Designation: D 5932 – 96 (Reapproved 2002)

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 Workplace[1]

This standard is issued under the fixed designation D 5932; 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 di*iso*cyanate (2,4-TDI) and 2,6-toluene di*iso*cyanate (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 0.02 to 4.2 µg of monomer 2,4- and 2,6-TDI/2.0 mL of desorption solution, which corresponds to concentrations of 0.001 to 0.28 mg/m^3 of TDI based on a 15-L air sample. This corresponds to 0.15 to 40 ppb(V) and brackets the established TLV value of 5 ppb(v).

1.6 The average correlation coefficient is 0.9999 and 0.9999 for the UV detector, for 2,6 and 2,4-TDI, respectively. For the fluorescence detector, the average correlation coefficient is 0.9803 and 0.9999 for 2,6 and 2,4-TDI, respectively. These values were obtained from seven standard solutions distributed along the calibration curve, each standard being injected six times, with the curve having been done twice by different operators.

1.7 The quantification limit for 2,6-TDI monomers is 0.007 µg/2 mL of desorption solution, which corresponds to 0.0005 mg/m^3 for 15-L sampled air volume for the UV detector. For the fluorescence detector, the quantification limit is 0.003 µg/2 mL of desorption solution, which correspond to 0.0002 mg/m^3 for a volume of 15 L collected in air. These values are equal to ten times the standard deviation obtained from ten measurements carried out on a standard solution whose concentration of 0.02 µg/2 mL is close to the expected detection limit.

1.8 The quantification limit for 2,4-TDI monomers is 0.015 µg/2 mL of desorption solution, which corresponds to 0.001 mg/m^3 for 15-L sampled air volume for the UV detector. For the fluorescence detector, the quantification limit is 0.012 µg/2 mL of desorption solution, which corresponds to 0.0008 mg/m^3 for a volume of 15 L of collected air. These values are equal to ten times the standard deviation obtained from ten measurements carried out on a standard solution whose concentration 0.02 µg/2 mL is close to the expected detection limit.

1.9 2,4- and 2,6-TDI isomers can be separated using a reversed phase C18 column for HPLC. The UV and fluorescence detector response factor (RF) ratio characterize each isomer.

1.10 A field blank sampling system is used to check the possibility of contamination during the entire analytical process.

[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] The sampling device for *iso*cyanates 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 Omega Specialty Instrument, Chelmsford, MA.

[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.

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

1.12 *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]

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

2.2 *Other Documents:*

Sampling Guide for Air Contaminants in the Workplace [6]

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D 1356.

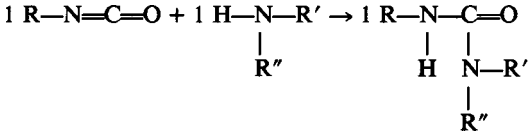
4. Summary of Test Method

4.1 A known volume of air is drawn through a segregating sampling device.

4.2 Gaseous and aerosol fraction are sampled simultaneously with a two filter loaded cassette.[2] The aerosol is collected 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 according to the procedure described in Ref (**1,2**).

4.4 The di*iso*cyanate present as a gas reacts with the secondary amine function of the MAMA impregnated on the GFF to form a urea derivative (**3,4**).



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) Ref (**5**).

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

4.8 The response factor is determined by the ratio of the concentration of the calibration solution and the area of the peak obtained.

4.9 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).

4.10 The amount of urea derivatives in the samples is calculated from the response factor and the area obtained for the sample peaks.

4.11 The amount of di*iso*cyanates is calculated from the amount of urea derivatives determined in the sample.

5. Significance and Use

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

5.2 *Iso*—cyanate use has been growing for the last ten years and the industrial need is still growing.

5.3 Di*iso*cyanates and poly*iso*cyanates are irritants to skin, eyes, and mucous membranes. They are recognized to cause respiratory allergic sensitization, asthmatic bronchitis, and acute respiratory intoxication (Refs **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/m^3 with a Short-Term Exposure Limit (STEL) of 0.14 mg/m^3 for 2,4-TDI (Ref **10**). (Ref. ACGIH 1993–4). 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/m^3 of TDI as a ceiling limit (**11**).

5.5 Monitoring of respiratory and other problems related to di*iso*cyanates and poly*iso*cyanates 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 detection 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 *iso*cyanate 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 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 laboratory manipulations.

7. Apparatus

7.1 *Sampling Equipment*:

[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 Division, Montreal, IRSST, 1995.

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 mL 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.

7.2.9 *Ointment Jars*, 30 mL, ointment jars and lid, capable of receiving 37-mm filters, used for desorption of samples.

7.2.10 *Reciprocating Shaker*, a reciprocating shaker or any other equivalent device.

7.2.11 *Vacuum Filtration System*, vacuum filtration system with 0.45-µm porosity nylon filters or any equivalent method to degas the mobile phase.

7.2.12 *Syringe Operated Filter Unit*, syringes with polyvinylidene fluoride 0.45-µm porosity filter unit, or any equivalent method.

7.2.13 *Injection Vials*, 1.5-mL vials with PTFE-coated septums for injection.

7.2.14 *Bottle*, amber-colored bottle with cap and PTFE-coated septum for conservation of stock and standard solutions of 2,4- and 2,6-TDIU or any equivalent method.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. All reagents shall 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.

8.2 *Purity of Water*—Unless otherwise indicated, water shall be reagent water as defined by Type 2 of Specification D 1193, HPLC grade.

8.3 *Acetonitrile (CH_3CN)*—HPLC grade.

8.4 *Buffer*—Place 30 mL of triethylamine (8.16) in water and dilute to 1 L in a volumetric flask. Add phosphoric acid (H_3PO_4) (8.11) to acidify to pH = 3.0. Filter the buffer under vacuum with a 0.45-µm porosity filter.

8.5 *Desorption Solution*—A solvent mixture of dimethylformamide (8.7) and mobile phase (8.10) in the percentage of 67 and 33 (v/v), respectively.

8.6 *Dichloromethane*—Reagent grade.

8.7 *Dimethylformamide*—Reagent grade.

8.8 *Helium (He)*—"High purity."

8.9 *9-(N-Methylaminomethyl) Anthracene (MAMA),* (F.W. 221.31) 99 % purity.

8.10 *Mobile Phase*—A solvent mixture of acetonitrile (CH_3CN) (8.3) and buffer (8.4) in the percentage of 70 and 30 (v/v), respectively, suitably degassed.

8.11 *Phosphoric Acid (H_3PO_4)*—Reagent grade.

8.12 *2,4-Toluene Diisocyanate (2,4-TDI)*—(F.W. 174.2) 97 % purity.

8.13 *2,6-Toluene Diisocyanate (2,6-TDI)*—(F.W. 174.2) 97 % purity.

8.14 *2,4-Toluene Diisocyanate 9-(N-Methylaminomethyl) Anthracene Derivative (2,4-TDIU).*

8.14.1 Add 320 µL of 2,4-TDI (8.13) (2 mmoles) to dichloromethane (8.6) and dilute to 25 mL in a volumetric flask. Place the 2,4-TDI solution in an additional flask.

8.14.2 Dilute approximately 1.3 g (6 mmoles) of 9-(*N*-methylaminomethyl) anthracene (MAMA) (8.9) in 50 mL of dichloromethane (8.6). Place the MAMA solution in a three-necked flask.

8.14.3 Add the TDI (8.13) drop by drop at a temperature of 25°C to the MAMA solution (8.14.2), stirring continuously for 60 to 90 min.

8.14.4 Cool the resulting solution on crushed ice.

8.14.5 Filter on a medium speed ashless filter paper[8] or any equivalent device.

8.14.6 Dissolve the precipitate in hot dichloromethane (8.6). Place in an ice bath to recrystallize and filter as in 8.14.5.

8.14.7 The compound has a melting point of 270°C.

8.14.8 Confirm that the urea derivative with the mass spectrum, the 2,4-TDI-MAMA has a molecular weight of 610.8 g.

8.14.9 The conversion factor for TDIU to TDI is 0.2823.

[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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[8] Whatman No. 40, ashless filter paper has been found satisfactory for this purpose.