Designation: ~~D817 – 96 (Reapproved 2010)~~ D817 – 12

Standard Test Methods of Testing Cellulose Acetate Propionate and Cellulose Acetate Butyrate[1]

This standard is issued under the fixed designation D817; 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 the testing of cellulose acetate propionates and acetate butyrates. These esters may vary widely in composition and properties, so certain of the procedures can be used only in the ranges of composition where they are suitable.

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

1.3 The test procedures appear in the following sections:

	Sections
Acetyl Propionyl or Butyryl Contents	28-37
Acetyl Content, Apparent	18-27
Acidity, Free	12-17
Ash	7-10
Color and Haze	77-81
Heat Stability	57-65
Hydroxyl Content	38-44
Hydroxyl Content, Primary	46-50
Intrinsic Viscosity	67-71
Moisture Content	5-6
Sulfur or Sulfate Content	51-56
Viscosity	74-75
Limiting Viscosity Number	67-71

1.4 *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:*[2]

D618 Practice for Conditioning Plastics for Testing

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

~~2.2 *ASTM Adjuncts:*~~

~~Color and Haze Apparatus[3]~~

3. Reagents

3.1 *Purity of Reagents*—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

[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.

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.

4. Conditioning

4.1 *Conditioning*—Condition the test specimens at 23 ± 2°C (73.4 ± 3.6°F) and 50 ± 5 % relative humidity for not less than 40 h prior to test in accordance with Procedure A of Practice D618, for those tests where conditioning is required. In cases of disagreement, the tolerances shall be ±1°C (±1.8°F) and ±2 % relative humidity.

4.2 *Test Conditions*—Conduct tests in the Standard Laboratory Atmosphere of 23 ± 2°C (73.4 ± 3.6°F) and 50 ± 5 % relative humidity, unless otherwise specified in the test methods. In cases of disagreements, the tolerances shall be ±1°C (±1.8°F) and ±2 % relative humidity.

MOISTURE CONTENT

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:

$$\text{Moisture, } \% = (A/B) \times 100 \tag{1}$$

~~*where:*~~
where:

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

ASH

7. Significance and Use

7.1 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.

8. Procedure

8.1 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. 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.

9. Calculation

9.1 Calculate the percentage of ash as follows:

$$\text{Ash, } \% = (A/B) \times 100 \tag{2}$$

~~*where:*~~
where:

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

10. Precision and Bias

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

[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.

FREE ACIDITY

11. Significance and Use

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

12. Reagents

12.1 *Acetone*, neutral.

12.2 *Methyl Red Indicator Solution (0.4 g/L)*—Dissolve 0.1 g of methyl red in 3.72 mL of 0.1000 *N* NaOH solution and dilute to 250 mL with water. Filter if necessary.

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

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

Test Method A—For Samples Containing Not More than About 30 % Propionyl or Butyryl

13. Procedure

13.1 Shake 5 g of the sample, 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 ester and wash it with water. Titrate the combined filtrate and washings with 0.01 *N* NaOH solution, using phenolphthalein indicator solution.

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

14. Calculation

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

$$\text{Free acetic acid, } \% = \{[(A - B)C \times 0.06]/W\} \times 100 \quad (3)$$

~~*where:*~~
where:

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

Test Method B—For Samples Containing More than About 7 % Propionyl or Butyryl and Particularly Suitable for Samples Containing More than 30 % Propionyl or Butyryl

15. Procedure

15.1 Dissolve 10.0 g of the sample, corrected for moisture content if necessary, in 200 mL of neutral acetone plus 20 mL of water. When completely dissolved, add 50 mL of water and shake well to precipitate the ester in a finely divided form. Add 3 drops of methyl red indicator solution and titrate to a lemon-yellow end point and 0.01 *N* NaOH solution.

15.2 Make a blank determination on the reagents.

16. Calculation

16.1 Calculate the free acid content as acetic acid as directed in Section 14.

17. Precision and Bias

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

APPARENT ACETYL CONTENT

18. Scope

18.1 The test methods described in the following Sections 20 to 26 cover the determination of the saponification value of the sample calculated as percentage of apparent acetyl, equivalent weight 43. This value is required in the calculation of acetyl and propionyl or butyryl contents in 36.1.

18.2 The test method used should be specified or agreed upon. The choice depends on the propionyl or butyryl content and the physical condition of the sample. Ordinarily, Test Method A is recommended for samples having less than about 35 % propionyl or butyryl and Test Method B for samples having more than that amount.

19. Significance and Use

19.1 Apparent acetyl content is a measure of the saponification value of the ester. Apparent acetyl value is required in the calculation of acetyl, propionyl, and butyryl content in 36.1.

Test Method A—For Samples Containing Less than About 35 % Propionyl or Butyryl

20. Apparatus

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

20.2 *Tray,* copper or aluminum, approximately 137 mm square, containing 25 compartments 25 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).

20.3 *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 NaOH solution (40 g/L).

20.4 *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.

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

20.6 *Magnetic Stirrer,* for single flask.

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

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

21. Reagents

21.1 *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 as above. The difference between the two titrations shall not exceed 0.05 mL.

21.2 *Dimethyl Sulfoxide.*

21.3 *Pyridine.*

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

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

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

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

22. Procedure

22.1 Dry the ground well-mixed sample in weighing bottle for 2 h at 105 ± 3°C and weigh 1.9 ± 0.05 g of the dried sample by difference to the nearest 1 mg into a 500-mL 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 above. 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.

22.2 For acetone-soluble sample, 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.

22.3 For acetone-insoluble samples of low propionyl or butyryl content, dissolve the sample by either of the following two methods:

22.3.1 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 22.4.

22.3.2 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 the mixture 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.

22.4 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 of 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 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 same 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.

23. Calculation

23.1 Calculate the percentage by weight of acetyl as ~~follows:~~ follows (see Note 4):

$$\text{Acetyl, \%} = \{[(D - C)N_a - (B - A)N_b + P] \times 0.04305\}/W \times 100 \quad (4)$$

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

(~~Note 4~~)

~~*where:*~~

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 of the H_2SO_4,
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.

Test Method B—For Cellulose Esters Containing More than 30 % Propionyl or Butyryl, by Varying the Reagents[4]

24. Reagents

24.1 *Acetone–Alcohol Mixture*—Mix equal volumes of acetone and methyl alcohol.

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

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

24.4 *Pyridine – Alcohol Mixture*—Mix equal volumes of pyridine and methyl alcohol.

[4] Malm, C. J., Genung, L. B., Williams, R. F., Jr., and Pile, M. A., "Analysis of Cellulose Derivatives: Total Acyl in Cellulose Organic Esters by Saponification in Solution," *Industrial and Engineering Chemistry*, Analytical Edition, IENAA, Vol 16, 1944, pp. 501–504.

24.5 *Sodium Hydroxide, Aqueous Solution (20 ~~g/L~~g/L)*—Dissolve 20 g of sodium hydroxide (NaOH) in water and dilute to 1 L with water.

24.6 *Sodium Hydroxide, Methanol Solution (20 ~~g/L~~g/L)*—Dissolve 20 g of NaOH in 20 mL of water and dilute to 1 L with methyl alcohol.

25. Procedure

25.1 Dry the sample for 2 h at 105 ± 3°C and cool in a desiccator. Weigh 0.5-g portions of the sample to the nearest 0.005 g and transfer to 250-mL glass-stoppered Erlenmeyer flasks. Dissolve each sample in 100 mL of appropriate solvent (see 25.2 and 25.3) and prepare at least two blanks, which shall be carried through all steps of the procedure.

25.2 *Samples Containing 30 to 45 % Propionyl or Butyryl*—Dissolve in 100 mL of the acetone–alcohol mixture. Add water and aqueous NaOH solution from a buret or pipet in the following order and swirl the contents of the flask vigorously during all additions: 10 mL of NaOH solution, 10 mL of water, 10 mL of NaOH solution, 5 mL of water, 20 mL of NaOH solution, and 5 mL of water. Stopper and allow to stand at room temperature for 16 to 24 h.

25.3 *Samples Containing More than 45 % Propionyl or Butyryl*—Dissolve in 100 mL of the pyridine–alcohol mixture. Add 30 mL of the methanol solution of NaOH from a pipet or buret slowly, with swirling. Add 20 mL of water slowly in about 2-mL portions, with swirling, and swirl the flask until the solution becomes turbid. Stopper and allow to stand overnight at room temperature.

25.4 Back-titrate the excess NaOH with 0.5 *N* HCl just to the disappearance of color, using phenolphthalein indicator solution.

26. Calculation

26.1 Calculate the apparent acetyl content as follows:

$$\text{Apparent acetyl, } \% = \{[(A - B)N_a \times 0.04305]/W\} \times 100 \quad (5)$$

~~*where:*~~
where:

A = HCl required for titration of the blank, mL,
B = HCl required for titration of the sample, mL,
N_a = normality of the HCl, and
W = sample used, g.

27. Precision and Bias

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

ACETYL AND PROPIONYL OR BUTYRYL CONTENTS

28. Scope

28.1 The test methods described in the following Sections 30 to 36 cover the determination of acetyl and propionyl or butyryl contents of cellulose mixed esters by calculation from the apparent acetyl content, determined in accordance with Sections 18 to 26, and the molar ratio of acetyl and propionyl or butyryl, determined in accordance with Sections 30 to 35. The molar ratio of acetyl and propionyl or butyryl is determined by saponifying, acidifying, vacuum distilling off the mixture of acids, and determining the distribution ratio of the acids between *n*-butyl acetate and water. The distribution ratios are also determined for acetic, propionic, and butyric acids, using samples of known high purity, and the molar ratio of the acids in the sample is calculated from these values.[5]

28.2 The saponification conditions are varied depending on the propionyl or butyryl content of the sample. Use Procedure A (Section 32) for samples containing less than about 35 % propionyl or butyryl, and use Procedure B (Section 33) for samples containing more than that amount.

28.3 Analyses for combined acetic, propionic, and butyric acids may be done by gas chromatographic methods. Difficulties encountered include ghosting in the columns, variation of factors with composition, and inconsistencies in the use of pure acids as standards. When such methods are used for this purpose, they shall be cross checked with the following partition method using suitable check batches to establish accuracy.

[5] Malm, C. J., Nadeau, G. F., and Genung, L. B., "Analysis of Cellulose Derivatives: Analysis of Cellulose Mixed Esters by the Partition Method," *Industrial and Engineering Chemistry*, Analytical Edition, IENAA, Vol. 14, 1942, pp. 292–297. This reference may be consulted for application to other mixed esters and to three-component mixtures.

29. Significance and Use

29.1 Acetyl and propionyl or butyryl content is a measure of the amount of each of these acids esterified onto the cellulose backbone of the polymer. The amount of substitution of these esters has a very strong effect on the polymer's solubility and physical properties.

30. Apparatus

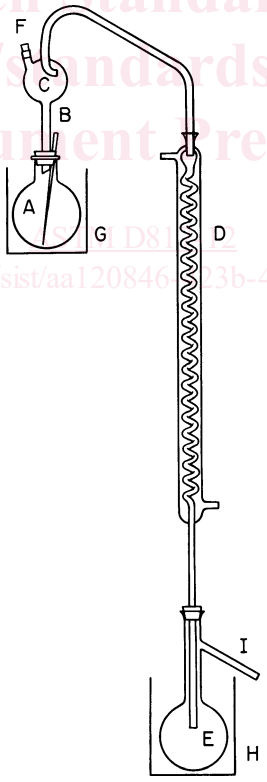
30.1 *Vacuum Distillation Apparatus*—The vacuum distillation apparatus shown in Fig. 1 will be required. The 500-mL round-bottom flask, *A*, shall be fitted with a stopper carrying a very small capillary inlet tube, *B*, and a Kjeldahl distilling head, *C*. The Kjeldahl distilling head shall be connected to a vertical condenser, *D*, having an outlet tube long enough to reach within 76.2 mm of the bottom of the 500-mL distilling flask, *E*, used as a receiver. The Kjeldahl distilling head shall be equipped with a funnel or stoppered opening, *F*, for adding extra water during the distillation. A water bath, *G*, for heating the sample and a cooling bath, *H*, for cooling the receiver shall be provided.

31. Reagents

31.1 *Acetic, Propionic, and Butyric Acids*—Acetic, propionic, and butyric acids of tested purity.

31.2 *Bromcresol Green Indicator Solution (0.4 g/L)*—Grind 0.1 g of tetrabromo-*m*-cresolsulfonphthalein in a mortar with 14.3 mL of 0.01 *N* NaOH solution and dilute to 250 mL.

31.3 *n-Butyl Acetate*—Prepare *n*-butyl acetate for use as an extraction solvent, free of acidity and water and containing not more than 2 % butyl alcohol. Check for acidity by shaking 60 mL of the *n*-butyl acetate with 30 mL of water in a 125-mL separatory funnel for about 1 min. Allow to settle, draw off the water layer, and titrate with 0.1 *N* NaOH solution, using phenolphthalein as the indicator. If this requires more than 0.02 mL of 0.1 *N* NaOH solution, the butyl acetate should be purified or a correction for acidity applied to each titration.



A—Flask containing sample (500-mL, round-bottom).
B—Capillary inlet tube.
C—Kjeldahl distilling head.
D—Condenser.
E—Receiver (500-mL distilling flask).
F—Opening for adding water.
G—Water bath for heating sample.
H—Cooling bath for receiver.
I—Side arm, connected to vacuum line.

FIG. 1 Vacuum Distillation Apparatus for Mixed-Ester Analysis

31.4 *Ethyl Alcohol*, Formula 2B, 3A, or 30 (denatured).

31.5 *Phosphoric Acid (1 + 14)*—Dilute 68 mL of phosphoric acid (H_3PO_4, 85 %) to 1 L with water. Titrate the NaOH solution (20 g/L) with this acid to a yellow end point, using bromcresol green indicator solution, and calculate the volume of the acid (approximately 50 mL) required for 100 mL of the NaOH solution.

31.6 *Sodium Hydroxide Solution (20 g/L)*—Dissolve 20 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

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

Isolation of the Mixed Acids

32. Procedure A—For Samples Containing Less than About 35 % Propionyl or Butyryl

32.1 Heat duplicate 3-g portions of the sample, not especially dried nor accurately weighed, with 100 mL of NaOH solution (20 g/L) in 500-mL, round-bottom, chemically resistant glass flasks in a water bath at 40°C for 48 to 72 h. At the end of this time add the required amount (approximately 50 mL) of H_3PO_4 (1 + 14) to each flask to form monosodium phosphate, which liberates the organic acids from their sodium salts.

32.2 Assemble the vacuum distillation apparatus as illustrated in Fig. 1. Heat the 500-mL round-bottom flask containing the sample in a water bath, and vacuum-distill the acid solutions to dryness, allowing a small stream of air bubbles to enter to avoid bumping. Keep the receiver cooled to 0°C. Add 25 mL of water to the residue in each flask and again distill to dryness. Repeat the distillation to dryness with a second 25-mL portion of water.

NOTE 5—In this operation it is not necessary to work with quantitative accuracy at all stages, but it is necessary to obtain water solutions of the acids in the same ratios as they occur in the esters. The volume of the distillate and rinsings is usually 200 to 250 mL, which in the majority of cases automatically adjusts the acidity of the distillate to 0.06 to 0.12 *N*, the range desired for subsequent extractions.

32.3 Continue as directed in Section 34.

33. Procedure B—For Samples Containing More than About 35 % Propionyl or Butyryl

33.1 Weigh duplicate 3-g samples, not especially dried nor accurately weighed, into 500-mL round-bottom flasks and add 100 mL of Formula 2B, 3A, or 30 denatured ethyl alcohol and 100 mL of NaOH solution (20 g/L) to each flask. Allow the samples to stand stoppered at room temperature for 48 to 72 h. At the end of this period, filter off the regenerated cellulose, collecting the filtrates in 500-mL round-bottom flasks.

33.2 Assemble the vacuum-distillation apparatus as illustrated in Fig. 1. Heat the flasks in the water bath and vacuum-distill off all the alcohol. After distilling to dryness, release the vacuum, rinse out the distillation heads, condensers, and receivers, and discard the distillates and rinsings.

33.3 Add the required amount, about 50 mL, of H_3PO_4 (1 + 14) to form monosodium phosphate, which liberates the organic acids from their sodium salts. Also add 100 mL of water to each flask and reassemble the distillation apparatus. Vacuum-distill the volatile acids as described in 32.2.

33.4 Continue as directed in Section 34.

Determination of the Molar Ratios of the Acids

34. Procedure

34.1 Titrate a 25-mL portion of the distillate (32.2) with 0.1 *N* NaOH solution, using phenolphthalein as the indicator. Designate the volume of NaOH solution required as *M*. Shake 30 mL of the distillate in a small separatory funnel with 15 mL of *n*-butyl acetate. Measure these volumes accurately using pipets and burets. Shake the mixture thoroughly for 1 min, allow the layers to separate for 2 min, and draw off the aqueous (lower) layer. Pipet out 25 mL of the solution and titrate with 0.1 *N* NaOH solution (Note 6). Designate the volume of NaOH solution required as M_1. Calculate *K*, the percentage partition ratio of the acids in the distillate, as follows:

$$K = (M_1/M) \times 100 \quad (6)$$

NOTE 6—It should be kept in mind that all these determination are ratios and not quantitative; however, accuracy of duplication is very important. All measurements must be made as exactly as those made by standardizations of the solutions and equipment.

34.2 In the same manner determine the distribution ratios for acetic, propionic, and butyric acids. Dilute a sample of each acid of tested purity with water to give an approximately 0.1 *N* solution. Titrate 25-mL portions and extract 30-mL portions, following exactly the same procedure as used for the mixtures (34.1). Calculate the partition ratios for the pure acids, as decimal fractions, as follows (Note 7):

$$k = M_1/M \quad (7)$$

where:

where:

k_a = distribution ratio for acetic acid under the conditions described,
k_p = distribution ratio for propionic acid under the conditions described, and
k_b = distribution ratio for butyric acid under the conditions described.

NOTE 7—The constants must be checked occasionally and must be determined by each operator for each supply of butyl acetate. Blanks should be run on the butyl acetate, since it may develop acidity on standing, particularly if it contains a little water. All measurements should be made with good pipets or burets and extreme care and cleanliness observed during the whole operation. The accuracy of the procedure can be checked by testing an acid mixture of known composition.

35. Calculation

35.1 Calculate the molar ratios of acetic and propionic or butyric acids in the mixed acids as follows (Note 8):

$$P = (100k_a - K)/(k_a - k_p) \quad (8)$$

$$A = 100 - P \quad (9)$$

$$B = (100k_a - K)/(k_a - k_b) \quad (10)$$

$$A = 100 - B \quad (11)$$

~~*where:*~~

where:

P = percentage of propionic acid, mol,
B = percentage of butyric acid, mol,
A = percentage of acetic acid, mol,
K = percentage distribution ratio of the acids in the distillate (34.1),
k_a = distribution ratio of acetic acid (34.2),
k_p = distribution ratio of propionic acid (34.2), and
k_b = distribution ratio of butyric acid (34.2).

NOTE 8—In order to evaluate two unknowns, two simultaneous algebraic equations involving the two unknown quantities are necessary. In the case of a binary acid mixture, the sum of the mol percentages of the acids present represents the total acidity, or 100 %. If A and B represent the mole percentages of acetic and butyric acids, respectively:

$$A + B = 100 \quad (12)$$

$$Ak_a + Bk_b = K \quad (13)$$

The distribution ratios k_a and k_b are known and refer to the pure individual acids, whereas the distribution ratio K refers to the binary mixture. By solving these equations for B, the equations given in this section may be derived.

Calculation of Acetyl, Propionyl, and Butyryl Contents

36. Calculation

36.1 Calculate the percentages by weight of acetyl, propionyl, and butyryl as follows:

$$\text{Acetyl, \%} = AC/100 \quad (14)$$

$$\text{Propionyl, \%} = (PC/100) \times (57/43) \quad (15)$$

$$\text{Butyryl, \%} = (BC/100) \times (71/43) \quad (16)$$

~~*where:*~~

where:

A = percentage of acetic acid (Section 35), mol,
P = percentage of propionic acid (Section 35), mol,
B = percentage of butyric acid (Section 35), mol, and
C = percentages by weight of apparent acetyl (Sections 23 and 26).

36.2 Hydroxyl can be measured precisely, particularly at high degrees of esterification (Sections 38 to 44). It is therefore sometimes advantageous to base the calculation of weight percentages of acetyl, propionyl, and butyryl on hydroxyl content rather than on apparent acetyl as in 36.1. The equations for this calculation are as follows:

For cellulose acetate propionates:

$$\text{Acetyl, \%} = 9.15A\ (31.5 - h)/(786 - A) \quad (17)$$

$$\text{Propionyl, \%} = 2.93P\ (31.5 - h)/(786 - A) \quad (18)$$

For cellulose acetate butyrates:

$$\text{Acetyl, \%} = 4.88A\ (31.5 - h)/(443 - A) \quad (19)$$

$$\text{Butyryl, \%} = 8.05B\ (31.5 - h)/(443 - A) \quad (20)$$

where, in addition to the definitions of terms in 36.1:
h = weight percentage of hydroxyl (Section 44).

NOTE 9—This calculation involves the assumption that there are exactly three hydroxyls, free plus esterified, for each anhydroglucose unit of cellulose.

37. Precision and Bias

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

HYDROXYL CONTENT

38. Scope

38.1 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).

38.2 A preferred method is available in Test Method D5897.

39. Summary of Test Method

39.1 Hydroxyl in cellulose esters 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.

40. Significance and Use

40.1 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.

41. Apparatus

41.1 *Spectrophotometer,* complete with hydrogen light source and a set of four 1.00-cm quartz cells or an equally suitable apparatus. The wavelength calibration, as checked against a mercury lamp, shall be within the manufacturer's tolerances. As a further check, measure the density 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 L 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.

41.2 *Bottles,* 112-g (4-oz), with screw caps, for washing the samples.

41.3 *Special Reflux Tubes* for the carbanilation, constructed as follows (see Fig. 2): Make a test tube approximately 20 by 150 mm from the outer part of a standard-taper 24/40 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 the 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.

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

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

41.6 *Automatic Shaker,* with speed regulator mechanism.

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

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

42. Reagents

42.1 *Acetone.*

42.2 *Ethyl Alcohol,* Formula 2B, 3A, or 30 (denatured).

42.3 *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 methyl alcohol should be selected to have low absorbance; otherwise, they should be redistilled.

42.4 *Phenyl Isocyanate.*

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