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.

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

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[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.

1.12 *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:*

D 1193 Specification for Reagent Water[5]

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[6]

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere[6]

2.2 *Other Documents:*

Sampling Guide for Air Contaminants in the Workplace[7]

3. Terminology

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

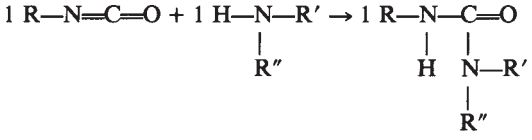
4. Summary of Test Method

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*:

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

[5] *Annual Book of ASTM Standards*, Vol 11.01.

[6] *Annual Book of ASTM Standards*, Vol 11.03.

[7] Available from Institut de Recherche en Santé et en Sécurité du Travail du Québec, Laboratory Division, Montreal, IRSST, 1995.

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.[8] 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[9] 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.

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.

[8] *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.

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

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 **(13)**.

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 D 1357 for general information on sampling.

10.2 This proposed test method recommends sampling according to the method described in **(12,14)** 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.

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 an ointment 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), according to 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 according to (8.14) and the 2,6-TDIU derivative according to (8.15). Confirm the expected urea derivatives by mass spectrometry. The molecular weight of 2,4- and 2,6-TDIU is 610.8 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 10 mg of 2,4- and 2,6-TDIU precisely into 50-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 for 2,4- and 2,6-TDI.

11.2.3 *External Calibration Standards of 2,4- and 2,6-TDIU*:

11.2.3.1 For the UV detector calibration standard, take 10 µL of 2,4-TDIU stock solution (11.2.2) with a 25-µL microsyringe and transfer it into 2 mL of desorption solution. Repeat with the 2,6-TDIU monomer. These solutions correspond approximately to 0.036 mg/m^3 of TDI for a sampled volume of 15 L. For the fluorescence detector calibration solution, dilute the stock solutions with desorption solution in proportion 1:10 and proceed in the same manner as for the UV detector calibration solutions. These solutions correspond to 0.0036 mg/m^3 of TDI for a volume of 15 L.

11.2.3.2 Transfer a fraction of each standard into injection vial and analyze according to the procedure in 13.2.

11.2.3.3 Use these standards daily to calibrate the instrument since the detector response may vary noticeably from one day to the next.

11.2.3.4 Prepare several vials of these solutions and inject into the chromatograph (minimum of three injections) before running the samples.

11.2.3.5 Calculate the response factor (*R.F.*) of the 2,4- and 2,6-TDI for each detector, using the following equation:

$$R.F. = \frac{B\ (\text{mg/mL})}{A} \quad (1)$$

where:

R.F. = response factor,
B = concentration of the calibration solution, in mg/mL, and
A = area of the peak obtained.

11.2.3.6 Before the samples are analyzed, verify that the response factors calculated fall within a maximum deviation of 5 %.

11.2.3.7 In daily routine procedures, every ten samples, inject one standard to check the reproducibility of the *R.F.*, and upgrade the *R.F.*, if necessary.

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 10 µL of 2,4- and 2,6-TDIU stock solutions onto an impregnated GFF. Put into an ointment 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 in desorption solution, with concentrations ranging from 0.02 to 4.2 µg of 2,4- and 2,6-TDI monomer/2 mL of desorption solution. This corresponds to 0.001 to 0.28 mg/m^3 of TDI for a sampled air volume of 15 L.

11.5.2 Place 2 mL of each standard solution with a calcined GFF into an ointment jar. Prepare three jars for each standard. Treat the standards as samples according to the procedures in 12.1.

11.5.3 Analyze by high performance liquid chromatography according to the method described in 12.2.

11.5.4 Use peak area integration. The peak area should agree within ±5 % per standard.

11.5.5 Prepare the calibration curve by plotting peak area values against µg per 2 mL of 2,4-TDI and 2,6-TDI.

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 an ointment jar. Treat blanks in the same manner as samples.

12.1.2 Add 2.0 mL of desorption solution (8.5) to the ointment 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 0.45-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, according to 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	2 mL/min
Ultraviolet	254 nm
Fluorescence	254 nm excitation
	412-nm emission
Injection volume	50 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 Verify the precision of the injector with three successive injections of an external standard. A difference of less than 5 % in the peak area must be obtained.

12.2.3 With each daily batch, prepare quality control samples according to 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 *R.F.* and the area. Use the following equation:

$$\text{C 2,4- or 2,6-TDI, mg/m}^3 = \frac{R.F. \times A}{V} \quad (2)$$

where:

C = concentration of 2,4- or 2,6-TDI, mg/m^3,
$R.F.$ = response factor,
A = area of the peak obtained, and
V = volume sampled, m^3.

13.2 If the total detector response for the field blank represents more than 5 % of the response obtained for the standard solution (0.02 µg/2 mL (0.036 mg/m^3 for 15-L sampled volume), field blank corrections might be necessary **(13,14)**.

14. Report

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

15. Precision and Bias

15.1 *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 according to the procedure in 11.5 (calibration curve) and contained 0.0212, 0.106, 0.212, 1.06, 2.12, and 4.24 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 0.001 to 0.280 mg/m^3 is equal to 0.02 for 2,4- and 2,6-TDI.

15.2 *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 102.6 ± 1.4 % for the UV detector and 100.3 ± 3.1 % for the fluorescence detector. The recovery percentage (n = 36) for all six 2,6-TDI concentrations is 101.8 ± 1.0 % for the UV detector and 101.9 ± 1.6 % for the fluorescence detector.

15.3 *Precision of the Apparatus*—The precision of the apparatus has been calculated from ten measurements carried out on a concentration equivalent to 0.014 mg/m^3. The operation has been done twice with different operators for a total of 20 measurements. For the UV detector, the average coefficient of variation is 0.30 and 0.55 % for the 2,6- and 2,4-monomers, respectively. For the fluorescence detector, the coefficient of variation is 0.67 and 0.67 % for the 2,6 and 2,4 monomers, respectively.

15.4 *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 0.14 mg of 2,4- and 2,6-TDI per cubic metre, the coefficient of variation is 6.8 and 4.8 %, respectively, for the UV detector. For the standard corresponding to 0.014 mg, the coefficient of variation is 19.6 % for the 2,4-TDI isomer and 15.7 % for the 2,6-TDI, using the fluorescence detector.

15.4.1 *Reproducibility of the Test Method*—Complete calibration curve—different labs.

15.4.2 *Reproducibility of the Test Method*—Spot checks—different labs, interlaboratory quality controls—one or more concentrations verified at the same time.

16. Keywords

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

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