Designation: D5932 – 08 (Reapproved 2013)ε1

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 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.

ε1 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.[2,3] 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 Workplace[6]

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.

[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/D5932-08R13E01.

[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 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.

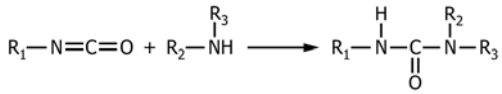
[5] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

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 in accordance with 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**), 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 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**).

5.4 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 (**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 as a ceiling limit and 0.005 ppm (V) or 0.036 mg/m^3 as a time-weighted average (**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 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 *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 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.

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,* 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 0.22-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,* 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 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 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, 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 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 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 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 D1357 for general information on sampling.

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

10.3 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.

[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.

10.4 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.

10.5 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.

10.6 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**).

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

11. Calibration and Standardization

11.1 *Sample Pump Calibration*—Calibrate the sampling pump (7.1.1) with a cassette (7.1.2) between the pump and the flow measuring device (7.1.3), in accordance with the method described in Ref (**1**). Calibrate the pump before and after the sampling. If the flow rate after the sampling is more than ±5 %, invalidate the sample.

11.2 *Reference Standards:*

11.2.1 *2,4- and 2,6-TDIU*—Prepare the 2,4-TDIU derivative in accordance with (8.14) and the 2,6-TDIU derivative in accordance with (8.15). Confirm the expected urea derivatives by mass spectrometry. The molecular weight of 2,4- and 2,6-TDIU is 616.75 g. Determine the melting point. 2,4-TDIU was a melting point of 270°C. 2,6-TDIU decomposes at 275°C.

11.2.2 *Stock Standard Solutions of 2,4- and 2,6-TDIU*—Prepare stock standard solutions separately of 2,4- and 2,6-TDIU dimethylformamide. This method recommends weighing approximately 12.5 mg of 2,4- and 2,6-TDIU precisely into 100-mL volumetric flasks and filling to the mark with dimethylformamide. Store in amber bottles. Express the TDIU as the free TDI. Multiply the amount of TDIU by the correction factor derived from the ratios of the respective molecular weights of the TDI and TDIU. The factor is 0.2823.

11.3 *Blanks:*

11.3.1 Use a field blank and treat as a sample.

11.3.2 Use desorption solution as a solution blank.

11.4 *Daily Quality Controls:*

11.4.1 For the UV detector, spike 15 µL of 2,4- and 2,6-TDIU stock solutions onto an impregnated GFF. Put into a glass jar and let dry with open lid. Treat as samples. For the fluorescence detector, dilute the stock solutions in desorption solution in a volume ratio of 1:10 and proceed in the same manner as for the UV detector.

11.4.2 Analyze at least one quality control preparation with each daily batch of samples.

11.5 *Calibration Curve:*

11.5.1 Prepare dilutions of the standard stock solutions (11.2.2) in desorption solution, with concentrations ranging from 0.029 to 1.16 µg of 2,4- and 2,6-TDI monomer/2 mL of desorption solution.

11.5.2 Place 2 mL of each standard solution with a calcined GFF into a glass jar. Process the standards as samples in accordance with the procedures in 12.1.

11.5.3 Analyze by high performance liquid chromatography in accordance with the method described in 12.2.

11.5.4 Prepare the calibration curve by plotting peak area values against µg per 2 mL of 2,4-TDI and 2,6-TDI. A coefficient of correlations equal or greater than 0.995 must be achieved.

11.5.5 In daily routine procedures, inject one working standard every ten samples to check the stability of the instrument response.

11.6 *Recovery Percentage*—Analyze the same standard solutions used for the calibration curve of the 2,4- and 2,6-TDI derivatives without contact with the GFF. Determine the ratio between the concentration obtained with and without contact with the filter.

12. Procedure

12.1 *Sample Preparation:*

12.1.1 Using tweezers, take the glass fiber filter from the cassette and place it in a glass jar. Treat blanks in the same manner as samples.

12.1.2 Add 2.0 mL of desorption solution (8.5) to the glass jar, using an automatic pipet or equivalent device. Close the jar tightly.

12.1.3 Shake for 30 min on a reciprocating shaker (7.2.10) or use any equivalent technique. Keep away from the light.

12.1.4 Filter the solution through a 0.22-µm porosity membrane (7.2.12) with a syringe operated filter device (7.2.12) and transfer the sample to an injection vial (8.8).

12.1.5 Analyze sample, blank, and quality control solutions in the same manner as external standard solutions in a batch at the same time, in accordance with the conditions described in 12.2. Use the same injection technique and injection volume for samples, blanks, quality controls, and external standards.

12.1.6 Inject each sample into a HPLC.

12.1.7 Calculate the 2,4- and 2,6-TDI concentration in the sample as specified in Section 13.

12.2 *HPLC Analysis:*

12.2.1 Analyze by high performance liquid chromatography using a suitable column and the mobile phase as described in 7.2 and 8.10, respectively. The typical conditions are as follows:

Column Temperature	Room Temperature
Flow rate	0.06 mL/min
Ultraviolet	254 nm
Fluorescence	254 nm excitation 412-nm emission
Injection volume	15 µL

Analytical conditions serve as a guideline and may need to be modified depending upon the specific samples, column condition, detector, and other parameters.

12.2.2 With each daily batch, prepare quality control samples in accordance with the method described in 11.4.1 and analyze in the same run as the samples.

13. Calculation and Interpretation of Results

13.1 Determine the concentration for the analyte by using the calibration curve (11.5) and the area. Use the following equation:

$$M_{TDI} = (A - b)/m \quad (1)$$

$$C_{TDI} = M_{TDI}/V \quad (2)$$

where:

M_{TDI} = Mass of the TDI monomer (2,4– or 2,6–TDI) in sample (µg),
A = area count of the peak,
b and m = Y intercept and slope, respectively, obtained from calibration curve,
C_{TDI} = concentration of 2,4- or 2,6-TDI (mg/m^3), and
V = volume sampled (L).

13.2 If the total detector response for the field blank represents more than the response obtained for the standard solution 0.029 µg/2 mL, field blank corrections might be necessary (**12**,**14**).

14. Report

14.1 Report the following information–concentration of gaseous 2,4- and 2,6-TDI in mg/m^3.

15. Performance, Precision, and Bias[9]

15.1 *Performance*

15.1.1 The average correlation coefficient is 0.9999 and 0.9997 for the UV detector, for 2,6 and 2,4-TDI, respectively. For the fluorescence detector, the average correlation coefficient is 0.9974 and 0.9998 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.

15.1.2 The instrumental quantification limit for 2,6-TDI monomers is 0.006 µg/2 mL of desorption solution. For the fluorescence detector, the instrumental quantification limit is 0.003 µg/2 mL of desorption solution. 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.

15.1.3 The instrumental quantification limit for 2,4-TDI monomers is 0.010 µg/2 mL of desorption solution. For the fluorescence detector, the instrumental quantification limit is 0.005 µg/2 mL of desorption solution. 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.

15.1.4 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.

15.2 *Precision*

15.2.1 *Precision on a Complete Calibration Curve (Same Lab, Same Operator)*—To measure the coefficient of variation and the recovery percentage, six concentration levels have been tested six times. The analytical standards have been prepared in accordance with the procedure in 11.5 (calibration curve) and contained 0.029 0.058, 0.146, 0.291, 0.582, and 1.16 µg/2 mL of desorption solution. The coefficient of variation of the UV and fluorescence detectors, for the entire analysis within the concentration, range from 0.002 to 0.078 mg/m^3 is equal to 2 % for 2,4- and 2,6-TDI.

15.2.2 *Recovery Percentage*—To evaluate the recovery percentage, the standards have been analyzed with and without contact with the GFF. The average recovery percentage (n = 36) for all six 2,4-TDI concentrations is 103.1 ± 1.5 % for the UV detector and 102 ± 0.6 % for the fluorescence detector. The recovery percentage (n = 36) for all six 2,6-TDI concentrations is 100.8 ± 0.6 % for the UV detector and 99.7 ± 0.8 % for the fluorescence detector.

15.2.3 *Precision of the Apparatus*—The precision of the apparatus has been calculated from ten measurements carried out on a concentration equivalent to 0.004 mg/m^3. The operation has been done once with the same operators for a total of ten measurements. For the UV detector, the average coefficient of variation is 1.7 and 1.5 % for the 2,6- and 2,4-monomers, respectively. For the fluorescence detector, the coefficient of variation is 1.1 and 0.98 % for the 2,6 and 2,4 monomers, respectively.

15.2.4 *Repeatability of the Daily Quality Controls*—(same lab, different operators, same lab procedure, two different concentrations)—Cumulation of daily quality controls prepared as described in 11.4 have been done on two different concentrations over a period of 42 months and including three different operators. For the standard corresponding to 0.036 mg/m^3 of 2,4- and 2,6-TDI, the coefficient of variation is 7 and 6 %, respectively, for the UV detector. For the standard corresponding to 0.0036 mg/m^3, the coefficient of variation is 12 % for the 2,4-TDI isomer and 10 % for the 2,6-TDI, using the fluorescence detector.

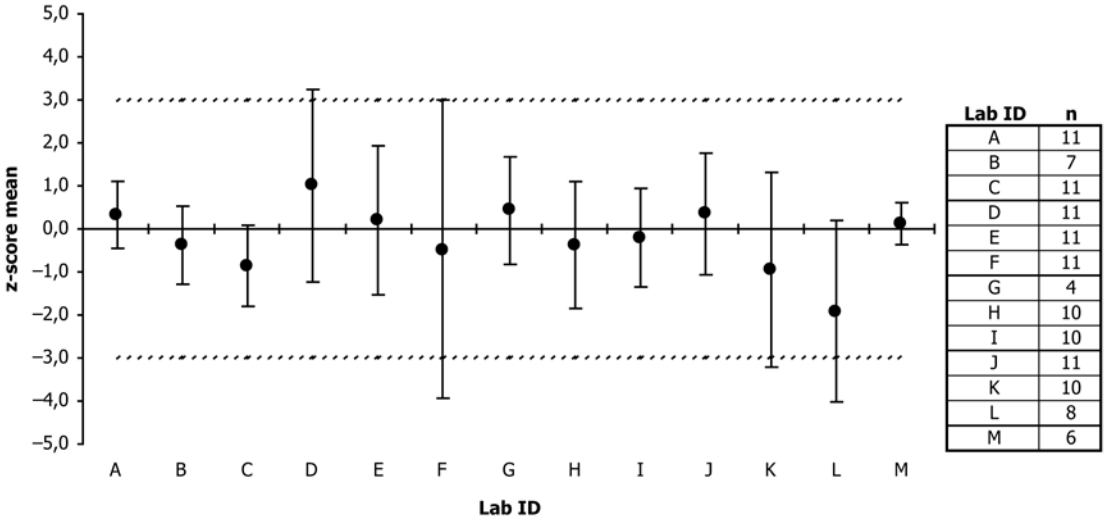
15.2.5 *Results of an Interlaboratory Evaluation*—The RSD calculated from an average of 13 participating laboratories over 11 rounds is 23 % (n = 242).

15.3 *Accuracy*—Figure 2 contains the average of the z-scores of thirteen different laboratories that participate to an on-going inter-laboratory evaluation using this test method. The evaluation is performed once a year.

16. Keywords

16.1 air monitoring; dual filter sampling system; high-performance liquid chromatography; sampling and analysis; toluene di*iso*cyanate; workplace atmospheres; 9-(N-methylaminomethyl) anthracene

[9] A research report has been submitted to ASTM headquarters. Its number will be available shortly.



Lab ID	n
A	11
B	7
C	11
D	11
E	11
F	11
G	4
H	10
I	10
J	11
K	10
L	8
M	6

FIG. 1 Means and Standard Deviations of the Z-Scores Obtained by 13 Laboratories after n ≥ 3 Participations to an Interlaboratory Evaluation

REFERENCES

(1) "Analyse du 2,4-Toluène Di *iso*cyanate (2,4-TDI) dans l'Air sous Forme Aérosol," Institut de Recherche en Santé et en Sécurité du Travail du Québec, Montréal, Québec, IRSST 236-1.

(2) "Analyse du 2,4–Toluène Di*iso*cyanate (2,4–TDI) et du 2,6-Toluène Di*iso*cyanate (2,6-TDI) dans l'Air sous Forme Gazeuse," Institut de Recherche en Santé et en Sécurité du Travail du Québec, Montréal, Québec, IRSST 226-1.

(3) Melcher, R. G., Langner, R. R., and Kagel, R. O., "Criteria for the Evaluation of Methods for the Collection of Organic Pollutants in Air Using Solid Sorbents," *American Industrial Hygiene Association Journal*, Vol 39, No. 5, May 1983, pp. 349–361.

(4) Dugehn, A., "Improved Chromatographic Procedure for Determination of 9-(N-Methylaminomethyl) Anthracene *Iso*cyanate Derivatives by High-Performance Liquid Chromatography," *Journal of Chromatography*, No. 301, 1984, pp. 484–484.

(5) Lesage, J., Goyer, N., Desjardins, F., Vincent, J.-Y., and Perrault, G., "Workers' Exposure to *Iso*cyanates," *American Industrial Hygiene Association Journal*, Vol 53, No. 2, 1992, pp. 146–153.

(6) Criteria for a Recommended Standard Occupational Exposure to Toluene Di*iso*cyanate, Department of Health, Education and Welfare, National Institute for Occupational Safety and Health, Cincinnati, OH, No. DHEW (NIOSH) 73-11022, 1973.

(7) Woolrich, P. F.," Toxicology, Industrial Hygiene and Medical Control of TDI, MDI and PMPPI," *American Industrial Hygiene Association Journal*, Vol 43, 1981, pp. 89–97.

(8) Moller, D. R., et al, "Chronic Asthma Due to Toluene Di*iso*cyanate," *Chest*, Vol 90, No. 4, 1986, pp. 494–499.

(9) Butcher, B. T., et al, "Poly*iso*cyanates and Their Prepolymers," *Asthma in the Workplace*, Bernstein, I. Leonard, Chan-Yeung, Moira, Malo, Jean-Luc, and Bernstein, David I., Eds., Cincinnati, Ohio, 1994, Chapter 20, pp. 415–436.

(10) *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*, American Conference of Government Industrial Hygienists, (ACGIH) Cincinnati, Ohio, 2007.

(11) Occupational Safety and Health Administration (OSHA): "OSHA Method 42: Di*iso*cyanates," OSHA Analytical Laboratory, Organic Methods Development Branch, Salt Lake City, Utah, 1989.

(12) Occupational Safety and Health Administration (OSHA): "Evaluation Scheme Methods that Use Filters as the Collection Medium," *OSHA Analytical Methods Manual*, Second Edition, Part 2, OSHA Technical Center, Salt Lake City, Utah, 1991.

(13) Lesage, J., and Perrault, G., "Sampling Device for *Iso*cyanates," U.S. Patent No. 4 961 916.

(14) *Guide d'echantillonnage des Contaminants de l'Air en Milieu de Travail*, Institut de Recherche en Santé et en Sécurité du Travail du Québec, Montréal, 2005.