



Standard Test Method for Polyurethane Raw Materials: Determination of Primary Hydroxyl Content of Polyether Polyols¹

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)³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

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.

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.

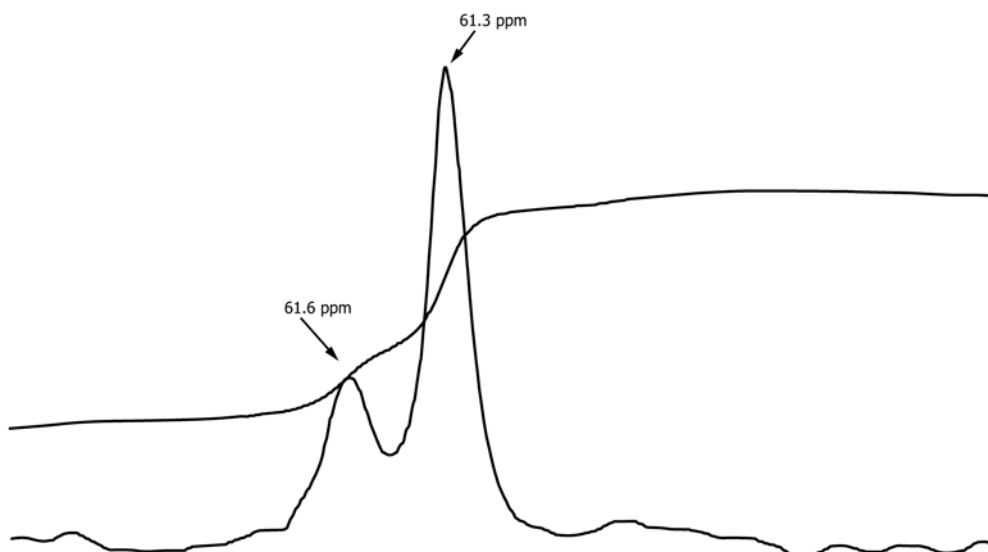


FIG. 1 Primary Hydroxyl Carbon Peaks of 3500 MW Triol (52 % Primary)

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:

$$\text{Primary hydroxyl, \%} = \frac{A_p}{A_p + A_s} \times 100 \quad (1)$$

where:

A_p = area of primary hydroxyl peaks, and

A_s = 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.

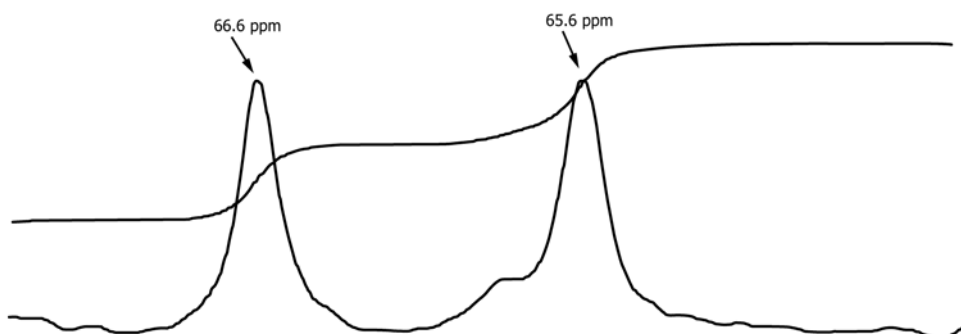


FIG. 2 Secondary Hydroxyl Carbon Peaks of 3500 MW Triol (52 % Primary)

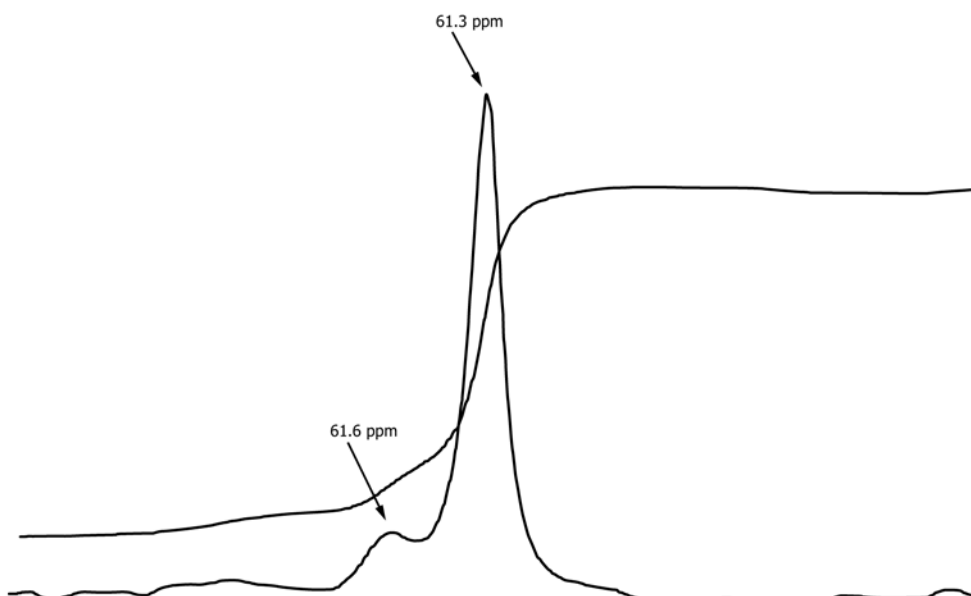


FIG. 3 Primary Hydroxyl Carbon Peaks of 5500 MW Triol (78 % Primary)



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