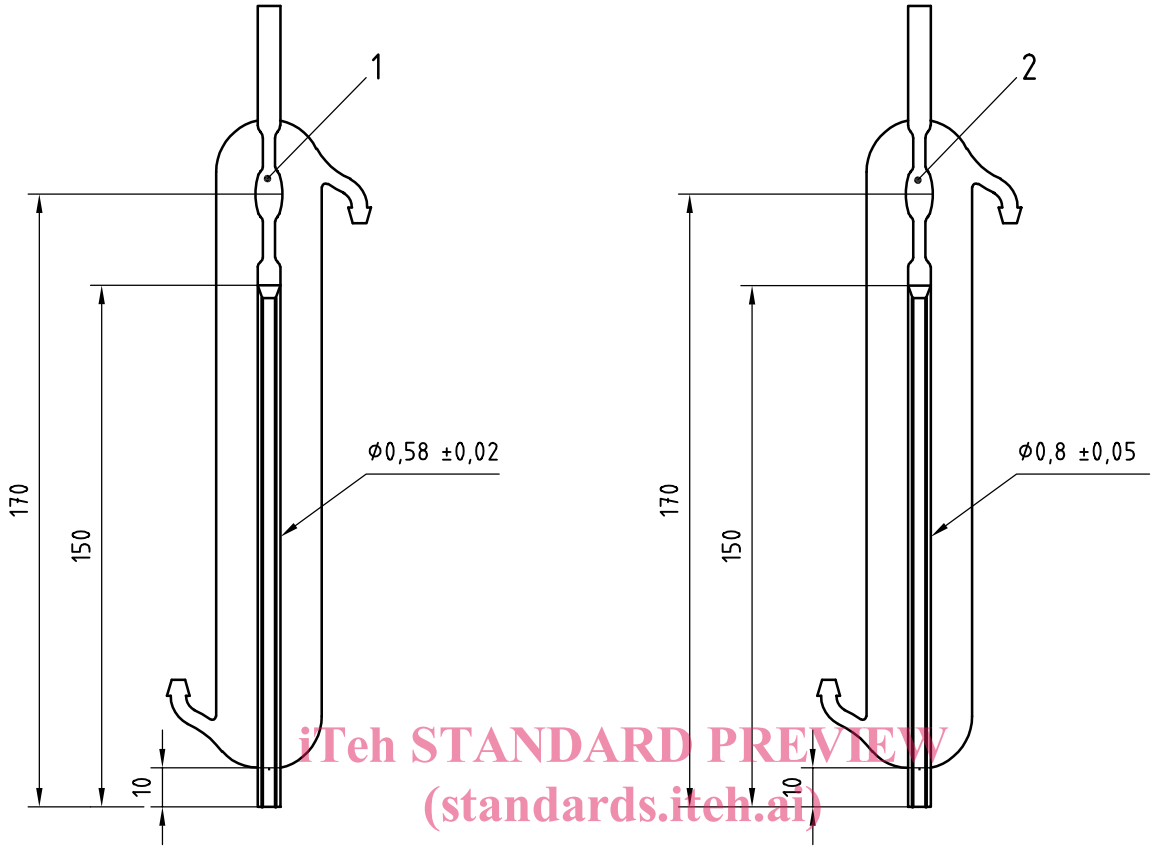
6.1.1 Capillary-tube viscometer for calibration purposes, with an efflux time of about 40 s for the 0,5 mol/l CED solution used for calibration.

NOTE The efflux time of the viscometer for distilled or deionized water will be about 60 s.

6.1.2 Capillary-tube viscometer for determination of limiting viscosity number at constant shear rate, with an efflux time of about 100 s for a solution of η/η_0 = 8,4 at a shear rate (see 3.1) of (200 ± 30) s^{-1}.

NOTE Solutions of polymers of high relative molecular mass are usually non-Newtonian. Their viscosity decreases as the shear rate (or in the present case the flow rate) increases. To avoid this complication, this International Standard specifies that the viscosity be determined at a shear rate of (200 ± 30) s^{-1}. The dimensions of the viscometer (see Figure 1b) are such that, for a solution of viscosity 10 mPa·s, the efflux time is about 90 s and the maximum shear rate (see 3.1) is then within the range (200 ± 30) s^{-1}.

Dimensions in millimetres



a) **Viscometer for calibration**

b) **Viscometer for determining viscosities of test solutions**

Key

1 volume 1,0 ml or 2,0 ml

2 volume 1,0 ml

Figure 1 — Capillary-tube viscometers

6.2 Dissolving bottles, capacity approximately 52 ml, designed so that, when the bottle is filled with 50 ml of test solution, the remaining air can be expelled by squeezing the bottle.

A polyethylene bottle with screw cap and rubber sealing ring can be used. Some practice will enable the analyst to expel the air and close the bottle with the screw cap in one operation. The air may also be expelled by a current of nitrogen.

If the pulp does not dissolve readily, use a flat-sided bottle.

6.3 Constant-temperature bath, capable of being maintained at (25 ± 0,1) °C, capable of accommodating the dissolving bottles (6.2) and provided with a pump for circulating the water through the jackets of the viscometers (6.1.1 and 6.1.2).

6.4 Pieces of copper wire, approximately 3 mm in diameter and between 10 mm and 20 mm long.

Clean the pieces of copper wire regularly with dilute nitric acid, rinsing them thoroughly afterwards with distilled or deionized water and letting them dry.

6.5 **Balance**, accurate to ± 0,1 mg.

6.6 **Timing device**, capable of being read to the nearest 0,1 s.

6.7 **Shaker** or **magnetic stirrer**, for dissolving the test portion.

7 Calibration of viscometers

7.1 Bring the temperature of the various calibration liquids (see below) to 25 °C and the viscometers (6.1.1 and 6.1.2) to (25,0 ± 0,1) °C.

7.2 Use the viscometer specified in 6.1.1 (see Figure 1a) as the calibration viscometer to measure the efflux times, in seconds, as described in 9.4, for

a) distilled or deionized water, t_w;

b) glycerol solution (5.2), t_c;

c) 0,5 mol/l CED solution, prepared by mixing equal volumes of distilled or deionized water and 1 mol/l CED solution (5.1), t_s.

In each case, make at least two measurements and calculate the mean.

The ratio of the efflux time for the CED solution to that of distilled water, t_s/t_w, shall lie between 1,27 and 1,29.

7.3 In the same way, measure the efflux time of the glycerol solution (5.2) in the viscometer to be calibrated (6.1.2) (see Figure 1b). Calculate the viscometer factor f and the viscometer constant h using the equations

$$f = \frac{t_c}{t_v} \tag{7}$$

$$h = \frac{f}{t_s} \tag{8}$$

where

t_c is the efflux time, in seconds, of the glycerol solution in the calibration viscometer (6.1.1) (see Figure 1a);

t_v is the efflux time, in seconds, of the glycerol solution in the viscometer to be calibrated (6.1.2) (see Figure 1b);

t_s is the efflux time, in seconds, of 0,5 mol/l CED solution in the calibration viscometer (6.1.1) (see Figure 1a).

The viscometer factor f is an apparatus constant and the viscometer constant h is dependent upon the solvent (CED solution) used. Consequently, h shall be determined each time a fresh CED solution is used.

7.4 If viscometers with an automatic timing device are used, carry out the calibration in accordance with the manufacturer's instructions.