Designation: D5836 – 08 (Reapproved 2013)

Standard Test Method for
Determination of 2,4-Toluene Diisocyanate (2,4-TDI) and 2,6-Toluene Diisocyanate (2,6-TDI) in Workplace Atmospheres (1-2 PP Method)[1]

This standard is issued under the fixed designation D5836; 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 This test method describes the determination of 2,4-toluene diisocyanate (2,4-TDI) and 2,6-toluene diisocyanate (2,6-TDI) in air samples collected from workplace atmospheres in a cassette containing a glass-fiber filter impregnated with 1-(2-pyridyl)piperazine (1-2 PP). This procedure is very effective for determining the vapor content of atmospheres. Atmospheres containing aerosols may cause TDI results to be underestimated.

1.2 This test method uses a high-performance liquid chromatograph (HPLC) equipped with a fluorescence or an ultraviolet (UV) detector (**1-4**).[2,3]

1.3 The validated range of the test method, as written, is from 1.4 to 5.6 µg of 2,4-TDI and 2,6-TDI which is equivalent to approximately 9.8 to 39 ppb for 2,4-TDI and 2,6-TDI based on a 20-L air sample. The HPLC method using an UV detector is capable of detecting 0.078 µg of 2,4-TDI and 0.068 µg of 2,6-TDI in a 4.0-mL solvent volume, which is equivalent to 0.55 ppb for 2,4-TDI and 0.48 ppb for 2,6-TDI based on a 20-L air sample.

1.4 The isomers of 2,4-TDI, and 2,6-TDI, can be separated utilizing a reversed phase column for the HPLC method. Because industrial applications employ an isomeric mixture of 2,4- and 2,6-TDI, the ability to achieve this separation is important.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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.* See Section 9 for specific precautions.

2. Referenced Documents

2.1 *ASTM Standards:*[4]

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D1356.

4. Summary of Test Method

4.1 A known volume of air is drawn through a cassette containing a glass-fiber filter impregnated with 1-(2-pyridyl)piperazine. The diisocyanate reacts with the secondary amine to form a urea derivative.

4.2 The coated glass-fiber filter is extracted with acetonitrile (ACN) containing 10 % dimethyl sulfoxide (DMSO) and the extract is analyzed by HPLC. The eluent is monitored with a fluorescence detector (240-nm excitation, 370-nm emission cutoff filter) or a UV detector (254 nm).

---

[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.

Current edition approved April 1, 2013. Published April 2013. Originally approved in 1995. Last previous edition approved in 2008 as D5836 - 08. DOI: 10.1520/D5836-08R13.

[2] Validation data and a preliminary draft of this test method were provided by the Salt Lake Technical Center of the U.S. Dept. of Labor, Occupational Safety and Health Administration, Salt Lake City, UT.

[3] The boldface numbers in parentheses refer to the references at the end of this test method.

[4] 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.

4.3 The amount of the urea derivative collected is determined by comparison of sample response (peak area integrations or peak heights) to a standard calibration curve for the urea derivative.

4.4 The amount of diisocyanate is calculated from the amount of urea determined in the analysis.

5. Significance and Use

5.1 Diisocyanates are used in the production of polyurethane foams, plastics, elastomers, surface coatings, and adhesives (**5**,**6**). It has been estimated that the production of TDI will steadily increase during the future years.

5.2 Diisocyanates are irritants to eyes, skin, and mucous membrane and are respiratory sensitizers. Chronic exposure to low concentrations of diisocyanates produces an allergic sensitization which may progress into asthmatic bronchitis (**7**,**8**).

5.3 The Occupational Safety and Health Administration (OSHA) has a permissible exposure limit (PEL) for 2,4-TDI of 0.02 ppm or 0.14 mg/m^3 as a ceiling limit. There is no OSHA PEL for 2,6–TDI(**9**). The American Conference of Governmental Industrial Hygienists (ACGIH) has a time–weighted average (TWA) Threshold Limit Value (TLV) of 0.005 ppm or 0.036 mg/m^3 and a short-term exposure limit (STEL) of 0.02 ppm or 0.14 mg/m^3 for either 2,4–TDI, or 2,6–TDI, or for a mixture of 2,4– and 2,6–TDI(**10**).

5.4 This proposed test method has been found satisfactory for measuring 2,4 and 2,6-TDI levels in the workplace.

6. Interferences

6.1 Any compound having the same retention time as the standards is a possible interference. Generally, chromatographic conditions can be altered to resolve an interference.

6.2 Compounds that can react with an isocyanate represent a potential interference. These would include molecules containing the functional groups: amines, alcohols, anhydrides, phenols, and carboxylic acids.

6.3 Strong oxidizing agents can potentially react with the 1-(2-pyridyl)piperazine.

6.4 Retention time data on a single column is not definitive proof of chemical identity. Analysis by an alternate column system, ratioing of wavelength response using two wavelengths or types of detector, should be performed to confirm chemical identity.

7. Apparatus

7.1 *Sampling Equipment:*

7.1.1 *Personal Sampling Pumps,* any pump capable of sampling at a rate of about 1.0 L/min for 8 h.

7.1.2 *Glass-Fiber Filters,* 37 mm, free of organic binder, impregnated with 1.0 mg of 1-(2-pyridyl)piperazine.[5,6]

7.1.3 *Cassette,* plastic holders of the three-piece personal monitor type, that accept filters of 37-mm diameter. Number the cassette for identification.

7.1.4 *Cellulose Backup Pad,* sized to fit the cassette (7.1.3).

7.2 *Analytical Equipment:*

7.2.1 *Liquid Chromatograph,* a high-performance liquid chromatograph (HPLC) equipped with a fluorescence detector capable of monitoring 240-nm excitation and 370-nm cutoff or a UV detector capable of monitoring 254-nm wavelength and a manual or automatic sample injector.

7.2.2 *Liquid Chromatographic Column,* an HPLC stainless steel column capable of separating the urea derivatives. Analytical columns recommended in this test method are the following: a 25-cm by 4.6-mm inside diameter stainless steel column packed with 10-µm Alltech C8[7]; 6-µm Zorbax CN[8]; 5-µm Zorbax TMS; 5-µm Chromegabond TMS[9]; 5-µm Spherisorb C6[10]; 5-µm Supelcosil LC-CN[11]; or an equivalent column.

7.2.3 *Electronic Integrator,* an electronic integrator or some other suitable method of determining peak areas or heights.

7.2.4 *Pipets and Volumetrics,* various sizes of volumetric pipets and flasks to prepare standards.

7.2.5 *Vials,* glass vials with a 4-mL volume and fitted with polytetrafluoroethylene-lined caps used for extraction of samples.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. It is intended that all reagents shall conform to the specifications of the Committees on Analytical Reagents of the American Chemical Society, where such specifications are available.[12] Other grades may be used provided it can be demonstrated that they are of sufficiently high purity to permit their use without decreasing the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference water shall be understood to mean Type II reagent water conforming to Specification D1193, HPLC grade.

8.3 *Acetonitrile* (CH_3CN) —HPLC grade.

8.4 *Ammonium Acetate*(CH_3COONH_4)—HPLC grade.

8.5 *Dimethyl Sulfoxide*($(CH_3)_2SO$)—HPLC grade.

8.6 *Extracting Solution*—A solvent mixture of acetonitrile and dimethyl sulfoxide in the percentage of 90 and 10 (v/v), respectively.

---

[5] ORBO-80 filters supplied by Supelco, Inc., Bellefonte, PA have been found satisfactory for this purpose.

[6] Isocyanate glass fiber filters supplied by Forest Biomedical, Salt Lake City, UT, have been found satisfactory for this purpose.

[7] 10-µm ALLTECH C8 supplied by Alltech Associates, Deerfield, IL, has been found satisfactory for this purpose.

[8] 6-µm ZORBAX CN and 5-µm ZORBAX TMS supplied by E.I. DuPont, Wilmington, DE, have been found satisfactory for this purpose.

[9] 5-µm Chromegabond TMS supplied by ES Industries, Marlton, NJ, has been found satisfactory for this purpose.

[10] 5-µm Spherisorb C6 supplied by PhaseSep, Hauppauge, NY, has been found satisfactory for this purpose.

[11] 5-µm Supelcosil LC-CN supplied by Supelco, Inc., Belleforte, PA has been found satisfactory for this purpose.

[12] *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.

8.7 *Glacial Acetic Acid* (CH_3COOH)—Reagent grade.

8.8 *Hexane* (C_6H_{14})—HPLC grade.

8.9 *Methylene Chloride*(CH_2 Cl_2)—HPLC grade.

8.10 *Mobile Phase*—A solvent mixture of acetonitrile (8.3) and water in the percentage of 37.5 and 62.5 (v/v), respectively. Add to the mobile phase enough ammonium acetate (8.4) (1.54 to 7.7 g/L of solution or 0.02 to 0.1 *N*) to optimize the chromatographic resolution. Add acetic acid (8.7) to the mixture to lower the pH to 6.0 to 6.2.

8.11 *1-(2-Pyridyl)piperazine* (1-2 PP) ($C_9H_{13}N_3$)—Reagent grade.[13]

8.12 *N,N'-(4-Methyl-1,3-phenylene)bis [4-(2-pyridinyl)-1-piperazinecarboxamide]* ($C_{27}H_{32}N_8O_2$)—(2,4-TDIP).[14]

8.13 *N,N'-(2-Methyl-1,3-phenylene)bis [4-(2-pyridinyl)-1-piperazinecarboxamide]* ($C_{27}H_{32}N_8O_2$)—(2,6-TDIP).[15]

8.14 *2,4-Toluene Diisocyanate* ($C_9H_6N_2O_2$)—Reagent grade.[16]

8.15 *2,6-Toluene Diisocyanate* ($C_9H_6N_2O_2$)—Reagent grade.[17]

9. Safety Precautions

9.1 The diisocyanates are potentially hazardous chemicals and are extremely reactive. Avoid exposure to the diisocyanate standards. Sample and standard preparations should be done in an efficient operating hood.

9.2 Avoid skin contact with all solvents.

9.3 Wear safety glasses at all times and other laboratory protective equipment as necessary.

10. Sampling

10.1 Refer to Practices D1357 and D3686 for general information on sampling.

10.2 Equip the worker, whose exposure is to be evaluated, with a filter holder connected to a belt-supported sampling pump. Collect personal samples by pointing the sampler downward in the breathing zone of the worker and remove the top for open-face sampling. Draw air through the filter at a calibrated rate of approximately 1.0 L/min and collect a maximum air sample of 15 L. Use a tripod or other support to locate the sampler in the general room area for stationary monitoring.

10.3 Treat field blanks in the same manner as samples. Open them in the environment to be sampled and immediately close and place with the samples to be sent to the laboratory for analysis. Provide an unopened, unused cassette assembly as a laboratory blank. Submit at least one laboratory blank and one field blank with each set of samples.

11. Preparation of Apparatus

11.1 *Glass-Fiber Filter*—Prepare a fresh solution of 2 mg/mL of 1-(2-pyridyl)piperazine (8.11) in methylene chloride every time a batch of filters is to be coated. In an exhaust hood, set several glass-fiber filters on an appropriate holder, one that will support and not contaminate the filters. Using a pipet that will deliver 0.5 mL, place 0.5 mL in the center of each filter. The liquid will just wet the filter; allow the filters to air-dry in the hood for several minutes. Place the filters in a jar that is large enough for the filters to lie flat. Place the jar in an unheated vacuum oven for 1 h (about 20-in. Hg vacuum) to remove residual methylene chloride. Install the top on the jar and store in a refrigerator until ready for use. Coated filters may be stored for up to six months if they are stored in small sealed jars in a refrigerator (4°C). The filters should not be stored at ambient temperature for more a day or two.

11.2 *Cassette*—Assemble the three-piece cassette, inserting the cellulose backup pad into the bottom, adding an impregnated filter, and installing the ring and top. Seal the assembly against air leakage by a wrap of masking tape or cellulose shrink bands, covering the crevice between the ring and bottom. Close the inlet and outlet openings of the cassette with plastic plugs.

12. Calibration and Standardization

12.1 *Sample Pump Calibration*—Calibrate the personal sampling pumps in accordance with Practice D3686, at the recommended flow rate with an assembled cassette between the pump and the flow-measuring device. Calibrate the pump before and after the sampling. If the postcalibration flow rate varies more than ±5 % from the precalibration flow rate, invalidate the sample.

12.2 *Standardization:*

12.2.1 Prepare a stock standard solution as micrograms of TDIP per millilitre of dimethyl sulfoxide. Express the TDIP as the free TDI. Multiply the amount of TDIP by the correction factor derived from the ratios of the respective molecular weights of the TDI and TDIP. The factor is 0.3479 for TDI.

12.2.2 Prepare working standards by diluting the stock standard with acetonitrile.

12.2.3 Prepare dilution standards at the necessary concentrations by diluting working standards with acetonitrile to generate a full calibration curve that brackets the sample concentrations.

12.2.4 Analyze by high-performance liquid chromatography using a suitable column and the mobile phase as described in 8.10. The typical operating conditions are as follows:

Column temperature	25°C
Flow rate	1.0 mL/min
Ultraviolet	254 nm
Fluorescence	240 nm, excitation 370 nm or none, emission cutoff filter
Injection size	5–25 µL

Analytical conditions serve as a guideline and may need to be modified depending upon the specific samples, column condition, detector, and other parameters.

---

[13] 1-(2-Pyridyl)piperazine supplied by Aldrich Chemical, Milwaukee, WI, has been found satisfactory for this purpose.

[14] 2,4-TDIP supplied by Supelco, Inc., Bellefonte, PA, is used for standardization purposes only.

[15] 2,6-TDIP supplied by Supelco, Inc., Bellefonte, PA, is used for standardization purposes only.

[16] 2,4-Toluene diisocyanate supplied by Bayer Corp. (formerly Miles, Inc.), Pittsburgh, PA, has been found satisfactory for this purpose.

[17] 2,6-Toluene diisocyanate supplied by Carbolabs, Inc., New Haven, CT has been found satisfactory for this purpose.

12.2.5 Analyze each diisocyanate standard solution in duplicate and utilize peak area integration if possible. Peak areas should agree within ±5 % per standard solution.

12.2.6 Prepare a calibration curve by plotting micrograms per millilitre of diisocyanate versus peak area or peak height values.

12.2.7 Periodically prepare quality control samples by spiking the underivatized TDI onto impregnated glass-fiber filters to verify the correctness of the calibration curve.

13. Procedure

13.1 Remove the filter from the cassette and, using forceps, insert into a 4-mL vial. Do not fold or crumple the filter, but lay it against the inside surface of the vial with the exposed surface inward. Treat the blanks in the same manner as the samples.

13.2 Pipet 4.0 mL of extracting solution into the vial. Seal immediately with a polytetrafluoroethylene-lined cap.

13.3 Shake the vial to remove large air bubbles from between the filter and the glass. Let the sample sit for 1 h.

13.4 Analyze the sample and quality control solutions in the same manner as the standard solutions in a batch at the same time. Use the same injection technique and injection volume for samples, quality controls, and standards.

13.5 Calculate the concentration of the diisocyanate in the sample as specified in Section 14. Determine the extraction efficiency periodically.

14. Calculation

14.1 Determine the concentration in micrograms per millilitre for the analyte from the integrated peak areas or peak heights by comparison of sample response with a least squares curve fit for standards.

14.2 Because the sample volume is 4.0 mL, the amount is directly known:

$$A = C \times 4.0 \text{ mL} \tag{1}$$

where:

A = amount of diisocyanate in the sample or blank solution, µg, and

C = concentration determined for the sample or blank from the calibration curve, µg/mL.

14.3 Subtract the quantity of diisocyanate found in the blank from the amount found in the sample:

$$A_{CORR} = A_S - A_B \tag{2}$$

where:

A_{CORR} = amount of diisocyanate in the sample minus the blank results, µg,

A_S = amount of diisocyanate found in the sample, µg, and

A_B = amount of diisocyanate found in the blank, µg.

14.4 Calculate the concentration of the diisocyanate in the air:

$$\text{TDI, mg/m}^3 = \frac{A_{CORR} \times \left(\frac{1000\text{L}}{\text{m}^3}\right)\left(\frac{\text{mg}}{1000\ \mu\text{g}}\right)}{(\text{air volume, L}) \times (EE)} \tag{3}$$

where:

EE = extraction efficiency in decimal form.

15. Precision and Bias[18]

15.1 *Precision.* An interlaboratory study was performed in accordance with Practice E691 to determine the precision of this test method. Thirteen sets of glass-fiber filters were spiked with four levels of TDIP and sent to 13 participating laboratories by overnight shipping. Each filter set consisted of four filters that were first coated with 1-2PP as described in the method, and then spiked with 2,4-TDIP and 2,6-TDIP from the same solution, plus a blank coated filter. The filters were shipped in separate 4-mL glass vials. A sample of the diluted TDIP mixture used to spike the coated filters was included with each filter set for use as an analytical standard. The amounts of TDIP present in the mixture solution were made known to the participating laboratories. The amounts of 2,4- and 2,6-TDIP (expressed as free TDI) spiked on the filters ranged from 1.4 to 5.4 µg per filter which is equivalent to 0.1 to 0.4 mg/m^3 TDI based on a 15-L air sample. The participating laboratories were told that the TDI amounts spiked on the filters were within the published range of the method. The average recovery for 2,4-TDI was 106 % with a relative standard deviation (RSD) of 5.6 %, and 104 % recovery with a RSD of 4.7 % for 2,6-TDI.

15.1.1 Within-laboratory precision, measured as repeatability RSD calculated from the interlaboratory study results, was 6.2 % for 2,4-TDI, and 5.7 % for 2,6-TDI (n=13).

15.1.2 Between-laboratory precision, measured as reproducibility RSD also calculated from the interlaboratory study results, was 7.8 % for 2.4-TDI, and 6.8 % for 2,6-TDI (n=13).

15.2 *Bias.* Method bias could not be directly measured because it was not possible to generate TDI test atmospheres. Estimated method bias is negligible, based on the fact that recoveries from the spiked samples were near 100 %.

16. Keywords

16.1 2,4-toluene diisocyanate; 2,6-toluene diisocyanate;1-(2-Pyridyl)piperazine; 2,4-TDI; 2,6-TDI; air monitoring; high-performance liquid chromatography; sampling and analysis; workplace atmospheres

---

[18] Supporting data are available from ASTM Headquarters. Request RR:D22-1030.

REFERENCES

(1) Hardy, H. L., and Walker, R. F., "Novel Reagent for the Determination of Atmospheric Isocyanate Monomer Concentrations," *Analyst*, No. 104, 1981, pp. 890–891.

(2) Goldberg, P. A., Walker, R. F., Ellwood, P. A., and Hardy, H. L., "Determination of Trace Atmospheric Isocyanate Concentrations by Reversed-Phase High-Performance Liquid Chromatography Using 1-(2-Pyridyl)Piperazine Reagent," *J. Chromatogr.* No. 212, 1981, pp. 93–104.

(3) Ellwood, P. A., Hardy, H. L., and Walker, R. F., *Analyst*, No. 106, 1981, p. 85.

(4) *OSHA Analytical Methods Manual*, 2nd ed., U.S. Department of Labor, Occupational Safety and Health Administration; OSHA Salt Lake Technical Center; Salt Lake, UT, 1983; Method 42—Diisocyanates; American Conference of Governmental Industrial Hygienists (ACGIH); Cincinnati, OH, Pub. No. 4542.

(5) "Criteria for a Recommended Standard...Occupational Exposure to Diisocyanates," Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health, Cincinnati, OH, No. DHEW (NIOSH), 1978, pp. 78–215.

(6) Hosein, H. R., and Farkes, S., "Risk Associated with the Spray Application of Polyurethane Foam," *Am. Ind. Hyg. Assoc. J.*, No. 42, 1982, pp. 663–665.

(7) "Criteria for a Recommended Standard...Occupational Exposure to Toluene Diisocyanate," Department of Health, Education and Welfare, National Institute for Occupational Safety and Health, Cincinnati, OH, No. DHEW (NIOSH) 1973, pp. 73–11022.

(8) Woolrich, P. F., "Toxicology, Industrial Hygiene and Medical Control of TDI, MDI and PMPPI," *Am. Ind. Hyg. Assoc. J.*, No. 43, 1981, pp. 89–97.

(9) *Code of Federal Regulations*, 29 CFR 1910.1000, Table Z-1.—Limits for Air Contaminants, U.S. Government Printing Office, Washington, DC, June 30, 1993 .

(10) *Threshold Limits Values for Chemical Substances and Physical Agents and Biological Exposure Indices* , American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 2007.