



Designation: E222 – 10

Standard Test Methods for Hydroxyl Groups Using Acetic Anhydride Acetylation¹

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)	15 – 21
Test Method C (Perchloric Acid Catalyzed Method)	22 – 28

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.

¹ These test methods are under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and are the direct responsibility of Subcommittee D16.15 on Industrial and Specialty General Standards.

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

1.5 *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 hazards statements are given in Section 7.

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

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
- 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

3. Terminology

3.1 Definitions:

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

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.⁴ 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 II or Type III 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.

TEST METHOD A (Pressure Bottle Method)

8. Summary of Test Method

8.1 The sample is acetylated with a solution of acetic anhydride in pyridine in a pressure bottle at 98°C. The excess reagent is hydrolyzed with water, and the acetic acid is titrated with standard sodium hydroxide solution. The hydroxyl content is calculated from the difference in titration of the blank and sample solutions.

9. Apparatus

9.1 *Bag*, heavy fabric, with draw string, to hold bottle (9.2). As an alternative a stainless steel mesh jacket fitted to cover the bottle may be used.

9.2 *Bottle*, pressure, heat-resistant, approximately 350 mL.

9.3 *Buret*, 100-mL total capacity, range of graduated portion 50 mL, 0.1-mL graduations, preferably equipped with PTFE stopcock (see Note 6).

9.4 *Steam Bath*, 98 ± 2°C, containing enough water to cover the liquid in the sample bottles. It is critical that the water level be as prescribed and that the temperature be within the prescribed range and uniform throughout the bath.

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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

10. Reagents

10.1 *Acetic Anhydride*. (**Caution:** see 7.1.)

10.2 *Acetylation Reagent*—Mix 127 mL of acetic anhydride with 1000 mL of pyridine (10.5). The reagent shall be prepared fresh daily and kept in a dark bottle. It should not be used if darker than a pale yellow color.

10.3 *Hydrochloric Acid, Standard Solution (0.5 meq/mL)*—Prepare and standardize in accordance with the appropriate sections of Practice E200. 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 as described in 10.6. 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 the presence of strong base in the sample being analyzed.

10.4 *Phenolphthalein Indicator Solution*—Dissolve 1 g of phenolphthalein in 100 mL of pyridine.

10.5 *Pyridine*, containing 0.30 to 0.45 % water. Determine the water content of the pyridine using Test Method E203, and add the required amount of water. The volume of water to add per litre of pyridine may be calculated as follows:

$$\text{Water to add, mL} = 4.0 - 9A \quad (2)$$

where:

A = percent water in pyridine.

10.6 *Sodium Hydroxide, Standard Solution (0.5 meq/mL)* (**Caution:** See 7.1)—Prepare and standardize in accordance with the appropriate sections of Practice E200. 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 by the following:

$$N_{t_2} = N_{t_1} + (t_1 - t_2) (F) \quad (3)$$

where:

N_{t_1} = meq/mL when standardized,

N_{t_2} = meq/mL during analysis of samples,

t_1 = temperature of solution (°C) during standardization,

t_2 = temperature of solution (°C) during analysis of samples, and

F = factor to correct for thermal expansion of the solution (see each solution for appropriate factor).

11. Procedure

11.1 To each of a sufficient number of pressure bottles to make all blank and sample determinations in duplicate, pipet 20.0 mL of the acetylation reagent. A uniform drainage time must be used for all aliquots.

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

NOTE 3—The sample size is based on a maximum of 9.8 meq of hydroxyl being present. Determine the sample weight using one of the following equations:

$$\text{Sample weight, g} = (561 \times 0.98) / \text{approximate hydroxyl number} \quad (4)$$

$$\text{Sample weight, g} = 0.0098 \times MW/n \quad (5)$$

where:

MW = molecular weight of the hydroxyl-containing compound, and
n = number of hydroxyl groups present in the molecule.

Since the calculated sample weight will be near the maximum permitted by the test method, adhere closely to the indicated weight. The sample should not exceed 10 g.

NOTE 4—If the sample contains an appreciable amount of water, the sample weight must be adjusted to accommodate this interference. In this case, determine the sample weight using one of the following equations:

$$\text{Sample weight, g} = \frac{0.1701 \times 0.98}{0.0094R + [0.01S \times (n \times 17.01) / MW]} \quad (6)$$

$$\text{Sample weight, g} = \frac{550}{\text{approximate hydroxyl number} + (31.2 \times R)} \quad (7)$$

where:

R = water in the sample, %,

S = purity of the sample, %,

MW = molecular weight of the hydroxyl-containing compound, and

n = number of hydroxyl groups present in the molecule.

Precision and accuracy are decreased when appreciable amounts of water are present because of the required decrease in sample size.

11.3 Stopper the bottle and swirl until the sample is completely dissolved. Enclose each bottle in a fabric bag and place all bottles as close together as possible in the steam bath at $98 \pm 2^\circ\text{C}$ for 2 h (Note 5). Maintain sufficient water in the bath to cover the level of liquid in the bottles.

NOTE 5—A reaction time of 2 h is satisfactory for most primary alcohols. Secondary alcohols react more slowly, and a general reaction time of 4 h is recommended. For some compounds a shorter or a longer reaction period may be required.

11.4 Remove the bottles from the bath and allow them to cool to room temperature. Untie the bags, uncap the bottles to release any pressure, and then remove the bags.

11.5 Carefully rinse any liquid on the stopper into the bottle and rinse the walls of the flask, using 20 to 30 mL of water. To each of the bottles add clean crushed ice until about one half full.

11.6 Add 1 mL of the phenolphthalein indicator solution and titrate (Note 6) immediately with the 0.5 meq/mL NaOH solution to the first faint pink end point permanent for 15 s. The solution should be swirled during the titration, with vigorous swirling as the end point is reached. Record the volume of titrant to 0.02 mL (Note 7). Record the temperature of the NaOH solution.

NOTE 6—As a substitute, if the 100-mL buret is not available, the first 50 mL of titrant may be added by pipet (uniform drainage time for all aliquots) and the titration completed with a 50-mL buret.

NOTE 7—If the volume of 0.5 meq/mL NaOH solution required for the sample is less than 80 % of that required for the blank, the sample was too large and the analysis should be repeated with a smaller weight of sample. In some cases, a smaller excess of acetylation reagent may be adequate, but this must be validated for the particular type compound; in no case should the sample titration be less than 65 % of that required for the blank.

12. Calculation

12.1 Calculate the hydroxyl content in terms of either hydroxyl number or percentage of the hydroxyl-containing compound as follows (Note 8):