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D1957 Test Method for Hydroxyl Value of Fatty Oils and Acids (Withdrawn 2007)[3]
D2195 Test Methods for Pentaerythritol (Withdrawn 2011)[3]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 D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.15 on Industrial and Specialty 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:

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

and:

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

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.

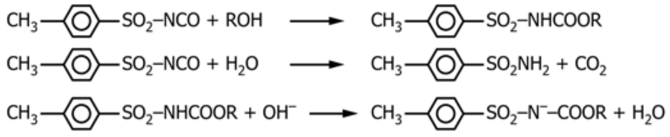

FIG. 1 Hydroxyl Group Reaction

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.

8.3 *Acetonitrile,* HPLC Grade must be used as it is sufficiently low in moisture so that molecular sieves are not needed to dry this solvent.

8.4 *2-Propanol, HPLC Grade.*

8.5 *p-Toluenesulfonyl Isocyanate (TSI), 96 %*—Maintain a nitrogen pad above this reagent after opening bottle.

8.6 *TSI Reagent*—Pipet 20 mL of TSI into a dry 500-mL volumetric flask half filled with acetonitrile. Dilute to the mark with acetonitrile and mix well. This reagent should be prepared fresh monthly.

8.7 *Potassium Hydrogen Phthalate, Primary Standard.*

8.8 *Tetrabutylammonium Hydroxide (Bu_4NOH), 1M Solution in Methanol,* 100 mL.

8.9 *Tetrabutylammonium Hydroxide (Titrant), 0.1 meq/mL*—Prepare by transferring the entire 100 mL of 1M Bu_4NOH in methanol (see 8.8) into a 1-L volumetric flask that is half filled with 2-propanol. Rinse the emptied bottle that contained the solution in 8.8 and transfer the rinsings to the contents of the 1-L volumetric flask. Swirl contents and dilute to the mark with 2-propanol. Stopper the flask and mix well. Finally, transfer the flask contents to the buret reservoir of a potentiometric autotitrator and standardize the titrate versus dried (2 h, 120°C) potassium hydrogen phthalate (KHP) as follows: dissolve approximately 0.18 g of KHP, weighed to 0.1 mg, in about 60 mL of water contained in a 100-mL beaker. Stir several minutes to ensure complete dissolution of the KHP. Perform a potentiometric titration directly on the KHP solution using the 0.1 meq/mL Bu_4NOH titrant. Perform three to five standardization titrations to obtain a reliable average value for the 0.1 meq/mL Bu_4NOH concentration.

$$N = \frac{\text{KHP, g}}{0.20423 \times \text{Bu}_4\text{NOH, mL}} \tag{2}$$

where:

N = concentration of the 0.1 meq/mL Bu_4NOH expressed to four decimal places, and

Bu_4NOH, mL = mL of this titrant to reach a potentiometric end point in the reaction with KHP.

8.10 *Methanol.*

8.11 *Acetone.*

9. Hazards

9.1 *p*-Toluenesulfonyl Isocyanate (TSI) is harmful by inhalation, in contact with skin and if swallowed. It may cause sensitization by inhalation and skin contact. It reacts violently with water. It causes severe irritation. It is a Lachrymator. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Never add water to this product.

9.2 Wear suitable protective clothing, gloves and eye/face protection when handling *p*-Toluenesulfonyl Isocyanate. Use only in a chemical fume hood. Do not breathe vapor. Do not get in eyes, on skin, or on clothing.

10. Sampling

10.1 Special precautions may be necessary to ensure that a representative sample is taken for analysis. General guidelines for sampling may be found in Practice E300. Samples which are solids at room temperature should be heated in a low temperature oven to obtain a clear liquid prior to weighing. Low temperature (50 to 70°C), should be tried first to avoid any undesirable changes in the sample. If higher temperatures are required to melt the sample, for example, 110°C, then the sample should be removed from the oven as soon as a clear liquid is obtained. After heating, invert the sample container twenty times to ensure complete homogenization. Samples that are liquid at room temperature only require inversion mixing.

11. Procedure

11.1 Tare a 100-mL glass or plastic beaker on an analytical balance and transfer a sample to the beaker using a glass or plastic transfer pipet. The optimum weight of sample is determined from the following relationship:

$$\text{sample, g} = \frac{40}{\text{expected OH\#}} \tag{3}$$

For expected OH# values of 2 or less, use 15 to 20 g of sample.

11.2 Using a graduated cylinder or other volumetric dispenser, add 10 mL of acetonitrile. Then add a magnetic stirring bar and stir slowly on a magnetic stirrer until sample is dissolved (30 s is usually sufficient) (see Note 2).

NOTE 2—Although acetonitrile has been found to dissolve a wide range of sample types (and should be used where possible), tetrahydrofuran or pentene stabilized chloroform may be used as solvent for samples which may be insoluble in acetonitrile. Alternatively, 3 mL of toluene may be used to dissolve a sample, followed immediately by addition of 7 mL of acetonitrile. Superior potentiometric titration curves are obtained in acetonitrile media. If there are difficulties in titrating while using less polar solvents, one may need to demonstrate the operation of the standard electrode (Section 7.2) and confirm its functionality under these conditions. Substitution of a more solvent compatible potentiometric electrode can be considered.

11.3 Pipet 10 ± 0.1 mL of TSI reagent into the sample solution, cover beaker with a watch glass and stir slowly on the magnetic stirrer for 5 min.

11.4 Add 0.5 mL of water to destroy excess TSI reagent. Stir for 1 min at slow speed.

11.5 Add 30 mL of acetonitrile using a graduated cylinder or other volumetric dispenser.

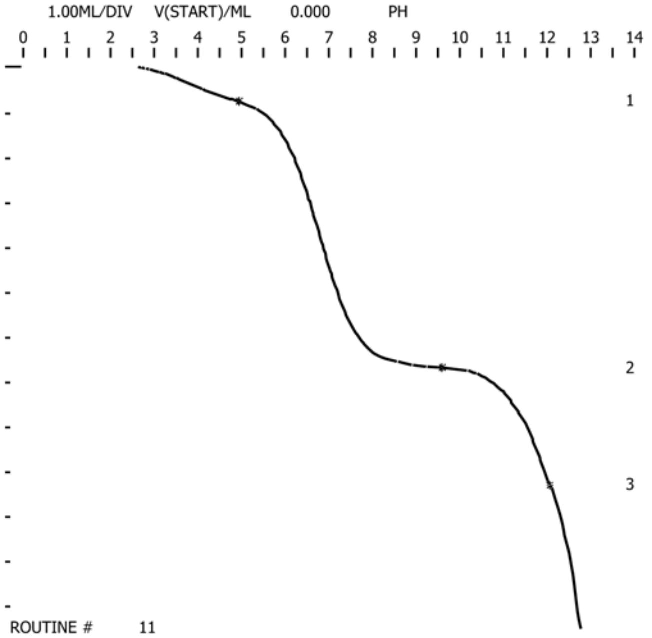
11.6 Using tissue paper, blot dry the end of the combination pH electrode and buret delivery tube tip. Immerse electrode and buret delivery tube tip into the sample solution, stir at a moderate speed, and begin the titration with 0.1 *N* standardized Bu_4NOH solution. Follow instruction manual for the autotitrator and be certain that all bubbles are expunged from the buret barrel and delivery tip tubing before beginning the titration. As is the case in all potentiometric titrations, it is advantageous if both normal and derivative titration curves can be run simultaneously, as complementary information can be gleaned from both modes regarding symmetry and spurious end points.

Otherwise, the analyst may choose which of the two modes to use. Ideally, the titration end point volumes are automatically marked.

11.7 When the titration has been complete, raise the electrode and buret delivery tube tip. Rinse electrode and delivery tube tip with methanol or acetone. This removes residual adhering organic material. Next, rinse electrode and tip with water and immerse the electrode in water to maintain good hydration of electrode bulb between titrations.

11.8 Record the volume in mL to the first potentiometric end point, V_1, and volume to the second end point, V_2. Although pH values will not enter into the calculations, record the "apparent" pH values at each of the potentiometric inflection points. They are useful reference points (see Note 3).

NOTE 3—A typical potentiometric titration curve (see Fig. 2), will have two or three inflections. The volume to V_1 is proportional to acidic species of the greatest strength and is reported to be related to age of reagent, catalysts present, and water in the sample. V_1 is usually 0.5 to 1.0 mL. The difference between V_2 and V_1 is related to the titration of the acidic carbamate of interest formed previously from the hydroxyl compound and the TSI reagent. The volume, V_2 is usually 5 to 10 mL. A third, less steep and spurious appearing inflection, V_3, sometimes occurs. Its identity has not been firmly established. Only V_1 and V_2 are used in the calculation. In acetonitrile medium, V_1 typically occurs at an "apparent" pH of about 5.0 to 5.5, V_2 at a pH of about 9.0 to 9.5, and V_3 at about pH 11 to 12. If V_2 and V_3 happen to occur rather close together, so that there is some question regarding which one is to be used as V_2 in the calculations, analyze a larger sample. V_3 will invariably move to higher pH values, further downscale, away from the unmoving V_2 value. If the program of the potentiometric titrator is set to detect extremely small end point breaks (that is, too high of a "sensitivity" setting), the titration curve occasionally may exhibit spurious end point markings, whether in the normal or derivative mode. It will be visually obvious that such breaks are spurious and the analyst should reduce the "sensitivity" setting for end point detection.



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ROUTINE #      11
#      7    PH(INIT)    2.776    V(TE)/ML    13.203
1   V/ML    0.778    PH(M)    4.953    PK(A)     3.82
2   V/ML    6.770    PH(M)    9.643    PK(A)     6.85
3   V/ML    9.415    PH(M)   12.141    PK(A)    11.59
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FIG. 2 Typical Potentiometric Titation Curve for Determination of Hydroxyl Number With TSI Reagent

12. Calculation

$$\text{hydroxyl number (OH\#)} = \frac{(V_2 - V_1) \times N \times 56.1}{\text{sample, g}} \quad (4)$$

where:

N = concentration of Bu_4NOH in meq/mL,
V_1 = mL Bu_4NOH to first potentiometric end point,
V_2 = mL Bu_4NOH to second potentiometric end point, and
sample, g = mass of sample in grams.

13. Report

13.1 Report the hydroxyl number to the nearest 0.1 unit if the value is above 100 and to the nearest 0.01 unit if the value is below 100.

14. Precision and Bias

14.1 *Precision*—The following criteria should be used for judging the acceptability of results:

14.1.1 *For Hydroxyl Values Greater Than 30 (See Note 4):*

14.1.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 0.500 % relative at 88 df. The 95 % limit for the difference between two such determinations is 1.40 % relative.

14.1.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The coefficient of variation of results (each the average of duplicates) obtained by the same analyst on different days, has been estimated to be 0.626 % relative at 44 df. The 95 % limit for the difference between two such averages is 1.75 % relative.

14.1.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be 1.151 % relative at 7 df. The 95 % limit for the difference between two such averages is 3.22 % relative.

NOTE 4—These precision estimates are based on an interlaboratory study conducted in 1996 involving Subcommittee E15.22 and Subcommittee D20.22.01. Single samples of four different materials were analyzed: Neodol 1-7[6] (alcohol ethoxylate); Terathane 1800[7] (poly 1,4 butanediol); Poly-G(R)74-376[8] (propoxylated sucrose); and Arcol Polyol E-648[9] (polyethylene-polypropylene glycol glycerol ether). Nominal hydroxyl number values for these samples were 123, 61, 367, and 35, respectively. One analyst in each of twelve laboratories performed duplicate determinations and repeated them on a second day, for a total of 192 determinations. Practice E180 was used in developing these statements.

14.1.2 *For Hydroxyl Values Less Than 2 (See Note 5):*

14.1.2.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.059 units absolute at 14 df. The 95 % limit for the difference between two such determinations is 0.16 units absolute.

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[6] Registered Trademark of Shell Oil Company.

[7] Registered Trademark of DuPont.

[8] Registered Trademark of Olin Corporation.

[9] Registered Trademark of ARCO Chemical Company.

14.1.2.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of duplicates) obtained by the same analyst on different days, has been estimated to be 0.10 units absolute at 7 df. The 95 % limit for the difference between two such averages is 0.29 units absolute.

14.1.2.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates) obtained by analysts in different laboratories has been estimated to be 0.10 units absolute at 6 df. The 95 % limit for the difference between two such averages is 0.29 units absolute.

NOTE 5—These precision estimates are based on an interlaboratory study[10] conducted in 1996 involving Subcommittee E15.22 and Subcommittee D20.22.01. A single sample of CR-39® Monomer[11] (diallyl diglycol carbonate) was analyzed. The nominal hydroxyl number can range from 0.5 to 5.0. One analyst in each of seven laboratories performed duplicate determinations and repeated them on a second day, for a total of 28 determinations. Practice E180 was used in developing these statements.

14.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable standard reference materials.

15. Keywords

15.1 hydroxyl number; *p*-Toluenesulfonyl isocyanate; polyacetals; polyols; potentiometric titration; tetrabutylammonium hydroxide

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[10] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1050. Contact ASTM Customer Service at service@astm.org.

[11] Registered Trademark of PPG Industries, Inc.

SUMMARY OF CHANGES

Committee E15 has identified the location of selected changes to this standard since the last issue (E1899 – 08) that may impact the use of this standard. (Approved April 1, 2016.)

(1) Changed "Material Safety Data Sheets (MSDS)" to "Safety Data Sheets (SDS)" in 1.2.