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

Pâtes — Détermination de l'indice de viscosité limite à l'aide d'une solution de cupri-éthylènediamine (CED)

Reference number
ISO 5351:2010(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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*.

This second edition cancels and replaces the first edition (ISO 5351:2004), Subclause 6.1.1, Clauses 8 and 9 and Annex A of which have 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 $\mathrm{d}v/\mathrm{d}z$ (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, which is normally the case with polymer solutions of high molecular mass 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 are derived by means of a capillary-tube viscometer (for terms and definitions, see Clause 3). The results of these measurements are seriously affected by the shear rate.

The mass concentration ρ of the pulp is therefore chosen so that, if multiplied by the limiting viscosity number $[\eta]$, it gives a product $[\eta] \times \rho$ 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 $(200 \pm 30)\ \mathrm{s}^{-1}$; this involves the employment of two viscometers, one for the calibration and one for the measurement of the viscosity of the pulp.

The viscosity of a pulp in cupri-ethylenediamine (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.

Care must be taken in drawing conclusions regarding the strength properties of the pulp strictly from viscosity measurement, 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 International Standard 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 that 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, *Paper, board and pulps — Determination of dry matter content — Oven-drying method*

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
relative viscosity (deprecated)
η_{ratio}
ratio of the viscosities η and η_0 of the polymer solution of stated concentration and of the solvent, respectively, at the same temperature

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

NOTE Viscosity ratio 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 Viscosity relative increment is dimensionless.

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

$$\frac{\eta - \eta_0}{\eta_0 \times \rho} \tag{5}$$

NOTE Viscosity number is measured in millilitres per gram.

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

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

NOTE 1 Limiting viscosity number 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 millipascal seconds (mPa·s) (see [7] in the Bibliography).

4 Principle

Measurement of the times of efflux of the diluted solvent and the pulp solution through a capillary-tube viscometer at a specified mass concentration at 25 °C. Calculation by Martin's formula (see [9] in the Bibliography) of the limiting viscosity number from these measurements, and from the known mass 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, $c(\text{CED}) = (1{,}00 \pm 0{,}02)$ mol/l, saturated with copper(II) hydroxide, for convenience referred to as CED solution.

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

WARNING — Because of the presence of allergens, avoid contact of the 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 to use a suitable destruction procedure 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 copper wire (6.4).

5.4 Acetone (CH_3COCH_3), analytical reagent grade.

WARNING — Acetone is inflammable. Keep away from open fire. Do not use a gas heater. Follow pertinent safety regulations.

5.5 Sulfuric-acid-based cleaning solution, designed for the washing of laboratory glassware.

5.6 Reagents, for calibration of 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 the 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 can 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 (5.4). If any residual material remains after cleaning, clean again with a sulfuric-acid-based cleaning solution (5.5) 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, having a capillary tube with a diameter of (0,58 ± 0,02) mm and, in other respects, the dimensions given in Figure 1a).

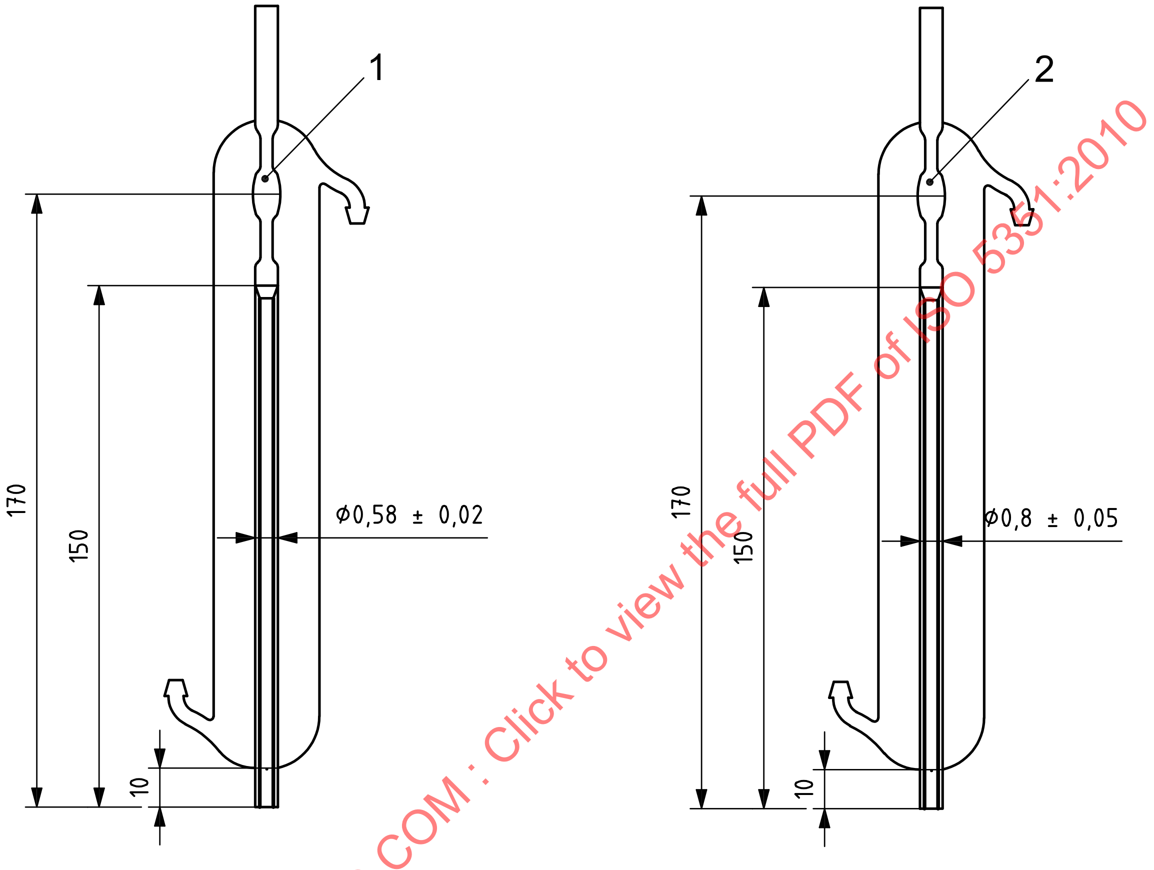
NOTE The efflux time of the viscometer for distilled or deionized water will be about 60 s.

6.1.2 Capillary-tube viscometer for determination of limiting viscosity number at constant shear rate, having a capillary tube with a diameter of (0,80 ± 0,05) mm and, in other respects, the dimensions given in Figure 1b).

NOTE 1 Efflux time is about 100 s for a solution of $\eta/\eta_0 = 8{,}4$ at a shear rate (3.1) of $(200 \pm 30)\ \mathrm{s}^{-1}$.

NOTE 2 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 $(200 \pm 30)\ \mathrm{s}^{-1}$. 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 (3.1) is then within the range $(200 \pm 30)\ \mathrm{s}^{-1}$.

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, of 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 a screw cap and rubber sealing ring can be used. 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 7.2) 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, and

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, $t_\mathrm{s}/t_\mathrm{w}$, 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

$$f = \frac{t_\mathrm{c}}{t_\mathrm{v}} \tag{7}$$

$$h = \frac{f}{t_\mathrm{s}} \tag{8}$$

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.

8 Sampling and preparation of sample

If the test is being made to evaluate a pulp lot, the sampling shall be carried out in accordance with ISO 7213. If it is not, report the source of the sample and, if possible, the sampling procedure used.

Take a sample corresponding to approximately 10 g of oven-dry mass. Examine the pulp sample. If shives are present, remove them by hand using a pair of tweezers or suspend the sample in water and remove the shives by screening. If shives have been removed from the sample, this shall be stated in the test report. If it is expected that the pulp will not disintegrate easily when the test solution is prepared (see 9.3), disintegrate the sample in water in a suitable apparatus and form thin sheets in a Büchner funnel. Dry the pulp sample or the prepared sheets at room temperature to constant mass (drying can also be performed at an elevated temperature, but not above 60 °C as over-drying can lower the viscosity). Tear the dry sample into small pieces by hand, wearing gloves, and using a pair of tweezers if convenient. Do not cut the dry sample or use a mechanical shredder because the viscosity is likely to be lowered as a result of this process of disintegration.

9 Procedure

9.1 Choice of mass concentration of solution

If the approximate value of the limiting viscosity number of the sample is not known, use a solution of mass concentration between 125 mg/50 ml and 150 mg/50 ml. If the limiting viscosity number obtained is not within the range specified by Table 1 for that mass concentration, adjust the concentration accordingly.

Table 1 — Example of the mass concentration ρ to be used, as a function of the limiting viscosity number $[\eta]$ which will be measured

Limiting viscosity number $[\eta]$ ml/g	**Quantity of sample** mg/50 ml	**Mass concentration,** ρ g/ml
< 650	250	0,005
651 to 850	200	0,004
851 to 1 100	150	0,003
1 101 to 1 400	120	0,002 4

NOTE The mass concentration ρ specified in Table 1 is an approximate value when $[\eta]$ is more than 1 100 ml/g. Determine the appropriate mass concentration ρ such that the product $[\eta] \times \rho$ is within the range $3{,}0 \pm 0{,}4$ for up to 1 100 ml/g and $3{,}0 \pm 0{,}1$ for more than 1 100 ml/g.

For samples of very high limiting viscosity number, the viscosity ratio is markedly dependent upon the shear rate. If a shear rate of $200\ \mathrm{s}^{-1}$ is to be obtained in the viscometer, it is necessary to use pulp mass concentrations selected in such a way that the measurements are made at exactly the same viscosity ratio. For pulps with a limiting viscosity number of less than 1 100 ml/g, shear rates of $(200 \pm 30)\ \mathrm{s}^{-1}$ and values for $[\eta] \times \rho$ of $3{,}0 \pm 0{,}4$ are allowable, as the error in the result will not exceed 2 %. For pulps with a limiting viscosity number of more than 1 100 ml/g, the error will be considerably larger if these tolerances are allowed. Accordingly, for accurate determinations at these high viscosities, it is necessary to select pulp mass concentrations such that the product $[\eta] \times \rho$ is as close to 3,0 as possible and, in no case, outside the range $3{,}0 \pm 0{,}1$. If the approximate viscosity of the sample is unknown, an exploratory determination shall first be made to enable the correct mass concentration to be selected.

9.2 Weighing of test portion

Weigh the chosen amount of sample to an accuracy of ± 0,5 mg into the dissolving bottle (6.2). At the same time, weigh a separate test portion for the determination of the dry-matter content in accordance with ISO 638, or any other method for the determination of dry-matter content giving similar results.

Carry out the determination in duplicate.

9.3 Preparation of test solution

Using a pipette, add 25,0 ml of distilled or deionized water to the test portion, together with 5 to 10 pieces of copper wire (6.4) if using a shaker (6.7), or a stirrer bar if using a magnetic stirrer. Close the bottle, and shake the mix until the test portion has been completely disintegrated.

Add 25,0 ml of the CED solution (5.1) and expel all of the remaining air by squeezing the bottle.

Re-close the bottle, and shake or stir again in the shaker or magnetic stirrer until the test portion is completely dissolved.

Complete dissolution should take less than 30 min.

Cold-alkali-treated pulps, and unbleached pulps of high viscosity, may sometimes be difficult to dissolve. In such cases, dissolution is facilitated if swelling is prevented by first dissolving the pulp in a solution of lower CED concentration. Consequently, prepare a slurry of the pulp in 25 ml of distilled or deionized water, add 5 ml of the CED solution (5.1) and shake. Add another 5 ml of CED solution and shake again, continuing until the total volume of CED solution added is 25,0 ml.

It is important that the sample dissolves completely. No lumps should be detectable.

Do not shake or stir for longer than necessary. When the pulp has dissolved, immerse the bottle in the constant-temperature bath (6.3) until a temperature of (25 ± 0,1) °C has been reached.

As oxygen has a degrading effect on cellulose in CED solution, care shall be taken to avoid contact between air and cellulose in CED solution. This can be done by using polyethylene dissolving bottles with screw caps.

9.4 Determination of efflux time

Using suction, draw into the viscometer (6.1.2) a sufficient quantity of the test solution prepared in 9.3. Allow the solution to drain out freely, without any obstruction. When the meniscus is at the upper mark, start the timer (6.6) and measure, to an accuracy of ± 0,2 s, the time to drain to the lower mark (the efflux time of the solution).

Make at least two determinations, the results of which shall agree within ± 0,5 %. Calculate the mean value.

10 Calculation

10.1 Viscosity ratio

The viscosity ratio η_{ratio} (η/η_0) (3.2) is given by the equation

$$\eta_{\mathrm{ratio}} = \frac{\eta}{\eta_0} = h \times t \qquad (9)$$

where

t is the efflux time of the test solution, in seconds;

h is the viscometer constant, in reciprocal seconds, determined as specified in 7.3.

10.2 Limiting viscosity number

Using the value of the viscosity ratio calculated in 10.1, obtain the corresponding value for $[\eta] \times \rho$ from Table B.1 in Annex B. Calculate the limiting viscosity number $[\eta]$ to the nearest 1 ml/g.

The values in Annex B were calculated using Martin's equation ([9] in the Bibliography).

$$\log\left[\eta\right] = \frac{\eta - \eta_0}{\eta_0 \times \rho} - k\left[\eta\right]\rho \qquad (10)$$

where

$\dfrac{\eta - \eta_0}{\eta_0 \rho}$	is the viscosity number, in millilitres per gram;
k	is an empirical constant (for the pulp/CED system, $k = 0{,}13$);
ρ	is the mass concentration (calculated on an oven-dry pulp basis), in grams per millilitre, of the pulp in the diluted solvent (0,5 mol/l CED solution).

EXAMPLE

h = 0,081 s^{-1} (obtained from the calibration procedure)

t = 100 s (measured)

ρ = 0,003 96 g/ml (calculated from the test portion mass and the dry-matter content)

$\eta_{\text{ratio}} = h \times t = 0{,}081 \times 100 = 8{,}21$

The corresponding value for $[\eta] \times \rho$, taken from Annex B, is 2,967 and thus

$$\left[\eta\right] = \frac{2{,}967}{0{,}003\ 96} = 749 \text{ ml/g} \approx 750 \text{ ml/g}$$

10.3 Expression of results

Report the limiting viscosity number to the nearest 10 ml/g.

11 Precision

11.1 General check using reference pulp

As a check on the procedures used, it is recommended that the viscosity of a reference pulp with a known limiting viscosity number in the same range as that of the sample be measured. Keep the reference pulp in a cool, dry, dark place.

11.2 Repeatability

To determine the precision, three pulp samples were analysed in ten different laboratories, five using manual time-recording and five using automatic time-recording. Each laboratory analysed the different pulp samples ten times in duplicate. Each laboratory calculated the mean result and the coefficient of variation (CV). The repeatability coefficient of variation is given in Table 2 separately for manual and automatic time-recording, at three viscosity levels.

Table 2 — Repeatability of determination of limiting viscosity number

Viscosity level ml/g	Manual time-recording		Automatic time-recording	
	Mean ml/g	CV %	Mean ml/g	CV %
650	637 to 664	0,4 to 1,2	638 to 662	0,1 to 0,7
800	773 to 806	0,4 to 0,9	770 to 806	0,2 to 1,4
1 150	1 150 to 1 182	0,5 to 0,8	1 097 to 1 183	0,3 to 1,0

11.3 Reproducibility

Three pulp samples were analysed in ten different laboratories, five using manual time-recording and five using automatic time-recording. The reproducibility is expressed as the coefficients of variation (CV) at three different viscosity levels.

Table 3 — Reproducibility of determination of limiting viscosity number

Viscosity level ml/g	CV %
650	1,4
800	1,7
1 150	2,1

12 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard;

b) all information necessary for complete identification of the sample;

c) the date and place of testing;

d) the result, expressed in millilitres per gram;

e) if and how shives were removed;

f) if an automatic time-recording device was used;

g) details of any unusual occurrences observed during the determination;

h) details of any departure from the requirement of this International Standard that could have affected the results, as well as details of any operations regarded as optional.

Annex A
(normative)

Preparation and analysis of the cupri-ethylenediamine (CED) solution

The preparation and analysis of the cupri-ethylenediamine (CED) solution described in this annex is based on Tappi T 230 om-04[13].

A.1 Reagents

During the analysis, use only reagents of recognized grade and only distilled or deionized water.

A.1.1 Ethylenediamine ($C_2H_8N_2$).

A.1.2 Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$).

A.1.3 Ammonia solution, containing about 250 g of ammonia (NH_3) per litre (mass concentration shall be confirmed).

A.1.4 Barium chloride solution, containing about 100 g of barium chloride ($BaCl_2$) per litre.

A.1.5 Potassium iodide solution, containing about 100 g of potassium iodide (KI) per litre.

A.1.6 Sodium thiosulfate ($Na_2S_2O_3$), 0,1 mol/l standard solution, freshly prepared.

A.1.7 Sulfuric acid (H_2SO_4), 2 mol/l and 0,5 mol/l standard solutions.

A.1.8 Sodium hydroxide (NaOH), 20 % standard solution.

A.1.9 Starch, 2 g/l indicator solution.

A.1.10 Phenolphthalein indicator solution.

Dissolve 50 mg of phenolphthalein ($C_{20}H_{14}O_4$) in 50 ml of ethanol (C_2H_5OH), and dilute with 50 ml of water.

A.1.11 20 % ammonium thiocyanate solution

Dissolve 10 g of thiocyanate crystal in 50 ml of water.

A.1.12 Methyl orange indicator solution, or any other acceptable indicator in the pH-range of 3 to 5.

A.2 Apparatus

Ordinary laboratory apparatus and the following.

A.2.1 Reagent bottle, made of glass, narrow necked (see Figure A.1).

A.2.2 Magnetic stirrer.

A.2.3 pH meter.

A.3 Preparation of copper(II) hydroxide

Dissolve 250,0 g of copper sulfate (A.1.2) in about 2 000 ml of hot water.

Heat to boiling and add ammonia solution (A.1.3) slowly with vigorous stirring until the solution is faintly alkaline (about 115 ml of ammonia solution are required). Let the precipitate settle, and wash by decantation with 1 000 ml portions of water, four times with hot water and twice with cold water. Then add sufficient cold water to make the volume of the slurry 1 500 ml; cool below 20 °C (preferably below 10 °C), and slowly add 850 ml of cold 20 % sodium hydroxide solution (A.1.8) with vigorous stirring.

Wash the precipitated copper(II) hydroxide [$Cu(OH)_2$] with water by decantation until the washings are colourless to phenolphthalein indicator solution (A.1.10) and give no precipitation of sulfate upon addition of barium chloride solution (A.1.4).

Copper(II) hydroxide purchased from chemical reagent suppliers may be used provided it is free from ammonia, chlorides, sulfates, and nitrates, and retains its blue-green colour when heated for 1 h at 100 °C. In this case, 97,5 ± 0,5 g of copper(II) hydroxide should be used in Clause A.4. Copper(II) hydroxide of good quality has a blue-green colour. If the sample is not pure, and particularly if it contains ammonia, it will gradually decompose and turn brown due to formation of the oxide. Such a discoloured product is not satisfactory for the preparation of the reagent. If the hydroxide contains chlorides, sulfates, or nitrates, the determination of ethylenediamine will give results that are too low.

A.4 Preparation of cupri-ethylenediamine solution

Transfer the washed copper(II) hydroxide slurries (A.3), using sufficient water to make a total volume of 500 ml, to a 1 000 ml reagent bottle (see Figure A.1). The bottle is equipped with a rubber stopper carrying two glass tubes, one of which (A) is straight and extends to within approximately 50 mm of the bottom of the bottle, and the other having two side tubes (B and C) at right angles and extending just through the rubber stopper. One of the side tubes (B or C) is connected to a suction source and the other to the nitrogen supply.

Clamp down the rubber stopper, exhaust the air with a laboratory water aspirator and refill the bottle three separate times with nitrogen at 14 kPa pressure. The rubber tubes and pinch clamps attached to the glass tubes of the reagent bottle, as shown in Figure A.1, are used for this purpose. Create a partial vacuum in the bottle and add 160 ml of 70 % ethylenediamine (A.1.1), taking care that no air enters the bottle. This is accomplished by inserting a funnel in the rubber tube attached to the longer glass tube of the solution bottle and opening the pinch clamp just enough to allow the ethylenediamine to be drawn into the bottle. Since considerable heat is evolved at this point, it is desirable to keep cold water running over the bottle during the initial phase of the reaction. After the addition of the ethylenediamine, the gas over the liquid should be alternately evacuated and flushed three times with nitrogen at 14 kPa pressure.

Shake the contents of the bottle several times during the course of an hour, and then let stand for 12 h to 16 h. A clear supernatant liquor will usually be obtained, but if desired, the solution may be filtered through a fritted-glass Büchner funnel, using suction, and again stored under nitrogen.

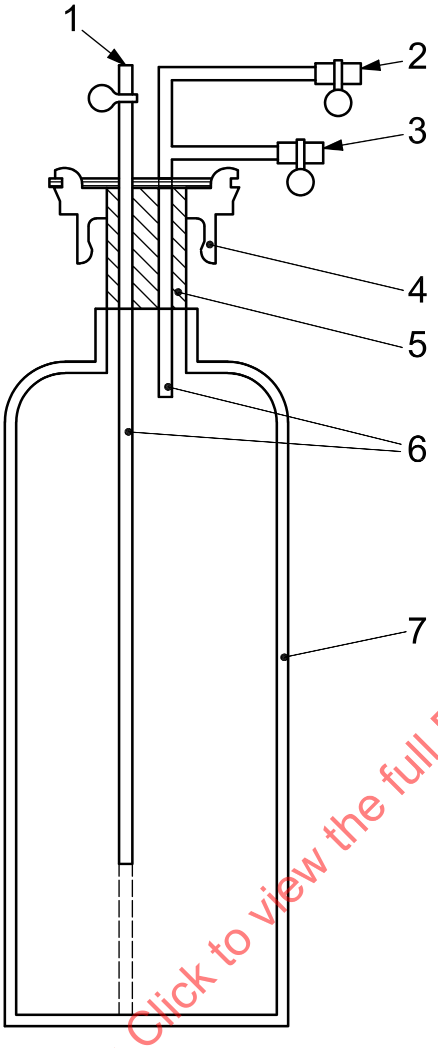
A.5 Determination of copper concentration of copper(II) hydroxide

Using a pipette, take a 25 ml sample of CED solution (A.4) in the cold room and dilute to 250 ml in a volumetric flask.

NOTE 1 Save the sample for the determination of ethylenediamine concentration (see A.6).

Using a pipette, transfer 25,0 ml of this solution to a 250 ml volumetric flask. Add 30 ml of potassium iodide solution (A.1.5) and 50 ml of 2 mol/l sulfuric acid (A.1.7) to acidify.

NOTE 2 The solution immediately takes on a dark brown colour that quickly changes to a dark greenish-brown colour. The colour is the result of a precipitate formed in the reaction.



Key

1 tube A
2 tube B
3 tube C
4 stopped clamp
5 rubber stopper
6 glass tubing
7 glass bottle

Figure A.1 — Cupri-ethylenediamine (CED) reagent bottle

Titrate the mixture with standard sodium thiosulfate solution (A.1.6) near to the starch end-point (the green colour remains for about 70 % to 75 % of the titration), using starch solution (A.1.9) as the indicator.

To perform the titration, it is necessary to constantly stir the mixture. This is achieved with best results using a magnetic stirrer.

For example, if an end-point of 25,0 ml is expected, the green colour should remain until about 17 ml to 19 ml of the titrant is consumed. At this point, the mixture takes on a very creamy coffee colour, and the effect of adding more of the titrant is like adding more cream to the coffee. After addition of about 3 ml to 4 ml more, a mauve colour will appear with each drop and quickly fade. The mixture remains a very light creamy colour. At this point, the starch should be added. If the starch is not added, the mixture will become completely mauve, and it is extremely difficult to see the end-point. Addition of the starch results in a creamy purple colour. The purple colour should fade with the addition of more titrant. Only about 0,3 ml to 0,5 ml of titrant should be needed after the addition of the starch. This should be the point right before the end-point.

Just before the starch end-point, add 10 ml of ammonium thiocyanate solution (A.1.11) to intensify the titration end-point. The mixture becomes purple again. Continue to titrate to the starch end-point until the mixture fades to a mauve colour and finally becomes white at the end-point.

NOTE 3 The end-point can appear as a salmon pink colour with the white colour of the precipitate developing only upon standing for a few minutes.

The copper concentration c_{Cu}, is given, in moles per litre (mol/l), by the equation

$$c_{\mathrm{Cu}} = 0{,}04 \times V_2 \tag{11}$$

where V_2 is the volume of sodium thiosulfate standard solution (A.1.6) used for the titration, in millilitres.

A.6 Determination of ethylenediamine concentration of ethylenediamine solution

Using a pipette, transfer 25 ml of the CED solution prepared in A.4 to a 250 ml Erlenmeyer flask. Add 75 ml of water and titrate to pH 3 using a pH meter (A.2.3) or methyl orange indicator solution (A.1.12) with 0,5 mol/l sulfuric acid standard solution (A.1.7) while stirring.

The ethylenediamine concentration c_{ED}, is given, in moles per litre (mol/l), by the equation

$$c_{\mathrm{ED}} = 0{,}2 \times V_1 - c_{\mathrm{Cu}} \tag{12}$$

where

V_1 is the volume of 0,5 mol/l sulfuric acid solution (A.1.7) used for the titration, in millilitres;

c_{Cu} is the copper concentration (A.5), in moles per litre.

A.7 Calculation of the ethylenediamine and the copper concentration and their ratio

Calculate the ethylenediamine concentration, c_{ED}, the cupric ion concentration, c_{Cu}, and their ratio, R, as follows:

$$c_{\mathrm{ED}} = \frac{M_1 \cdot V_1 - M_2 \cdot V_2}{V_3 \cdot V_5} \cdot V_4 \tag{13}$$

$$c_{\mathrm{Cu}} = \frac{M_2 \cdot V_2}{V_3 \cdot V_5} \cdot V_4 \tag{14}$$

$$R = \frac{c_{\mathrm{ED}}}{c_{\mathrm{Cu}}} \tag{15}$$

where

V_1 is the volume of 0,5 mol/l sulfuric acid solution (A.1.7) used for the titration, in millilitres;

V_2 is the volume of sodium thiosulfate solution (A.1.6) used for the titration, in millilitres;

V_3 is the volume of sample solution used for initial dilution, in millilitres;

V_4 is the volume of sample dilution, in millilitres;

V_5 is the volume of diluted solution used for titration, in millilitres;

M_1 is the molarity of sulfuric acid solution (= 0,5 mol/l);

M_2 is the molarity of sodium thiosulfate solution (= 0,1 mol/l);

c_{ED} is the ethylenediamine concentration, in moles per litre;

c_{Cu} is the copper concentration, in moles per litre;

R ratio ethylenediamine/copper.

The ratio R shall be 2,00 ± 0,04 and the copper concentration shall be 1,00 ± 0,02 mol/l. If the ratio exceeds 2,00:1, add fresh copper (II) hydroxide and repeat the stirring and determination of the solution as given above. If the ratio falls below 1,92:1, start with fresh copper(II) hydroxide and increase the volume of ethylenediamine accordingly.

After preparation, solutions shall be stored under a nitrogen atmosphere at all times. The concentrations of copper and ethylenediamine should be checked as specified in this annex, no less frequently than monthly.