Designation: E1899 – 16

Standard Test Method for
Hydroxyl Groups Using Reaction with *p*-Toluenesulfonyl Isocyanate (TSI) and Potentiometric Titration with Tetrabutylammonium Hydroxide[1]

1. Scope*

1.1 This test method covers the determination of hydroxyl groups attached to primary and secondary carbon atoms in aliphatic and cyclic compounds and phenols. It is not suitable for determination of hydroxyl groups attached to tertiary carbon atoms. This test method is applicable to polyacetals, temperature sensitive materials, high solids polymer polyols, and rigid polyols. Other available test methods listed in Note 1 are not suitable for many of the sample types listed above.

1.1.1 This test method is currently recommended for neutral refined products. Successful application has been made, however, to some in-process samples that contain an excess of acidic species. Proper validation must be performed, of course, to show that the acidic species either does not interfere, or that the acidic species interference has been obviated.

NOTE 1—Other methods for determination of hydroxyl groups are given in Test Methods D817, D871, D1957, D2195, D4252, D4273, D4274, E222, E326, and E335.

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

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 *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.* For specific hazards see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D817 Test Methods of Testing Cellulose Acetate Propionate and Cellulose Acetate Butyrate
D871 Test Methods of Testing Cellulose Acetate
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D1957 Test Method for Hydroxyl Value of Fatty Oils and Acids (Withdrawn 2007)[3]
D2195 Test Methods for Pentaerythritol (Withdrawn 2011)[3]
D4252 Test Methods for Chemical Analysis of Alcohol Ethoxylates and Alkylphenol Ethoxylates
D4273 Test Method for Polyurethane Raw Materials: Determination of Primary Hydroxyl Content of Polyether Polyols
D4274 Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols
E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]
E222 Test Methods for Hydroxyl Groups Using Acetic Anhydride Acetylation
E300 Practice for Sampling Industrial Chemicals
E326 Test Method for Hydroxyl Groups by Phthalic Anhydride Esterification (Discontinued 2001) (Withdrawn 2001)[3]
E335 Test Method for Hydroxyl Groups by Pyromellitic Dianhydride Esterification (Withdrawn 2002)[3]

3. Terminology

3.1 *Definitions:*

3.1.1 *hydroxyl number (OH#)*—the milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of sample.

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[1] This test method is under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and is the direct responsibility of Subcommittee E15.01 on General Standards.

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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**

3.1.1.1 *Discussion*—In the case of a pure compound, the hydroxyl number is inversely proportional to the hydroxyl equivalent weight and the molecular weight:

$$\text{equivalent weight} \left(\text{g/equivalent}\right) = \frac{56100}{\text{OH\#}} \qquad (1)$$

and:

$$\text{molecular weight} \left(\text{g/mol}\right) = \frac{56100 \times \text{number of OH groups per molecule}}{\text{OH\#}}$$

4. Summary of Test Method

4.1 According to a reaction given in Manser et al.[4] (see Fig. 1) the hydroxyl group is reacted with excess p-toluenesulfonyl isocyanate (TSI), to form an acidic carbamate. Water is added to convert unreacted isocyanate to sulfonamide, followed by direct potentiometric titration of the acidic carbamate with tetrabutylammonium hydroxide (Bu_4NOH) in nonaqueous medium.

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.

5.2 This test method has the following advantages over other hydroxyl number methods: It is rapid (10 min), pyridine-free, ambient temperature, small sample size, applicable to extremely low hydroxyl numbers (<1), and is amenable to automation.

6. Interferences

6.1 Primary and secondary amines derivatize quantitatively with the TSI reagent and contribute to the hydroxyl value.

6.2 High levels of water in the sample can interfere by consuming reagent. The amount of excess TSI reagent prescribed by this test method is quite large, however, so that rather high water levels can be accommodated. Optimum titration curves are obtained, however, when the water is <1 %.

6.3 Any acidic species with a pKa value close to that of the acidic carbamate (formed between TSI and the hydroxyl compound), will contribute to the hydroxyl number and cause high values. Excess base in a sample may potentially react with the acidic carbamate to cause low hydroxyl number values. If this test method is to be used for samples other than neutral refined products, the analyst must first validate this test method on a case by case basis. For example, an in-process sample containing excess acid or base may be analyzed using Test Method B of Test Methods E222, to establish concordance of results with the current TSI test method for that particular matrix. The identities of acidic or basic species contained in in-process samples are frequently known, so that known addition of these moieties to the sample can establish whether or not there is interference exhibited. For example, methane sulfonic acid titrates sufficiently before the acidic carbamate formed between TSI and ROH, and therefore does not interfere. At the other extreme, methacrylic acid titrates well after the acidic carbamate of interest and thus causes no interference.

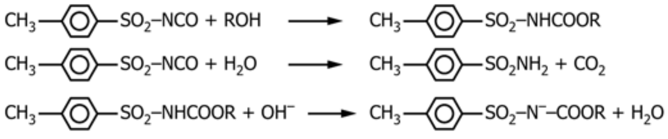

FIG. 1 Hydroxyl Group Reaction

7. Apparatus

7.1 *Potentiometric Autotitrator,* equipped with a 10- or 20-mL delivery buret. Ideally, the autotitrator should be capable of generating the potentiometric titration curve in the normal and derivative modes with automatic marking of end points. However, an older model titrator without automatic marking of end points was shown to give excellent hydroxyl number results obtained by manually evaluating the mid-point of the normal "S" shaped curve.

7.2 *Glass Combination pH Electrode,* consisting of a glass sensing membrane and Ag/AgCl internal reference element.

7.3 *Automatic Pipetter,* 500 µL.

7.4 *Glass or Plastic Beakers,* 100 mL.

7.5 *Magnetic Stirrer and Stirring Bars,* (3-cm length is optimum).

7.6 *Glass Pipet,* 10 and 20 mL, Class A.

7.7 *Volumetric Flasks,* 500 and 1000 mL.

7.8 *Analytical Balance,* accurate to 0.1 mg.

7.9 *Standard Bulb Transfer Pipets,* plastic, approximately 15-cm length.

7.10 *Graduated Cylinder,* 10 mL, or *Bottle Type Volumetric Dispenser*.

8. Reagents

8.1 *Purity of Reagents*—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.

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 D1193.

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[4] Manser, G.E., Fletcher, R.W., and Knight, M.R., *High Energy Binders Final Report*, Defense Technical Information Center, Ft. Belvoir, VA, Contract No. N00014-82-C-0800, p. 1-3 of Appendix A, August, 1985.

[5] *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 *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USP), Rockville, MD.