Designation: D6562 – 12

Standard Test Method for Determination of Gaseous Hexamethylene Diisocyanate (HDI) in Air with 9-(N-methylaminomethyl) Anthracene Method (MAMA) in the Workplace[1]

This standard is issued under the fixed designation D6562; 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 hexamethylene diisocyanate (HDI) in air samples collected from workplace and ambient atmospheres. The method described in this test method collects separate fractions. One fraction will be dominated by vapor, and the other fraction will be dominated by aerosol. It is not known at the present time whether this represents a perfect separation of vapor and aerosol, and in any case, there are not separate exposure standards for vapor and aerosol. Therefore, in comparing the results for isocyanate against a standard, results from the two fractions should be combined to give a single total value. The reason for splitting the sample into two fractions is to increase analytic sensitivity for the vapor fraction and also to give the hygienist or ventilation engineer some information concerning the likely state of the isocyanate species. The analyses of the two fractions are different, and are provided in separate, linked, standards to avoid confusion. This test method is principally used to determine short term exposure (15 min) of HDI in workplace environments for personal monitoring or in ambient air. The analysis of the aerosol fraction is performed separately, as described in Test Method D6561.

1.2 Differential air sampling is performed with a segregating device.[2] The vapor 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 range of application of this test method, using UV and fluorescence detectors both connected in serial, has been validated from 0.006 to 1.12 µg of monomeric HDI/2.0 mL of desorption solution, which corresponds to concentrations equivalent to 0.0004 to 0.075 mg/m^3 of HDI based on a 15-L air sample. Those concentrations correspond to a range of vapor phase concentrations from 0.06 ppb(V) to 11 ppb(V) and cover the established threshold limit value (TLV) value of 5 ppb(V).

1.5 The quantification limit for the monomeric HDI, using the UV detection, has been established as 0.012 µg/2 mL of desorption solution and as 0.008 µg/2 mL, using the fluorescence detector. These limits correspond to 0.0008 mg/m^3 and 0.0005 mg/m^3 respectively for an air sampled volume of 15 L. These values are equal to ten times the standard deviation (SD) obtained from ten measurements carried out on a standard solution in contact with the GFF, whose concentration of 0.02 µg/2 mL is close to the expected detection limit.

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 additional hazards.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

D5337 Practice for Flow Rate Adjustment of Personal Sampling Pumps

D6561 Test Method for Determination of Aerosol Monomeric and Oligomeric Hexamethylene Diisocyanate (HDI)

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

Current edition approved April 1, 2012. Published May 2012. Originally approved in 2000. Last previous edition approved in 2011 as D6562 - 06(2011). DOI: 10.1520/D6562-12.

[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. If you are aware of an alternative to this patented item, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[3] 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.

in Air with (Methoxy-2–phenyl-1) Piperazine (MOPIP) in the Workplace

2.2 *Other Standard:*

Sampling Guide for Air Contaminants in the Workplace[4]

3. Terminology

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

4. Summary of Test Method

4.1 Vapor and aerosol fractions are sampled simultaneously by using a segregating sampling device. The aerosols are collected on a polyterafluoroethylene (PTFE) filter while the gaseous fraction is being adsorbed on the second filter made of glass fiber impregnated with MAMA.

4.2 The analysis of the oligomer in the aerosol fraction is performed separately in accordance with the procedure described in Test Method D6561.

4.3 Diisocyanates present as vapors react with the secondary amine function of the MAMA, impregnated on the GFF to form a urea derivative (**1,2**) as shown in Fig. 1.[5]

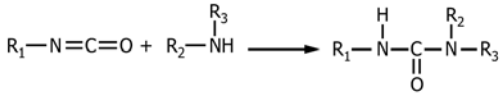

FIG. 1

Desorption of the GFF is done by using a solution mixture of 67 % N,N-dimethylformamide and 33 % of a 30:70 buffer-acetonitrile mixture. Monomeric and oligomeric diisocyanates are separated by using a reversed phase HPLC column, followed by UV (254 nm) and fluorescence detectors (254-nm excitation and 412-nm emission) in series (**3**).

4.4 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 HDI is mostly used in the preparation of paints. For the last ten years, the use of isocyanates and their industrial needs have been in constant growth.

5.2 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 (**4-7**).

5.3 The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a threshold limit value - time weighted average (TLV - TWA) of 0.005 ppm (V) or 0.034 mg/m^3 (**8**). The Occupational Safety & Health Administration of the U.S. Department of Labor (OSHA) has not listed a permissible exposure limit (PEL) for HDI (**9**).

5.4 Due to its low LOD and low required volume (15 L), this test method is well suited for monitoring of respiratory and other problems related to diisocyanates and polyisocyanates. Its short sampling times are compatible with the duration of many industrial processes, and its low detection limit with the concentrations often found in the working area.

6. Interferences

6.1 Any substances, including strong oxidizing agents, that can react with the MAMA reagent impregnated on the GFF can affect the sampling efficiency.

6.2 Any compound that has the same retention time as the hexamethylene diisocyanate 9-(N-methylaminomethyl) anthracene (HDIU) derivative and contributes to the UV signal is an interference. Chromatographic conditions can sometimes be changed to eliminate an interference. The response factor (RF) ratio from the UV and fluorescence detectors gives a good indication to the analyst about the possibility of an interference.

7. Apparatus

7.1 *Sampling Equipment:*

7.1.1 *Personal Sampling Pump*—Equipped with a flow-monitoring device (rotameter, critical orifice) or a constant-flow device capable of drawing 1.0 L/min through the sampling device for a period of at least 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 GFF impregnated with MAMA and by a plastic back-up pad.[6] The GFF is impregnated with an amount of MAMA in the range from 0.07 to 0.25 mg.

7.1.3 *Flow Measuring Device,* used in accordance with Practice D5337.

7.2 *Analytical Equipment:*

7.2.1 Liquid Chromatograph, an HPLC, equipped with a UV (254-nm wavelength) and fluorescence detectors (412-nm emission and 254-nm excitation) and equipped with an automatic or manual sampling port injection.

7.2.2 *Liquid Chromatographic Column,* an HPLC stainless steel column, capable of separating the urea derivatives. This test method recommends a 150 by 3.2-mm internal diameter stainless steel column packed with 3 µm C-18, or an equivalent column.

7.2.3 *Electronic Integrator,* or any other effective method for determining peak area counts.

7.2.4 *Analytical Balance,* with a precision of ± 0.0001 g.

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

[4] Available from Institut de recherche en sante et en securite du travail du Quebec, Laboratory Division, Montreal, IRSST.

[5] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[6] The sole source of supply of the apparatus known to the committee at this time is Omega Specialty Instrument, Chelmsford, MA and is prepared in accordance with Patent No. 4 961 916 (**10**). If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.