Designation: D1696 – 95 (Reapproved 2011)

Standard Test Method for Solubility of Cellulose in Sodium Hydroxide[1]

This standard is issued under the fixed designation D1696; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method[2] is intended for application to dissolving-type cellulose pulps prepared from cotton or wood. The procedure is not directly applicable to unrefined pulps for use in chemical conversion processes because solubility equilibrium may not be attained within the specified extraction time.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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 consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1193 Specification for Reagent Water

D1347 Test Methods for Methylcellulose (Withdrawn 2003)[4]

D1348 Test Methods for Moisture in Cellulose

2.2 *TAPPI Standard:*

T 429 Method for Alpha-Cellulose in Paper[5]

3. Summary of Test Method

3.1 Pulp is steeped in a sodium hydroxide solution of a specified concentration for 1 h at 20°C. The soluble fraction is estimated by dichromate oxidation of the filtered steeping alkali. The concentration of sodium hydroxide used in the pulp extraction process must be reported as part of the analytical result. Sodium hydroxide concentrations of 10, 18, and 21.5 % are most frequently used. Data are reported as percent of dry sample weight.

3.2 The extraction procedure avoids dilution sequences, and therefore, the results are not comparable to data obtained by the alpha, beta, gamma methods of pulp fractionation (see TAPPI Method T 429). The terms "alpha-," "beta-," or "gamma-" cellulose must not be applied to any test values obtained by this procedure since they are defined only by the method of their determination.

3.3 The essential feature of the method is to prepare sodium hydroxide extracts and oxidize the soluble material with dichromate as described. Alternative methods of estimating dichromate by titration with ferrous ammonium sulfate and sodium thiosulfate are described.

4. Significance and Use

4.1 The measurement of soluble oxidizable components of cellulose in sodium hydroxide is indicative of the purity of the cellulose sample, since pure cellulose is insoluble in sodium hydroxide. The extracted components are typically hemicelluloses, which are naturally present in the wood. Differences in pulp purity can have a dramatic impact on the processing and properties of the cellulose derivatives produced from the pulp.

5. Apparatus

5.1 *Constant-Temperature Bath*—A water bath maintained at 20 ± 0.2°C.

5.2 *Stirrer*—Mechanical stirrer as shown in Fig. 1. All parts in contact with solutions must be of stainless steel. The stirrer motor shall be a variable speed laboratory motor with 1500 rpm max speed.

5.3 *Fritted-Glass Filter Crucible*—A fritted-glass filter crucible, coarse porosity (pore size 40 to 60 µm), of 30-mL capacity.

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[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.36 on Cellulose and Cellulose Derivatives.

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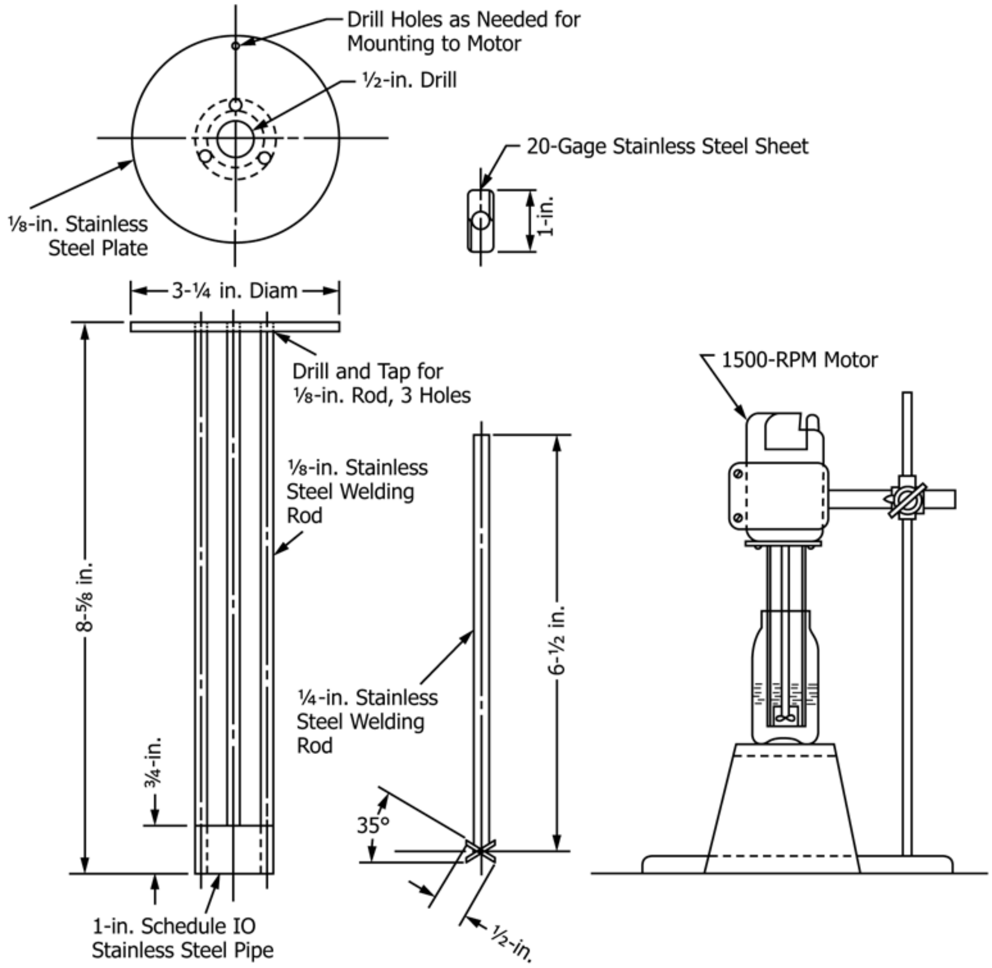
[2] This test method is an adaptation of the method designated CCA 8:55 by the Analysis Committee of the Central Committee of the Cellulose Industry of the Swedish Association of Pulp and Paper Engineers. This test method is also comparable with the TAPPI Tentative Standard T 235 m-58, Solubility of Pulp in Cold Sodium Hydroxide.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] The last approved version of this historical standard is referenced on www.astm.org.

[5] Available from Technical Association of the Pulp and Paper Industry (TAPPI), P.O. Box 105113, Atlanta, GA 30348; 15 Technology Parkway South, Norcross, GA 30092.



Metric Equivalents

in.	⅛	¼	½	¾	1	3¼	6½	8⅝
mm	3.2	6.4	12.7	19.0	25.4	82.6	165.1	219.1

FIG. 1 Design Details of Mechanical Stirrer

5.4 *Electrometric Titration Apparatus*—For estimation of dichromate by titration with ferrous ammonium sulfate. An indicator may be used as described in 8.6, but for rapid, accurate analysis an electrometric apparatus is recommended.

6. Purity of Reagents

6.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,[6] where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193.

7. Reagents

7.1 *Ferroin (0.025 M)*—Dissolve 1.48 g of orthophenanthroline monohydrate (or 1.624 g of the hydrochloride) with 0.695 g of ferrous sulfate ($FeSO_4$) in water and dilute to 100 mL.

7.2 *Ferrous Ammonium Sulfate Solution* (0.1 *N*)—Dissolve 40 to 41 g of ferrous ammonium sulfate ($FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$) in water containing 10 mL of H_2SO_4 and dilute to 1 litre in a volumetric flask. Standardize the solution daily against potassium permanganate ($KMnO_4$).

7.3 *Potassium Dichromate Solution (20 g/L)*—Weigh 20.0 g of potassium dichromate ($K_2Cr_2O_7$), transfer to a 2-L beaker, and dissolve in approximately 700 mL of water. Add, with constant stirring, 150 mL of H_2SO_4. Allow to cool to room temperature. Dilute to 1 L with water.

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[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.4 *Potassium Iodide* (KI).[7]

7.5 *Sodium Hydroxide Solution*—Dissolve solid sodium hydroxide (NaOH) in an equal weight of water. Cover and allow to stand about one week to permit settling of sodium carbonate (Na_2CO_3). Prepare the dilute NaOH solutions listed below by approximate addition of freshly boiled water to portions of the concentrated stock solution. Use a siphon to withdraw the required volume of 50 % NaOH solution from the stock bottle; do not disturb the Na_2CO_3 precipitate. The Na_2CO_3 content of the dilute solutions should not exceed 1 g/L. Standardize the final dilute solutions by titration with standard acid.

7.5.1 *Sodium Hydroxide Solution (10 %)*—Prepare a solution containing 10.0 ± 0.1 g NaOH per 100 g of solution. Specific gravity at 20/4°C is 1.1089. This solution is 2.77 *N*.

7.5.2 *Sodium Hydroxide Solution (18 %)*—Prepare a solution containing 18.0 ± 0.1 g NaOH per 100 g of solution. Specific gravity at 20/4°C is 1.1972. This solution is 5.39 *N*.

7.5.3 *Sodium Hydroxide Solution (21.5 %)*—Prepare a solution containing 21.5 ± 0.1 g NaOH per 100 g of solution. Specific gravity at 20/4°C is 1.2356. This solution is 6.64 *N*.

7.6 *Sodium Thiosulfate Solution (0.1 N)*[6]—Prepare and standardize 0.1 *N* sodium thiosulfate ($Na_2S_2O_3$) solution as directed in 23.11 of Test Methods D1347.

7.7 *Starch Solution* (5 g/L).

7.8 *Sulfuric Acid* (sp gr 184)—Concentrated sulfuric acid (H_2SO_4).

8. Preparation of Samples

8.1 Condition the air-dry pulp samples to obtain moisture equilibrium by exposing them to the atmosphere for 24 h in the room where the portions of this sample will be weighed for moisture and solubility analysis.

8.2 If the pulp is in sheeted form, tear it into pieces about 10 mm square. Do not use cut edges. Weigh a portion for moisture analysis and immediately also weigh, to the nearest 1 mg, about 1.6 g of the air-dry sample for the solubility determination.

8.3 Determine the moisture content of the air-dry sample in accordance with Test Methods D1348. Calculate the oven-dry weight of the sample for the solubility determination.

9. Procedure

9.1 Precool the NaOH solutions to 20°C. Pulp solubility in 18 and 21.5 % NaOH solutions is not affected by a few degrees variation in temperature. Hence, temperatures of 20 ± 2°C are satisfactory in this case. However, pulp solubility in 10 % NaOH solution is very sensitive to temperature variation. The operator must control temperature to 20 ± 0.2°C in all phases of pulp extraction with 10 % NaOH solution.

9.2 With a pipet or buret, transfer 100 mL of the NaOH solution of the desired concentration (10, 18, or 21.5 %) into a 250-mL beaker. Add the 1.6 g air-dry pulp sample to the solution. Allow the pulp to swell for 2 min; then introduce the stirring apparatus into the beaker so that the surface of the liquid coincides with the draft tube top. Disintegrate the pulp by stirring for 3 min (Note 1). Adjust the stirring speed to prevent addition of air to the slurry (about 1500 rpm). Remove the stirrer. Carefully clean the stirring apparatus and walls of the beaker with a glass rod so that all pulp fibers are retained in the alkali. Cover the beaker with a watch glass and leave in the 20°C bath until a total of 60 min have elapsed from the time of addition of NaOH to the sample. For solubility determinations in 10 % NaOH solution, all extraction operations must be performed with the sample container in the constant-temperature water bath. In work with 18 or 21.5 % NaOH, the sample container may be removed from the bath for the disintegration process.

NOTE 1—Most pulps are completely disintegrated after 3 min. A reasonable increase in the time of disintegration does not sensibly affect the solubility. On the other hand, low values are obtained if the disintegration is not complete. The stirrer should, therefore, be run until complete disintegration is obtained, even if the time required exceeds 3 min.

9.3 At the end of the 1-h total extraction time, remove the beaker from the bath and immediately filter the slurry through a coarse fritted-glass filter. Apply suction but do not pull air through the cellulose mat on the filter. Discard the first 10 mL of filtrate. If suspended fibers are noted in the filtrate, recycle the filtrate through the cellulose mat to clarify. Retain the filtrate in a stoppered Erlenmeyer flask.

9.4 Transfer 10-mL aliquots of the NaOH filtrates to 250-mL Erlenmeyer flasks. Add 10 mL $K_2Cr_2O_7$ solution to each flask; then *carefully* add 30 mL of H_2SO_4 to each flask. After 10 min (Note 2), cool to room temperature. Include a blank test with the original NaOH extraction solution in this operation.

NOTE 2—It is suggested that heat be applied to maintain a temperature in the range of 125 to 130°C for the entire 10-min period. A reflux system is highly satisfactory.

9.5 The 10-mL aliquot of the NaOH filtrates specified in 9.4 is generally suitable for dissolving-type pulps; however, if the alkali solubility is greater than 16 %, reduce the volume of filtrate to 5 mL and the volume of H_2SO_4 to 25 mL. For pulps with alkali solubility less than 5 %, use 20 mL of filtrate and 45 mL of H_2SO_4.

9.6 After dichromate oxidation, add 50 mL of water to each sample and the blank. Cool again to room temperature. Titrate the excess $K_2Cr_2O_7$ with 0.1 *N* ferrous ammonium sulfate solution. An electrometric titrimeter is preferred for this operation. If this equipment is not available, ferroin indicator may be used to detect the end point.

9.7 An acceptable alternative for measuring dichromate concentration is to use iodometric methods. In this case, transfer the cooled solution with about 500 mL of water to a 1-L Erlenmeyer flask. Add about 2 g of Kl and after 5 min titrate the solution to a visual end point with 0.1 *N* $Na_2S_2O_3$ solution, using starch as the indicator. Make a blank test on the original NaOH extraction solution in the same manner.

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[7] This reagent is required only for the iodometric method for measuring dichromate (see section 9.7). Thyodene, supplied by Fisher Scientific Co., Pittsburgh, PA is an acceptable substitute.

10. Calculations

10.1 Calculate the results, when obtained by titration with ferrous ammonium sulfate, as follows:

$$\text{Alkali solubility, \%} = \left[\left(b - a \right) N \times 68.5 \right] / mw \tag{1}$$

where:

a = ferrous ammonium sulfate solution required for titration of the sample, mL,

b = ferrous ammonium sulfate solution required for titration of the blank, mL,

N = normality of the ferrous ammonium sulfate solution,

68.5 = cellulose equivalent to 1 milliequivalent of $K_2Cr_2O_7$, times 10 (Note 3), mg,

m = filtrate used for oxidation, mL, and

w = oven-dry weight of sample used, g.

NOTE 3—The factor 68.5 is the experimental value recommended in method CCA 8:55.[2] As an alternative, the problem of standardization of ferrous ammonium sulfate can be handled in terms of oxidation of a reference cellulose solution prepared at each occasion for analysis as follows: Dissolve 200 mg (oven-dry weight) of high-quality cotton linters pulp in H_2SO_4 (3 + 1) (prepared by mixing 3 volumes of H_2SO_4 (sp gr. 1.84) with 1 volume of water) and dilute to 100 mL with H_2SO_4 (3 + 1). Do not use heat in the preparation of this solution. Immediately after preparation, oxidize 2-mL aliquots of this solution in the procedure described in Section 8 for blank and sample treatment. Compare the cellulose solution and blank to express the concentration of ferrous ammonium sulfate solution in terms of milligrams of cellulose per millilitre of solution. The calculation then becomes:

$$\text{Alkali solubility, \%} = \left[10\, C \left(b - a \right) \right] / mw \tag{2}$$

where:

C = concentration of ferrous ammonium sulfate solution in terms of milligrams of cellulose per millilitre, and b, a, m, w are defined as in 10.1.

10.2 Calculate the results, when obtained by titration with $Na_2S_2O_3$ solution, as follows:

$$\text{Alkali solubility, \%} = \left[\left(V_1 - V_2 \right) N \times 68.5 \right] mw \tag{3}$$

where:

V_1 = $Na_2S_2O_3$ solution required for titration of the sample, mL,

V_2 = $Na_2S_2O_3$ solution required for titration of the blank, mL, and

N = normality of the $Na_2S_2O_3$ solution, and m and w are defined as in 10.1.

11. Report

11.1 Report the alkali solubility as a percentage of oven-dry pulp to one decimal place. Use the symbol *S* for alkali solubility. Denote the strength of the sodium hydroxide solution by a numerical suffix, for example, designate the solubility in 10 % NaOH solution by the symbol S_{10}.

11.2 If it is of interest to report the insoluble fraction, subtract the *S* value from 100. Use the symbol *R*, with the appropriate subscript, to report this value. For example: $R_{10} = 100 - S_{10}$.

12. Precision and Bias

12.1 *Precision*—Statistical analysis indicates a precision of no less than ±8 % at the 95 % confidence level for all concentrations of sodium hydroxide.

12.2 *Bias*—No statement of bias can be made as no suitable reference material exists for determining bias.

13. Keywords

13.1 cellulose; sodium hydroxide solubility