



Standard Test Method for Unreacted Toluene Diisocyanates in Urethane Prepolymers and Coating Solutions by Gas Chromatography¹

This standard is issued under the fixed designation D 3432; 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.

This standard has been approved for use by agencies of the Department of Defense.

^{ε1} NOTE—Editorial changes were made throughout in November 1996.

1. Scope

1.1 This test method covers the determination of free toluene diisocyanates in urethane prepolymers and unpigmented coating solutions.

NOTE 1—This test method may also be useful for the determination of free isocyanate monomers of other types upon taking precautions to confirm suitability.

1.2 There is no reason to believe this test method would not work for pigmented coatings.

1.3 The values stated in inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *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 a specific hazard statement, see Section 8.

2. Referenced Documents

2.1 ASTM Standards:

D 2372 Practice for Separation of Vehicle from Solvent-Reducible Paints²

D 2698 Test Method for Determination of Pigment Content of Solvent-Reducible Paints by High-Speed Centrifuging²

E 260 Practice for Packed Column Gas Chromatography³

3. Summary of Test Method

3.1 A standard solution of the diisocyanate is analyzed by gas chromatography using an internal standard technique. The unknown specimen is then chromatographed, again using an internal standard, and a response factor is calculated from the standard solution. The unreacted diisocyanate content of the

unknown is calculated from the chromatogram of the specimen.

4. Significance and Use

4.1 This test method provides a measurement of the unreacted diisocyanate content of urethane prepolymers and coating solutions. This measurement is of basic importance to the health of the users.

5. Interferences

5.1 Under the test conditions described in this test method, other diisocyanates or impurities having identical or nearly identical elution times may interfere. It is generally necessary to know the identity of the diisocyanate being used in the specimen being tested, either by knowledge of the composition or by a separate analysis.

5.2 The temperature specifications for the injection port and column oven must be strictly followed to prevent thermal decomposition of the specimen. Decomposition can be detected by the failure of the recorder pen to return to the baseline after elution of the diisocyanate monomer.

5.3 Since resin solution specimens leave a nonvolatile residue in the injection port, the use of glass injection port liners is recommended. The glass liner should be changed daily or after each group of 10 specimens that are analyzed.

5.4 Since diisocyanates are highly reactive with water, a suitable drying cartridge should be used in the carrier gas line.

6. Apparatus

6.1 *Gas Chromatograph* equipped with flame ionization detector (FID) and capable of linear temperature programming to 300°C.

6.2 *Chromatographic Column*, 6.6 ft (2 m) by 0.125-in. (3.2-mm) outside diameter, 0.085-in. (2.1-mm) inside diameter stainless steel (or glass, 2-mm inside diameter), packed with a 10 % methyl vinyl silicone on 80/100 mesh high performance, white, flux-calcined diatomaceous earth. The packing is prepared by dissolving 1.0 g of the methyl vinyl silicone in 50 mL of methylene chloride. This solution is placed in an evaporating dish and 9 g of the diatomaceous earth is added with gentle

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² *Annual Book of ASTM Standards*, Vol 06.01.

³ *Annual Book of ASTM Standards*, Vol 14.02.

stirring. The evaporating dish may be gently heated on a steam bath or evaporated at room temperature. The packing should be gently stirred, periodically, until dry and free-flowing. A newly packed column should be conditioned overnight at 200°C with a flow of dry carrier gas.

NOTE 2—Any other column, either packed or capillary, may be substituted if the required separation is obtained.

NOTE 3—Other methods of packing preparation may be used, provided a free-flowing, uniformly coated packing results.

6.3 *Chromatographic Syringe*, 10 μL .

6.4 *Analytical Balance*, accurate to 0.1 mg.

6.5 *Glassware*—All glassware used should be oven-dried to eliminate moisture.

6.6 *Recorder, Recording Integrator or Computer* with appropriate software.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ 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 *Ethyl Acetate* (99 + %), urethane grade, dried over a Type 5A molecular sieve.

7.3 *Standard Solution A*—Weigh about 5.0 g of 1,2,4-trichlorobenzene (TCB) to 0.1 g and dilute to 500 mL with ethyl acetate (1 mL = 10 mg TCB).

7.4 *Standard Solution B*—Weigh about 0.25 g of the diisocyanate to 1 mg into a dried 100 mL volumetric flask and add 10 mL of Standard Solution A by pipet. Dilute to 100 mL with ethyl acetate and mix well. This solution has a shelf life of one day.

7.4.1 If the unreacted diisocyanate content of the prepolymer or coating solution exceeds 1 %, then Standard Solution B should be made by diluting 0.25 g of the diisocyanate monomer, weighed to 1 mg, with Standard Solution A to 10 mL in a dried 10-mL volumetric flask. No additional solvent is added in this case.

7.5 *Toluene Diisocyanate (TDI)*, 99.5 + % assay, mixture of 80 % 2,4- and 20 % 2,6-isomers.

7.6 *1,2,4-Trichlorobenzene (TCB)*.

8. Hazards

8.1 Diisocyanates can be toxic when inhaled or adsorbed through the skin. Provide adequate ventilation and wear impermeable gloves (for example, rubber, polyethylene, etc.) when handling these materials. Consult the manufacturer's Material Safety Data Sheet (MSDS) before handling any of these materials.

9. Procedure

9.1 Prepare the gas chromatograph (refer to Practice E 260) as follows:

9.1.1 *Injection Port Temperature*—150°C. When first using the method, it may be desirable to experiment with slightly higher and lower temperatures to determine if the injection port temperature is high enough for complete volatilization of the monomer, but low enough to avoid decomposition of the polymer (see 5.2).

9.1.2 *Oven Temperature*—150°C (for TDI). For other isocyanates, isothermal or temperature programmed analysis may be necessary.

9.1.3 *Detector Temperature*—300°C.

9.1.4 *Carrier Gas*—Dry helium or nitrogen (see 5.4), flow rate adjusted to obtain proper elution time (3.7 min) of the internal standard (30 mL/min nominal).

9.2 Separation may be required for products containing pigments. Pigments may be removed using procedures given in Methods D 2372 or D 2698. Report the values for unreacted diisocyanate in the product on a pigment-free basis.

9.3 Calibrate by injecting a 1 μL aliquot of Standard Solution B (7.4) and obtain a chromatogram.

9.4 *Specimens Having 0.1 to 1.0 % Unreacted Diisocyanate*:

9.4.1 Weigh a 5-g specimen (± 0.01 g) into a tared 25-mL (7-dram) vial. Pipet 1 mL of Standard Solution A into the vial. Add 10 mL of ethyl acetate and mix thoroughly.

NOTE 4—Additional solvent may be added if required to reduce viscosity of the specimen. Increase the specimen size to be injected proportionally.

9.4.2 Inject a 1 μL aliquot of the test solution (Note 5). Obtain a chromatogram, internally or by temperature programming as required.

NOTE 5—One-microlitre syringes tend to “freeze” during use with polymer solutions; therefore, a 10 μL syringe is recommended. Employ the proper technique to inject the desired specimen size.

9.5 *Specimens Having 1 to 10 % Unreacted Diisocyanate*:

9.5.1 Weigh a 5-g specimen (± 0.01 g) into a tared 25 mL (7-dram) vial. Pipet 10 mL of Standard Solution A into the vial and mix thoroughly. No additional solvent is added in this case.

9.5.2 Inject a 1 μL aliquot of the test solution (Note 5).

9.6 The order of elution (see Fig. 1) is:

Compound	Retention Time, min
Ethyl acetate	0.4
TCB	1.9
TDI	3.7

9.7 Construct baselines under the internal standard and isocyanate peaks by drawing a straight line from valley to valley under the respective peaks. With the standard solution, the isocyanate peak may return to the baseline more promptly than with sample solutions that contain polymeric species. However, it is important that the tail of the diisocyanate peak returns to the baseline. Failure to do so indicates thermal breakdown that will result in high values. Illustrations of peak shapes are shown in Fig. 1. Due to the nonsymmetrical shape of the peaks, measure peak areas by electronic integrator or planimeter.

⁴ *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.