Designation: D 6561 – 06

Standard Test Method for Determination of Aerosol Monomeric and Oligomeric Hexamethylene Diisocyanate (HDI) in Air with (Methoxy-2–phenyl-1) Piperazine (MOPIP) in the Workplace[1]

This standard is issued under the fixed designation D 6561; 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 aerosol 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 vapor fraction is performed separately, as described in Test Method D 6562.

1.2 Differential air sampling is performed with a segregating device.[2] The aerosol fraction is collected on a polytetrafluoroethylene (PTFE) filter.

1.3 Immediately after sampling, the PTFE filter is transferred into a jar containing a (methoxy-2 phenyl-1) piperazine (MOPIP) solution in toluene.

1.4 The analysis of the aerosol fraction is performed by using a high performance liquid chromatograph (HPLC) equipped with an ultraviolet (UV) detector. The range of application of the test method has been validated from 0.052 to 1.04 µg of monomeric HDI/mL, which corresponds, based on a 15 L air sample, to concentrations from 0.004 to 0.070 mg/m^3 of HDI. Those concentrations correspond to a range of aerosol phase concentrations from 0.5 ppb (V) to 10 ppb (V) and cover the established threshold limit valve (TLV) value of 5 ppb (V).

1.5 The quantification limit for the monomeric HDI is 0.041 µg per mL, which corresponds to 0.003 mg/m^3 for a 15 L sampled air volume. This value is equivalent to ten times the standard deviation obtained from ten measurements carried out on a standard solution in contact with the PTFE filter whose concentration of 0.1 µg/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]

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 5337 Practice for Flow Rate Calibration of Personal Sampling Pumps

D 6562 Test Method for Determination of Gaseous Hexamethylene Diisocyanate (HDI) in Air with 9-(N-methylaminomethyl) Anthracene Method (MAMA) in the Workplace

[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 Atmospheres.

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[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.

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2.2 *Other Standard:*[4]
Sampling Guide for Air Contaminants in the Workplace

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 Vapor and aerosol fractions are sampled simultaneously by using a segregating sampling device. The aerosols are collected on PTFE filter while the gaseous fraction is being adsorbed on a second filter made of glass fiber, impregnated with a 9-(N-methylaminomethyl) anthracene (MAMA).

4.2 The analysis of the monomer in the gaseous fraction is performed separately in accordance with the procedure described in Test Method D 6562.

4.3 Diisocyanates present as aerosols are collected on the PTFE filter and derivatized in a MOPIP solution (**1**, **2**).[5] See Fig. 1.

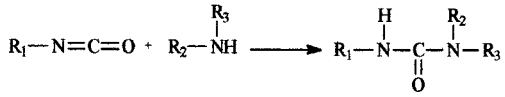

FIG. 1 MOPIP Solution

4.3.1 The solution is then evaporated to dryness and redissolved, using the acetic anhydride solution (see 8.11). Monomeric and oligomeric HDI are separated by using a reversed phase HPLC column, and detection is made by using an HPLC equipped with UV detection.

4.4 Concentration of monomeric and oligomeric diisocyanates contained in a sample is calculated by using an external standard of the monomeric HDI.

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 (**3-6**).

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 for monomeric HDI (**7**). The Occupational Safety & Health Administration of the U.S. Department of Labor (OSHA) has not listed a permissible exposure limit (PEL) for HDI (**8**).

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 substance, including strong oxidizing agents, that can be deposited on the PTFE filter and react with MOPIP reagent can affect the analysis efficiency.

6.2 Any compound that has the same retention time as the HDI-MOPIP derivative and contributes to UV response is an interference. Chromatographic conditions can sometimes be changed to eliminate 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 of air 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 glass fiber filter (GFF) impregnated with MAMA and 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 D 5337.

7.2 *Analytical Equipment*:

7.2.1 *Liquid Chromatograph*, HPLC, equipped with a UV detector (242 nm wavelength), connected in series with a diode detector, 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 areas.

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.

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

7.2.7 *Culture Tubes*, 16 by 100 mm, disposable, in borosilicate glass for evaporation of derivatized samples.

7.2.8 *Glass Jars*, 30 mL, and lids, capable of receiving 37-mm filters, used for derivatization of samples.

7.2.9 *Vacuum Filtration System*, filter 47 mm, with 0.22-µm pore size polyamide filters, or any equivalent method.

[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 (**9**). 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.