



Designation: D 4876 – 98

Standard Test Method for Polyurethane Raw Materials: Determination of Acidity of Crude or Modified Isocyanates¹

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1. Scope *

1.1 This test method determines the total acidity, expressed as HCl, of crude or modified isocyanates. The test method is applicable to products derived from toluene diisocyanate, methylene-bis-(4-phenylisocyanate), and polymethylene polyphenylisocyanates. (See Note 1.)

1.2 The values stated in SI units are to be regarded as the 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. For specific hazards statements see 7.1 and Note 2.*

NOTE 1—There is no equivalent ISO standard.

2. Referenced Documents

2.1 ASTM Standards:

D 841 Specification for Nitration Grade Toluene²

D 883 Terminology Relating to Plastics³

D 1193 Specification for Reagent Water⁴

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁵

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁶

3. Terminology

3.1 Definitions—For definitions of terms used in this test method see Terminology D 883.

4. Summary of Test Method

4.1 Labile chlorine compounds react with methanol to liberate hydrogen chloride. The hydrogen chloride is titrated potentiometrically with alcoholic potassium hydroxide.

5. Significance and Use

5.1 These test methods can be used for research or for quality control to characterize isocyanates used in polyurethane products.

6. Apparatus

6.1 *Potentiometric Titrator or pH Meter.*

6.2 *Calomel Electrode.*

6.3 *Glass Electrode.*

6.4 *Lunge Pipet*, or any weighing device suitable for weighing a liquid sample by difference to the nearest 0.001 g.

6.5 *Magnetic Stirrer.*

6.6 *Thermometer*, –10 to 100°C range.

7. Reagents

7.1 *Purity of Reagents*—Use reagent-grade chemicals in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁷ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type 1 of Specification D 1193.

7.3 *Methanol-Anhydrous* reagent grade with a water content of 0.10 % maximum.

7.4 *Potassium Hydroxide, Methanolic Solution (0.02 N)*—Prepare a 0.02 N methanolic potassium hydroxide (KOH) solution and standardize frequently enough to detect changes of 0.001.

7.5 *Toluene*—Dry, conforming to Specification D 841 and dried by a drying agent.

¹ This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D 20.22 on Cellular Plastics.

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² *Annual Book of ASTM Standards*, Vol 06.04.

³ *Annual Book of ASTM Standards*, Vol 08.01.

⁴ *Annual Book of ASTM Standards*, Vol 11.01.

⁵ *Annual Book of ASTM Standards*, Vol 15.05.

⁶ *Annual Book of ASTM Standards*, Vol 14.02.

⁷ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

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

8. Sampling

8.1 Since organic isocyanates react with atmospheric moisture, special precautions must be taken in sampling (**Caution:** Note 2). Usual sampling methods (for example, sampling an open drum with a thief), even when carried out rapidly, can cause contamination of the sample with insoluble urea. Therefore, the sample must be blanketed with dry air or nitrogen at all times.

NOTE 2—Organic isocyanates are toxic when they are absorbed through the skin, or when the vapors are breathed. Adequate ventilation should be provided and protective gloves and eyeglasses should be worn.

9. Test Conditions

9.1 Since isocyanates react with moisture, laboratory humidity should be kept low, preferably around 50 % relative humidity.

10. Procedure

10.1 Weigh to the nearest 1 mg 1.0 to 1.5 g of crude isocyanate into each of two clean, dry, 250-mL beakers. Add by graduated cylinder 50-mL of toluene and 50-mL of anhydrous methanol to each beaker. Add a stirring bar and a thermometer to each beaker and place them on a hot plate. Rapidly heat the solutions with stirring so that they reach a temperature of 60 to 65°C in 2 to 3 min. Do not allow the beakers to remain on the heater for more than 60 s after the temperature reaches 60°C and do not allow the temperature to exceed 65°C. If either of these conditions is violated, discard the sample and repeat the analysis. Remove the beakers from the hot plate, cover with a watch glass, and allow to cool in air for 60 ± 5 min. Remove the thermometer from the beaker and wash the thermometer and the beaker walls with 25 mL of anhydrous methanol.

10.2 Titrate the solution potentiometrically with 0.02 N methanolic KOH solution, using a 10-mL buret. Titrate to a pH of 7.0 which is stable for 30 s.

10.3 Titrate a blank exactly as described above, but without adding the sample.

11. Calculation

11.1 Calculate the acidity as follows:

$$\text{HCl, \%} = \frac{3.65(A - B)N}{W}$$

where:

- A = KOH solution required for titration of the sample, mL,
- B = KOH solution required for titration of the blank, mL,
- N = normality of the KOH solution in milliequivalents/mL,
- W = sample used, g, and
- 3.65 = a constant combining 1) the equivalent weight of HCl (36.5) is mg/meq, 2) conversion from mg to g (1000), and 3) conversion to percent (100).

$$\text{HCl, \%} = \frac{36.5(A - B)(N)(100)}{W(1000)} = \frac{3.65(A - B)N}{W}$$

12. Precision and Bias⁸

12.1 *Precision*—Table 1 is based on a round robin conducted in 1994 in accordance with Practice E 691, involving three materials tested by nine laboratories. All of the samples for each material were prepared at one source, but the individual specimens were prepared at the laboratories that tested them. Each test result was the average of two individual determinations. Each laboratory obtained two test results for each material on each of two days.

NOTE 3—The following explanations of *r* and *R* (12.1 through 12.1.3) are intended only to present a meaningful way of considering the approximate precision of this test method. The data in Table 1 should not be applied rigorously to the acceptance or rejection of material, as those data are specific to the round robin and may not be representative of other lots, conditions, materials, or laboratories. Users of this test method should apply the principles outlined in Practice E 691 to generate data specific to their laboratory and materials or between specific laboratories. The principles of 12.1 through 12.1.3 would then be valid for such data.

12.1.1 *Repeatability, (r)*—(Comparing two replicates for the same material, obtained by the same operator using the same equipment on the same day.) The two replicate results should be judged not equivalent if they differ by more than the *r* value for that material.

12.1.2 *Reproducibility, (R)*—(Comparing two results for the same material, obtained by different operators using different equipment on different days.) The two test results should be judged not equivalent if they differ by more than the *R* value for that material.

12.1.3 Any judgment per 12.1.1 and 12.1.2 would have an approximate 95 % (0.95) probability of being correct.

12.2 *Bias*—There are no recognized standards by which to estimate the bias of this test method.

13. Keywords

13.1 acidity; aromatic isocyanates; isocyanates; methylene diphenyldiisocyanate; MDI; prepolymer; polyurethane; raw materials; test method; titration; toluene diisocyanate

⁸ Supporting data are available from ASTM Headquarters. Request RR: D20-6099.

TABLE 1 Round Robin Percent Acidity Data According to Practice E 180

Sample	Values in units of percent HCl					
	Average	<i>S_r</i> ^A	<i>S_R</i> ^B	<i>r</i> ^C	<i>R</i> ^D	df ^E
Mondur	0.0379	0.0012	0.0031	0.0034	0.0087	8
Rubinate	0.0184	0.0018	0.0142	0.0050	0.0400	7
TDI	0.0093	0.0008	0.0040	0.0022	0.0112	8

^A *S_r* = The within-laboratory standard deviation of replicates.

^B *S_R* = The between-laboratory standard deviation of average of duplicates.

^C *r* = The within-laboratory repeatability limit, 2.8^*S_r .

^D *R* = The between-laboratory reproducibility limit, 2.8^*S_R .

^E df = The df for the between-laboratory data.