



Designation: D5932 – 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 Air (with 9-(N-Methylaminomethyl) Anthracene Method) (MAMA) in the Workplace¹

This standard is issued under the fixed designation D5932; 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 covers the determination of gaseous 2,4-toluene diisocyanate (2,4-TDI) and 2,6-toluene diisocyanate (2,6-TDI) in air samples collected from workplace and ambient atmospheres.

1.2 Differential air sampling is performed with a segregating device.^{2,3} The gaseous fraction is collected on a glass fiber filter (GFF) impregnated with 9-(N-methylaminomethyl) anthracene (MAMA).

1.3 The analysis of the gaseous fraction is performed with a high performance liquid chromatograph (HPLC) equipped with ultraviolet (UV) and fluorescence detectors.

1.4 The analysis of the aerosol fraction is performed separately as described in Ref (1).⁴

1.5 The range of application of this test method, utilizing UV and a fluorescence detector, is validated for 0.029 to 1.16 μg of monomer 2,4- and 2,6-TDI/2.0 mL of desorption solution, which corresponds to concentrations of 0.002 to 0.077 mg/m^3 of TDI based on a 15-L air sample. This

corresponds to 0.28 to 11 ppb(V) and brackets the established TLV value of 5 ppb(v).

1.6 A field blank sampling system is used to check the possibility of contamination during the entire sampling and analysis.

1.7 The values stated in SI units are to be regarded as the standard.

1.8 *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:⁵

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

2.2 Other Documents:

Sampling Guide for Air Contaminants in the Workplace⁶

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 segregating sampling device.

4.2 Gaseous and aerosol fraction are sampled simultaneously with a two filter loaded cassette.² The aerosol is collected

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 1996. Last previous edition approved in 2008 as D5932 - 08. DOI: 10.1520/D5932-08R13.

² The sampling device for isocyanates is covered by a patent held by Jacques Lesage et al, IRSST, 505 De Maisonneuve Blvd West, Montreal, Quebec, Canada. Interested parties are invited to submit information regarding the identification of acceptable alternatives to this patented item to the Committee on Standards, ASTM International Headquarters, 100 Barr Harbor Dr., PO Box C700, West Conshohocken, PA 19428. Your comments will receive careful consideration at a meeting of the committee responsible, which you may attend. This sampling device is currently commercially available under license from SKC Omega Specialty Division, Eighty-Four, PA.

³ The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

⁴ The boldface numbers in parentheses refer to the list of references at the end of this test method.

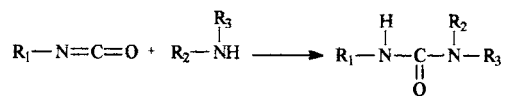
⁵ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

⁶ Available from Institut de Recherche en Santé et en Sécurité du Travail du Québec, Laboratory Services and Expertise Department, Montreal, IRSST, 2005.

on the first filter made of polytetrafluoroethylene (PTFE), the gaseous counterpart being adsorbed on the second filter made of glass fiber (GFF) impregnated with MAMA.

4.3 The analysis of the monomer and oligomer in the aerosol fraction is performed separately in accordance with the procedure described in Ref (1,2).

4.4 The diisocyanate present as a gas reacts with the secondary amine function of the MAMA impregnated on the GFF to form a urea derivative (3,4), as shown below.



4.5 Desorption is done with dimethylformamide 67 % containing 33 % mobile phase (70 % acetonitrile, 30 % buffer).

4.6 The resulting solution is analyzed by HPLC with two detectors in series: UV (254 nm) and fluorescence (254-nm excitation and 412-nm emission) (5).

4.7 2,4- and 2,6-TDI urea derivatives are separated using reversed phase HPLC column.

4.8 A complete calibration curve, covering the range of application of the test method, was obtained to determine the linearity of the method (see 1.5).

4.9 Concentration of urea derivative contained in the samples is calculated by using an external standard of the appropriate urea derivative.

5. Significance and Use

5.1 TDI is used mostly in the preparation of rigid and semi-rigid foams and adhesives.

5.2 Isocyanate use has been growing for the last 20 years and the industrial need is still growing.

5.3 Diisocyanates and polyisocyanates are irritants to skin, eyes, and mucous membranes. They are recognized to cause respiratory allergic sensitization, asthmatic bronchitis, and acute respiratory intoxication (6-9).

5.4 The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a Threshold Limit Value—Time Weighted Average (TLV—TWA) of 0.036 mg/m³ with a Short-Term Exposure Limit (STEL) of 0.14 mg/m³ for 2,4-TDI (10). The Occupational Safety and Health Administration of the U.S. Department of Labor (OSHA) has a permissible exposure limit of 0.02 ppm(V) or 0.14 mg/m³ of TDI as a ceiling limit and 0.005 ppm (V) or 0.036 mg/m³ as a time-weighted average (11).

5.5 Monitoring of respiratory and other problems related to diisocyanates and polyisocyanates is aided through the utilization of this test method, due to its sensitivity and low volume requirements (15 L). Its short sampling times are compatible with the duration of many industrial processes and its low quantification limit also suits the concentrations often found in the working area.

5.6 The segregating sampling device pertaining to this proposed test method physically separates gas and aerosol

allowing isocyanate concentrations in both physical states to be obtained, thus helping in the selection of ventilation systems and personal protection.

5.7 This test method is used to measure gaseous concentrations of 2,4- and 2,6-TDI in air for workplace and ambient atmospheres.

6. Interference

6.1 Any substance that can react with MAMA reagent impregnated on the GFF can affect the sampling efficiency. This includes strong oxidizing agents.

6.2 Any compound that has the same retention time as the TDIU derivative and gives the same UV/fluorescence detector response factor ratio can cause interference. Chromatographic conditions can be changed to eliminate an interference.

6.3 A field blank double-filter sampling system is used to check contamination during the combined sampling, transportation, and sample storage process. A laboratory blank is used to check contamination occurring during the analytical process.

7. Apparatus

7.1 Sampling Equipment:

7.1.1 *Personal Sampling Pump*, capable of sampling 1.0 L/min or less for 4 h.

7.1.2 *Double Filter Sampling Device*, 37 mm in diameter, three-piece personal monitor, plastic holder loaded with a PTFE filter close to the mouth, followed by a glass fiber filter impregnated with MAMA and a plastic back-up pad.² The glass fiber filter is impregnated with an amount of MAMA in the range of 0.07 to 0.25 mg.

7.1.3 Flow Measuring Device.

7.2 Analytical Equipment:

7.2.1 *Liquid Chromatograph*, a high-performance liquid chromatograph equipped with UV (254-nm wavelength) and fluorescence detectors (412-nm emission and 254-nm excitation) and an automatic or manual sample injector.

7.2.2 *Liquid Chromatographic Column*, an HPLC stainless steel column, capable of separating the urea derivatives. This proposed method recommends a 150- by 4.6-mm internal diameter stainless steel column packed with 0.5-μm C18, or an equivalent column.

7.2.3 *Electronic Integrator*, an electronic integrator or any other effective method for determining peak areas.

7.2.4 *Analytical Balance*, an analytical balance capable of weighing to 0.001 g.

7.2.5 *Microsyringes and Pipets*, microsyringes are used in the preparation of urea derivatives and standards. An automatic pipet, or any equivalent method, is required for sample preparation.

7.2.6 *pH Meter*, a pH meter or any equivalent device capable of assaying a pH range between 2.5 and 7.

7.2.7 *Specialized Flasks*, three-necked flask and an additional flask for the synthesis of the TDIU standard.

7.2.8 *Magnetic Stirrer*, a magnetic stirrer or any other equivalent method.