Designation: E 335 – 96

AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Hydroxyl Groups by Pyromellitic Dianhydride Esterification[1]

This standard is issued under the fixed designation E 335; 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 Department of Defense.

1. Scope

1.1 This test method covers the determination of hydroxyl groups attached to primary and secondary carbon atoms in aliphatic and alicyclic compounds. It is not suitable for the determination of hydroxyl groups attached to tertiary carbon atoms. Phenolic hydroxyl groups do not react.

NOTE 1—Other methods for determination of hydroxyl groups are given in ASTM Test Method D 1957, Test Method for Hydroxyl Value of Fatty Oils and Acids,[2] ASTM Methods D 2849, Methods of Testing Urethane Foam Polyol Raw Materials,[3] ASTM Test Methods E 222, Test Methods for Hydroxyl Groups by Acetic Anhydride Acetylation,[4] ASTM Test Method E 326, Test Method for Hydroxyl Groups by Phthalic Anhydride Esterification,[4] ASTM Test Method E 567, Test Method for Tertiary Hydroxyl Groups with Hydrogen Bromide,[4] and Test Methods D 2195, Test Methods for Pentaerythritol.[2]

1.2 *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.* Specific precautionary statements are given in Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[5]
E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[4]
E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[4]
E 203 Test Method for Water Using Karl Fischer Reagent[4]
E 287 Specification for Burets[6]
E 300 Practice for Sampling Industrial Chemicals[4]

3. Terminology

3.1 *Definition:*

3.1.1 *hydroxyl number*—the milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of material. In the case of pure compound, the hydroxyl number is inversely proportional to the hydroxyl equivalent weight:

$$\text{Equivalent weight (g/equivalent)} = \frac{56100}{\text{hydroxyl number}} \quad (1)$$

4. Summary of Test Method

4.1 The hydroxyl group is esterified by reaction with pyromellitic dianhydride in a dimethyl sulfoxide-pyridine medium at approximately 100°C. The excess anhydride is hydrolyzed with water and the pyromellitic acid formed is titrated to the phenolphthalein end point with standard sodium hydroxide solution. The hydroxyl content is calculated from the difference in titration of the blank and the sample solution.

5. Significance and Use

5.1 Hydroxyl is an important functional group and knowledge of its content is required in many intermediate and end-use applications. This test method is for the determination of primary and secondary hydroxyl groups and can be used for the assay of compounds containing them.

6. Interferences

6.1 Primary and secondary amines and mercaptans usually will react quantitatively along with the hydroxyl group. Tertiary aliphatic amines may be sufficiently basic to cause end-point errors in the titration. In this case, potentiometric determination of the end point may improve the precision of this test method.

6.2 Tertiary alcohols will interfere with the accuracy of this test method. Easily saponified esters will interfere during the titration. This interference, usually indicated by a fading end point, can be minimized by cooling the solution before titration.

6.3 Ethers other than epoxides-saturated aldehydes or compounds that produce a free carbonyl group under the conditions of the reaction do not interfere.

6.4 Excessive amounts of water in the sample will interfere by consuming the reagent. A small amount of water can be accommodated by adjustment of the sample size used for analysis (Note 4).

6.5 Free acids interfere by consuming the standard alkali solution and strong bases interfere by consuming an equivalent

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[1] This test method is under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and is the direct responsibility of Subcommittee E15.22 on Functional Groups.

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[2] *Annual Book of ASTM Standards*, Vol 06.03.
[3] *Annual Book of ASTM Standards*, Vol 08.02.
[4] *Annual Book of ASTM Standards*, Vol 15.05.
[5] *Annual Book of ASTM Standards*, Vol 11.01.
[6] *Annual Book of ASTM Standards*, Vol 14.02.

amount of pyromellitic acid. Provisions for determining and applying corrections for these interferences are included in this test method. Some of the higher fatty acids may be converted to anhydrides, releasing water which will consume the esterification reagent.

6.6 Due to reaction of alcohol, even at room temperature, the indicator solution must not be prepared in this solvent.

7. Apparatus

7.1 *Buret,* 100-mL total capacity, range of graduated portion 50 mL, 0.1-mL graduation, preferably equipped with a PTFE stopcock (Note 7). Complete specifications are given in Specification E 287.

7.2 *Flasks*, Erlenmeyer, 300 mL with glass stoppers.

7.3 *Pipet,* 50-mL transfer.

7.4 *Steam Bath,* 100°C.

8. Reagents

8.1 *Purity of Reagents*—Use reagent grade chemicals 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.[7] 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water as defined in Specification D 1193.

8.3 *Dimethylsulfoxide*—**Caution**—See 9.1.

8.4 *Pyridine*—**Caution**—See 9.2.

8.5 *Pyromellitic Dianhydride*, [8] 90 % minimum assay. A method for assaying the material is given in the Appendix X1.

NOTE 2—Pyromellitic dianhydride that is low in anhydride content due to pickup of water, may be regenerated by drying at 170°C for 48 h.

8.6 *Esterification Reagent* (0.5 *M*)—Dissolve a weight of reagent containing 109 g of pyromellitic dianhydride (gram reagent × 100/percent of pyromellitic dianhydride) in 525 mL of dimethylsulfoxide, then add 425 mL of pyridine. The solution should be clear. If necessary filter through a sintered glass funnel (do not use filter paper).

8.7 *Hydrochloric Acid, Standard* (0.5 *N*)—Prepare and standardize hydrochloric acid (HCl) in accordance with the appropriate sections of Practice E 200. Determine and record the temperature at which the standardization was performed. The concentration of the solution shall be corrected to the temperature at which the determination is performed using the Eq 2 given in 8.9. The factor for the thermal expansion of this solution is 0.00014. This solution is required only if a correction is to be applied for presence of strong base in the sample being analyzed.

8.8 *Phenolphthalein Solution in Pyridine* (10 g/L)—Dissolve 1 g of phenolphthalein in pyridine and dilute with pyridine to 100 mL[9].

8.9 *Sodium Hydroxide, Standard Solution* (1.0 *N*)—Prepare and standardize sodium hydroxide (NaOH) solution in accordance with the appropriate sections of Practice E 200. Determine and record the temperature at which the standardization was performed. The factor for thermal expansion of this solution is 0.00035. For calculation of the hydroxyl content, the normality of the solution shall be corrected to the temperature at which the determination is performed using the following Eq 2:

$$N_{t2} = N_{t1} + (t_1 - t_2)(\ 0.00035) \quad (2)$$

where:

N_{t1} = normality when standardized,
N_{t2} = normality during analysis of samples,
t_1 = temperature of solution during standardization, °C, and
t_2 = temperature of solution during analysis of samples, °C.

9. Precautions

9.1 *Dimethylsulfoxide* — Dimethylsulfoxide is recognized as an experimental teratogen by the National Institute of Occupational Safety and Health. Precautions should be taken, especially by women of childbearing capability, to avoid exposure by skin contact or inhalation of vapors.

9.1.1 Also, dimethylsulfoxide penetrates the skin rapidly and could act as a carrier for other substances dissolved in it or present on the skin. It has analgesic properties.

9.1.2 If solutions containing dimethylsulfoxide contact the skin, the affected area should immediately be washed thoroughly with water.

9.2 *Pyridine*—Pyridine is mildly irritating to the skin. Inhalation of vapors can cause damage to the central nervous system. Kidney and liver damage have been reported in experimental animals. Avoid unnecessary exposure to vapors of pyridine. If solutions containing pyridine contact the skin, the affected area should be washed immediately with water.

10. Sampling

10.1 Special precautions may be necessary to ensure that the sample taken for analysis is representative of the whole. Refer to Practice E 300 for a detailed discussion of sampling procedures.

11. Procedure

11.1 To each of a sufficient number of flasks to make all blank and sample determinations in duplicate, pipet 50.0 mL of the esterification reagent. A uniform drainage time must be used for all aliquots.

11.2 Reserve two of the flasks for the blank determination. Into the other flasks add an appropriate weight of sample (Note 3, Note 4, and Note 7).

NOTE 3—Determine the sample weight as follows:

[7] *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.

[8] The practical grade available from E. I. DuPont de Nemours or from Distillation Products is suitable.

[9] This reagent is also described in Practice E 200.