Designation: D 871 – 96

Standard Test Methods of Testing Cellulose Acetate[1]

This standard is issued under the fixed designation D 871; 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 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

This standard does not purport to address 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 1193 Specification for Reagent Water[2]

D 1343 Test Method for Viscosity of Cellulose Derivatives by Ball-Drop Method[3]

D 2929 Test Method for Sulfur Content of Cellulosic Materials by X-Ray Fluorescence[3]

D 5897 Test Method for Determination of Percent Hydroxyl on Cellulose Esters by Potentiometric Titration—Alternative Method[3]

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.[4] 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 D 1193.

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.

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

[1] These test methods are under the jurisdiction of ASTM Committee D-1 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] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 06.03.

[4] *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.

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 5 ⅜in. (136.5 mm) square, containing 25 compartments 1 in. (25.4 mm) 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. Then add 3 drops of phenolphthalein indicator solution to each flask and titrate the small excess of acid with 0.1 *N* NaOH solution to a persistent phenolphthalein end point. Take extreme care to locate this end point; after the sample is titrated to a faint pink end point, swirl the mixture vigorously or place it for a moment on the magnetic stirrer. If the end point fades because of acid soaking from the cellulose, continue the addition of 0.1 *N* NaOH solution until a faint persistent end point remains after vigorous swirling or stirring. Titrate the blank in the same manner as the sample.

NOTE 2—While the amount of magnetic stirring is somewhat optional, such stirring during the entire period of the determination is strongly recommended. Solution is more rapid, titrations are more rapid, and the end point can be approached directly and without a back titration.

NOTE 3—It is important to correct all 1.0 *N* H_2SO_4 buret readings for temperature and buret corrections.

22. Calculation

22.1 Calculate the percentage by weight of acetyl and acetic acid as follows:

$$\text{Acetyl or acetic acid, \%} = [(D - C)N_a + (A - B)N_b + P] \times (F/W) \quad \text{(Note 4)} \tag{2}$$

$$P = (GH \times 1000)/204.2$$

where:
A = NaOH solution required for titration of the sample, mL,
B = NaOH solution required for titration of the blank, mL,
N_b = normality of the NaOH solution,
C = H_2SO_4 required for titration of the sample, mL,
D = H_2SO_4 required for titration of the blank, mL,
N_a = normality the H_2SO_4,
F = 4.305 for acetyl and 6.005 for acetic acid,
P = milliequivalents of potassium acid phthalate,
G = potassium acid phthalate used, g,
H = purity factor for potassium acid phthalate, and
W = sample used, g.

NOTE 4—When equal volumes of alkali or acid are added to samples and blank, these amounts cancel out. Thus only the amounts of each added in the titration enter into the calculations. Use of potassium acid phthalate in the blank is recommended. When it is not used, the term P drops out of the equation.

23. Precision and Bias

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

Test Method B—Heterogeneous Saponification Method

24. Reagents

24.1 *Ethyl Alcohol* (75 Volume %)—Mix 790 mL of Formula 2B, 3A, or 30 denatured ethyl alcohol and 210 mL of water.

24.2 *Hydrochloric Acid* (0.5 *N*)—Prepare and standardize a 0.5 *N* solution of hydrochloric acid (HCl).

24.3 *Sodium Hydroxide, Standard Solution* (0.5 *N*)—Prepare and standardize a 0.5 *N* solution of sodium hydroxide (NaOH).

25. Procedure

25.1 Grind the sample in a Wiley mill or other suitable grinder so that 100 % will pass a No. 20 (850-µm). (Grinding may be omitted if the sample has suitable texture.) Dry about 1 g of the sample in a weighing bottle at 105 ± 3°C for 2 h, stopper, and cool in a desiccator. (An oven with mechanical circulation is to be preferred over a convection-type oven).

25.2 Weigh the bottle containing the sample to the nearest 0.001 g, transfer the sample to a 250-mL Erlenmeyer flask, and weigh the bottle again to the nearest 0.001 g. Handle the bottle with either tongs or a clean dry cloth during these manipulations. Add 40 mL of ethyl alcohol (75 %) to each sample. Include a blank determination with each set of samples and carry the blank determination through the complete procedure, including the back titration.

25.3 Heat the flasks, loosely stoppered, for 30 min at 50 to 60°C. Add 40 mL of 0.5 *N* NaOH solution to each flask and heat again at 50 to 60°C for 15 min. Stopper the flasks tightly and allow to stand at room temperature for about 48 h. If the acetyl content of the sample is over 43 %, or if the sample is hard and horny, allow to stand for about 72 h. At the end of this time back titrate the excess NaOH with 0.5 *N* HCl, using phenolphthalein as the indicator. Add an excess of about 1 mL of 0.5 *N* HCl and allow the NaOH to diffuse from the regenerated cellulose for several hours, or, preferably overnight. The disappearance of the pink color indicates the complete neutralization of the NaOH. Titrate the small excess of HCl with 0.5 *N* NaOH solution to a phenolphthalein end point. Extreme care must be taken to locate this end point. After the sample is titrated to a faint pink end point, stopper the flask and shake vigorously. The end point may fade because of acid diffusing from the cellulose. Continue the addition of 0.5 *N* NaOH solution and shaking until the faint pink end point persists after vigorous shaking of the flask.

26. Calculation

26.1 Calculate the percentage of combined acetyl or acetic acid as follows:

$$\text{acetyl or acetic acid, \%} = [(D - C)N_a + (A - B)N_b] \times (F/W) \quad (3)$$

where:
A = NaOH solution required for titration of the sample, mL,
B = NaOH solution required for titration of the blank, mL,
N_b = normality of the NaOH solution,
C = HCl required for titration of the sample, mL,
D = HCl required for titration of the blank, mL,
N_a = normality of the HCl solution,
F = 4.305 for acetyl or 6.005 for acetic acid, and
W = sample used, g.

HYDROXYL CONTENT

27. Scope

27.1 This test method is applicable to pyridine-soluble cellulose esters and is especially useful when the hydroxyl content is low. Samples containing plasticizer may be analyzed directly by this test method because the plasticizer is removed during washing of the carbanilate.

27.2 A preferred method is available in Test Method D 5897.

28. Summary of Test Method

28.1 Hydroxyl in cellulose acetate is determined by reaction with phenyl isocyanate in pyridine solution under anhydrous conditions to form the carbanilate derivative. The derivative is then analyzed for its carbanilate content by ultraviolet absorption.

28.2 The acetyl content of cellulose acetates may be calculated provided that the degree of polymerization is not excessively low.

29. Significance and Use

29.1 Hydroxyl content is a measure of the free hydroxyl on the cellulose backbone of the polymer. Hydroxyl content has a strong effect on the polymer's solubility and physical properties. Hydroxyl content also impacts the propensity for this polymer to crosslink with various crosslinking agents.

30. Apparatus

30.1 *Spectrophotometer*, complete with hydrogen light source and a set of four 1.00-cm quartz cells, or an equally

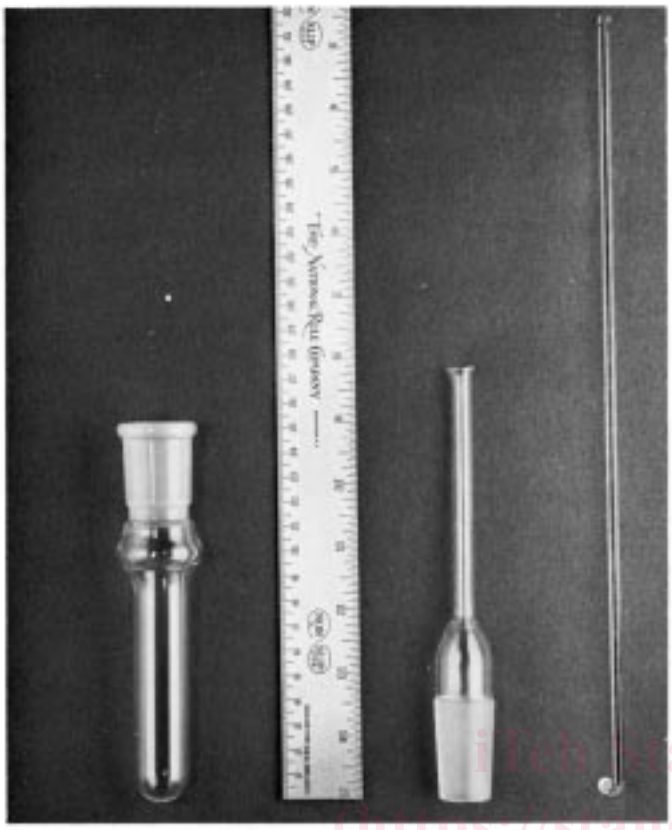

FIG. 1 Special Reflux Tube for Carbanilation

suitable apparatus. The wavelength calibration, as checked against a mercury lamp, shall be within the manufacturer's tolerances. As a further check, measure the absorbance of a potassium chromate (K_2CrO_4) solution prepared as follows: Dissolve 0.0400 g of K_2CrO_4 or 0.0303 g of potassium dichromate $K_2Cr_2O_7$ in 0.05 *N* potassium hydroxide (KOH) solution and dilute to 1 litre in a volumetric flask with 0.05 *N* KOH solution. Using the hydrogen lamp, measure the absorbance at 280 nm of a silica cell filled with the K_2CrO_4 solution and also of the same cell filled with water. The absorbance of the solution minus that of the blank shall be 0.723 ± 0.023.

30.2 *Bottles*, 4-oz, with screw caps, for washing the samples.

30.3 *Special Reflux Tubes* for the carbanilation, constructed as follows (see Fig. 1): Make a test tube approximately 20 by 150 mm from the outer part of a 24/40 standard-taper ground glass joint by closing the open end in a blast lamp. Draw the tubing on the inner joint to a constriction just above the joint. Cut the glass at that point and seal on a short length of 8-mm tubing to provide a bearing for a glass stirrer. Make a stirrer of 4-mm glass rod with a semicircle at right angles to the shaft at the bottom and small enough to fit into the test tube. When properly constructed this unit acts as an air condenser, thus preventing the loss of solvent by evaporation.

30.4 *Pipet*, serological-type, 5-mL capacity, graduated in 0.1-mL divisions.

30.5 *Büchner Funnel*, of a size accommodating 90-mm filter paper.

30.6 *Automatic Shaker*, with speed regulator mechanism.

30.7 *Electric Oven*, maintained at 105 ± 3°C.

30.8 *Oil Bath*, equipped with a rack to hold several of the special reflux tubes. This bath shall be kept between 115 and 120°C.

31. Reagents

31.1 *Acetone*.

31.2 *Ethyl Alcohol*, denatured, Formula 2B, 3A, or 30.

31.3 *Methylene Chloride-Methyl Alcohol Mixture*—Mix 9 parts by weight of methylene chloride with 1 part of methyl alcohol. This mixture should have an absorbance of less than 0.2 at 280 nm in a 1.00-cm silica cell measured against air. Pure methylene chloride has an absorbance of about 0.05, but the commercial product may have an absorbance as high as 1.00. The methylene chloride and methanol should be selected to have low absorbance; otherwise, they should be redistilled.

31.4 *Phenyl Isocyanate*.

31.5 *Pyridine*, redistilled, low water content, preferably less than 0.05 %.

32. Procedure

32.1 In the following procedure the phenyl isocyanate reagent shall be used under anhydrous conditions. Therefore, the sample, containers, pipet, and all other equipment shall be thoroughly dried.

32.2 Place a 0.5-g sample in a special reflux tube and dry in an electric oven at 105°C for 2 h. Remove the tube from the oven, add 5 mL of pyridine, assemble the reflux apparatus complete with glass stirring rod, and place in the 115 to 120°C oil bath. Stir occasionally until the sample is completely dissolved. Add 0.5 mL of phenyl isocyanate, stir thoroughly, and reflux in the oil bath for ½ h to complete the reaction. Use 0.1 mL of phenyl isocyanate for each percent of estimated hydroxyl content, but never less than 0.5 mL.

32.3 At the end of the reaction time, remove the sample and dilute it with acetone to the proper viscosity for precipitation. The amount of acetone used to thin the solution is a critical factor in acquiring a good precipitate. Samples having low viscosity require little, if any, dilution. The average sample requires the addition of about an equal volume of acetone. Precipitate the carbanilate by pouring the solution into about 200 mL of ethyl alcohol. The precipitate should be fluffy and white. Sticky precipitates indicate too little dilution. Stir the alcohol vigorously during precipitation. Filter off the precipitate, using paper on a Büchner funnel, with suction applied only as long as is necessary to remove the bulk of the solvent; prolonged suction may cause undesirable clumping together of the precipitate.

32.4 Wash by transferring the precipitate to a 4-oz screw cap bottle containing 75 mL of ethyl alcohol, capping securely, and shaking for ½ h on an automatic shaker at medium speed. Filter the precipitate on the Büchner funnel, pressing out as much liquid as possible with a glass stopper. Repeat the washing and filtering operations twice more. Allow the precipitate to air-dry 1 to 2 h at room temperature with good ventilation or preferably overnight to ensure complete removal of the alcohol. (Samples wet with alcohol may sinter and stick to paper or glass when dried at 105°C.) Dry the sample at

105°C in the oven for 1 h and cool in a desiccator. Small manila envelopes are convenient for drying and cooling the samples.

32.5 Weigh 0.1231 g of the dry precipitate into a 100-mL volumetric flask fitted with a ground-glass stopper. Add 60 to 80 mL of the methylene chloride-methyl alcohol mixture, and shake occasionally until complete solution occurs. Dilute to 100 mL and mix thoroughly. Using the spectrophotometer with a 1-cm silica cell measure the absorbance of the solution at 280 nm against the solvent mixture as a reference.

33. Calculation

33.1 Calculate the percentage of carbanilate, *c*, for a sample weight of 0.1231 g as follows:[5]

$$\text{Carbanilate, \%} = A \times 17.1 \quad (4)$$

where:

A = absorbance.

33.2 Calculate the percentage of hydroxyl as follows:

$$\text{Hydroxyl, \%} = 14.3c/(100 - c)$$

33.3 Calculate the percentage of acetyl as follows:

$$\text{Acetyl, \%} = (4480 - 65.1c) / (100 - c)$$

NOTE 5—The calculation for acetyl content assumes exactly three hydroxyls per anhydroglucose unit and applies to cellulose acetates only.

PRIMARY HYDROXYL CONTENT

34. Summary of Test Method

34.1 The primary hydroxyl content of cellulose acetate is determined by formation of the triphenylmethyl (trityl) ether and measurement of the trityl group by ultraviolet absorbance.[5] Trityl chloride reacts preferentially with primary hydroxyls. Since there is also a slight reaction with secondary hydroxyls, standardized reaction conditions are important.[6]

35. Apparatus

35.1 See Section 30.

36. Reagents

36.1 *Acetone*.

36.2 *Ethyl Alcohol*, denatured, Formula 2B, 3A, or 30.

36.3 *Methylene Chloride-Methyl Alcohol Mixture*—Mix 9 parts by weight of methylene chloride with 1 part of methyl alcohol. This mixture should have an absorbance of less than 0.2 at 259 nm in a 1-cm silica cell measured against air; otherwise the solvents should be redistilled.

36.4 *Pyridine*, redistilled to a water content less than 0.05 %. The water content may be reduced further by storing over a suitable drying agent, such as a molecular sieve, Type 4A.

36.5 *Trityl Chloride (Chlorotriphenylmethane or Triphenylmethyl Chloride)*, reagent grade.

37. Procedure

37.1 The reagents shall be used under anhydrous conditions. It is imperative that the sample and all equipment be thoroughly dry.

37.2 Place a 0.5-g sample in the test tube of the special reflux apparatus and dry for 2 h at 105 ± 3°C. Add 5 mL of pyridine, insert the top of the reflux apparatus and the stirrer and heat with stirring in a 115 to 120°C oil bath. After the sample has dissolved, add 0.5 g of trityl chloride. If the total hydroxyl content exceeds 3 %, use an additional 0.075 g of trityl chloride for each additional 1 % hydroxyl. Stir the mixture thoroughly and reflux in the oil bath for exactly 2 h at 115 to 120°C. Remove the tube and cool.

37.3 Dilute the sample with acetone to the proper viscosity for precipitation. The amount of acetone used to thin the solution is a critical factor in obtaining a good precipitate. Samples having low viscosity require little, if any, dilution. The average sample requires the addition of about an equal volume of acetone. Precipitate the trityl derivative by pouring the solution into about 200 mL of ethyl alcohol with vigorous stirring. The precipitate should be fluffy and white. Sticky precipitates indicate too little dilution. Separate the precipitate by filtering through paper on a Büchner funnel, with suction applied only as long as necessary to remove the bulk of the solvent; prolonged suction may evaporate the alcohol and cause the precipitate to partially redissolve in the remaining pyridine.

37.4 Wash the precipitate by transferring it to a 4-oz screw cap bottle containing 75 mL of ethyl alcohol, capping securely, and shaking for ½ h on a shaker at medium speed. Again collect the precipitate on a Büchner funnel, pressing out as much liquid as possible with a glass stopper. Repeat this washing and filtering operation twice more, or until the absorbance of the filtrate at 259 nm is about the same as that of an alcohol blank. Allow the precipitate to air-dry on the filter paper for ½ h at room temperature with good ventilation, or preferably overnight, to remove most of the alcohol. (Samples wet with alcohol may sinter or stick to paper or glass when dried at 105°C.) Transfer the sample to a manila envelope, dry it for 1 h at 105°C, and cool in a desiccator.

37.5 Weigh 0.1231 g of the dry trityl ether derivative into a 100-mL volumetric flask fitted with a ground-glass stopper, and dissolve in the methylene chloride-methyl alcohol mixture. Dilute to 100 mL and mix thoroughly. Measure the absorbance of this solution in a 1-cm silica cell using a spectrophotometer at 259 nm against the solvent as a reference.

38. Calculation

38.1 Calculate the trityl content, *t*, for this concentration of 0.1 g/100 g and with a correction of 0.015 for the absorbance of the cellulose acetate as follows:[7]

[5] Malm, C. J., Tanghe, L. J., Laird, B. C., and Smith, G. C., "Determination of Total and Primary Hydroxyl in Cellulose Esters by Ultraviolet Absorption Methods," *Analytical Chemistry*, ANCHA, Vol 26, 1954, p. 189.

[6] Malm, C. J., Tanghe, L. J., and Laird, B. C., "Primary Hydroxyl Groups in Hydrolyzed Cellulose Acetate," *Journal of the American Chemical Society*, JACSA, Vol 72, 1950, p. 2674.

[7] Wagner, R. H., and Russell, John, "Capillary Tube Viscometer for Routine Measurement of Dilute High Polymer Solutions," *Analytical Chemistry*, ANCHA, Vol 20, 1948, pp. 151–157.