Designation: D871 – 96 (Reapproved 2019)

Standard Test Methods of Testing Cellulose Acetate[1]

This standard is issued under the fixed designation D871; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These test methods cover procedures for testing cellulose acetate.

1.2 The test procedures appear in the following sections:

	Sections
Ash	8 to 11
Color and Haze	67 to 72
Combined Acetyl or Acetic Acid Content	
Test Method A. Solution Method	17, 19 to 23
Test Method B. Heterogeneous Saponification Method	17, 24 to 26
Free Acidity	12 to 16
Heat Stability	47 to 56
Hydroxyl Content	27 to 33
Intrinsic Viscosity	57 to 62
Moisture Content	4 to 7
Primary Hydroxyl Content	34 to 39
Sulfur or Sulfate Content	40 to 45
Viscosity	63 to 66

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D1343 Test Method for Viscosity of Cellulose Derivatives by Ball-Drop Method

D2929 Test Method for Sulfur Content of Cellulosic Materials by X-Ray Fluorescence

D5897 Test Method for Determination of Percent Hydroxyl on Cellulose Esters by Potentiometric Titration—Alternative Method

3. Purity of Reagents

3.1 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, where such specifications are available.[3] 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.

3.2 Unless otherwise indicated, references to water shall be understood to mean reagent tared, low, wide-form weighing bottle and water, conforming to Specification D1193.

MOISTURE CONTENT

4. Significance and Use

4.1 Moisture content of the cellulose ester can be used to estimate the dry weight of the cellulose ester. Since cellulose esters are desiccants, their moisture content can vary greatly depending on storage.

5. Procedure

5.1 Transfer about 5 g of the sample to a tared, low, wide-form weighing bottle and weigh to the nearest 0.001 g. Dry in an oven for 2 h at 105 ± 3°C. Remove the bottle from the oven, cover, cool in a desiccator, and weigh.

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

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[2] 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.

[3] *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.

6. Calculation

6.1 Calculate the percentage of moisture as follows:

$$\text{Moisture, \%} = (A/B) \times 100$$

where:

A = weight loss on heating, g, and
B = sample used, g.

7. Precision and Bias

7.1 No statement on bias can be made as no reference material is available as a standard.

ASH

8. Significance and Use

8.1 Ash content gives an estimate of the inorganic content of cellulose ester samples. The presence of high levels of inorganic content (ash) can be detrimental to the melt stability and optical clarity of a cellulose ester in melt processing or act as a potential source of insolubles when the ester is used in solution.

9. Procedure

9.1 Dry the sample for 2 h at 105 ± 3°C and weigh 10 to 50 g, to the nearest 0.01 to 0.1 g, depending on its ash content and the accuracy desired. An air-dried sample may be used and calculated to dry weight using the value for moisture determined as in Sections 5 and 6. Burn directly over a flame in a 100-mL tared platinum crucible that has been heated to constant weight and weighed to the nearest 0.1 mg. Add the sample in portions if more than 10 g is taken. The sample should burn gently and the portions should be added as the flame subsides. Continue heating with a burner only as long as the residue burns with a flame. Transfer the crucible to a muffle furnace and heat at 550 to 600°C for 3 h, or longer if required, to burn all the carbon. Allow the crucible to cool and then transfer it, while still warm, to a desiccator. When the crucible has cooled to room temperature, weigh accurately to the nearest 0.1 mg.

10. Calculation

10.1 Calculate the percentage of ash as follows:

$$\text{Ash, \%} = (A/B) \times 100$$

where:

A = ash, g, and
B = sample used, g.

11. Precision and Bias

11.1 No statement on bias can be made as no reference material is available as a standard.

FREE ACIDITY

12. Significance and Use

12.1 Free Acidity is a measure of unesterified organic acid in the ester. The presence of high levels of free acid is potentially detrimental to the melt processing of the ester and can impact the odor of the ester.

13. Reagents

13.1 *Phenolphthalein Indicator Solution (1 g/100 mL)*—Dissolve 1 g of phenolphthalein in 100 mL of ethyl alcohol (95 %).

13.2 *Sodium Hydroxide, Standard Solution*—(0.01 *N*)—Prepare and standardize a 0.01 *N* solution of sodium hydroxide (NaOH).

14. Procedure

14.1 Shake 5 g of the sample, ground to pass a No. 20 (850 µm) sieve and corrected for moisture content if necessary, in a 250-mL Erlenmeyer flask with 150 mL of freshly boiled, cold water. Stopper the flask and allow it to stand for 3 h. Filter off the cellulose acetate and wash it with water. Titrate the combined filtrate and washings with 0.01 *N* NaOH solution, using phenolphthalein indicator solution.

14.2 Run a blank determination on the water, using the same volume as was used in extracting the sample.

15. Calculation

15.1 Calculate the percentage of acidity as free acetic acid as follows:

$$\text{Free acetic acid, \%} = [(A - B)N \times 0.06 \times 100]/W \quad (1)$$

where:

A = NaOH solution used to titrate the sample, mL,
B = NaOH solution used to titrate the blank, mL,
N = normality of the NaOH solution, and
W = sample used, g.

16. Precision and Bias

16.1 No statement on bias can be made as no reference material is available as a standard.

COMBINED ACETYL OR ACETIC ACID CONTENT

17. Scope

17.1 Two test methods are described for determining the combined acetyl or acetic acid content. The first, described in Sections 19 to 22, is more precise, but less widely applicable, than the method described in Sections 24 to 26.

18. Significance and Use

18.1 Acetyl or acetic acid content is a measure of the amount of acetic acid esterified onto the cellulose backbone of the polymer. The amount of substitution of acetate ester has a very strong effect on the polymer's solubility and physical properties.

Test Method A—Solution Method

19. Apparatus

19.1 *Weighing Bottle,* glass-stoppered, 15-mL capacity, 25-mm diameter by 50-mm high.

19.2 *Tray,* copper or aluminum, approximately 136.5 mm (5 ⅜ in.) square, containing 25 compartments 25.4 mm (1 in.) square. Each compartment shall have the correct dimensions to contain one weighing bottle. The entire tray shall fit inside a desiccator and should have a basket-type handle to facilitate the introduction and removal of the tray (convenient but not essential).

19.3 *Buret,* automatic zero, 35-mL, 25-mL bulb, stem graduated from 25 to 35 mL in 0.05-ml increments; or pipet, automatic zero, 30-mL, for 1.0 *N* NaOH solution.

19.4 *Buret,* automatic zero, 15-mL, 10-mL bulb, stem graduated from 10 to 15 mL in 0.05-mL increments, for 1 *N* H_2SO_4.

19.5 *Buret,* 5-ml, in 0.01 or 0.1-mL divisions, for back titration with 0.1 *N* NaOH solution.

19.6 *Magnetic Stirrer,* for single flask.

19.7 *Magnetic Stirrer,* capacity twelve or more flasks.

19.8 *Stirring Bars,* stainless steel Type 416, length 50 mm, diameter 5 to 6 mm, or equivalent, dimensions not critical.

20. Reagents

20.1 *Acetone*—Add one 30-mL portion of 1.0 *N* NaOH solution to a mixture of 150 mL acetone and 100 mL hot water, allow to stand with frequent swirling for 30 min, and titrate with 1.0 *N* H_2SO_4. Add another 30-mL portion of 1.0 *N* NaOH solution to 100 mL of hot water, allow to stand for 30 min, and titrate. The difference between the two titrations shall not exceed 0.05 mL.

20.2 *Dimethyl Sulfoxide.*

20.3 *Pyridine.*

20.4 *Sodium Hydroxide Solution (40 g/L)*—Dissolve 40 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

20.5 *Sodium Hydroxide, Standard Solution* (0.1 *N*)—Prepare and standardize a 0.1 *N* solution of NaOH.

20.6 *Sulfuric Acid* (1.0 *N*)—Prepare and standardize a 1.0 *N* solution of sulfuric acid (H_2SO_4).

20.7 *Phenolphthalein Indicator Solution (1 g/100 mL)*—Dissolve 1 g of phenolphthalein in 100 ml of ethyl alcohol (95 %).

21. Procedure

21.1 Dry 1.9 ± 0.05 g of the ground well-mixed sample in a weighing bottle for 2 h at 105 ± 3°C and weigh the dried sample by difference to the nearest 1 mg into a 500-mL wide-mouth Erlenmeyer flask. Prepare a blank by drying approximately 3.8 g of potassium acid phthalate and weighing it by difference into a flask as described. Carry the blank through the entire procedure.

NOTE 1—Potassium acid phthalate is used so that the concentration of the NaOH in contact with the solvent in the blank will be approximately the same as that in contact with the sample and so that the titration of the blank will be approximately the same as the titration of the sample, thus avoiding errors caused by using a different buret for the titration of the blank and the sample or by refilling the 15-mL buret. If desired, however, the potassium acid phthalate may be omitted.

21.2 If the acetyl content is 32 to 41 % or the acetic acid content is 45 to 57 %, put the sample into solution as follows: Add 150 mL of acetone and 5 to 10 mL of water and swirl to mix. Stopper the flask and allow it to stand with occasional swirling until solution is complete. Solution may be hastened by magnetic stirring or by any suitable mechanical shaking that will provide a gentle rocking type of agitation to avoid splashing the solution on the stopper. It is essential that complete solution be effected. Proceed in accordance with 21.4.

21.3 If the acetyl content is 41 to 44.8 % or the acetic acid content is 57 to 62.5 %, dissolve the sample by either of the following two methods:

21.3.1 Gently rotate the flask by hand to distribute and spread the sample in a thin layer over the bottom of the flask. Add 70 mL of acetone to the flask and swirl gently until the sample particles are completely wetted and evenly dispersed. Stopper the flask and allow it to stand undisturbed for 10 min. Carefully add 30 mL of dimethyl sulfoxide from a graduate to the flask, pouring the solvent down the sides of the flask to wash down any sample particles clinging to the side. Stopper the flask and allow it to stand with occasional swirling until solution is complete. Magnetic stirring or gentle mechanical agitation that will not splash the solution is recommended. When solution appears to be complete, add 50 mL of acetone and swirl or stir for 5 min. Proceed in accordance with 21.4.

21.3.2 Dimethyl sulfoxide is the preferred solvent, but if it is not available, spread the sample in a thin layer over the bottom of the flask, add 15 mL of acetone, swirl to wet the particles with acetone, stopper the flask, and allow the mixture to stand undisturbed for 20 min. Add 75 mL of pyridine without shaking or swirling, and allow to stand for 10 min. Heat the solution just to boiling and swirl or stir for 5 min. Again heat to boiling and swirl or stir for 10 min. Continue to heat and stir until the mixture is homogeneous and all large gel masses are broken down into individual highly swollen particles. When these highly swollen gel particles are well dispersed and are not fused together in large gel masses, no further heating is necessary. Cool the flask, add 30 mL of acetone, and swirl or stir for 5 min. Proceed in accordance with 21.4.

21.4 Add 30 mL of NaOH solution (40 g/L) with constant swirling or stirring to the solution of the sample and also to the blank. Use of a magnetic stirrer is recommended (Note 2). It is absolutely necessary that a finely divided precipitate of regenerated cellulose, free from lumps, be obtained. Stopper the flask and let the mixture stand with occasional swirling, or stir on the magnetic stirring unit. Allow 30 min for saponification of lower acetyl samples, 2 h for high acetyl samples when dimethyl sulfoxide is the solvent, and 3 h when pyridine is the solvent. At the end of the saponification period, add 100 mL of hot water, washing down the sides of the flask, and stir for 1 or 2 min. Add 4 or 5 drops of phenolphthalein indicator solution and titrate the excess NaOH solution with 1.0 *N* H_2SO_4 (Note 3). Titrate rapidly with constant swirling or stirring ring until the end point is reached; then add an excess of 0.2 or 0.3 mL of H_2SO_4. Allow the mixture to stand with occasional stirring or preferably stir on the magnetic stirrer for at least 10 min.