Designation: ~~D5932 – 08 (Reapproved 2013)ε1~~ D5932 – 20

Standard Test Method for Determination of 2,4-Toluene ~~Diisocyanate~~Di*iso*cyanate (2,4-TDI) and 2,6-Toluene ~~Diisocyanate~~Di*iso*cyanate (2,6-TDI) in Air (with 9-(N-Methylaminomethyl) Anthracene Method) (MAMA) in the Workplace[1]

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.

~~ε[1] NOTE—Editorial corrections were made to 8.14.8 and 11.2.1 in March 2015.~~

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]. 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. An ultra high performance liquid chromatograph (UPLC) can also be used, provided that its performance is equivalent to what is stated in this standard.

1.4 The analysis of the aerosol fraction is performed separately as described in Ref (**1**).[3]

1.5 The range of application of this test method, utilizing UV and a fluorescence detector, is validated for ~~0.029~~0.014 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~~0.001 to 0.077 mg/m^3 of TDI based on a 15-L air sample. This corresponds to ~~0.28~~0.0.14 to 11 ppb(V) and brackets the established TLV value of ~~5~~1 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. No other units of measurement are included in this 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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.* See Section 9 for additional hazards.

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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

D4840 Guide for Sample Chain-of-Custody Procedures

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[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.

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[2] ~~The American Society for Testing and Materials~~ ASTM International 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.

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

[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.

D5337 Practice for Flow Rate Adjustment of Personal Sampling Pumps

2.2 *Other Documents:*

Sampling Guide for Air Contaminants in the Workplace[5]

3. Terminology

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

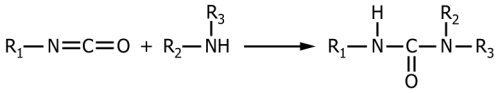
4. Summary of Test Method

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. 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 in accordance with the procedure described in ~~Ref~~Refs (**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**), 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 a 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.~~

5.2 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 ~~((~~**(6-9)**.~~)~~.

5.3 The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a Threshold Limit Value–Time Weighted Average ~~(TLV—TWA) of 0.036~~ (TLV-TWA) of 0.001 ppm of 0.007 mg/m^3 with a Short-Term Exposure Limit (STEL) of ~~0.14~~ 0.005 ppm or 0.036 mg/m^3 for ~~2,4-TDI~~ (either 2,4–TDI, or 2,6–TDI, or for a mixture of 2,4– and 2,6–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/m^3 of ~~TDI~~2,4-TDI as a ceiling limit and 0.005 ppm (V) or 0.036 mg/m^3 as a time-weighted average (**11**).

5.4 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 quantification limit also suits the concentrations often found in the working area.

5.5 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.

5.6 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.

[5] Available from Institut de Recherche en Santé et en Sécurité du Travail ~~du Québec, Laboratory Services and Expertise Department, Montreal, IRSST, 2005.~~(IRSST), Laboratory Division, Montreal, QC, 2012, http://www.irsst.qc.ca/media/documents/Pubirsst/T-15.pdf.

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. 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.*~~ *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. A second UV wavelength is recommended for identify confirmation if no fluorescence detector is utilized. An ultra high performance liquid chromatography (UPLC) providing at least the same or equivalent performance of HPLC can be also used.

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~~3.5-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,*~~ *Pipets*—~~microsyringes~~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,*~~ *Meter*—~~a~~A pH meter or any equivalent device capable of assaying a pH range between 2.5 and 7.

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

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

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

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

7.2.11 *Vacuum Filtration* ~~*System,*~~ *System*—~~vacuum~~Vacuum filtration system with ~~0.45-µm~~0.22-µm porosity nylon filters or any equivalent method to degas the mobile phase.

7.2.12 *Syringe Operated Filter* ~~*Unit,*~~ *Unit*—~~syringes~~Syringes with polyvinylidene fluoride 0.22-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,*~~ *Bottle*—~~amber-colored~~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.[6] 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 D1193, 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~~0.22-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.

[6] ~~*Reagent Chemicals, American Chemical Society Specifications,*~~*ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* 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 *Dimethylformamide*—Reagent grade.

8.8 *Helium (He)*—~~High~~ Ultra high purity, 99.999 %.

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~~575 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~~25 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 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 616.75 g.

8.14.9 The conversion factor for TDIU to TDI is 0.2823.

8.15 *2,6-Toluene Diisocyanate 9-(N-Methylaminomethyl) Anthracene Derivative (2,6-TDIU)*—Same preparation as 2,4-TDIU but use 2,6-TDI. The compound starts to show decomposition at 275°C.

8.16 *Triethylamine*—Purity 98 % min.

9. Hazards

9.1 **Warning—**Di*iso*cyanates are ~~potentially~~ hazardous chemicals and extremely reactive. Warning on compressed gas cylinders. Refer to ~~MSD sheets~~SD datasheets for reagents.

9.2 **Precaution**—Avoid exposure to di*iso*cyanate standards. Sample and standard preparations should be done in an efficient operating hood. For remedial statement see Ref **(12)**.

9.3 **Precaution**—Avoid skin contact with all solvents and *iso*cyanates.

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

10. Sampling

10.1 Refer to the ~~Practices~~Practice D1357 for general information on sampling.

10.2 Adjust the personal sampling pumps to the recommended flow rate with an assembled cassette between the pump and the flow-measuring device in accordance with Practice D5337. After the sampling, perform a post sampling flow rate verification. If the post sampling flow rate varies more than ±5 % from the recommended flow rate, invalidate the sample.

10.3 This proposed test method recommends sampling in accordance with the method described in ~~Ref~~Refs **(13, 14)** of this test method.

10.4 Equip the worker, whose exposure is to be evaluated, with a filter holder connected to a belt-supported sampling pump. Place the filter, holder pointing downward, in the breathing zone of the worker. Draw air through the sampling device and collect 15 L at a rate of approximately 1.0 L/min.

10.5 For stationary monitoring, use a tripod or any other support to locate the sampler in a general room area at a height equivalent to the breathing zone.

10.6 Open the field blanks in the environment to be sampled and immediately close them. Treat field blanks in the same manner as samples. Submit at least one field blank with each set of samples.

10.7 Once the sampling is done, open the cassette, withdraw the PTFE filter, place it in a glass jar, and close the jar. This filter is used to analyze the aerosol fraction of di*iso*cyanates **(1, 2)**.

10.8 Close the cassette, send it to be analyzed with the field blanks, and keep it away from light.

10.9 The samples are stable for 14 days at room temperature and 42 days at 4°C.