Designation: E 326 – 96

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

This standard is issued under the fixed designation E 326; 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 the determination of hydroxyl groups attached to primary and secondary carbon atoms in aliphatic and alicyclic compounds. It is not suitable for determination of hydroxyl groups attached to tertiary carbon atoms. Phenolic hydroxyl groups do not react and also certain sterically hindered hydroxyl groups may not react.

NOTE 1—Other methods for determination of hydroxyl groups are given in Test Method D 1957, Test Method for Hydroxyl Value of Fatty Oils and Acids[2], Methods D 2849, Methods of Testing Urethane Foam Polyol Raw Materials[3], Test Methods E 222, Test Methods for Hydroxyl Groups by Acetic Anhydride Acetylation[4], Test Method E 335, Test Method for Hydroxyl Groups Using Pyromellitic Dianhydride Esterification[4], 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]

D 1209 Test Method for Color of Clear Liquids (Platinum—Cobalt Scale)[6]

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[7]

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 sample. In the case of a 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 phthalic anhydride in a pyridine medium at approximately 100°C. The excess anhydride is hydrolyzed with water and the phthalic 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 accuracy and precision of the test method.

6.2 Tertiary alcohols may interfere by dehydration or by partial reaction. 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 Saturated aldehydes or compounds that produce a free carbonyl group under the conditions of the reaction do not interfere. Secondary hydroxyl compounds containing a beta-carbonyl group do not esterify but are dehydrated. The epoxide group interferes.

6.4 Glycols react slowly and may require a longer reaction period than specified in this test method for the usual

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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 06.04.

[7] *Annual Book of ASTM Standards*, Vol 14.02.

compound. The 1,2-glycols require a longer esterification period than glycols with more widely separated hydroxyl groups.

6.5 Excessive amounts of water in the sample will interfere by consuming the reagent. Provisions are made to accommodate a small amount of water by adjustment of the sample size used for analysis (see Note 4).

6.6 Free acids interfere by consuming the standard alkali solution and strong bases interfere by consuming an equivalent amount of phthalic 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 phthalation reagent.

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

7. Apparatus

7.1 *Bag*, heavy fabric, with drawstring, to contain bottle (7.2). As an alternative, a stainless steel mesh jacket fitted to cover the bottle may be used.

7.2 *Bottle*, pressure, heat-resistant, approximately 350 mL[8].

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

7.4 *Steam Bath*, 98± 2°C, containing enough water to cover the liquid in the sample bottles. The temperature should be uniform throughout the bath.

8. Reagents

8.1 *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 such specifications are available[9]. 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 *Hydrochloric Acid Standard Solution* (0.5 *N)*—Prepare and standardize 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 hydrochloric acid (HCl) solution shall be corrected to the temperature at which the determination is performed using the equation given in 8.8. The factor for the thermal expansion of this solution is 0.00014. This solution is required only if a sample correction is to be applied for presence of strong base in the sample being analyzed.

8.4 *Pyridine*—**CAUTION** (See 9.1)—To be acceptable, each lot should be tested and should pass the following quality test (Note 2). Place 7 g of phthalic anhydride and 50 mL of pyridine in a glass-stoppered flask. Shake vigorously until dissolved, heat at 50 to 60°C for 30 min, allow to stand at room temperature in the dark for 24 h, then measure the color of the solution. The pyridine is acceptable if the color is lighter than 200 Pt-Co scale (see Test Method D 1209).

NOTE 2—Commercial refined pyridine and other material which is marginal for the quality test may be further refined by distilling from phthalic anhydride through a packed column using a low (5 + 1) reflux ratio until the head temperature is 114°C, then collecting all overhead distilling at 114 to 116°C.

8.5 *Phthalation Reagent* (1 *M)*—Dissolve 130 ± 3 g of phthalic anhydride in 800 mL of pyridine, shaking vigorously to effect solution. Store in a brown, glass-stoppered bottle. The solution preferably should stand overnight before using. However, the solution may be heated at 70°C for 1 h, then cooled to room temperature and used immediately. This reagent may be used until it becomes badly discolored (greater than 200 Pt-Co scale) (see Test Method D 1209).

8.6 *Phthalic Anhydride.*

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

8.8 *Sodium Hydroxide, Standard Solution* (0.5 *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 0.00014. 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 equation:

$$N_{t_2} = N_{t_1} + (t_1 - t_2)(0.00014) \quad (2)$$

where:

N_{t_1} = normality when standardized,
N_{t_2} = 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 *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 immediately be washed 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

[8] A suitable bottle may be obtained from B. Preiser Co., Inc., Charleston, W VA, Catalog No. 10-5485; SGA Scientific, Bloomfield, NJ, Catalog No. B5317; or Sargent-Welch Scientific Co., Catalog No. S9015.

[9] *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.

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