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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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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 D 5897; 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 %.

2. Referenced Documents

2.1 *ASTM Standards:*

D 817 Test Methods of Testing Cellulose Acetate Propionate and Cellulose Acetate Butyrate[2]

D 871 Test Methods of Testing Cellulose Acetate[2]

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 D 817 and D 871.

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*,[3] equipped with *Glass Electrode*, or equivalent.

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

6.3 *Heating/Stirring Block*, cut from polished-finish aluminum block to fit stirrer in 7.2 (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.

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[4] 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.

[1] This test method is under the jurisdiction of ASTM Committee D-1 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] *Annual Book of ASTM Standards*, Vol 06.03.

[3] Titrator and instruction manual such as Mettler DL77 equipped with DG-115-SC glass electrode available from Mettler Toledo Inc., 69 Princeton-Hightestown, P.O. Box 71, Hightestown, NJ 08520 has been found suitable for this purpose.

[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

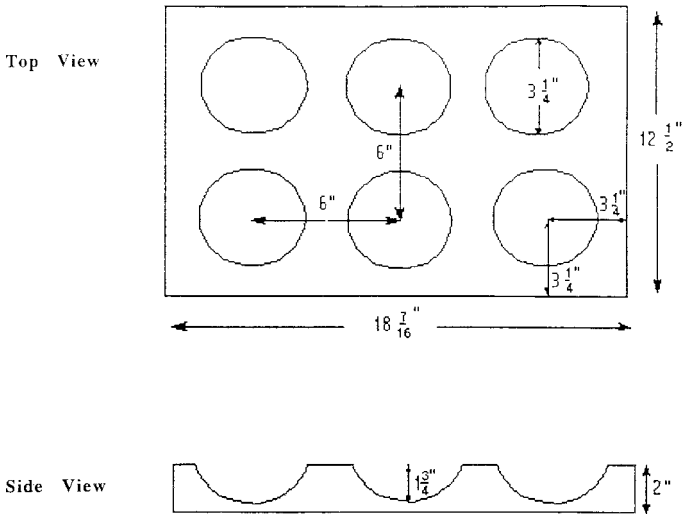


FIG. 1 Heating/Stirring Block Dimensions

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.

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 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 9.1.1-9.1.3 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.

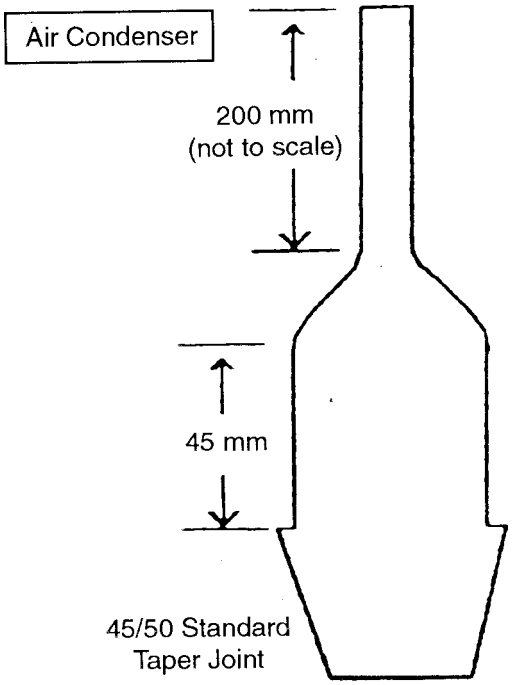
8.2 *Standardization of Methanolic 0.5 N Sodium Hydroxide*:

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:



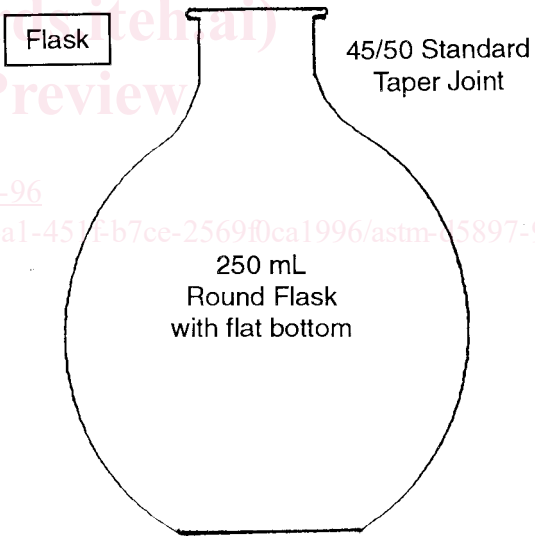


FIG. 2 Flask and Air Condensor Dimensions

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

where:

W = weight of KHP in g,

mL = volume of titrant used for titration, and

204.23 = formula weight of KHP.

9. Procedure[5,6]

9.1 *Blank Determination*—This has to be done everytime

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