Designation: ~~D4273 – 18~~ D4273 – 23

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* (^{13}C NMR) measures the primary hydroxyl content of ethylene oxide (EO)-propylene oxide (PO) polyether polyols used in preparing flexible polyurethane foams. This method is best suited for polyether polyols with primary hydroxyl contents of 10 to 90 %.

1.2 The values stated in SI units are to be regarded as 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, health, and 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
E456 Terminology Relating to Quality and Statistics
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E2935 Practice for Evaluating Equivalence of Two Testing Processes
E2977 Practice for Measuring and Reporting Performance of Fourier-Transform Nuclear Magnetic Resonance (FT-NMR) Spectrometers for Liquid Samples

3. Terminology

3.1 *Definitions*—~~For definitions of terms that appear in this method, refer to~~ Terms used in this standard are defined in accordance with Terminology D883 and Practice E2977, unless otherwise specified. For terms relating to precision and bias and associated issues, the terms used in this standard are defined in accordance with Terminology E456.

[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**

4. Summary of Test Method

4.1 Peaks of the primary and secondary hydroxyl carbons of polyether polyols used in flexible polyurethane foams are well-resolved in high-resolution ^{13}C NMR spectra. The primary hydroxyl content is determined from the ratio of the primary hydroxyl area to the total hydroxyl (primary and secondary) area.

5. Significance and Use

5.1 The primary hydroxyl content provides information about the relative reactivities of ~~polyols.~~polyols in the urethane forming reaction with isocyanates.

6. Interferences

6.1 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. Any additional non-polyether polyol compounds in the sample that produce NMR peaks in the 68-60 ppm region may interfere with the measurement.

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 spectroscopic-grade and free of magnetic materials.

8.1.1 *Deuterated chloroform or deuterated acetone,* containing tetramethylsilane (TMS) as an internal standard.

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.~~away, outside the 5-gauss perimeter.

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~~ ~100 ppm.

10.1.6 *Acquisition Time*—1 to 2 s.

11. Calibration and Standardization

11.1 This test method does not require standards. To evaluate the test method, ~~standards can be prepared~~ it is feasible to prepare standards by blending commercially available poly(propylene oxide) and poly(ethylene oxide) diols. ~~The~~ Ideally, the molecular weights of the diols ~~should ideally~~are to 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. 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 deuterium lock on the solvent.

12.5 Tune and match the ~~probe.~~probe for ^{13}C and ^{1}H channels.

12.6 Shim the sample to optimize magnetic field-homogeneity.

12.7 Acquire the NMR data.

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

13. Calculation

13.1 Calculate the percent primary hydroxyl content using the following equation:

$$\text{Primary hydroxyl, \%} = A^{*}\frac{100}{\text{A}+B} \quad (1)$$

where:

A = area of terminal EO methylene carbons (primary hydroxyl peaks),

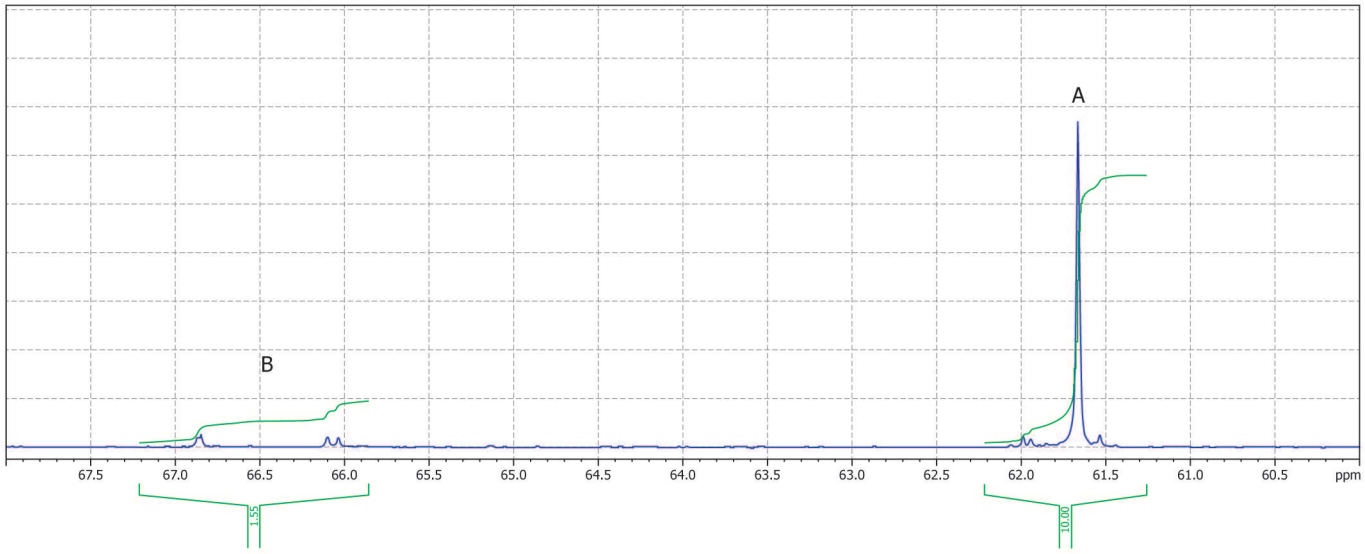

FIG. 1 ^{13}C NMR Spectrum of an EO-PO Polyol (BB23796)

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

14. Report

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

15. Precision and Bias[3]

15.1 Table 1 is based on a round robin conducted in 2016 in accordance with Practice E691, involving five materials tested by eight laboratories. For each material, all the samples were prepared at one source, but the individual specimens were prepared at the laboratories which tested them. Each test result was a single determination. Each laboratory obtained two test results for each material.

15.2 *Caution*—The explanation of repeatability (*r*) and reproducibility (*R*) 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 to generate data specific to their materials and laboratory (or between specific laboratories). The principles would then be valid for such data.

15.3 *Repeatability*—Precision under repeatability conditions.

15.4 *Reproducibility*—Precision under reproducibility conditions.

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

15.6 There are no recognized standards by which to estimate bias of this method.

15.7 For information on equivalence, refer to Practice E2935.

16. Keywords

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

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

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

[A] 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 = $2.8 \times S_r$
[E] R = between-laboratories critical interval between two test results = $2.8 \times S_R$

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