Designation: ~~D4273 – 11~~ D4273 – 18

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~~(~~13~~ ~~NMR),~~C NMR) measures the primary hydroxyl content of ethylene ~~oxide-propylene oxide polyethers~~ oxide (EO)-propylene oxide (PO) polyether polyols used in preparing flexible polyurethane foams. ~~It~~ This method is best suited for ~~polyethers~~ polyether polyols 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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

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

1.4 *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]

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]~~

~~E386 Practice for Data Presentation Relating to High-Resolution Nuclear Magnetic Resonance (NMR) Spectroscopy (Withdrawn 2015)[3]~~

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

E2977 Practice for Measuring and Reporting Performance of Fourier-Transform Nuclear Magnetic Resonance (FT-NMR) Spectrometers for Liquid Samples

3. Terminology

3.1 *Definitions*—~~The terminology in this test method follows the standard terminology defined in Practice~~ For definitions of terms that appear in this method, refer to Terminology ~~E386~~D883 and ~~in Terminology~~ Practice ~~D883~~E2977.

4. Summary of Test Method

4.1 ~~The resonance peaks~~ Peaks of the primary and secondary hydroxyl carbons of ~~the polyethers~~polyether polyols used in flexible ~~urethane~~polyurethane foams are well-resolved in high-resolution ~~13~~~~carbon-13~~C 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.~~hydroxyl (primary and secondary) area.

[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.

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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.

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

5. Significance and Use

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

6. Interferences

6.1 ~~Any primary hydroxyl propoxylate carbons present~~ Primary hydroxyl PO methylene carbons (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.~~

7. Apparatus

7.1 *Fourier-Transform NMR (FT-NMR) Spectrometer,* with carbon-13 capability and a carbon-13 resonance frequency of 50 MHz (proton resonance frequency of 200 MHz) or higher. The spectrometer is to have a minimum carbon-13 signal-to-noise ratio of 70:1 based on the benzene carbon signal in a 60 % benzene-d6, 40 % p-dioxane (v/v) sample (ASTM NMR standard) that has been pulsed once using a 90° pulse angle under the conditions specified in Practice E2977.

7.2 *NMR sample tubes* having outside diameters of 5 mm or more.

7.3 *NMR spinners.*

8. Reagents and Materials

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

8.1 ~~*Deuterated Chloroform or Deuterated Acetone,* containing tetramethylsilane (TMS) as an internal standard.~~All reagents are to be spectroscopic-grade and free of magnetic materials.

8.1.1 *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.~~

9. Hazards

9.1 *Magnetic Fields*—Follow the manufacturer's recommendation for the safe operation of the instrument.

9.1.1 Persons with implanted or attached medical devices such as pacemakers and prosthetic parts must remain outside the 5-gauss perimeter.

9.1.2 Objects made of ferromagnetic material will be attracted to the magnet and are to be kept a safe distance away.

~~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.~~

10. Preparation of Apparatus

10.1 Prepare a proton decoupled carbon-13 NMR experiment, selecting appropriate parameters to obtain quantitative integration of the peaks in the 68-60 ppm region.

10.1.1 *Inverse Gated Decoupling*—Decouple only during acquisition.

10.1.2 *Pulse Angle and Sequence Delay Time*—Select a 90 degree pulse angle with a sequence delay of 5 to 10 × T_1 of the peak with the longest relaxation time in the 68-60 ppm region. It is acceptable to use a different pulse angle/sequence delay combination to reduce acquisition time provided that quantitative data acquisition is not compromised.

10.1.3 *Number of Scans*—Select the appropriate number to yield a minimum signal to noise of > 10:1 for the smallest peak integrated over the 68-60 ppm region (usually 1024 to 2048).

10.1.4 *Sweep Width*—~ 220 ppm.

10.1.5 *Transmitter Frequency*—~100 ppm.

10.1.6 *Acquisition Time*—1 to 2 s.

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

11. Calibration and Standardization

11.1 This test method does not require standards. To evaluate the test method, standards can be prepared by blending commercially available poly(propylene oxide) and poly(ethylene oxide) diols. The molecular weights of the diols should ideally be 300 or more since lower molecular weight polyols can contain structural configurations that are not typical of polyether polyols used in flexible polyurethane foams.

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.

12. Procedure

12.1 Prepare a solution of the polyol sample in deuterated chloroform or deuterated acetone containing TMS as an internal standard. A 30-60 % solution is recommended. (See Note 2.)

12.2 Transfer an appropriate amount of the sample solution to an NMR tube.

12.3 Place the NMR tube into a spinner, adjust it to the appropriate depth and insert it into the spectrometer probe.

12.4 Obtain a stable lock on the solvent.

12.5 Tune and match the probe.

12.6 Shim the sample to optimize field-homogeneity.

12.7 Acquire the NMR data.

12.8 Zero fill the data. The recommended value is 1 or 2 × number of points.

12.9 Apply a spectral weighting function (apodization) and Fourier Transform the Free Induction Decay (FID). The recommended apodization is an exponential window multiplication and a typical line broadening value is 1/acquisition time.

12.10 Phase and baseline correct the spectrum.

12.11 Set the internal TMS reference to 0 ppm.

12.12 Expand and integrate the peaks of interest. The primary hydroxyl peaks typically resonate in the 61.0 to 62.5 ppm region and the secondary hydroxyl peaks typically resonate in the 65.5 to 67.5 ppm region. An example is shown in Fig. 1.

NOTE 2—The use of 0.025 to 0.05 M $Cr(acac)_3$ has been found to shorten relaxation times allowing for shorter data acquisition times.

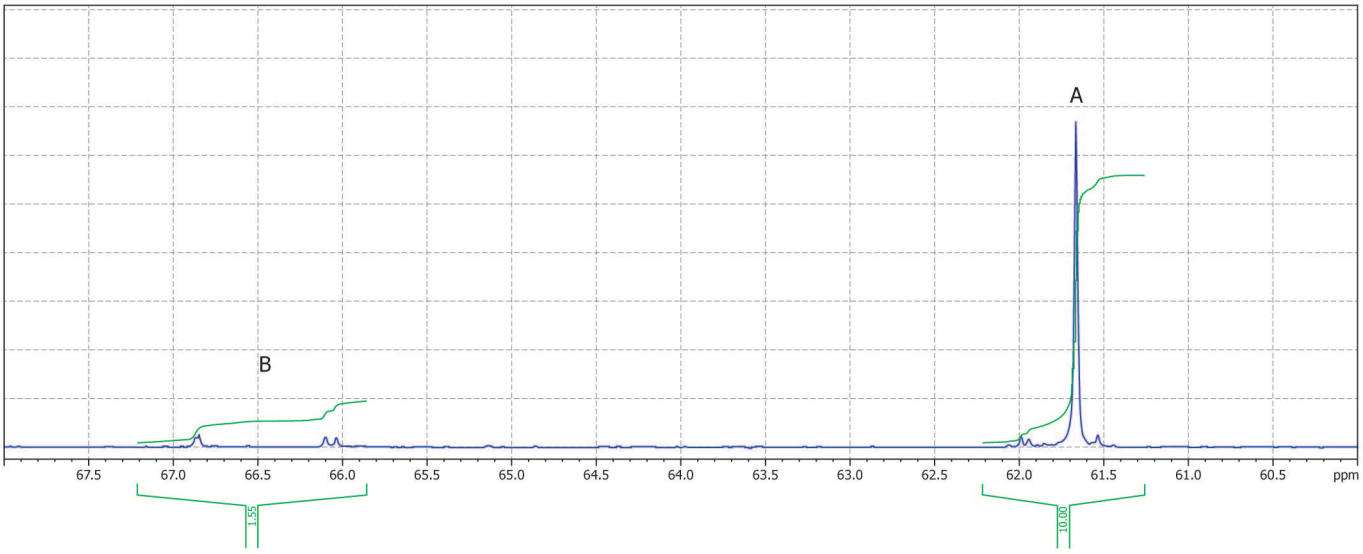

FIG. 1 [13] ~~Primary Hydroxyl Carbon Peaks of 3500 MW Triol (52 % Primary)~~C NMR Spectrum of an EO-PO Polyol (BB23796)

13. Calculation

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

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

$$\text{Primary hydroxyl, \%} = A * \frac{100}{\text{A} + B} \tag{1}$$

where:~~*where:*~~

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

A = area of terminal EO methylene carbons (primary hydroxyl peaks),
B = area of terminal PO methine carbons (secondary hydroxyl peaks—does not correct for primary hydroxyl PO terminations).

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

14. Report

14.1 Report ~~results~~ the % primary hydroxyl content to the nearest ~~percent primary hydroxyl.~~two decimal places.

15. Precision and Bias[3]

15.1 Table 1 is based on a round robin conducted in ~~1979~~2016 in accordance with Practice E691, involving ~~six polyol samples with primary hydroxyl contents from 11 to 76 % and hydroxyl numbers from 24 to 109 (~~five materials ~~Table 2)~~ tested by eight laboratories. For each ~~polyol,~~material, all ~~of~~ the samples were prepared at one source, but the individual specimens were prepared at the laboratories ~~that~~which tested them. Each test result was ~~obtained from one individual NMR run.~~ a single determination. Each laboratory obtained two test results for each ~~material on two separate days.~~material.

15.2 *Caution*—~~In~~The ~~Table 1, for~~ explanation of repeatability (*r*) and reproducibility (*R*~~the polyols indicated and the test results that are derived~~) is only intended to present a meaningful way of considering the approximate precision of this test method. Do not apply the data in Table 1 to accept or reject materials, as these data apply only to the materials tested in the round robin and are unlikely to be rigorously representative of other lots, formulations, conditions, materials, or laboratories. Users of this test method need to apply the principles outlined in Practice E691 ~~from testing two specimens of each polyol on each of two separate days:~~to generate data specific to their materials and laboratory (or between specific laboratories). The principles would then be valid for such data.

~~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.)~~

[3] Supporting data are available from ASTM Headquarters. Request ~~RR:D20-1108~~RR:D20-1270.

~~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 1 Primary Hydroxyl Content of Polyether Polyols

Sample	Material	OH Value (mg KOH/g)	Mean	S_r[B]	S_R[C]	r[D]	R[E]
BB23792	Blend of PPG 2000 and PEG	61	10.85	0.45	0.56	1.27	1.56
BB23793	Blend of PPG 2000 and PEG[A]	71	24.38	0.63	1.72	1.75	4.80
BB23794	Glycerol/EO-PO (EO + PO > 6.5) mixed feed	43	42.55	0.73	1.05	2.03	2.95
BB23795	DPG/EO-PO (EO + PO > 4.5)	43	71.39	0.39	1.46	1.10	4.08
BB23796	EO-PO	30	87.75	1.09	2.36	3.04	6.62

~~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.~~Phase separation was observed in sample BB23793. Data for this sample are expected to include this variability.

[B] S_r = within-laboratory standard deviation for the indicated material. It is obtained by pooling the within-laboratory standard deviations of the test results from all of the participating laboratories:

$S_r = [[(S_1) 2 + (S_2)^2 \ldots \ldots + (S_n)^2]/n]^{1/2}$ where n = number of participating laboratories.

[C] S_R = between-laboratories reproducibility, expressed as standard deviation:

$S_R = [S_r^2 + S_L^2]^{1/2}$ where S_L = standard deviation of laboratory means.

[D] r = within-laboratory critical interval between two test results = 2.8 × S_r

[E] R = between-laboratories critical interval between two test results = 2.8 × S_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 *Repeatability*—~~For further information on the methodology used in this section, see Practice~~ Precision under repeatability conditions.~~E691~~.

15.4 *Reproducibility*—Precision under reproducibility conditions.

15.5 Any judgment in accordance with the repeatability and reproducibility statements shown would have an approximate 95% (0.95) probability of being correct.

15.6 ~~*Bias*—~~There are no recognized standards ~~on~~by which to ~~base an~~ estimate ~~of~~ bias ~~for~~of 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

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.~~

X1.1 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).