Designation: E222 – 23

Standard Test Methods for Hydroxyl Groups Using Acetic Anhydride Acetylation[1]

This standard is issued under the fixed designation E222; 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 the determination of hydroxyl groups attached to primary and secondary carbon atoms in aliphatic and alicyclic compounds and phenols.

1.2 Three test methods are given as follows:

	Sections
Test Method A (Pressure Bottle Method)	8 – 14
Test Method B (Reflux Method)	16 – 22
Test Method C (Perchloric Acid Catalyzed Method)	24 – 30

1.2.1 Test Method A is recommended for general use. Test Method B is included to give a standard procedure for the method that has been used widely. Test Method C is recommended when the results are required in a minimum period of time or where ambient temperature for the reaction is desired.

1.2.2 The results obtained using Test Methods A and B will be essentially the same, but the results obtained using Test Method C will be higher (up to approximately 4 % relative) than those obtained using the other two methods.

1.2.3 Statements on precision are included with each test method. The precision of Test Methods A and C is consistent over a wide range of hydroxyl content (tested over hydroxyl number range of 250 to 1600), whereas Test Method B is less precise at the higher hydroxyl content level than it is at the lower hydroxyl content level. In general, Test Method A is approximately two-fold as precise as Test Method C. Test Method B has approximately the same precision as Test Method C at the lower hydroxyl content level but poorer precision at the higher hydroxyl content level.

1.2.4 The interferences are essentially the same for the three methods. Some compounds can be analyzed using Test Methods A or B but not using Test Method C because of interfering reactions of the strong acid catalyst with the compound being analyzed or the acetate product formed in the determination. However, because of its increased reactivity, Test Method C is applicable for determination of some compounds, particularly sterically hindered secondary alcohols, which react too slowly or not at all in Test Methods A and B.

NOTE 1—Other methods for determination of hydroxyl groups are given in Test Methods D1957, D2195, E326, E335, and E567.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded in accordance with the rounding off methods of Practice E29.

1.5 Review the current appropriate Safety Data Sheets (SDS) for detailed information concerning toxicity, first aid procedures, and safety precautions.

1.6 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazards statements are given in Section 7.

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D1957 Test Method for Hydroxyl Value of Fatty Oils and Acids (Withdrawn 2007)[3]

D2195 Test Methods for Pentaerythritol (Withdrawn 2011)[3]

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

[1] These test methods are under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and are the direct responsibility of Subcommittee D16.12 on Caustics and Peroxides.

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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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

***A Summary of Changes section appears at the end of this standard**

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]
E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis
E203 Test Method for Water Using Volumetric Karl Fischer Titration
E326 Test Method for Hydroxyl Groups by Phthalic Anhydride Esterification (Withdrawn 2001)[3]
E335 Test Method for Hydroxyl Groups by Pyromellitic Dianhydride Esterification (Withdrawn 2002)[3]
E567 Test Method for Tertiary Hydroxyl Groups with Hydrogen Bromide (Withdrawn 1996)[3]
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *Other Document:*

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.1200 – Air Contaminants Exposure Limits and Hazard Communication[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *hydroxyl number*—the milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of material. 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. Significance and Use

4.1 Hydroxyl is an important functional group, and knowledge of its content is required in many intermediate and end use applications. The test methods described herein are for the determination of primary and secondary hydroxyl groups and can be used for the assay of compounds containing them.

5. Interferences

5.1 Unless stated otherwise, the following interferences apply to all three test methods:

5.1.1 Pentavalent nitrogen compounds, amides, some ethers, and some carbonyl compounds may interfere with the accuracy of the test method.

5.1.2 Tertiary alcohols, cyanohydrins, some hydroxylated fatty acids, certain substituted phenols, and some polyhydroxyl compounds will react in a nonstoichiometric manner.

5.1.3 Primary and secondary amines and mercaptans usually will react quantitatively along with the hydroxyl group.

5.1.4 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 the analysis.

5.1.5 Free acids interfere by consuming the standard alkali solution, and strong bases interfere by consuming an equivalent amount of acetic acid; provisions for determining and applying corrections for these interferences are included in the test methods. Some of the higher fatty acids may be converted to anhydrides, releasing water which will consume acetylation reagent.

5.1.6 In Test Method C, epoxy, poly(oxyethylene), poly(oxypropylene), and furan rings interfere. Enols, imides, hydrazides, and some oximes will react in a nonstoichiometric manner.

5.1.7 Phenol (in contrast to other phenolics) gives low results with Test Methods A and B.

5.1.8 With Test Methods A and B, epoxy compounds will give erroneously high results.

NOTE 2—In a study performed by the American Oil Chemists' Society, satisfactory results were obtained with epoxidized soybean oil, epoxidized tall oil, and epoxidized castor oil when the acetylation was carried out at room temperature for 24 h.

5.1.9 Presence of an olefinic or acetylenic unsaturation in the hydroxyl-containing compound should have no effect on the hydroxyl content result obtained with Test Methods A and B, but may give a positive interference with Test Method C.

5.1.10 Test Methods A and B as written (using a visual indicator) may not be applicable to samples containing heat-sensitive impurities, leading to high color in the reacted solution.

6. Reagents

6.1 *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.[5] 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.

6.2 Unless otherwise indicated, references to water shall be understood to mean Type I or Type II reagent water conforming to Specification D1193.

7. Hazards

7.1 Acetic anhydride, pyridine, and 1,2-dichloroethane are eye, skin, and respiratory irritants. Avoid bodily contact with these reagents and use only in a well-ventilated area.

7.2 Perchloric acid is commonly available in 60 % to 72 % concentrations. These solutions may form explosive mixtures with certain organic materials. Dehydrating agents may cause the formation of the anhydrous acid which is unstable at ambient temperature and explodes on contact with most organic materials. The acid is an acute irritant to the eyes, skin, and mucous membranes. Avoid bodily contact. Wash all spills with copious amounts of water.

[4] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

[5] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.