Standard Test Method for
Polyurethane Raw Materials: Determination of Primary Hydroxyl Content of Polyether Polyols[1]

This standard is issued under the fixed designation D4273; 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 *Carbon-13 Nuclear Magnetic Resonance Spectroscopy* (carbon-13 NMR), measures the primary hydroxyl content of ethylene oxide-propylene oxide polyethers used in preparing flexible foams. It is best suited for polyethers with primary hydroxyl contents of 10 to 90 %.

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

1.3 *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.*

NOTE 1—There is no known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E386 Practice for Data Presentation Relating to High-Resolution Nuclear Magnetic Resonance (NMR) Spectroscopy

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 The terminology in this test method follows the standard terminology defined in Practice E386 and in Terminology D883.

4. Summary of Test Method

4.1 The resonance peaks of the primary and secondary hydroxyl carbons of the polyethers used in flexible urethane foams are well-resolved in high-resolution carbon-13 NMR spectra. The peak areas are measured by the spectrometer's integration system, and the relative primary hydroxyl content is determined from the ratio of the primary hydroxyl area to the total area of the primary and secondary hydroxyl resonance peaks.

5. Significance and Use

5.1 Measurements of primary hydroxyl content are useful for providing information regarding the relative reactivities of polyols.

6. Interferences

6.1 Any primary hydroxyl propoxylate carbons present (where the methylene carbon is next to the hydroxyl group and the methine carbon is next to the ether oxygen) are integrated with the secondary hydroxyl carbons and are therefore not included in the primary hydroxyl content as measured by this method.

7. Equipment

7.1 *Pulse Fourier-Transform NMR (FT-NMR) Spectrometer,* with carbon-13 capability and a carbon-13 resonance frequency of 15 MHz (proton resonance frequency of 60 MHz) or higher. The spectrometer is to have a minimum signal-to-noise ratio of 70:1, based on the largest aromatic peak of 90 % ethylbenzene sample that has been pulsed one time using a 90° pulse.

7.2 *NMR Sample Tubes,* with outer diameters of 5 mm or more.

---

[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.22 on Cellular Materials - Plastics and Elastomers.

Current edition approved April 1, 2011. Published April 2011. Originally approved in 1983. Last previous edition approved in 2005 as D4273 - 05. DOI: 10.1520/D4273-11.

[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**

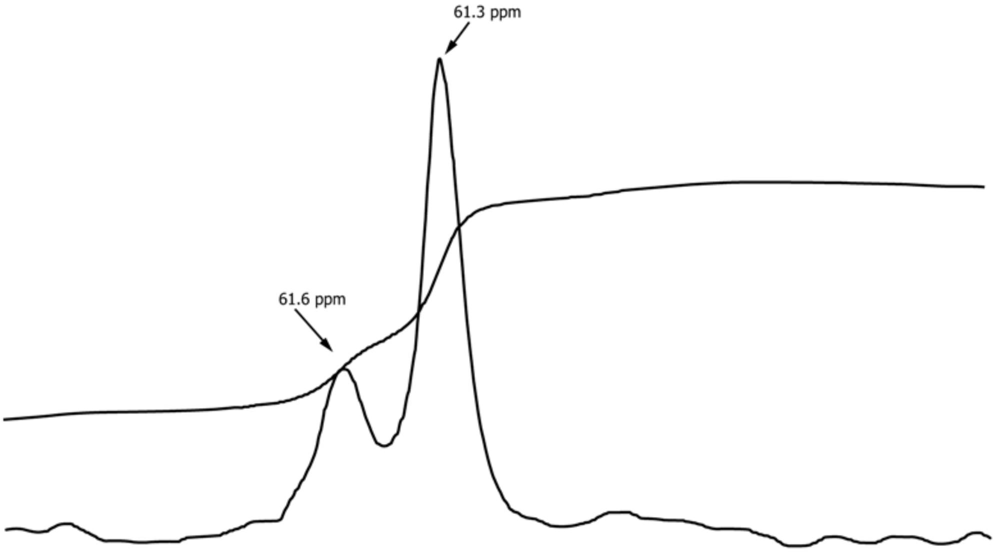

FIG. 1 Primary Hydroxyl Carbon Peaks of 3500 MW Triol (52 % Primary)

8. Reagents

8.1 All reagents are to be NMR-grade, deuterated solvents.

8.2 *Deuterated Chloroform or Deuterated Acetone,* containing tetramethylsilane (TMS) as an internal standard.

9. Standards

9.1 This test method does not require standards. To evaluate the test method, standards can be prepared by mixing in solution commercially available poly(propylene oxide) and poly(ethylene oxide) diols. The molecular weight of the standard would ideally be 300 or more since lower-molecular-weight polyols can contain structural configurations that are not typical of polyethers used in flexible urethane foams.

10. Preparation of Sample

10.1 Mix 3 mL of polyol with 1.5 to 2 mL of deuterated chloroform or deuterated acetone. Transfer an appropriate amount to the NMR tube.

11. Instrument Preparation

11.1 Prepare a decoupled carbon-13 NMR experiment, selecting appropriate parameters to obtain quantitative integration of the peaks in the 67-60 ppm region.

11.2 The settings presented here are examples that apply to a Bruker WP-80 spectrometer and a Varian AC 300 spectrometer. Instrument settings for other spectrometers vary. Consult the manufacturer's operating manual.

11.2.1 Typical Bruker WP-80 spectrometer parameters are as follows:

Nucleus observed	Carbon-13
Spectral width	3000 Hz
Pulse angle	30°
Data points	8K
Acquisition time	1.36 s
Delay between pulses	0.0 s
^{1} H decoupler	Broadband

11.2.2 Typical Varian AC 300 spectrometer parameters are as follows:

Nucleus observed	Carbon-13
Spectral width	100 ppm
Pulse angle	90°
Data points	32K
Acquisition time	~2 s
Pulse delay	5 s
^{1} H decoupler	on, or gated decoupling

12. NMR Analysis

12.1 Place the NMR tube containing the sample solution into the spectrometer probe. After a stable lock is obtained, optimize the field homogeneity. Collect a sufficient number of repetitive scans for the analysis. The number required depends on the spectrometer, the molecular weight of the polyol, and the functionality of the polyol. Some samples will require repetitive scanning for 30 min or less, while some will require an hour or more. After scanning, transform the free induction decay (FID) to the frequency-domain spectrum. The primary hydroxyl peaks at about 61 ppm and the secondary hydroxyl peaks at about 66 ppm are then expanded, amplified, and integrated (the chemical shifts are based on TMS set at 0.0 ppm). See Figs. 1-4 for examples of spectra obtained for two different polyols.

13. Calculation

13.1 Determine the areas of the primary and secondary peaks from the integration curves. Calculate the mole percent primary hydroxyl from the following equation:

$$\text{Primary hydroxyl, \%} = \frac{Ap}{Ap+As} \times 100 \qquad (1)$$

where:

Ap = area of primary hydroxyl peaks, and
As = area of secondary hydroxyl peaks.

The area of each peak type is in accordance with Fig. 1 and Fig. 2.

14. Report

14.1 Report results to the nearest percent primary hydroxyl.

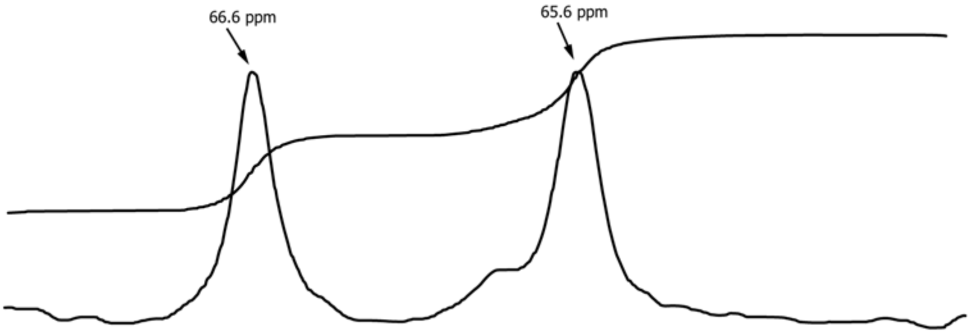

FIG. 2 Secondary Hydroxyl Carbon Peaks of 3500 MW Triol (52 % Primary)

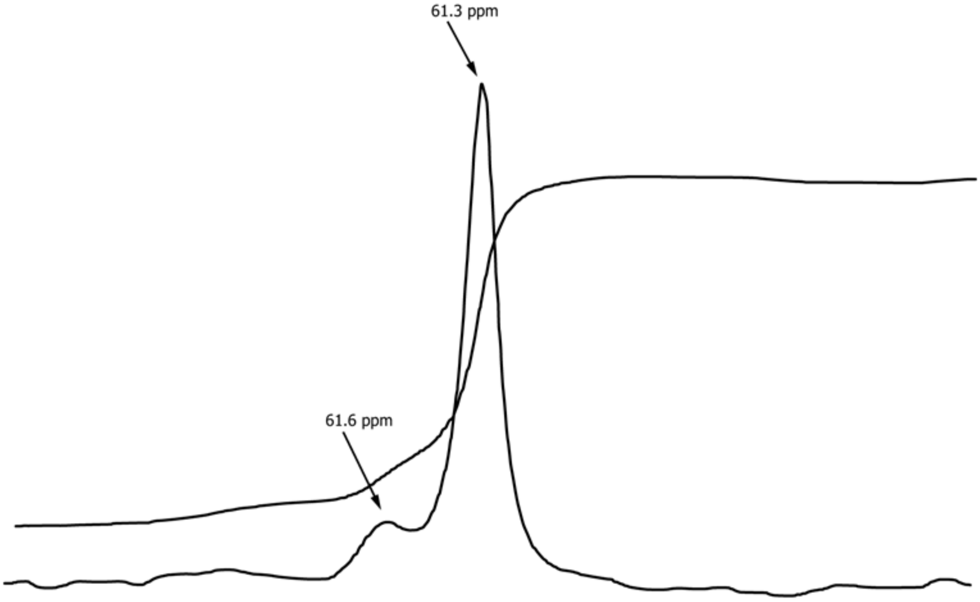

FIG. 3 Primary Hydroxyl Carbon Peaks of 5500 MW Triol (78 % Primary)

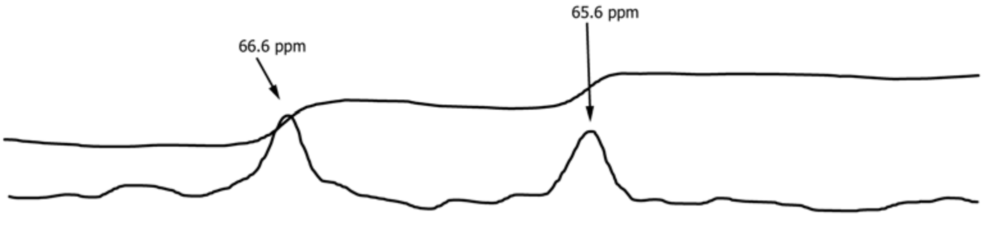

FIG. 4 Secondary Hydroxyl Carbon Peaks of 5500 MW Triol (78 % Primary)

15. Precision and Bias[4]

TABLE 1 ^{13}C Method, % Primary OH Content for Eight Laboratories, Six Polyols

Sample	Mean	S_r	S_R	I_r	I_R
1	11.1	0.96	1.71	2.72	4.83
2	39.6	1.95	1.51	5.52	4.27
3	75.4	0.83	1.43	2.35	4.05
4	71.7	2.00	3.46	5.66	9.79
5	52.0	2.50	3.40	7.08	9.62
6	74.4	1.27	2.22	3.59	6.28

TABLE 2 Description of Samples Analyzed

Sample	Composition	Hydroxyl Number
1	0.34 g PEG + 19.6 g PPG[A]	61
2	1.89 g PEG + 18.1 g PPG[A]	84
3	6.37 g PEG + 13.6 g PPG[A]	152
4	ethoxylated poly(propylene oxide)	24
5	ethoxylated poly(propylene oxide)	52
6	ethoxylated poly(propylene oxide)	74

[A] PEG refers to a polyethylene glycol of Hydroxyl Number 358. PPG is a polypropylene glycol of Hydroxyl Number 55.9.

15.1 Table 1 is based on a round robin conducted in 1979 in accordance with Practice E691, involving six polyol samples with primary hydroxyl contents from 11 to 76 % and hydroxyl numbers from 24 to 109 (Table 2) tested by eight laboratories. For each polyol, all of the samples were prepared at one source, but the individual specimens were prepared at the laboratories that tested them. Each test result was obtained from one individual NMR run. Each laboratory obtained two test results for each material on two separate days.

15.2 In Table 1, for the polyols indicated and the test results that are derived from testing two specimens of each polyol on each of two separate days:

15.2.1 S_r = within-laboratory standard deviation of the average: $I_r = 2.83\ S_r$. (See 15.2.3 for application of I_r.)

15.2.2 S_R = between-laboratory standard deviation of the average: $I_R = 2.83\ S_R$. (See 15.2.4 for application of I_R.)

15.2.3 *Repeatability*—In comparing two test results for the same polyol, obtained by the same operator using the same equipment on the same day, those test results are to be judged not equivalent if they differ by more than the I_r value for that polyol and condition.

15.2.4 *Reproducibility*—In comparing two test results for the same polyol, obtained by different operators using different equipment on different days, those test results are to be judged not equivalent if they differ by more than the I_R value for that polyol and condition. (This applies between different laboratories or between equipment within the same laboratory.)

15.2.5 Any judgement in accordance with 15.2.3 and 15.2.4 will have an approximate 95 % (0.95) probability of being correct.

15.2.6 Other polyols can yield somewhat different results.

15.3 For further information on the methodology used in this section, see Practice E691.

15.4 *Bias*—There are no recognized standards on which to base an estimate of bias for this test method.

15.5 The precision statements in 15.1 – 15.3 are based on a 1979 interlaboratory study of six samples with primary hydroxyl contents from 11 to 76 % described in Table 2. One analyst in each of eight laboratories performed duplicate determinations and repeated them on a second day. Practice E180 was used in developing these precision estimates. The NMR spectrometers used in this study were five Varian CFT-20's (80 MHz), two Jeol FX 60's (60 MHz), and one Bruker WP-80 (80 MHz).

16. Keywords

16.1 NMR; nuclear magnetic resonance spectroscopy; polyurethane raw materials; primary hydroxyl, polyether polyol

---

[4] Supporting data are available from ASTM Headquarters. Request RR:D20-1108.

APPENDIX

(Nonmandatory Information)

X1. FLUORINE-19 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY METHOD FOR DETERMINATION OF PRIMARY HYDROXYL CONTENT OF POLYETHER POLYOLS

X1.1. Scope

X1.1.1 *Fluorine-19 Nuclear Magnetic Resonance Spectroscopy* (fluorine-19 NMR), measures the primary hydroxyl content in ethylene oxide-propylene oxide polyethers used in flexible urethane foams. It is suitable for polyethers with hydroxyl numbers of 24 to 300 and primary hydroxyl percentages of 2 to 98.

X1.2. Summary of Test Method

X1.2.1 Hydroxyl-terminated polyethers are reacted with trifluoroacetic anhydride, converting them quantitatively to trifluoroacetate esters. High-resolution fluorine-19 NMR spectra of the esters have well-resolved resonance peaks for the esters of primary and secondary alcohols. Areas of these peaks are measured by the spectrometer's integration system, and the relative primary hydroxyl content is calculated from the ratio of the areas of the primary hydroxyl peaks to the total area of primary and secondary hydroxyl peaks.

X1.2.2 Mixtures of polyethers can be analyzed provided none of the trifluoroacetylation derivatives extract preferentially into aqueous bicarbonate solution. Extractable polyethers are polyethylene glycols of molecular weight greater than 300.

NOTE X1.1—A blend of polypropylene glycol (hydroxyl number equals 60) and polyethylene glycol (hydroxyl number equals 75) had a calculated primary hydroxyl of 49.7 % and an observed value by the fluorine-19 NMR derivatization method of 39.9 %. This example is extreme since these components are incompatible. Nevertheless, a test is described in Section 12 to determine the test method's applicability to a particular blend.

X1.2.3 The hydroxyl contribution of chain extenders in polyethers can be determined provided that (*1*) their trifluoroacetate derivatives are not volatile under the derivatization conditions, (*2*) their derivatives do not extract into aqueous bicarbonate, and (*3*) their fluorine-19 NMR peaks are well-resolved.

NOTE X1.2—A test of the test method's applicability to samples containing chain extenders is given in Section X1.9.

X1.3 Equipment

X1.3.1 *NMR Spectrometer,* with a fluorine-19 resonance frequency of 75 MHz or higher.

NOTE X1.3—There was only a small loss in precision when this test method was used with 56-MHz spectrometers. Although this test method is written for continuous-wave instruments, Fourier-transform NMR has been used with comparable precision.

X1.3.2 *NMR Sample Tubes,* having an outside diameter of at least 5 mm.

X1.3.3 *Centrifuge,* bench-top type that can provide a relative centrifugal force (RCF) of about 800.

X1.4. Reagents and Materials

X1.4.1 All reagents should be ACS certified or reagent grade unless otherwise specified and are to be reasonably free of paramagnetic materials (less than 100 ppm iron, for example).

X1.4.2 *Trifluoroacetic Anhydride*—Aldrich Gold Label or the equivalent.

X1.4.3 *Methylene Chloride*—Alcohol-free.

X1.4.4 *Chloroform-d_1-alcohol-free* —Deuterated chloroform is used because non-deuterated chloroform usually contains ethanol.

X1.4.5 *Sodium Bicarbonate Solution* —Prepare a saturated solution by adding 10 g of sodium bicarbonate to 100 mL of water.

X1.4.6 *Anhydrous Magnesium Sulfate*, or other drying agent.

X1.4.7 *Fluorotrichloromethane*—Stabilized grade.

X1.5 Standards

X1.5.1 This test method does not require standards. To evaluate this test method, standards can be prepared from commercially available poly(oxypropylene oxide) and poly(ethylene oxide) of known hydroxyl numbers. Polyethylene glycol of molecular weight less than 300 is preferred since the trifluoroacetate derivatives of higher-molecular-weight polyethylene glycols may partially extract into aqueous bicarbonate solution (see Note X1.1).

X1.6 Preparation of Sample

X1.6.1 Add about 1 g of sample, the appropriate trifluoroacetic anhydride volume as follows, and 4 mL of methylene chloride to a 4-mm vial or test tube. Mix well.

Trifluoroacetic Anhydride Volume

Hydroxyl Number of Polyol	Volume Anhydride, mL
24 to 75	1.0
76 to 150	2.0
151 to 225	3.0
226 to 300	4.0

X1.6.1.1 Heat the uncapped vial or tube on a hot plate or steam bath in an exhaust hood for about 10 min or until the excess methylene chloride and trifluoroacetic anhydride have boiled off. Cool the concentrate (about 2 mL) to ambient temperature. Add 0.54 mL of chloroform-d_1 and 2 mL of saturated aqueous bicarbonate solution (Note X1.4). Cap the vial or tube and shake vigorously with venting. Decant into a 10-mL centrifuge tube and centrifuge at an RCF of about 800. Transfer the organic layer (bottom) to a 1-dram vial containing about 0.3 g of drying agent. After 5 min, filter the trifluoroacetylated polyol solution into an NMR tube.

NOTE X1.4—Trifluoroacetate derivatives are hydrolytically unstable. The analysis must not be interrupted once water is added.

X1.7 Instrument Preparation

X1.7.1 The instrument settings given here are for a Varian EM-390 spectrometer. Instrument preparation may vary with the spectrometer. For a description of a particular spectrometer and details of its operation, refer to the manufacturer's operating manual.

X1.7.2 Typical EM-390 console settings are as follows:

Lock	–30 ppm (fluorotrichloromethane)
Offset	+ 46.3 ppm
Sweep width	1 ppm
Sweep time	2 min
Integration time	1 min
Spectrum amplitude	1000 to 3000
Filter time constant	0.05 s
RF power	0.15 mG
Lock gain	3 to 4
Lock power	0.006 mG
Mode	Autoshim

X1.8 NMR Analysis

X1.8.1 Add sufficient chloroform-d_1 or fluorotrichloromethane to the NMR tube containing the sample to obtain a stable lock signal. Optimize the field homogeneity and scan the trifluoroacetate region (75 to 76 ppm downfield from fluorotrichloromethane, see Fig. X1.1). Integrate the spectrum six times at a power level below that which causes saturation.

X1.8.2 *Derivatization Check*—Add 10 µL of trifluoroacetic anhydride to the NMR tube and rescan the spectrum. If hydrolysis has occurred or if not enough reagent was used, the measured primary hydroxyl content will change by 3 % or more. If this happens, add 10-µL increments of anhydride until the percent primary hydroxyl remains constant or the anhydride peak appears (see Fig. X1.2).

NOTE X1.5—Hydrolysis or insufficient reagent is rarely a problem if the procedure is followed closely. Accelerated hydrolysis has been observed in polyethers containing tertiary amines. Trifluoroacetylated esters of primary alcohols hydrolyze faster than those of secondary alcohols.

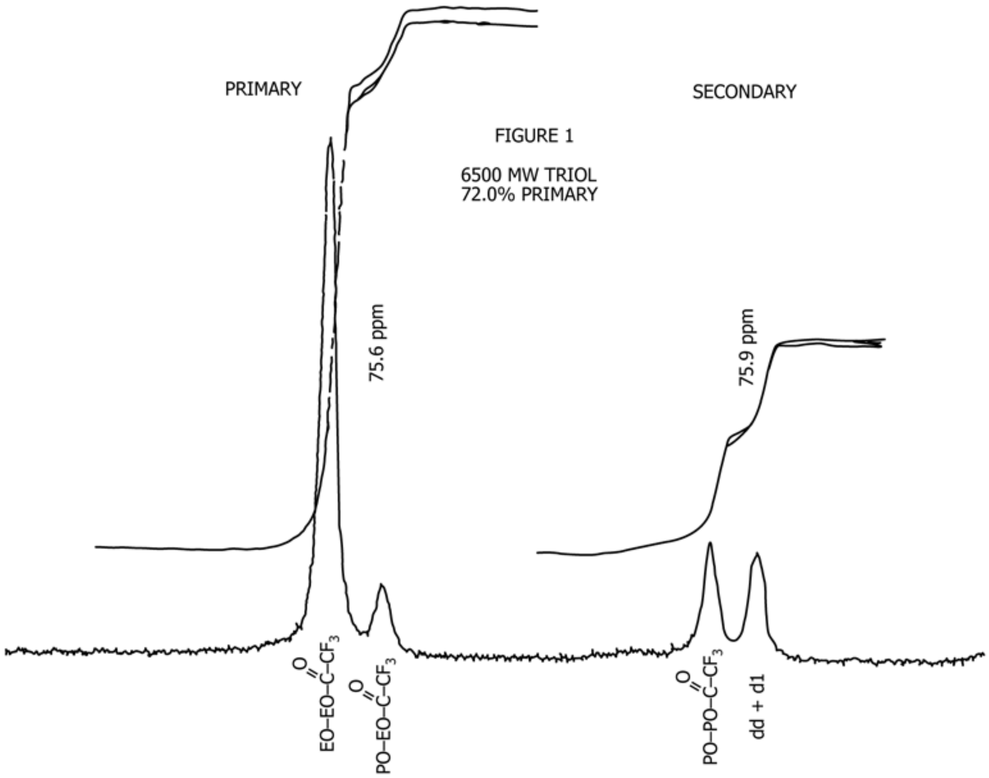

FIG. X1.1 6500 MW Triol (72.0 % Primary)

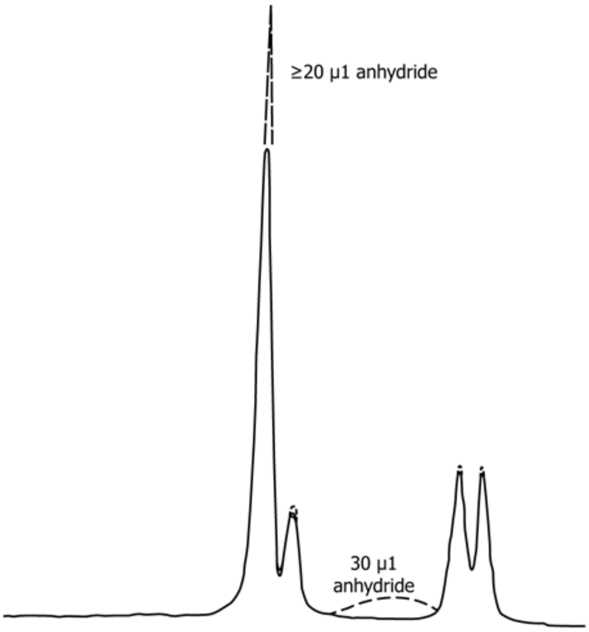

FIG. X1.2 Addition of Anhydride to Partially Hydrolyzed Polyol

NOTE X1.6—You can eliminate the trifluoroacetic anhydride peak by adding 10 µL of water. Add water only after the anhydride peak has appeared in the spectrum.

X1.9 Mixtures of Polyethers and Chain Extenders

X1.9.1 The following procedure determines if the test method is applicable to a particular mixture. Because of interference from trifluoroacetic acid, this procedure is not as precise as the procedure in Sections X1.6 – X1.8. The higher the hydroxyl number of the sample, the more severe the interference.

X1.9.2 Prepare a 30 % solution of polyether in chloroform-d$_1$ or fluorotrichloromethane. Transfer about 0.5 mL to an NMR tube. Proceed as in X1.8.2 using 25-µL aliquots of trifluoroacetic anhydride (Note X1.7). Minimize interferences from the spinning side bands of trifluoroacetic acid by changing the spinning rate. After complete derivatization, compare the relative areas of primary and secondary peaks with those obtained by derivatizing in accordance with Section X1.6 (Note X1.8). The test method described in Section X1.6 is applicable if the relative areas agree to within ±5 %. Peak shapes and chemical shifts can vary slightly since they are dependent on trifluoroacetic acid concentration (see Fig. X1.3).

NOTE X1.7—NMR sample sizes and anhydride aliquots were chosen based on a 5-mm NMR tube and a polyol having a hydroxyl number of 28. If different diameter NMR tubes are used or if the polyol has a higher hydroxyl number, adjust volumes accordingly. Complete derivatization requires about 60 µL of anhydride.

NOTE X1.8—Primary alcohols derivatize slightly faster than secondary alcohols. Insufficient anhydride will give a primary hydroxyl value about 10 % higher than the actual value.

X1.10. Calculation

X1.10.1 Determine the average areas of the primary and secondary peaks from the integration curves. Calculate the percent primary hydroxyl from the following equation:

$$\text{Primary hydroxyl, \%} = \frac{\text{Ap}}{\text{Ap} + \text{As}} \times 100 \qquad (X1.1)$$

where:

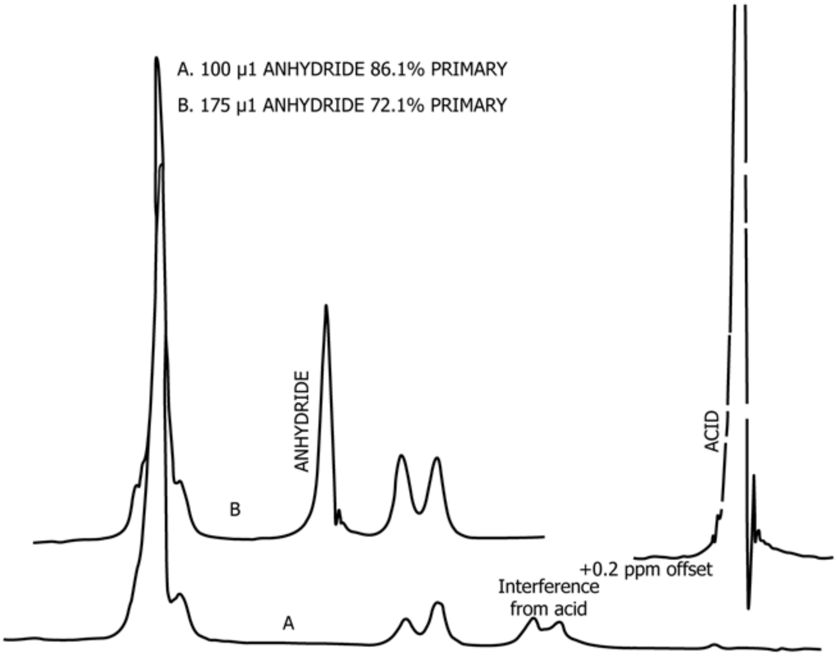

FIG. X1.3 Derivatization in NMR Tube 1000 MW Diol (72.6 % Primary)

Ap = area of primary hydroxyl peaks, and
As = area of secondary hydroxyl peaks.

Areas of each peak type are in accordance with Fig. X1.1.

X1.11. Report

X1.11.1 Report data to nearest 0.1 % primary hydroxyl. Duplicate runs which agree within two primary hydroxyl units are accepted for averaging.

X1.12. Precision and Bias[5]

X1.12.1 Attempts to develop a precision and bias statement for this test method have not been successful. For this reason, data on precision and bias cannot be given. Contact the Chairman, Subcommittee D20.22, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428–2959 if you want to participate in the development of precision and bias data.

X1.12.2 A limited round robin was run involving four laboratories testing six polyols ranging in primary hydroxyl content from 12 to 73 %. The intralaboratory repeatability is estimated to be 1.6 % absolute (2.8 standard deviations) from these data.

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue, D4273 - 05, that may impact the use of this standard. (April 1, 2011)

(1) Revised Note 1 to reflect the format (language and location) specified in D4968.
(2) Added an interference statement (Section 6). This required that all succeeding sections be renumbered.
(3) Added the proton resonance frequency of the spectrometer in 7.1.
(4) Revised 10.1 to allow mixing of the solution before addition to the NMR tube.
(5) Added 11.1 to explicitly state that quantitative conditions are required.
(6) Revised 11.2 to introduce both examples shown below and to remove non-mandatory language.
(7) Revised 11.2.2 to include the complete name of the instrument referenced.
(8) Revised 13 to remove a duplicate sentence and correct a typographical error. Changed percent to mole percent for clarity.
(9) Revised 15.5 to correct a typographical error.

---

[5] Supporting data are available from ASTM Headquarters. Request RR:D20-1107.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/