Designation: D 5836 – 03

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 D 5836; 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 produce low results.

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 *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]

D 1193 Specification for Reagent Water

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)

E 691 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 D 1356.

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 Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.04 on Workplace Atmospheres.

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[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 for 2,4-TDI of 0.02 ppm or 0.14 mg/m^3 as a ceiling limit **(9)**. The American Conference of Governmental Industrial Hygienists (ACGIH) has a 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**(10)**. No exposure limits have been established for 2,6-TDI.

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 D 1193, 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.

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

8.8 *Hexane* (C_6H_{14})—HPLC grade.

8.9 *Methylene Chloride* (CH_2Cl_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.

[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.