



Standard Test Method for Intrinsic Viscosity of Cellulose¹

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1. Scope

1.1 This test method covers the determination of the intrinsic viscosity of purified celluloses such as bleached wood pulps, cotton linters, and regenerated cellulose. It is applicable to all cellulose samples with an intrinsic viscosity of 15 dl/g or less. Most native (unpurified) celluloses have intrinsic viscosity values too high for measurement by this test method.

NOTE 1—The use of cuprammonium hydroxide solution for regular viscosity determination is described in Test Methods D 539, Method T 206 m-55 of the Technical Association of Pulp and Paper Industry on “Cuprammonium Disperse Viscosity of Pulp,” and Joint Army-Navy Specifications JAN-C-206.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

- D 445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)²
- D 539 Test Methods for Apparent Fluidity of Dispersions of Cellulose Fibers³
- D 629 Test Methods for Quantitative Analysis of Textiles⁴
- E 1 Specification for ASTM Thermometers⁵

3. Summary of Test Method

3.1 A weighed sample of the material is dissolved in a 0.5 M cupriethylenediamine hydroxide solution. The viscosity of this solution, and also that of the solvent, is determined at 25°C by means of a calibrated glass capillary-type viscometer. The relative viscosity is calculated and the corresponding intrinsic viscosity is read from a table.

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² *Annual Book of ASTM Standards*, Vol 05.01.

³ Discontinued, see *1973 Annual Book of ASTM Standards*, Part 24.

⁴ *Annual Book of ASTM Standards*, Vol 07.01.

⁵ *Annual Book of ASTM Standards*, Vol 14.03.

4. Significance and Use

4.1 This test is a sensitive measure of the degradation of cellulose resulting from the action of heat, light, acids, alkalis, oxidizing and reducing agents, and the like, used in its processing or purification. The intrinsic viscosity value may be converted to degree of polymerization (DP) or to intrinsic fluidity, if desired.

4.2 Solutions of cellulose are not Newtonian liquids; that is, their viscosity depends upon the rate-of-shear or velocity gradient during measurement. This effect is smaller for samples of low molecular mass (DP) and at low concentrations than for high- DP samples and at high concentrations. For the celluloses and concentrations included within the limits set forth in this test method, the effect of rate-of-shear is assumed to be negligible for referee purposes. For other conditions and for research purposes this assumption may be invalid, but to discuss ways of accounting for this effect is beyond the scope of the present test method.

5. Apparatus

5.1 *Viscometer, Glass, Capillary Type*—The Cannon-Fenske, Ubbelohde, or similar capillary type instrument as described in Test Method D 445 is recommended. Viscometers described in Test Methods D 539 are also suitable. In order to avoid correction for the kinetic energy effect, choose a viscometer with a small enough capillary to give an outflow time of 80 s or more for the Cannon-Fenske type. (A size 100 viscometer is normally used for the sample solution and a size 50 for the solvent.)

5.2 *Thermometer*—ASTM Kinematic Viscosity Thermometer for use at 25°C, having a range from 19 to 27°C and conforming to the requirement for Thermometer 17C as prescribed in Specification E 1.

5.3 *Bath*—A constant-temperature bath at 25°C suitable for immersion of the viscometer so that the reservoir or the top of the capillary, whichever is uppermost, is immersed at least 50 mm, and with provision for visibility of the instrument and the thermometer. Firm supports for the viscometer shall be provided; or the viscometer may be sealed in as an integral part of the bath. Either a liquid bath with thermostatic regulation and a stirrer or a vapor bath with pressure regulation is permissible. The efficiency of the stirring and the balance between heat losses and heat input must be such that the temperature of the bath medium does not vary by more than $\pm 0.1^\circ\text{C}$ over the

length of the viscometer, or from viscometer to viscometer in the various bath positions. If a vapor bath is used, there must be no temperature gradient over the length of the viscometer greater than that permitted in a liquid bath.

5.4 *Timer*—A stop watch or other spring-activated timing device or electrical timing device shall be used, graduated in divisions of 0.2 s or less, and accurate to within 0.05 % when tested over not less than a 10-min period. Such electrical timing devices shall be used only on electrical circuits of continuously controlled frequency. Frequency-controlled devices of suitable capacity for laboratory purposes, accurate to within 1 part in 10 000 should be used. Errors exceeding 0.05 % of a 10-min interval may occur in timing devices actuated by electrical synchronous motors driven by most public power systems, which are intermittently and not continuously controlled.

6. Reagent

6.1 *Cupriethylenediamine Hydroxide Solution* ($1.00 \pm 0.01 M$), in copper, with the molar ratio of ethylenediamine to copper of 2 ± 0.1 to 1. This solvent may be prepared in the laboratory as described in Test Methods D 539. It is also commercially available.⁶

7. Reference Materials

7.1 *Viscosity Oil Standards*—Calibrating oils in the specified ranges of viscosity.⁶ Aqueous solutions of glycerol may be used instead of standardized oils; the compositions for various viscosities are given in chemical handbooks. The applicable viscosity oil standards (Note 2) are listed in Table 1.

TABLE 1 Viscosity Oil Standards

Viscometer		Viscosity Oil Standard	
Size	Absolute Viscosity Range, cP ^A	Designation	Approximate Absolute Viscosity at 77°F (25°C), cP
50	0.9 to 3.5	S-3	3.3
100	3.3 to 13.3	S-6	7.7

^A For solution with density of 0.9.

NOTE 2—The viscosity oil standards are available only as 1-pt (4.7- m³) samples. More than 1 pt of any given oil (for example, duplicate samples) are supplied only when it is established that 1 pt is inadequate.⁶

8. Calibration of Viscometer

8.1 The following directions apply to the Cannon-Fenske viscometer (Note 3). They should be modified according to the operating instructions for other types of viscometers. The viscometers shall be calibrated (Note 4) by means of liquids having known viscosities approximately equal to those of the solvent and cellulose solutions respectively (1.2 and 12 cP, approximately).

NOTE 3—Detailed specifications and directions for filling, calibrating, and measurement with types of capillary viscometers most used are given in Test Method D 445.

⁶ The sole source of supply of the viscosity oil standards known to the committee at this time is Cannon Instrument Co., P. O. Box 16, State College, PA 16801. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

NOTE 4—Calibration of the viscometers may be avoided if both solvent and solution are measured in the same instrument. Then the relative viscosity is nearly the ratio of outflow times for solution and solvent, respectively. This simplification involves two assumptions. The first, that the densities of solution and solvent are equal, holds very well for the dilute solutions used in these tests. The second, that the kinetic energy correction is zero, depends upon the choice of viscometer. If the one used gives convenient outflow times for the solution of less than 150 s, then it will be too fast for the solvent. The kinetic energy correction is zero, depending upon flow. On the other hand, if one is chosen so that the outflow time for the solvent is large enough (80 s or more), then the times for the solutions will in most cases be inconveniently long. For some work, however, it may be desirable to make some sacrifice in accuracy or in convenience during measurement in order to avoid calibration and using two sizes of viscometers.

8.2 By means of a pipet, add 7.0 mL of the calibrating liquid to the viscometer, in a constant-temperature bath at $25 \pm 0.1^\circ\text{C}$ (or fill as described in Test Method D 445, Appendix A).

8.3 When the liquid has reached temperature equilibrium with the bath (in about 5 min), determine the outflow time t by drawing the top meniscus of the liquid above the mark between the two bulbs and measuring the time required for the meniscus to pass from this mark to the mark below the lower bulb. Take the average of two or more observations, which should differ by not more than 0.2 s.

8.4 Determine the viscometer constant C by the equation:

$$C = \eta/dt \quad (1)$$

where:

η = viscosity of the calibrating liquid, cP,

d = density, g/mL, and

t = time, s.

9. Preparation of Sample

9.1 To avoid undesirable effects from long heating at high temperature, samples should be air-dried and the moisture content determined on a portion that is not used for measurement of viscosity. The mass of air-dried samples is then corrected for moisture to obtain the mass of oven-dried cellulose used to calculate concentration.

9.2 Soft, sheeted pulp should be picked apart with tweezers or scraped with a dull knife. Hard-pressed or harsh pulp should be slurried in water, formed into thin sheets on a Büchner funnel, and dried at a temperature below 100°C (preferably room temperature). Loose pulp should be picked apart by hand to break up any lumps. Slurried or slush pulps should be formed into thin sheets and dried. Yarn and staple should be washed in warm water containing a little detergent to remove the finish, rinsed thoroughly, dried (at low temperature), and fluffed. (It will be found helpful to cut yarn and long staple into short lengths, say $\frac{1}{2}$ in. (13 mm), before washing.) Fabrics should be cut into small pieces, desized (see Test Methods D 629, Section 8), thoroughly washed, and dried. Raveling will be helpful before dissolving samples that tend to get in the solvent. Materials containing a considerable amount of non-cellulosic matter must first be purified; such treatments lie outside the scope of this test method.

10. Preparation of Solution

10.1 The sample size is dependent upon the nature of the material, smaller masses of high-viscosity celluloses and larger

TABLE 2 Intrinsic Viscosities of Typical Samples

Type of Material	Intrinsic Viscosity, dL/g	Approximate Concentration, g/dL
Regenerated cellulose (rayons)	2 to 3	1
Dissolving pulps:		
Low viscosity	3 to 4	1
Regular viscosity	4 to 7	0.5
High viscosity	7 to 10	0.3
Cotton linters, for rayon and acetate	6 to 9	0.4
Paper (wood) pulps	3 to 8	0.4
Native celluloses ⁴	15 to 30	0.1 to 0.2

⁴ Serious error may be introduced when this test method, which neglects effects of rate of shear upon viscosity, is used for native celluloses of high intrinsic viscosity.

masses of low-viscosity celluloses being used in order to keep the viscosity of the solutions within rather narrow limits. (Working at nearly constant viscosity reduces the effect of rate of shear upon the measurements.) The concentration for each sample is chosen according to the rule:

$$[\eta]c = 3.09 \pm 0.5 \quad (2)$$

where:

$[\eta]$ = intrinsic viscosity, dL/g, and
 c = cellulose concentration, g/dL.

Obviously, use of this rule requires knowledge of the approximate intrinsic viscosity of the sample before the concentration can be estimated. In routine control work, such information is available. If it is not, Table 2 will serve as an approximate guide.

10.2 Make up a preliminary solution of about the indicated concentration, and determine the viscosity as described in Sections 11 and 12. From the relative viscosity thus obtained, find the approximate value of the intrinsic viscosity by means of Table 3. From this determine the concentration needed to give: $[\eta]c = 3.0$. If this preliminary solution does not give a value of $[\eta]c$ of 3.0 ± 0.5 , prepare a second solution of the indicated concentration for the final viscosity measurement.

10.3 Alkaline solutions of cellulose are known to be sensitive to oxidation. Hence it is usually necessary to exclude air during solution of the sample; several ways of doing this are described in the literature, but the following is simple and adequate: Weigh out the calculated amount of air-dried cellulose (corrected to oven-dry mass) and transfer quantitatively to a suitable glass or polyethylene container (capacity somewhat more than 50 mL) that can be tightly closed by a stopper or screw cap. Add 25.0 mL of distilled water from a pipet or buret, insert the stopper or cap, and shake in order to wet out and disperse the sample. Sweep the air from the vessel with a stream of nitrogen and, with the nitrogen still flowing, add 25.0 mL of solvent. Stopper or cap tightly and shake vigorously by hand or in a mechanical shaker until the cellulose is completely dissolved.

NOTE 5—Most work pulp and regenerated celluloses dissolve within 5 min. Mercerized celluloses do not dissolve as easily in cupriethylenediamine as in cuprammonium solvent and require longer times (up to 1 h). Some operators report difficulty in dissolving native celluloses including cotton linters with degree of polymerization (DP) as low as that of wood pulps. The difficulty shows up by much poorer precision of results than the 1 to 2 % that is normally obtained between measurements made with two or more solutions of the same sample. Even solutions that leave no residue

on fritted-glass filters have been observed to give erratic results. Inadequate dispersion of the sample is apparently the cause, and two modifications in procedure have been recommended in such cases. One is to add about 0.04 % wetting agent to the water used to wet out the sample.⁷ The other requires use of cupriethylenediamine solutions of two concentrations: The sample is wetted out with one solution that is 0.167 M in copper and dispersion is completed by adding the second solution, 1.000 M in copper, in such volume as to make the final copper concentration 0.500 M (see Section 14 of Test Methods D 539).

11. Measurement of Viscosity

11.1 Transfer 7.0 mL of the solution by means of a syringe or pipet to a viscometer previously placed in the bath at 25°C and flushed with nitrogen (or fill as described in Test Method D 445, Appendix A). Allow at least 5 min for the solution to reach bath temperature.

11.2 By applying either pressure (with nitrogen) or suction, draw the solution into the lower bulb of the viscometer until the top meniscus is a little above the mark between the two bulbs. Measure the time t required for the meniscus to pass from this mark to the mark below the lower bulb. Repeat at least twice and average the observations, which should not differ by more than 0.3 %.

11.3 In the same way, measure the outflow time t_0 for the solvent. This of course must be determined not for the 1.00 M solvent as prepared or purchased, but for this solvent diluted with an equal volume of water.

12. Calculations

12.1 Calculate the viscosity, η , in centipoises, as follows:

$$\eta = Ct \quad (3)$$

where:

C = viscometer constant (Section 8),

t = outflow time, s, and

d = density, g/mL.

Calculate the relative viscosity, η_{rel} , as follows:

$$\eta_{rel} = \eta/\eta_0$$

where η_0 is the viscosity of the solvent. Since the densities of solvent and solution are practically the same, they cancel in determining relative viscosity. Hence a little work may be saved by determining the kinematic viscosity, ϵ , in centistokes, for solution and solvent:

$$\epsilon = Ct \quad (4)$$

and then

$$\eta_{rel} = \epsilon/\epsilon_0 \quad (5)$$

If both solution and solvent are measured in the same viscometer (see Note 4), relative viscosity may be obtained directly from the ratio of outflow times:

$$\eta_{rel} = t/t_0 \quad (6)$$

12.2 By means of Table 3, determine the product $[\eta]c$ corresponding to the value of the relative viscosity. From this value and the concentration, calculate the intrinsic viscosity in decilitres per gram.

⁷ Lindsley, C. H., "Rapid Dispersion of Cellulose in Cupriethylenediamine," *Textile Research Journal*, Vol 21, 1951, p. 286.