Designation: D5897 – 13

Standard Test Method for Determination of Percent Hydroxyl on Cellulose Esters by Potentiometric Titration—Alternative Method[1]

This standard is issued under the fixed designation D5897; 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 covers a procedure for determining the percent hydroxyl on cellulose esters by potentiometric titration. The typical range of percent hydroxyl measured is 0.7 to 10.0 %.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D817 Test Methods of Testing Cellulose Acetate Propionate and Cellulose Acetate Butyrate

D871 Test Methods of Testing Cellulose Acetate

3. Summary of Test Method

3.1 The cellulose ester is dissolved in pyridine and the hydroxyl sites on the cellulose ester are acetylated with acetic anhydride in the presence of basic catalyst, 1-methylimidazole. The excess acetic anhydride is hydrolyzed and the resulting acetic acid is titrated with sodium hydroxide. An automatic titrator dispenses the titrant, potentiometrically determines the endpoint, and calculates the percent hydroxyl on the cellulose ester based on a blank determination.

4. Significance and Use

4.1 This test method provides a simpler means for the determination of the hydroxyl content of cellulose esters than the preparation and measurement of the carbanilate derivative described in Test Methods D817 and D871.

4.2 The hydroxyl content is an important indicator of solubility and reactivity.

5. Interferences

5.1 Undissolved ester may accumulate on the sides of the flask and on top of the stirring-star during dissolution, leading to low results. Gently swirling the solution during titration can reduce this problem.

5.2 The ground glass joints of the flask and the air condenser must always be rinsed into the flask with hydrolyzing solution at the point of hydrolysis and before titration. This will prevent erroneous results from material that may have refluxed into the joint.

6. Apparatus

6.1 *Titrator,* equipped with *Glass Electrode*.

6.2 *Heating/Stirring Module,* six-place.

6.3 *Heating/Stirring Block,* cut from polished-finish aluminum block to fit stirrer in 6.2 (see Fig. 1 for dimensions).

6.4 *Stirrer,* six place.

6.5 *Magnetic Stirrers,* size 25 mm and 50 mm.

6.6 *Stirring Bar.*

6.7 *Flask and Air Condenser,* (see Fig. 2 for dimensions).

6.8 *Bottle-Top Dispensers,* capable of dispensing 20 mL, 35 mL, and 50 mL, or equivalent.

6.9 *Analytical Balance,* capable of weighing 250 g to the fourth decimal place.

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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] 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.

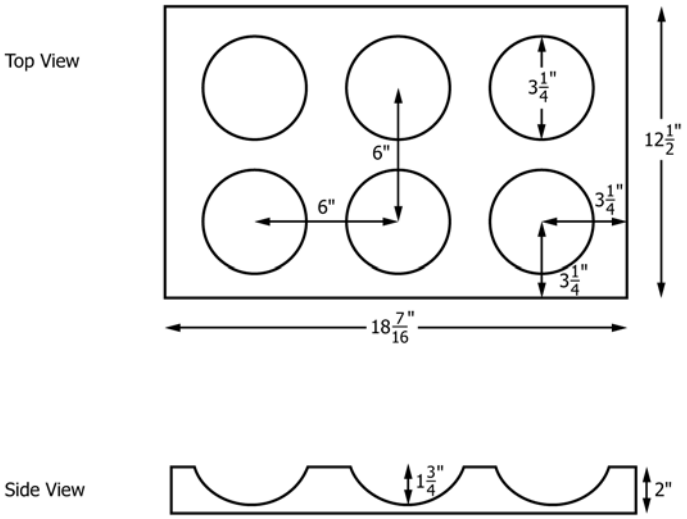


FIG. 1 Heating/Stirring Block Dimensions

6.10 *Analytical Balance,* capable of weighing 1000 g to the second decimal place.

7. Reagents and Materials

7.1 *Purity of Reagents*—American Chemical Society[3] reagent grade chemicals shall be used throughout this test unless otherwise indicated.

7.2 *Pyridine.*

7.3 *Acetic Anhydride.*

7.4 *Acetylating Solution*—115 ± 0.50 g of acetic anhydride per litre of pyridine. The container needs to be equipped with 20-mL buret. The shelf-life of this solution is 5 days.

7.5 *Dimethylformamide.*

7.6 *Deionized Water,* purified to 18.3 MΩ resistance.

7.7 *Hydrolyzing Solution*—Mix 600 mL dimethylformamide, 300 mL pyridine, and 100 mL water in a 1-L bottle equipped with a bottle top dispenser capable of dosing 35 mL. Stir for at least 10 min prior to use. The shelf-life of this solution is 1 month.

7.8 *1-Methylimidazole.*

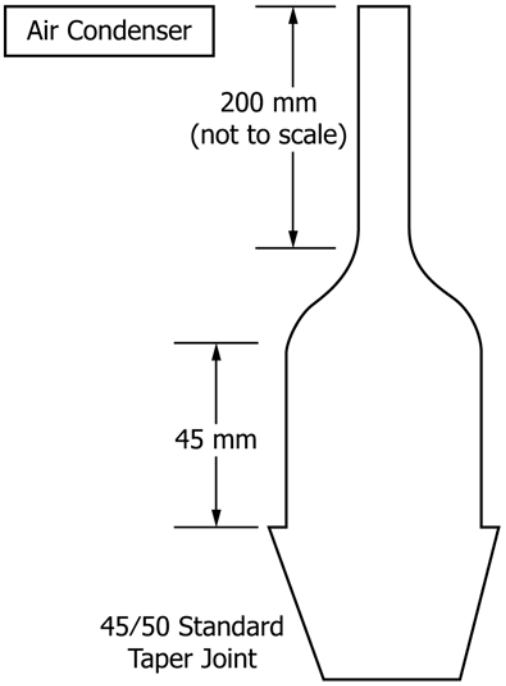
7.9 *Sucrose.*

7.10 *Acetone.*

7.11 *Potassium Acid Phthalate (KHP),* National Institute of Standards and Technology primary standard grade. Store in desiccator, after drying for 1 h at 105°C (±5°C).

7.12 *Methanol.*

7.13 *Sodium Hydroxide,* 0.5 *N* in methanol. This solution has a shelf life of 2 weeks.



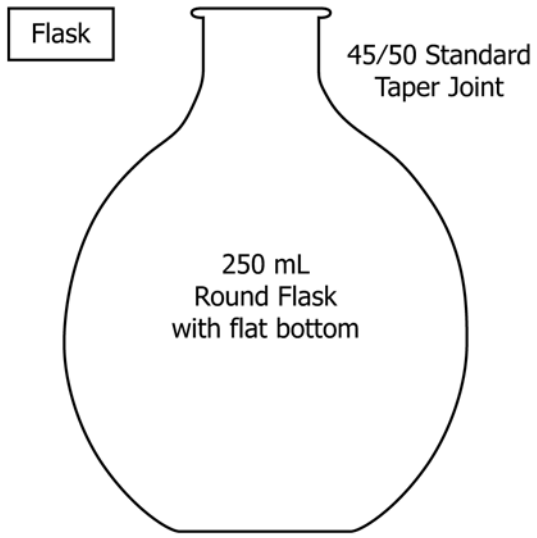


FIG. 2 Flask and Air Condenser Dimensions

7.14 *Traceable Buffers,* pH 4 and pH 7, available from National Institute of Standards and Technology.

7.15 *Potassium Chloride (KCl),* 5 *M*, weigh 37.3 g (±0.3000 g) of KCl into a 100-mL volumetric flask. Dilute to the mark with purified water. Shake into solution.

7.16 1,2-*Dichloroethane*.

8. Calibration and Standardization

8.1 *Calibration of the Electrode:*

NOTE 1—If the electrode is new, perforate the nipple on the rubber cap

[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.

and soak the electrode in 5 M potassium chloride for 1 h. Store in pH 4 buffer until use.

8.1.1 Select from the titrator menu the procedure for calibration of the electrode.

8.1.2 Add about 50 mL of pH 4 buffer into a titration cup and lower the electrode into it.

8.1.3 Run the procedure for the titrator to read the correct pH.

8.1.4 Repeat process 8.1.1 – 8.1.3 for buffer pH 7.

8.1.5 Make sure that the calibration is done when a new electrode is put into use and then check once/month thereafter or when a problem is suspected.

8.2 *Standardization of Methanolic 0.5 N Sodium Hydroxide:*

8.2.1 Weigh approximately 1.5 ± 0.1000 g of KHP into a titration cup and record the weight. Add about 35 mL of purified water and allow to dissolve.

8.2.2 Ensure that the burette is flushed with the 0.5 *N* NaOH.

8.2.3 Titrate the sample.

8.2.4 Normality is calculated as follows:

$$N = \frac{W \times 1000}{\text{mL} \times 204.23} \quad (1)$$

where:

W = weight of KHP in g,
mL = volume of titrant used for titration, and
204.23 = formula weight of KHP.

9. Procedure[4,5]

9.1 *Blank Determination*—This has to be done every time new reagents are used.

9.1.1 Flush burettes delivering the reagent, clearing tubing of air bubbles.

9.1.2 Dispense 1.0 mL 1-methylimidazole and 20 mL acetylating solution into three flasks.

9.1.3 Immediately place air condenser in the flask, and dispense 35 mL of the hydrolyzing solution into the flask through the air condenser.

NOTE 2—Dispense 35 mL immediately through the air condenser after addition of the acetylation solution, one sample at the time.

9.1.4 Let the three blanks stir for at least 20 min at room temperature, then dose 50 mL of 1,2-dichloroethane into the flask through the air condenser. Remove the air condensers from each flask, and rinse them including the ground-glass joint with the hydrolyzing solution.

9.1.5 Titrate the solutions. The average of the three blanks will be used for this test if their relative standard deviation <0.3 %.

9.2 *Control Percent Hydroxyl Determination*—Sucrose is used as a statistical control sample for this test. The sucrose control sample is run on a regular schedule, and when the reagents or equipment has changed.

9.2.1 Dispense 1.0 mL 1-methylimidazole and 20 mL acetylating solution into the flask containing a spin-type stirring bar. Set the flask into a heating block at 115 ± 5°C.

9.2.2 Weigh 0.25 g ± 0.0100 g of sucrose into a weighing pan, and then tare the balance. Remove the condenser from the flask and add the sample into the solution while it is still stirring. Immediately replace the condenser and set the weighing pan back on the balance. Record the weight from the balance as the weight of the sucrose.

9.2.3 Let the sucrose solution stir at 115 ± 5°C for 30 min.

9.2.4 Dispense 35 mL of the hydrolyzing solution into the flask through the air condenser. Remove the air condensers from each flask, and rinse them, including the ground-glass joint into the flask with the hydrolyzing solution. Replace the air condenser in the flask and let stir for at least 20 min at room temperature.

9.2.5 Dose 50 mL of 1,2-dichloroethane into the flask through the air condenser. Remove the air condensers from each flask, and rinse them, including the ground-glass joint with the hydrolyzing solution.

9.2.6 Lower the buret tip and electrode into the flask and titrate the solution.

9.2.7 The percent hydroxyl is calculated as follows:

$$\frac{[(\text{mL blank} - \text{mL sample}) \times N \times 17]}{\text{grams sample} \times 1000} \times 100\,\% \quad (2)$$

where:

N = normality of NaOH (~0.5),
17 = molecular weight hydroxyl group, and
1000 = conversion of mL to L.

9.2.8 Plot the sucrose percent hydroxyl on a control chart with the following parameters: Average: 39.85 %, Upper control limit: 41.00 %, and lower control limit: 38.70 %. Follow normal statistical process control (SPC) procedures.

9.3 *Cellulose Esters Samples Percent Hydroxyl Determination:*

9.3.1 Dry the sample at 105 ± 5°C for 1 h. Remove from the oven, cap, and allow to cool for 15 min in a desiccator.

9.3.2 Dispense 1.0 mL of 1-methylimidazole and 20.0 mL of acetylating solution into the flask containing a stirring bar in the same way as the preparation for the blanks.

9.3.3 Weigh 1.5 ± 0.1000 g of the sample into a weighing pan. Tare the balance with the weighing pan and sample on it. Remove the condenser from the flask and add the sample into the flask containing the solution. Immediately replace the condenser and set the weighing pan back on the balance. Record the weight from the balance as the weight of the sample. Set the flask into a heating block at 115 ± 5°C.

9.3.4 Let the sample stir at 115 ± 5°C for 30 min.

9.3.5 Dispense 35 mL of the hydrolyzing solution into the flask through the air condenser. Remove the air condensers from each flask, and rinse them, including the ground-glass joint into the flask with the hydrolyzing solution. Replace the air condenser in the flask and let stir for at least 20 min at room temperature.

9.3.6 Dose 50 mL of 1,2-dichloroethane into the flask through the air condenser. Remove the air condensers from

[4] Siggia, S. and Hanna, J. G., "Quantitative Organic Analysis via Functional Groups," *Wiley-Interscience Publication*, New York, 1979.

[5] Conners, K. A. and Pandit, N. K., "N-methylimidazole as a Catalyst for Analytical Acetylations of Hydroxy Compounds," *Analytical Chemistry*, Vol 50, No. 11, 1978.

each flask, and rinse them including the ground-glass joint with the hydrolyzing solution.

9.3.7 Lower the buret tip and electrode into the flask and titrate the solution.

9.3.8 The percent hydroxyl is calculated in the same way as for the sucrose control.

10. Report

10.1 Report the percent hydroxyl to two decimal places.

11. Precision and Bias

11.1 *Precision*—The precision data is based on 30 pairs of cellulose acetate samples. The data was gathered over a period of three months by two analysts. At the 95 % confidence interval the percent hydroxy at a level of 3.65 % should differ no more than 0.06 % absolute for duplicate analysis.

11.2 *Bias*—No suitable reference material is available to determine a bias.

12. Keywords

12.1 cellulose esters; percent hydroxyl; potentiometric titration