International Standard 5351/1

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Cellulose in dilute solutions — Determination of limiting viscosity number — Part 1 : Method in cupri-ethylene-diamine (CED) solution

Cellulose en solutions diluées — Détermination de l'indice de viscosité limite — Partie 1 : Méthode utilisant une solution de cupri-éthylène-diamine (CED)

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

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It has been approved by the member bodies of the following countries:

Australia	France	Philippines
Austria	Germany, F.R.	Poland
Belgium	Hungary	Romania
Brazil	India	South Africa, Rep. of
Canada	Italy	Spain
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No member body expressed disapproval of the document.

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Cellulose in dilute solutions — Determination of limiting viscosity number — Part 1 : Method in cupri-ethylene-diamine (CED) solution

0 Introduction

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

$$\tau = \eta \cdot \dot{\gamma}$$

where

τ is the shear stress;

η is the viscosity;

$\dot{\gamma} = \frac{dv}{dz}$ is the velocity gradient (v is 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-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 cellulose in dilute solutions (for definitions and symbols, see clause 4) are derived by means of a capillary-tube viscometer. the results of these measurements are seriously affected by the shear rate. The solution to the problem that thereby arises can be sought either by determination of the viscometric properties at so low a concentration of cellulose that the effect of shear rate is small, or by determination at a shear rate closely reproducible in different laboratories. In this document, both alternatives are given, as it has been proved that the results they provide are equal so long as the limiting viscosity number is less than 1 000 ml/g. For values which exceed this, alternative procedure B gives somewhat higher results by reason of the lower shear rate.

In **alternative A**, the concentration c of cellulose is chosen that if multiplied by the limiting viscosity number it gives a product of $[\eta] \cdot c$ = 1,0 to 1,5, corresponding to viscosity ratio $\frac{\eta}{\eta_0}$ equal to 2,3 to 3,4. At this low concentration, the effect of shear rate can be ignored, and determinations of the efflux times of the solution and diluted solvent can be made in the same viscometer.

In **alternative B**, the concentration c of cellulose is so chosen that if multiplied by the limiting viscosity number it gives a product of $[\eta] \cdot c = 3{,}0 \pm 0{,}4$, corresponding to viscosity ratio $\frac{\eta}{\eta_0}$ equal to 6 to 10. The determination shall then be carried out at a reproducible shear rate of 200 ± 30 s^{-1}; this involves the employment of two viscometers, one for the diluted solvent, and one for the solution. This alternative should be applied when there is reason to expect that the narrow capillary specified in alternative A will become clogged by undissolved particles, or when difficulty is experienced in attaining the prescribed degree of accuracy in weighing the small amounts of sample implied by alternative A in some cases.

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1 Scope and field of application

This part of ISO 5351 specifies a method for the determination of the limiting viscosity number of cellulose in dilute cupri-ethylene-diamine (CED) solution.

This method is applicable to CED-soluble samples of cellulose, for instance in pulps and textiles.

NOTE — The viscosity test is a means for determining the extent of cellulose degradation produced by cooking and bleaching. This degradation greatly affects the suitability of pulp for dissolving purposes and papermaking.

ISO 5351/2 specifies a method for the determination of the limiting viscosity number of cellulose in dilute iron(III) sodium tartrate complex ($EWNN_{mod\ NaCl}$) solution.

2 References

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

ISO 1833, *Textiles — Binary fibre mixtures — Quantitative chemical analysis.*

ISO 5089, *Textiles — Preparation of laboratory test samples and test specimens for chemical testing.*

ISO/TR 5090, *Textiles — Methods for the removal of non-fibrous matter prior to quantitative analysis of fibre mixtures.*

3 Principle

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

4 Definitions

For the purpose of this International Standard, the following definitions apply.

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

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

where

V is the volume between two arbitrary calibration marks of 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.

4.2 viscosity ratio : The ratio of the viscosities η and η_0 of the polymer solution of stated concentration and of the solvent respectively at the same temperature :

$$\frac{\eta}{\eta_0}$$

This ratio, as a number, is dimensionless.

4.3 viscosity relative increment : The viscosity ratio (4.2) minus one :

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

As a number, it is dimensionless.

4.4 viscosity number : The ratio of the viscosity relative increment (4.3) to the polymer concentration c in the solution :

$$\frac{\eta - \eta_0}{\eta_0 \cdot c}$$

Its unit is the millilitre per gram.

4.5 limiting viscosity number (L.V.N.) $[\eta]$: The limiting value of the viscosity number (4.4) at infinite dilution :

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

Its unit is the millilitre per gram.[1)]

5 Pretreatment of test samples

5.1 Pulp samples

Take a sample corresponding to approximately 10 g of oven-dry mass. Split and tear the pulp into small pieces. If it is expected that the pulp will not disintegrate easily on being shaken in distilled water with copper pieces (6.2.3), disintegrate the sample in water in a suitable apparatus, and form thin sheets on a Büchner funnel. Dry the sheets at a temperature below 60 °C.

5.2 Textile samples

5.2.1 Generally

Prepare the sample as specified in ISO 5089.

Extract a sample of at least 3 g of air-dry mass in a Soxhlet apparatus with light petroleum for 1 h at a minimum rate of 6 cycles per hour. Allow the light petroleum to evaporate from the sample; soak the specimen in cold distilled or deionized water for 1 h, and then in a fresh portion of water at 65 + 5 °C for a further 1 h. In both cases, use a liquor/specimen ration of 100 : 1. Agitate the liquor from time to time. Remove the excess water from the sample by squeezing, suction or by means of a centrifuge and then allow the sample to become air-dry. For additional information, see ISO 1833 and ISO/TR 5090.

5.2.2 For bast fibres

Prepare the sample as described in annex D.

6 Alternative A — Determination of limiting viscosity number at low concentration of cellulose

6.1 Reagents

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

6.1.1 Cupri-ethylene-diamine (CED) solution, solution of cupri-ethylene-diamine saturated with copper(II) hydroxide, for convenience referred to as cupri-ethylene-diamine solution.

The solution contains 1,0 mol of copper, and 2,0 mol of ethylene-diamine per litre. It is commercially available, or prepared and analysed as described in annex A. When a commercial solution is used, check the conformity of the copper and ethylene-diamine contents by determination (as indicated in clause A.7 of annex A).

If the copper and the ethylene-diamine concentrations differ by more than ± 2 % from the values given above a new solution has to be prepared.

NOTE — By reason of allergens, avoid contact of skin with CED and ethylene-diamine solutions. Ethylene-diamine is volatile and repeated exposure may lead to severe respiratory allergic reactions with subsequent sensitization. Cupri-ethylene-diamine solutions should not be pipetted by mouth.

6.1.2 Diluted cupri-ethylene-diamine solution, 50 % (V/V).

With a pipette, using a pipette filler, measure 25,0 ml of the cupri-ethylene-diamine solution (6.1.1) into the dissolving

1) The SI unit of $[\eta]$ is the cubic metre per kilogram. Information from ISO/TC 61, *Plastics*, indicates plans in TC 61 to adopt this unit in practice.

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flask (6.2.2). Add, with a pipette, 25,0 ml of distilled or deionized water. Shake until dissolved.

6.2 Apparatus

Ordinary laboratory apparatus and

6.2.1 Constant-temperature bath, capable of being controlled at 25 ± 0,1 °C, accommodating the dissolving flask (6.2.2) and provided with a pump for water circulation through the jacket of the viscometer (6.2.6 and 7.2.1).

6.2.2 Dissolving flask, so constructed that the remaining air can be expelled when the flask is filled with 50 ml of test solution.

NOTE — A polyethene flask with screw cap and rubber gasket can be used. Some practice will enable the analyst to expel the air and lock the flask with the screw cap in one operation. If the pulp does not dissolve readily, use a flat-sided bottle. The air may also be expelled by a current of nitrogen.

6.2.3 Copper pieces, made of electrolytic copper.

6.2.4 Balance, accurate to ± 0,1 mg.

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

6.2.6 Capillary-tube viscometer, with water jacket, connected to the constant-temperature bath (6.2.1) and having an efflux time of about 40 s for the diluted solvent (6.1.2), and a shear rate (4.1) of about 400 s^{-1} for a concentration of cellulose such that $[\eta] \cdot c = 1{,}5$ and $\frac{\eta}{\eta_0} = 3{,}4$.

A suitable viscometer is shown in figure 1.

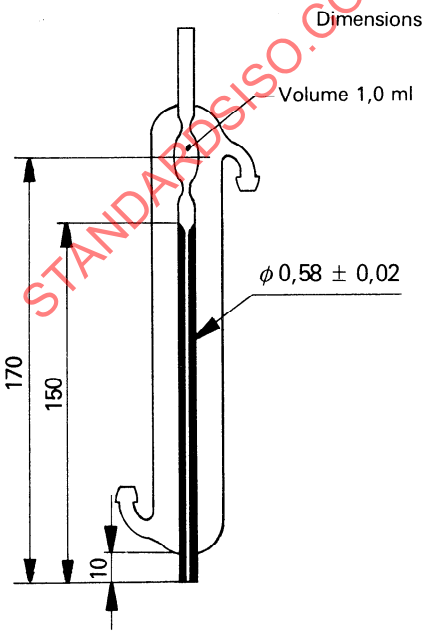

Figure 1 — Viscometer suitable for determination of the limiting viscosity number in accordance with alternative A

6.2.7 Shaking device.

6.3 Procedure

6.3.1 Choice of concentration of solution (see also annex C)

6.3.1.1 If the approximate limiting viscosity number of the sample is known, choose the concentration from table 1.

Table 1 — Concentration c to be used, as a function of the limiting viscosity number $[\eta]$ which will be measured

Limiting viscosity number $[\eta]$	Quantity of sample	Concentration c
ml/g	mg/50 ml	g/ml
< 200	250	0,005
201 to 400	200	0,004
401 to 600	125	0,002 5
601 to 900	80	0,001 6
901 to 1 200	60	0,001 2
1 201 to 1 500	45	0,000 9

6.3.1.2 If the approximate value of the limiting viscosity number of the sample is not known, test a sample of 125 mg/50 ml. If the limiting viscosity number so obtained is not within the range prescribed by table 1 for that concentration, make the test by choice of the correct concentration according to the value of the limiting viscosity number so derived.

6.3.2 Weighing of sample

Weigh the chosen amount of sample to an accuracy of ± 0,5 mg into the dissolving flask (6.2.2). At the same time, weigh out a separate sample for the determination of dry matter in accordance with ISO 638 or ISO 1833, sub-clause 1.7.

6.3.3 Preparation of test solution

With a pipette, add 25,0 ml of distilled or deionized water to the sample, together with some copper pieces (6.2.3). Close the flask, and shake it continuously until the sample has been completely disintegrated. With a pipette, using a pipette filler, add 25,0 ml of the CED solution (6.1.1) and expel all of the remaining air. Re-close the flask, shake in the shaking device (6.2.7) for 2 h, with the flat-sided bottles placed in the direction of movement of the device (see note 1). Immerse the flask in the constant-temperature bath (6.2.1) until a temperature of 25 ± 0,1 °C has been reached.

NOTES

1 Cold-alkali-treated pulps, and unbleached pulps of high viscosity, may sometimes be difficult to dissolve; this is effected more easily 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, and add 5 ml of the CED solution (6.1.1); shake, and add another portion of 5 ml of CED solution (6.1.1), until the total added volume is 25,0 ml. Minimize degradation by shaking for as short a time as possible. For low viscosity pulps, about 3 min will be enough.

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2 As oxygen has a degrading effect on the cellulose in CED-solution, care must be taken to avoid contact between air and cellulose in CED solution. This can be done by using dissolving flasks made of polyethylene.

6.3.4 Determination of efflux times

By suction, draw into the viscometer (6.2.6) a portion of the diluted solvent (6.1.2) thermostatted to 25 ± 0,1 °C (see 6.3.3). Allow the fluid to drain. When the meniscus is at the upper mark, start the timing device (6.2.5), and measure to an accuracy of ± 0,2 s the efflux time of the fluid to drain to the lower mark. If a free-flow viscometer is used, the efflux volume shall drain along the wall of a beaker to preclude the influence of surface tension. Rinse the viscometer with the test solution, and then, as described above, measure the efflux time of the test solution.

Make at least two determinations, the results of which shall agree within ± 2,5 %.

6.4 Calculation

6.4.1 Viscosity ratio

The viscosity ratio $\frac{\eta}{\eta_0}$ is given by the formula

$$\frac{\eta}{\eta_0} = \frac{t}{t_0}$$

where

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

t_0 is the efflux time of the diluted solvent, in seconds.

6.4.2 Limiting viscosity number

By means of the values of the viscosity ratio obtained according to 6.4.1, obtain from the table in annex B the values for $[\eta] \cdot c$. Calculate $[\eta]$ and report the limiting viscosity number to the nearest unit.

For calculating the values in annex B, the Martin's formula has been used :

$$\lg (\text{L.V.N.}) = \lg [\eta] = \lg \frac{\eta - \eta_0}{\eta_0 \cdot c} - k\,[\eta] \cdot c$$

where

$\frac{\eta - \eta_0}{\eta_0 \cdot c}$ is the viscosity number, in millilitres per gram;

k is an empirical constant (for cellulose-CED system, $k = 0{,}13$);

c is the concentration (oven-dry basis), in grams per millilitre, of the cellulose in the diluted solvent (6.1.2).

7 Alternative B — Determination of limiting viscosity number at reproducible shear rate

7.1 Reagents

Cupri-ethylene-diamine (CED) solutions, as specified in 6.1.1 and 6.1.2, and

7.1.1 Glycerol, 65 % (m/m) solution in water, having a viscosity of about 10 mPa · s.

7.2 Apparatus

Ordinary laboratory equipment and a constant-temperature bath, dissolving flask, copper pieces, balance, timing device and a viscometer, as specified in 6.2.1 to 6.2.6 are required, and

7.2.1 Capillary-tube viscometer, with water jacket connected to the constant-temperature bath (6.2.1), and having an efflux time of about 100 s for a solution of $\frac{\eta}{\eta_0} = 8{,}4$ at a shear rate (4.1) of 200 ± 30 s^{-1}. A suitable viscometer is shown in figure 2.

Dimensions in millimetres

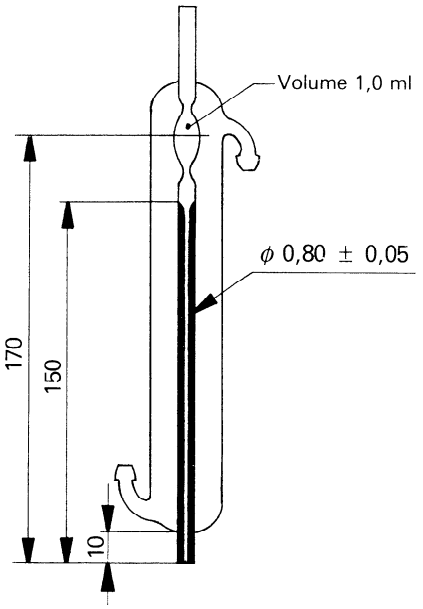

Figure 2 — Viscometer suitable for determination of the limiting viscosity number in accordance with alternative B

7.3 Calibration of viscometers

Use the viscometer specified in 6.2.6 as a calibration viscometer for measurement, at 25 ± 0,1 °C, of the efflux times of the glycerol solution (7.1.1) and the diluted solvent (6.1.2). Carry out the measurements as specified in 7.4.4.

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In the same way, measure the efflux time of the glycerol solution in the viscometer to be calibrated (7.2.1). Calculate the viscometer factor f and the viscometer constant h using the equations

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

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

where

t_c is the efflux time, in seconds, of the glycerol solution in the calibration viscometer;

t_v is the efflux time, in seconds, of the glycerol solution in the viscometer to be calibrated;

t_s is the efflux time, in seconds, of the diluted solvent in the calibration viscometer.

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

7.4 Procedure

7.4.1 Choice of concentration of solution (see also annex C)

7.4.1.1 If the approximate limiting viscosity number of the sample is known, choose the concentration from table 2.

Table 2 — Concentration c to be used, as a function of the limiting viscosity number $[\eta]$ which will be measured

Limiting viscosity number $[\eta]$	Quantity of sample	Concentration c
ml/g	mg/50 ml	g/ml
< 400	250	0,005
400 to 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

7.4.1.2 If the approximate value of the limiting viscosity number of the sample is not known, test a sample of 150 mg/50 ml. If the limiting viscosity number so obtained is not within the range prescribed by table 2 for that concentration, make the test by choice of the correct concentration according to the value of the limiting viscosity number so derived.

7.4.2 Weighing of sample

Weigh the chosen amount of sample to an accuracy of ± 0,5 mg into the dissolving flask (6.2.2). At the same time, weigh out a separate sample for the determination of dry matter, in accordance with ISO 638, or ISO 1833, sub-clause 1.7.

7.4.3 Preparation of test solution

With a pipette, add 25,0 ml of distilled or deionized water to the sample together with some copper pieces (6.2.3). Close the flask, and shake it continuously until the sample has been completely disintegrated. With a pipette, add 25,0 ml of the CED solution (6.1.1), and expel all of the remaining air. Re-close the flask, shake it continuously until the sample is completely dissolved (see the note to 6.3.3). Immerse the flask in the constant-temperature bath (6.2.1) until a temperature of 25 ± 0,1 °C has been reached.

7.4.4 Determination of efflux time

By suction, draw into the viscometer (7.2.1) a portion of the test solution (7.4.3). Allow the fluid to drain. When the meniscus is at the upper mark, start the timing device (6.2.5) and measure to an accuracy of ± 0,2 s the efflux time of the fluid to drain to the lower mark. If a free-flow viscometer is used, the efflux volume shall drain along the wall of a beaker to preclude the influence of surface tension.

Make at least two determinations, the results of which shall agree within ± 2,5 %.

7.5 Calculation

7.5.1 Viscosity ratio

The viscosity ratio $\frac{\eta}{\eta_0}$ is given by the formula

$$\frac{\eta}{\eta_0} = h \cdot t$$

where

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

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

7.5.2 Limiting viscosity number

By means of the value of the viscosity ratio (7.5.1), obtain from the table in annex B the values for $[\eta] \cdot c$. Calculate $[\eta]$, and report the limiting viscosity number to the nearest unit.

For calculating the values in annex B, the Martin's formula has been used :

$$\lg (\text{L.V.N.}) = \lg [\eta] = \lg \frac{\eta - \eta_0}{\eta_0 \cdot c} - k [\eta] \cdot c$$

where

$\frac{\eta - \eta_0}{\eta_0 \cdot c}$ is the viscosity number, in millilitres per gram;

k is the empirical constant (for cellulose-CED system, $k = 0{,}13$);

c is the concentration (oven-dry basis), in grams per millilitre, of the cellulose in the diluted solvent.

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8 Test report

The test report shall include the following particulars :

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

b) reference to this International Standard;

c) the alternative procedure employed, A or B;

d) the result expressed in millilitres per gram;

e) any unusual features observed during the course of the test;

f) any operations not specified in this International Standard or in the International Standards to which reference is made, or regarded as optional, which might have affected the results.

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Annex A

Preparation and analysis of the cupri-ethylene-diamine solution

(Forms part of the standard)

A.1 Reagents

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

A.1.1 Ethylene-diamine ($C_2H_8N_2$).

A.1.2 Copper sulphate pentahydrate ($CuSO_4.5H_2O$).

A.1.3 Acetone (CH_3COCH_3).

A.1.4 Ammonia solution, containing approximately 250 g of ammonia (NH_3) per litre.

A.1.5 Nitric acid (HNO_3), concentrated, ϱ = 1,4 g/ml.

A.1.6 Barium chloride solution, containing about 100 g of barium chloride ($BaCl_2$) per litre.

A.1.7 Potassium iodide solution, containing about 100 g of potassium iodide (KI) per litre.

A.1.8 Sodium hydroxide solution, containing about 100 g of sodium hydroxide (NaOH) per litre.

A.1.9 Hydrochloric acid, 1,0 mol/l solution.

A.1.10 Sodium thiosulphate ($Na_2S_2O_3$), 0,05 mol/l standard volumetric solution, freshly standardized.

The concentration shall be known to ± 0,000 2 mol/l.

A.1.11 Sulphuric acid, 0,5 mol/l standard volumetric solution.

The concentration shall be known to ± 0,002 mol/l.

A.1.12 Sodium hydroxide, 0,1 mol/l standard volumetric solution.

The concentration shall be known to ± 0,004 mol/l.

A.1.13 Starch, 2 g/l indicator solution.

A.1.14 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 distilled water.

A.1.15 Methyl orange indicator solution or any acceptable indicator in the pH-range of 3 to 5.

A.2 Apparatus

Ordinary laboratory apparatus and

A.2.1 Flask, made of brown glass, narrow necked, with a ground glass stopper.

A.3 Preparation of copper(II) hydroxide

Dissolve 330,0 g of the copper sulphate (A.1.2) in about 1 650 ml of hot water, and heat to boiling. Cool to about 45 °C, and slowly add the ammonia solution (A.1.4) with vigorous stirring until the solution is faintly violet. (About 150 ml of ammonia solution is required.) Let the precipitate settle, and wash by decantation with cold water until the washings remain colourless. By careful cooling, keep the temperature below 20 °C, and slowly add 800 ml of the sodium hydroxide solution (A.1.8), with vigorous stirring, to the pasty precipitate. Wash the precipitated copper(II) hydroxide by decanting with distilled water until the washings show neutral reaction to the phenolphthalein indicator solution (A.1.14). Wash the precipitate twice with water, and once with the acetone (A.1.3) and dry at room temperature in a vacuum desiccator.

Grind and homogenize before proceeding with the determination of copper content in copper hydroxide.

A.4 Determination of copper content in copper hydroxide

Weigh approximately 2,0 g of the copper(II) hydroxide (A.3) to an accuracy of ± 0,1 mg, and dissolve in 50 ml of the sulphuric acid solution (A.1.11). Transfer the solution quantitatively into a 250 ml one-mark volumetric flask and dilute to the mark. With a pipette, measure 25,0 ml of this solution, add 25 ml of potassium iodide solution (A.1.7), and titrate with the standard volumetric sodium thiosulphate solution (A.1.10) to the starch end-point.

The copper content X is given, as a percentage by mass, by the formula

$$X = 10 \times V_1 \times 0{,}05 \times 0{,}063\,6 \times \frac{100}{m_1} - \frac{V_1 \times 3{,}18}{m_1}$$

where

V_1 is the volume of the standard volumetric sodium thiosulphate solution (A.1.10) used for the titration, in millilitres;

m_1 is the mass of copper hydroxide precipitate dissolved, in grams.

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NOTES

1 The copper(II) hydroxide shall be completely soluble in the concentrated nitric acid (A.1.5), and give no precipitate of sulphate upon the addition of the barium chloride solution (A.1.6).

2 Commercial copper(II) hydroxide of acceptable quality is usually available. the product shall not bear marks of brown colour indicating its gradual decomposition to copper oxide.

A.5 Determination of ethylene-diamine content in the ethylene-diamine solution

Weigh, to the nearest 0,000 1 g, approximately 2,0 g of the ethylene-diamine solution (A.1.1) into a 250 ml conical flask. Carefully cool and dilute with water to a volume of about 100 ml. Determine the content of ethylene-diamine by titration with the standard volumetric sulphuric acid solution (A.1.11), with methyl orange (A.1.15) as indicator.

The ethylene-diamine content Y is given, as a percentage by mass, by the formula

$$Y = \frac{V_2 \times 3{,}01}{m_2}$$

where

V_2 is the volume of the standard volumetric sulphuric acid solution (A.1.11) used for the titration, in millilitres;

m_2 is the mass of the ethylene-diamine solution (A.1.1) tested, expressed in grams.

A.6 Preparation of cupri-ethylene-diamine solution

Calculate the masses m_3 and m_4, to the nearest gram, of the copper hydroxide and ethylene-diamine respectively required for the preparation of 1 litre of the cupri-ethylene-diamine solution (6.1.1) using the formulae

$$m_3 = \frac{63{,}6 \times 100}{X}$$

$$m_4 = \frac{120{,}2 \times 100}{Y}$$

where

X is the copper content, as a percentage by mass, calculated in accordance with clause A.4;

Y is the ethylene-diamine content, as a percentage by mass, calculated in accordance with clause A.5.

Weigh the calculated mass m_3 of copper hydroxide (prepared as specified in clause A.3) (see the note) into a 400 ml beaker, and slowly add the calculated mass m_4 of ethylene-diamine solution (A.1.1) while stirring with a glass rod. Keep the temperature below 20 °C by careful cooling. Dilute the solution with distilled water to a volume of 800 ml in the brown glass flask (A.2.1), carefully avoiding any increase in temperature. Leave the solution to stand overnight, and then, subsequent to centrifugation or filtration through a glass filter, transfer it into a 1 000 ml measuring flask, and dilute to the mark. Pour the solution back to the brown glass flask, which has been cleaned and dried. Check the concentration of the solution as specified in clause A.7.

NOTE — When commercial copper(II) hydroxide is used, it is recommended that an excess amount be taken and the undissolved amount separated by filtration or centrifugation.

A.7 Determination of the concentration of the cupri-ethylene-diamine solution (A.6)

Reaction equations :

$$Cu(en)_2(OH)_2 + 2\,HCl \quad Cu(en)_2Cl_2 + 2\,H_2O$$

$$Cu(en)_2Cl_2 + 4\,HCl \quad CuCl_2 + 2(en).2\,HCl$$

$$Cu(en)_2(OH)_2 + 6\,HCl \quad CuCl_2 + 2\,H_2O + 2(en).2\,HCl$$

$$2\,CuCl_2 + 4\,KI \quad Cu_2I_2 + 4\,KCl + I_2$$

With a pipette, measure 5 ml of the cupri-ethylene-diamine solution into a 250 ml conical flask. Acidify with the hydrochloric acid solution (A.1.9) and 30 ml of the potassium iodide solution (A.1.7), and then without further dilution titrate with the standard volumetric sodium thiosulphate solution (A.1.10) to the starch end-point. Record the volume of sodium thiosulphate solution used.

Add 5 more drops of the sodium thiosulphate solution. Transfer the solution quantitatively to a 1 000 ml conical flask, using in all 400 ml of distilled water for rinsing the 250 ml flask and for dilution of the solution. Titrate with the standard volumetric sodium hydroxide solution (A.1.12), using the methyl orange indicator (A.1.15), until the end-point is reached.

Calculate the copper concentration (c_{Cu}), and ethylene-diamine concentration (c_{en}), in moles per litre, by the formulae

$$c_{Cu} = \frac{V_3 \times 100}{1\,000 \times 10} = \frac{V_3}{100}$$

$$c_{en} = \frac{\left(50 - \frac{V_3}{10} - \frac{V_4}{10}\right) \times 200}{2 \times 1\,000} = \frac{1}{10}\left(50 - \frac{V_3}{10} - \frac{V_4}{10}\right)$$

where

V_3 is the volume of the standard volumetric sodium thiosulphate solution (A.1.10) used for the titration, in millilitres;

V_4 is the volume of the standard volumetric sodium hydroxide solution (A.1.12) used for the titration, in millilitres.

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