



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

This standard is issued under the fixed designation D 4273; 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 *Test Method A—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.

1.2 *Test Method B—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 suitable for polyethers with hydroxyl numbers of 24 to 109 and primary hydroxyl contents of 10 to 90 % (see Note 2).

NOTE 1—There are no equivalent ISO standards.

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.*

2. Referenced Documents

2.1 ASTM Standards:

D 883 Terminology Relating to Plastics²

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals³

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁴

¹ These test methods are under the jurisdiction of ASTM Committee D-20 on Plastics and are the direct responsibility of Subcommittee D20.22 on Cellular Plastics. These test methods were recommended to ASTM by the Society of the Plastics Industry Polyurethane Raw Materials Analysis Committee.

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² *Annual Book of ASTM Standards*, Vol 08.01.

³ *Annual Book of ASTM Standards*, Vol 15.05.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

3. Terminology

3.1 *Definitions*: The terminology in these test methods follows the standard terminology defined in Terminology D 883.

3.2 *Acronym Specific to This Standard*:

3.2.1 *RCF, n*—relative centrifugal force, expressed as a multiple of gravitational force.

4. Summary of Test Methods

4.1 *Test Method A*—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.

4.1.1 Mixtures of polyethers may 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 2—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.

4.1.2 The hydroxyl contribution of chain extenders in polyethers may 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 3—A test of the test method's applicability to samples containing chain extenders is given in Section 12.

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

4.2 *Test Method B*—The resonance bands 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 band 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 bands.

5. Significance and Use

5.1 Measurements of primary hydroxyl content are used in research to estimate the reactivities of polyols.

TEST METHOD A—FLUORINE-19 NMR

6. Equipment

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

NOTE 4—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.

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

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

7. Reagents and Materials

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

7.2 *Trifluoroacetic Anhydride*—Aldrich Gold Label or the equivalent.

7.3 *Methylene Chloride*—Alcohol-free.

7.4 *Chloroform-d₁-alcohol-free*—Deuterated chloroform is used because non-deuterated chloroform usually contains ethanol.

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

7.6 *Anhydrous Magnesium Sulfate*, or other drying agent.

7.7 *Fluorotrichloromethane* — Stabilized grade.

8. Standards

8.1 This test method does not require standards. To evaluate this test method, standards may 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 2).

9. Preparation of Sample

9.1 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

9.1.1 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-d₁ and 2 mL of saturated aqueous bicarbonate solution (Note 5). 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 5—Trifluoroacetate derivatives are hydrolytically unstable. The analysis should not be interrupted once water is added.

10. Instrument Preparation

10.1 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.

10.2 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

11. NMR Analysis

11.1 Add sufficient chloroform-d₁ 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. 1). Integrate the spectrum six times at a power level below that which causes saturation.

11.2 *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. 2).

NOTE 6—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.

NOTE 7—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.

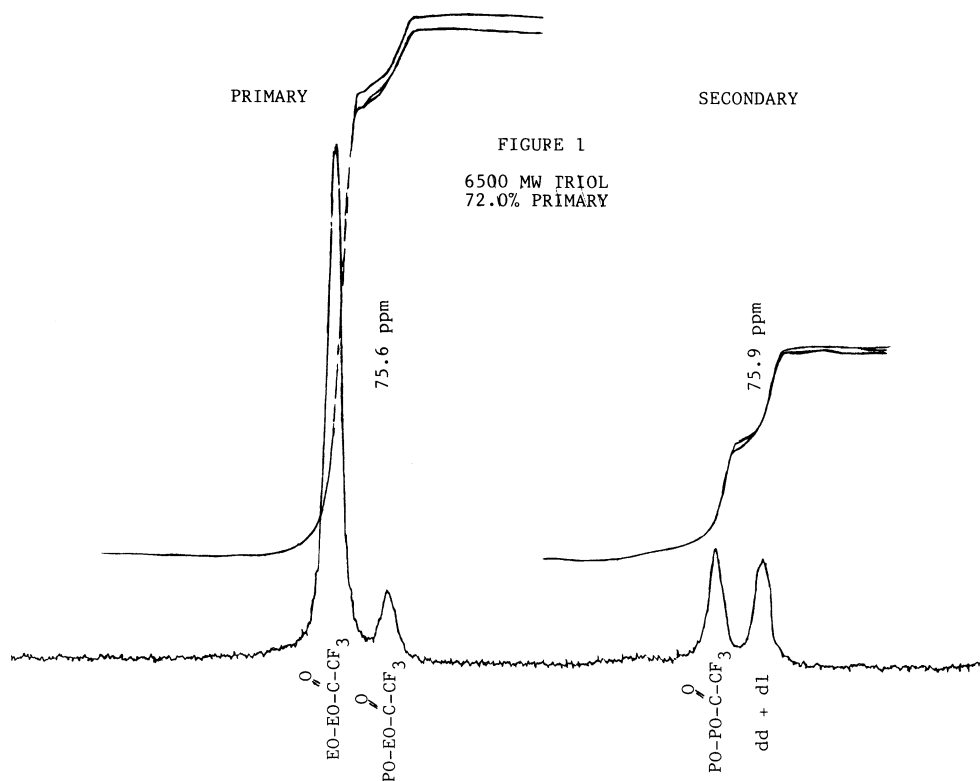


FIG. 1 6500 MW Triol (72.0 % Primary)

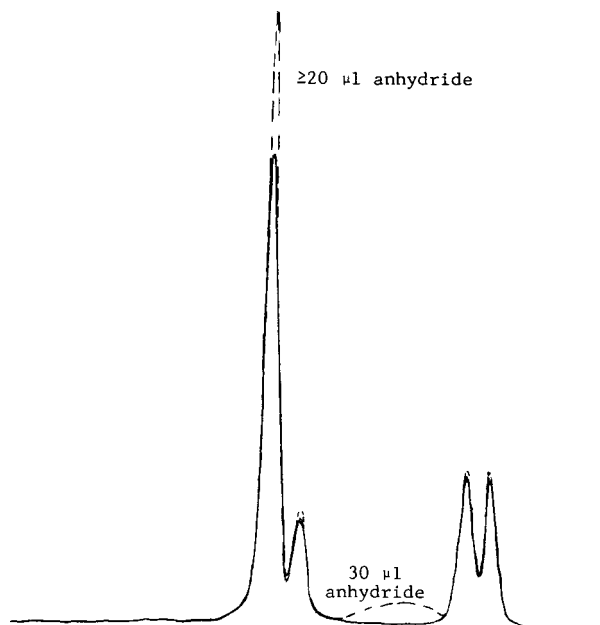


FIG. 2 Addition of Anhydride to Partially Hydrolyzed Polyol

12. Mixtures of Polyethers and Chain Extenders

12.1 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 9-11. The higher the hydroxyl number of the sample, the more severe the interference.

12.2 Prepare a 30 % solution of polyether in chloroform-d₁ or fluorotrichloromethane. Transfer about 0.5 mL to an NMR tube. Proceed as in 11.2 using 25-μL aliquots of trifluoroacetic anhydride (Note 8). 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 according to Section 9 (Note 9). The test method described in Section 9 is applicable if the relative areas agree to within ±5 %. Peak shapes and chemical shifts may vary slightly since they are dependent on trifluoroacetic acid concentration (see Fig. 3).

NOTE 8—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 9—Primary alcohols derivatize slightly faster than secondary alcohols. Insufficient anhydride will give a primary hydroxyl value about 10 % higher than the actual value.

13. Calculation

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

$$\begin{aligned} & \text{Primary hydroxyl, \%} & (1) \\ & = \frac{\text{area primary hydroxyl peaks}}{\text{area of primary hydroxyl peaks} + \text{area of secondary hydroxyl peaks}} \\ & \times 100 \end{aligned}$$

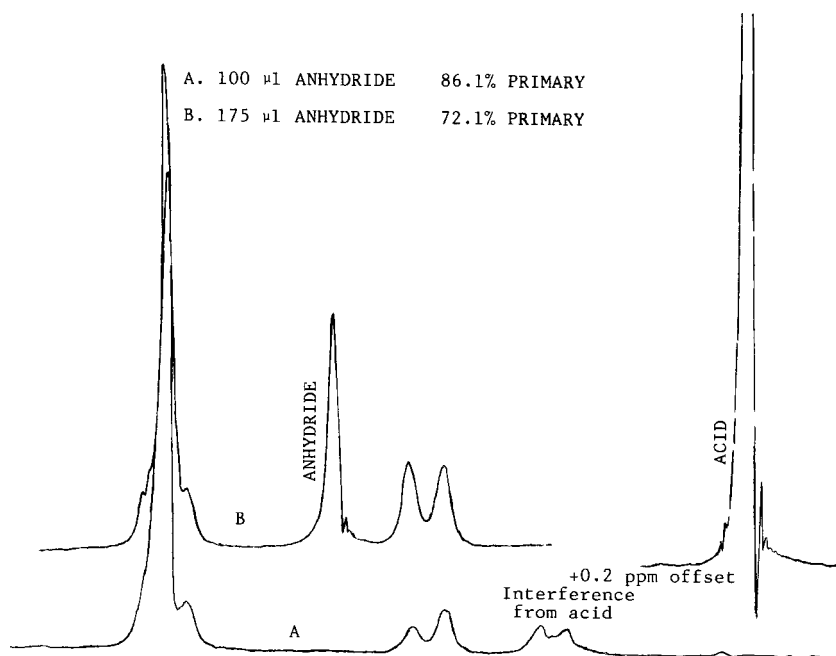


FIG. 3 Derivatization in NMR Tube 1000 MW Diol (72.6 % Primary)

where the areas of each peak type are in accordance with Fig. 1.

14. Report

14.1 Report data to nearest 0.1 % primary hydroxyl. Duplicate runs which agree within 2 primary hydroxyl units are accepted for averaging.

15. Precision and Bias

15.1 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. Anyone wishing to participate in the development of precision and bias data should contact the Chairman, Subcommittee D20.22, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

15.2 A limited round robin was run⁵ 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.

TEST METHOD B—CARBON-13 NMR

16. Equipment

16.1 *Pulse Fourier-Transform NMR (FT-NMR) Spectrometer*, with carbon-13 capability and a carbon-13 resonance frequency of 15 MHz or higher. The spectrometer should 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. There should be a minimum of 8K computer words available for the analysis.

16.2 *NMR Sample Tubes*, with outer diameters of 8 mm or more.

17. Reagents

17.1 All reagents should be spectroscopic grade deuterated solvents and should be reasonably free of paramagnetic materials (less than 100 ppm iron, for example).

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

18. Standards

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

19. Preparation of Sample

19.1 Add 3 mL of the polyol and 1.5 to 2 mL of deuterated chloroform or deuterated acetone to the NMR tube. Cap the tube and mix the contents thoroughly.

20. Instrument Preparation

20.1 The settings presented here apply to a Bruker WP-80 spectrometer. Instrument settings for other spectrometers may be different. Consult the manufacturer's operating manual.

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

Nucleus observed	Carbon-13
Spectral width	3000 Hz
Pulse angle	27°
Data points	8K
FT transform	8K or 16K if available (using zero fill in the second 8K)
Acquisition time	1.36 s
Delay between pulses	0.0 s

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

Exponential weighing function 1.5 Hz
 Detection method Quadrature phase (if available) or

 single phase
¹H decoupler Broadband
 Mode Auto shim

21. NMR Analysis

21.1 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 bands at about 61 ppm and the secondary hydroxyl bands at about 66 ppm are then expanded, amplified, and integrated (the chemical shifts are based on TMS set at 0.0 ppm). See Figs. 4-7 for examples of spectra obtained on two different polyols.

22. Calculation

22.1 Determine the areas of the primary and secondary bands from the integration curves. Calculate the percent primary hydroxyl from the following equation:

$$\begin{aligned} & \text{Primary hydroxyl, \%} & (2) \\ & = \frac{\text{area primary hydroxyl peaks}}{\text{area of primary hydroxyl peaks} + \text{area of secondary hydroxyl peaks}} \times 100 \end{aligned}$$

23. Report

23.1 Report results to the nearest percent primary hydroxyl.

24. Precision and Bias ⁶

⁶ Supporting data are available from ASTM Headquarters. Request RR: D20-1108.

TABLE 1 ¹³C 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.

24.1 Table 1 is based on a round robin conducted in 1979 in accordance with Practice E 691, 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.

24.2 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:

24.2.1 S_r = within-laboratory standard deviation of the average: I_r = 2.83 S_r. (See 24.2.3 for application of I_r.)

24.2.2 S_R = between-laboratory standard deviation of the average: I_R = 2.83 S_R. (See 24.2.4 for application of I_R.)

24.2.3 *Repeatability*—In comparing two test results for the same polyol, obtained by the same operator using the same

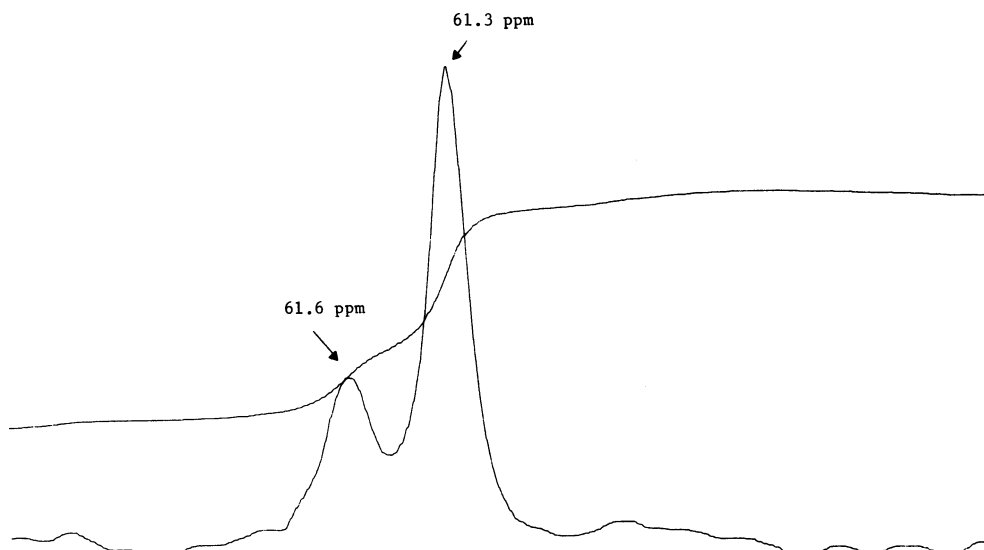


FIG. 4 Primary Hydroxyl Carbon Bands of 3500 MW Triol (52 % Primary)

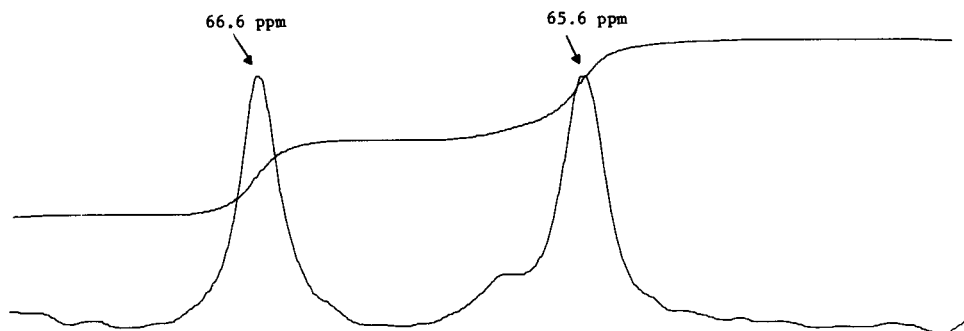


FIG. 5 Secondary Hydroxyl Carbon Bands of 3500 MW Triol (52 % Primary)

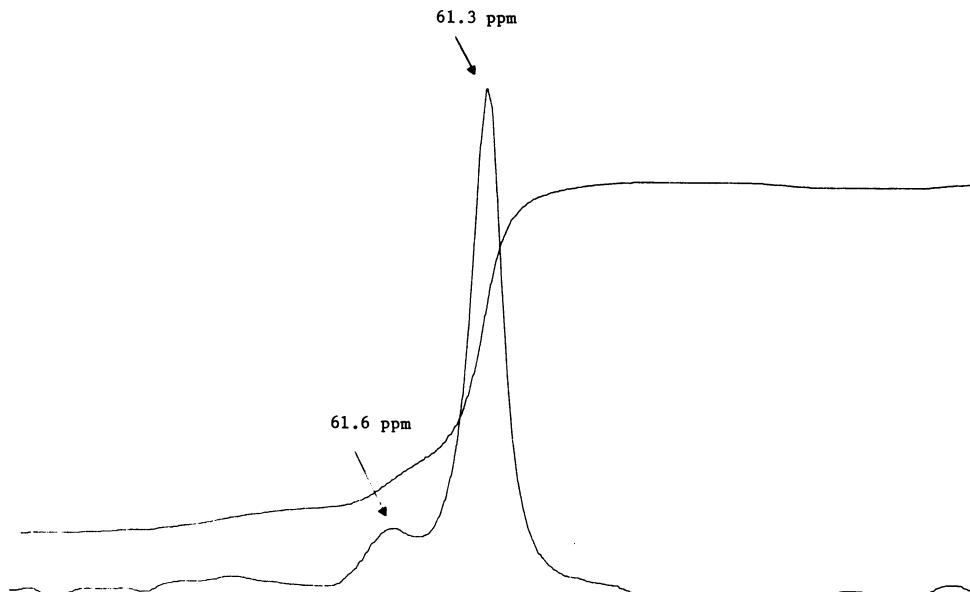


FIG. 6 Primary Hydroxyl Carbon Bands of 5500 MW Triol (78 % Primary)

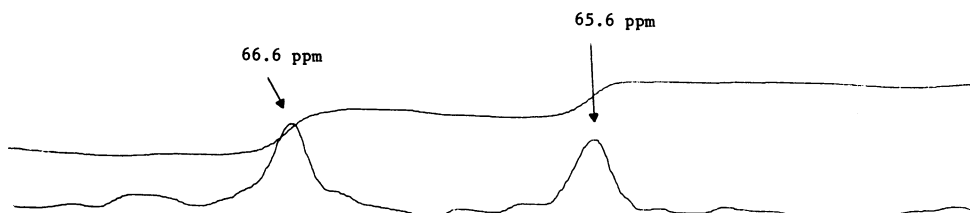


FIG. 7 Secondary Hydroxyl Carbon Bands of 5500 MW Triol (78 % Primary)

equipment on the same day, those test results should be judged not equivalent if they differ by more than the I_r value for that polyol and condition.

24.2.4 *Reproducibility*—In comparing two test results for the same polyol, obtained by different operators using different equipment on different days, those test results should 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.)

24.2.5 Any judgement in accordance with 24.2.3 and 24.2.4 will have an approximate 95 % (0.95) probability of being correct.

24.2.6 Other polyols may yield somewhat different results.

24.3 For further information on the methodology used in this section, see Practice E 691.

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

24.5 The precision statements in 24.1-24.3 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 E 180 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 Mz).

25. Keywords

25.1 NMR; nuclear magnetic resonance spectroscopy; polyether polyol; polyurethane raw materials

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this edition of these test methods since the last issue that may impact the use of these test methods:

D 4273–99:

(1) In 1.2, removed hyphen in ethylene oxide.

(2) In 4.1, pluralized “Area.”

(3) In 6.3, moved comma and hyphen to clarify “*Centrifuge, bench-top type.*”

(4) In 3.2, made editorial changes.

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