
**Workplace atmospheres —
Determination of toluene diisocyanate
vapours using 1-(2-pyridyl)
piperazine-coated glass fibre filters
and analysis by high performance
liquid chromatography with
ultraviolet and fluorescence detectors**

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Air des lieux de travail — Détermination des vapeurs de toluène diisocyanate à l'aide de filtres en fibre de verre enduits de pipérazine-1-(2-pyridyl) et par analyse par chromatographie liquide à haute performance avec détecteurs à ultraviolets et à fluorescence

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 14382 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

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Introduction

The most common form of toluene diisocyanate (TDI) marketed commercially is a mixture containing 80 % 2,4-TDI and 20 % 2,6-TDI. It is also available as a mixture containing 65 % 2,4-TDI and 35 % 2,6-TDI, and as the pure 2,4-TDI isomer. The main commercial use for TDI is the manufacture of polyurethane (PU) flexible foams used in upholstery, mattresses, shoe soles, and automotive seats. The PU foams are prepared by reacting the TDI with a polyol to produce the product. Depending on the components selected and how they are combined, end products with quite different properties can be achieved.

The majority of flexible foams are produced by the slabstock foaming process, in which the mixture of polyurethane raw materials is dispensed onto paper linings in an open trough, where it gradually expands into a large bun of foam. These buns are cut into blocks or slices, which are then processed into the final desired products.

In the majority of workplace atmospheres, TDI is present as a vapour and the 2,6-isomer may be predominant. In those rare instances where TDI is emitted into workplace environments as an aerosol, the aerosols are collected efficiently by the glass fibre filter. The TDI in the aerosol readily evaporates during sampling and is captured by the liquid reagent [1-(2-pyridyl)piperazine] coated on the filter. This International Standard provides a simple, well-tested and reliable method for the sampling and analysis of TDI using instrumentation readily available in most commercial laboratories. This International Standard is based on the United States Occupational Safety and Health Administration (OSHA) Method 42^[9] for diisocyanates, ASTM D5836^[8] (which is based on the OSHA Method 42^[9]) and on modifications to OSHA Method 42^[9] recommended by Bayer MaterialScience Environmental Analytics Laboratory^[10]. The Bayer modifications include the use of 2 mg of reagent to coat the sampling filter and the use of cellulose spacer rings in the air sampling cassette.

OSHA Method 42 is widely used throughout the world. In an interlaboratory evaluation of the ASTM D5836^[8] with 13 participating laboratories, the average recovery from spiked media for 2,4-TDI was $(106 \pm 5,6) \%$ and $(104 \pm 5,7) \%$ for 2,6-TDI. Laboratory precision, measured as a repeatability coefficient of variation, was 6,2 % for 2,4-TDI and 5,7 % for 2,6-TDI.

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WARNING — This document does not purport to address all safety concerns, if any, associated with its use. It is the responsibility of the user of this document to establish appropriate health and safety practices and to determine the application of regulatory limitations prior to use.

1 Scope

This International Standard gives general guidance for the sampling and analysis of airborne toluene diisocyanate (TDI) in workplace atmospheres. The procedure specified in this International Standard is especially suitable for short (15 min) and long-term (4 h) sampling and analysis of 2,4- and 2,6-TDI vapours.

The upper limit for this method is approximately 85 µg of TDI per sample. This is a conservative upper limit based on the requirement of maintaining a sufficient amount of reagent on the coated glass fibre filter while permitting a 4 h sample to be collected at 1 l/min from an atmosphere containing 50 nl/l of TDI.

The quantitation limits for this method are 0,039 µg for 2,4-TDI and 0,034 µg for 2,6-TDI using a fluorescence detector. These limits, for a 15-min sample collected at 1 l/min, are equivalent to 0,36 nl/l for 2,4-TDI, and 0,32 nl/l for 2,6-TDI. For a 4 h sample collected at 1 l/min, the limits are equivalent to 0,022 nl/l for 2,4-TDI and 0,020 nl/l for 2,6-TDI.

The commercial availability of the specified reagents, the use of common analytical instrumentation, and the current widespread use of the method make this standard method ideally suited for the determination of TDI in workplace environments.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 16200-1, *Workplace air quality — Sampling and analysis of volatile organic compounds by solvent desorption/gas chromatography — Part 1: Pumped sampling method*

3 Principle

Samples are collected by drawing a known volume of workplace air through glass fibre filters coated with 2 mg of 1-(2-pyridyl)piperazine (1-2PP) which are contained in open-face cassettes. Samples are collected at 1 l/min for 15 min; up to a maximum sampling time of 4 h. Bayer^[10] has methods that use both 13 mm and 37 mm filters (both sizes are coated with 2 mg of 1-2PP), but OSHA Method 42^[9] uses only 37 mm filters. The Bayer 13 mm filters are coated with 5 µl of diethylphthalate per filter in addition to 2 mg of 1-2PP. The samples are extracted with 90 + 10 parts by volume acetonitrile/dimethyl sulfoxide (90 + 10 parts by volume ACN + DMSO) and are analysed by high performance liquid chromatography (HPLC) using an ultraviolet (UV) or a fluorescence detector. Use of both detectors in series allows the analyst to have high confidence in HPLC peak identification and quantitation. Other mixture ratios of ACN + DMSO can be used, providing they are tested and their use is consistent throughout the analysis.

4 Reagents and materials

Use only reagents of recognized analytical grade, unless otherwise specified. Always evaluate the derivatization and/or chromatographic effects when a reagent is changed.

- 4.1 Methylene chloride [CAS 75-0-2], HPLC grade.
- 4.2 Hexane [CAS 110-54-3], HPLC grade.
- 4.3 Acetonitrile (ACN) [CAS 75-05-8], HPLC grade.
- 4.4 Dimethyl sulfoxide (DMSO) [CAS 67-68-5], HPLC grade.
- 4.5 Water [CAS 7732-18-5], HPLC grade.
- 4.6 1-(2-Pyridyl)piperazine [CAS 34803-66-2], ≥99,5 % (mass fraction) grade.
- 4.7 2,4-TDI [CAS 584-84-9].
- 4.8 2,6-TDI [CAS 91-08-7].
- 4.9 Ammonium acetate [CAS 631-61-8], HPLC grade.
- 4.10 Acetic acid, glacial [CAS 64-19-7], HPLC grade.
- 4.11 Acetone [CAS 67-64-1], HPLC grade.

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5 Reagent solutions

5.1 Preparation of TDI urea derivatives

Prepare a solution containing 3,5 g of 2,4-TDI in 25 ml of methylene chloride and slowly add it to a stirred solution of 7,25 g of 1-2PP in 100 mL of methylene chloride. Slowly heat the solution to about 35°C, stirring constantly for several minutes. Reduce the volume of methylene chloride to about 10 ml with a stream of dry nitrogen. Precipitate the product by slowly adding approximately 50 ml of hexane to the solution (precipitation may start without adding the hexane). Filter the precipitate and then redissolve it in a minimal volume of methylene chloride and reprecipitate. Filter the solution and wash the collected precipitate with hexane. The approximate yield is 9 g of the derivative after being dried by a vacuum. This preparation is a modification of the procedure reported by Goldberg et al.^[11]. The purity of the TDI urea shall be checked using the melting point, elemental analysis, and/or NMR spectroscopy. The solid urea, when stored in a well-sealed dark bottle, is stable for more than 10 years. The 1-2PP derivative of 2,6-TDI is prepared by a similar procedure.

5.2 Analytical standards

5.2.1 Preparation of analytical standards using TDI urea derivatives

Stock analytical standard solutions are prepared by accurately weighing (to three significant figures) the TDI urea derivatives (5.1) and then dissolving them in DMSO. To express the derivative as free TDI,

weigh the amount of 2,4-TDI and 2,6-TDI ureas and multiply by the conversion factor of 0,3479, the ratio of molecular masses.

$$\frac{M_r(\text{TDI})}{M_r(\text{TDI urea})} = \frac{174,6}{500,1} = 0,3479$$

All dilutions of the stock solutions are made to arrive at the working range in 90 + 10 parts by volume ACN + DMSO. For example, a stock standard prepared in DMSO can be diluted 1→10 with pure ACN to arrive at 90 + 10 parts by volume ACN + DMSO. Any further dilutions are made with 90 + 10 parts by volume ACN + DMSO.

5.2.2 Preparation of analytical standards using pure TDI

Analytical standard solutions can also be prepared by reacting TDI (either pure 2,4-TDI or pure 2,6-TDI isomer) with 1-2PP in solution. Prepare a solution containing 1 mg/ml (0,006 mmol/l) 1-2PP by diluting 100 mg of 1-2PP to the mark with 90 + 10 parts by volume ACN + DMSO in a 100 ml volumetric flask, ISO 1042,[1] class A. Prepare a separate solution of 1 mg/ml (0,006 mmol/l) pure TDI by carefully and accurately weighing 50 mg of TDI (to three significant figures) and diluting it to the mark with 90 + 10 parts by volume ACN + DMSO in a 50 ml volumetric flask. Pipette 1 ml to 3 ml of the 1 mg/ml TDI solution into a 25 ml volumetric flask and dilute to the mark with the 1 mg/ml 1-2PP solution. Mix the solution well and allow it to react overnight. Do not use more than 3 ml of the TDI solution in order to ensure a proper excess of 1-2PP. Do *not* use the conversion factor in 5.2.1 to calculate the concentration of these standards. Use fresh solutions. The amount of pure TDI isomer shall be accurately known to prepare accurate standards.

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5.2.3 Commercial standard solutions

Analytical standard solutions are commercially available.

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5.3 Filter extraction solution

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This solution is composed of 90 + 10 parts by volume ACN + DMSO.

5.4 1-2PP filter coating solution

This solution is composed of 4 mg/ml (0,025 mmol/l) 1-2PP in methylene chloride.

5.5 HPLC mobile phase

This solution is composed of 0,01 M ammonium acetate (buffered to pH 6,2 with acetic acid) in water and acetonitrile. The exact composition of the mobile phase depends on the HPLC column selected for use. The buffered ammonium acetate solution can be prepared separately and used in a solvent programmed gradient with acetonitrile.

6 Apparatus

6.1 Air sampler

The air sampler consists of a three piece 37 mm polystyrene cassette with a glass fibre filter (type A/E binder free) coated with 2 mg of 1-2PP (see Figure 1).

6.1.1 Preparation of coated filters

Prepare a sufficient volume of a solution containing 4 mg/ml 1-2PP in methylene chloride. The volume is based on the number of filters to be coated. Use 0,5 ml of this solution to coat each filter. Use a properly functioning fume hood to evaporate the solvent and minimize exposure of the filters to light during coating, drying, and subsequent operations. Separately place the uncoated glass fibre filters on a

nickel-chromium wire grid or on the rims of 40 ml glass beakers so that only the edges of the filter are supported. Carefully, and slowly, pipette 0,5 ml of the 1-2PP solution onto the centre of the filter. This volume of solution is sufficient to fully wet the filter. Allow the methylene chloride solvent to evaporate in the hood for about 1 h. Transfer the coated filters to a clean dry container, loosely cap the container, and place the container in a vacuum desiccator equipped with a cold trap. Further dry the filters at reduced pressure for about 2 h. Analyse at least three of the coated filters for TDI after they are dry and store the remaining filters in a closed container in a freezer at $-20\text{ }^{\circ}\text{C}$. There are various recommendations for the shelf life of these filters, however, they have been successfully used for up to 1 year after preparation when stored in a freezer until use. Do not store isocyanates, anhydrides, alcohols, carboxylic acids, or amines in the same freezer.

6.1.2 Commercial coated filters

Glass fibre filters coated with 1-2PP are commercially available; however, the amount of 1-2PP coated on the filter may be different than specified in this International Standard.

6.1.3 Assembly of sampling cassettes

Store the coated filters and assembled cassettes in a freezer. Do not store isocyanates, anhydrides, alcohols, carboxylic acids, or amines in the same freezer.

Try to anticipate sampling needs and to minimize storage time for assembled sampling cassettes.

Place a cellulose spacer ring on the cassette bottom, then put a coated filter on top of the spacer ring, and place a cassette ring on top of the coated filter. Use sufficient pressure to completely seal the assembled sampling cassette. Seal the cassette with a shrink band. Sampling is performed with an open-face cassette; therefore, the cassette top need not be firmly attached to the sampler unless the assembled sampler is to be stored where it could become contaminated or if it is to be stored for more than 1 day or 2 days before use.

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6.2 Sampling pump

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The pump shall fulfil the requirements of EN 1232^[5] or equivalent. The sampling pump shall be capable of maintaining a flow rate of $(1,00 \pm 0,05)$ l/min with the air sampler in-line.

6.3 Sampling pump calibration

Calibrate the sampling pump with a representative air sampling cassette in-line using a calibrated external flowmeter that is accurate to within $\pm 2\%$.

6.4 Tubing

Use about 90 cm of flexible plastic tubing to connect the sampling cassette to the sampling pump. Clips shall be provided to secure the sampler and the tubing to the wearer's lapel within their breathing zone.

6.5 Flowmeter

Use a portable calibrated flowmeter, capable of measuring 1,00 l/min to within $\pm 0,05$ l/min with the air sampling cassette in-line, to check the flow rate. The flowmeter is not the principal calibration device.

6.6 Liquid chromatography system

6.6.1 HPLC system

An HPLC system consisting of an autosampler, a column oven, an HPLC pumping system capable of gradient elution, a fluorescence detector, and/or an ultraviolet detector, is required for the analysis of samples. A computerized data system is useful to acquire and reduce data.

6.6.2 HPLC analytical column

There are many excellent C-8 and C-18 HPLC columns that are capable of separating 2,4- and 2,6-TDI isomers from potential interferences. The selected analytical column can be operated with an appropriate guard column. Use of a guard column is optional.

6.6.3 Syringes and syringe filters

Use disposable syringes and 0.2 µm pore size PTFE syringe filters that are both compatible with ACN + DMSO mixtures to filter sample solutions.

7 Air sampling

7.1 Calibration of sampling pump

Calibrate each sampling pump with a representative sampling filter cassette in-line to $(1 \pm 0,05)$ l/min using a certified flowmeter traceable to national standards. Pump calibration shall be performed before sampling and shall be verified after sampling. The sampling rates shall agree to within 5 % or the sample is invalid. Use the same type sampler but not the same samplers that are intended to be used for air sampling to calibrate the sampling pumps.

7.2 Safety practices

Follow all safety practices that apply to the workplace being sampled. The sampling equipment shall be attached to the wearer in such a manner that it does not interfere with work performance or safety.

7.3 Preparation of air sampler

Remove the cassette top piece for open-face sampling. Remove the cassette bottom plug and connect the air sampler to the flexible plastic tubing with a Luer fitting. Minimize exposure of the sampling filter to light. Connect the calibrated sampling pump to the flexible plastic tubing and an air sampler. Use the portable calibrated flowmeter to check the flow rate.

7.4 Collection of air samples

In an isocyanate-free location, using the supplied clips, attach the open-face air sampler and tubing to the wearer's lapel in their breathing zone with the open-face down. Attach the sampling pump to the wearer's belt or to another secure location. When ready to begin sampling, turn on the sampling pump and record the start time. Collect samples at 1 l/min for 15 min; up to a maximum sampling time of 4 h. Take two consecutive samples for 4 h each for 8 h time-weighted average measurements. Minimize exposure of the sampling filter to light. After sampling is complete, record the stop time, turn off the sampling pump, and remove the sampling equipment from the wearer. Replace the cassette top and bottom end plug. Store the collected sample at ambient temperature in the dark for up to six days. Store the collected samples in a freezer at $-20\text{ }^{\circ}\text{C}$, if they are not analysed within 6 days. Accurately determine and record the temperature and atmospheric pressure at the sampling site. If TDI aerosols are present, it may be advisable to extract collected samples in the field by following the instructions in 8.2.

7.5 Blanks

Submit at least one blank per 10 air samples. Blank air samplers shall be handled identically to the actual air samples, except that no air is drawn through them.

7.6 Sample shipment

Ship the collected air samples and the blank air samplers to the analytical laboratory as soon as possible by overnight delivery. If delay is unavoidable, store the air samples and blanks in an isocyanate-free