American Chemistry Council
Diisocyanates Panel
Considerations for Modifications to OSHA Method 42
Air Monitoring Method: Toluene Diisocyanate (TDI)

PURPOSE

The purpose of this document is to provide considerations for modifications to the Occupational Safety and Health Administration (OSHA) air sampling method for TDI: OSHA Method 42. These modifications can help improve the ability of the method to sample and derivatize TDI. The information provided in this document is not a directive or an industry standard. The information is intended as guidance. Users should independently determine what constitutes an appropriate practice relative to their own needs and circumstances.

1. SUMMARY OF THE METHOD

1.1 Analytes: 2,6-Toluene diisocyanate (2,6-TDI, Tolylene 2,6-diisocyanate); CAS [91-08-7]. 2,4-Toluene diisocyanate (2,4-TDI, Tolylene 2,4 diisocyanate); CAS [584-84-9].

1.2 Matrix: Air

1.3 Procedure: Adsorption on a 37-mm glass fiber filter coated with 1-(2-pyridyl)piperazine (PP) at a flow rate of 1 L/min for 0.25- to 4-h time intervals; desorption into 90/10 acetonitrile/DMSO and analysis using reverse-phase liquid chromatography with UV or fluorescence detection (HPLC/UV or HPLC/FLD).

1.4 Basis and Validation: This method is an adaptation of OSHA Method 42 (1); the validation conducted for that method applies to this method. Several of the adaptations were made to improve the ability of the method to sample and derivatize TDI. The areas of the method in which changes were made from OSHA 42 are:

- Working standards and spiking solutions can be made with a prepared stock of the PP derivatives of 2,4-TDI (2,4-TDIP) and 2,6-TDI (2,6-TDIP).
- To prevent migration of PP to the back-up pad, ,do one of the following: 1) do not use the back-up pad, or 2) coat the back-up pad with PP.
- PP loading on the filters was increased to a minimum of 2 mg.

2. SAFETY

2.1 Good laboratory practices dictate that each analyst should be thoroughly acquainted with potential hazards of the reagents, products, and solvents before commencing laboratory work. SOURCES OF INFORMATION INCLUDE: SAFETY DATA SHEETS, LITERATURE AND OTHER RELATED DATA. Safety information on reagents may be obtained from the supplier. Disposal of reagents, reactants, and solvents must be in compliance with local, state, and federal laws and regulations.

2.2 Exposure to airborne concentrations of TDI above the occupational exposure limit (OEL = 5 parts per billion as an 8-hr average) can irritate (burning sensation) the mucous membranes in the respiratory tract (nose, throat, lungs) causing runny nose, sore throat, coughing, chest discomfort, shortness of breath and reduced lung function (breathing obstruction). As a result of repeated overexposures (above the OEL) or exposure to a single large dose, certain individuals may develop sensitization to TDI (asthma or asthma-like symptoms) that may cause them to react to a later exposure to TDI at levels below the OEL. TDI can also cause irritation of the skin (upon direct skin contact) with symptoms of reddening, itching and swelling. Direct splashing of liquid TDI into the eye can cause irritation with symptoms of reddening, tearing, stinging, and swelling. Refer to the SDS for more information including first aid measures.

2.3 Acetonitrile is extremely flammable and can cause respiratory irritation. Prevent contact with the skin or eyes. Work in a well-ventilated area from any source of ignition.

2.4 Exposure to dimethyl sulfoxide (DMSO) can occur primarily by skin contact. DMSO readily penetrates the skin and may significantly enhance absorption of other dissolved chemicals into the body. Skin adsorption may cause Central Nervous System effects such as headache, nausea, and dizziness. DMSO's ability to increase absorption of other chemicals is its most significant occupational hazard. Direct contact with DMSO may also cause skin and eye irritation (burning sensation). Refer to the SDS for more information including first aid measures.

2.5 Methylene chloride is a clear, colorless, volatile liquid with a chloroform-like odor. OSHA considers methylene chloride to be a potential occupational carcinogen. Short-term exposures to high concentrations may cause mental confusion, lightheadedness, nausea, vomiting, and headache. Continued exposure may also cause eye and respiratory tract irritation. Exposure to methylene chloride may make symptoms of angina more severe. Skin exposure to liquid methylene chloride may cause irritation or chemical burns.

3 APPARATUS

3.1 Portable battery operated pumps, capable of maintaining a flow rate of approximately 1 L/min.

3.2 37-mm Glass fiber filter coated with a minimum of 2 mg of PP, available from Supelco (Orbo 80) or equivalent.

3.3 37-mm polystyrene, 3-section filter housing, P/N 225-3050LF, obtained from SKC Inc. or equivalent.

3.4 10-µL Syringe, blunt-tip, (Hamilton 701 SNR), or equivalent.

3.5 Repipet dispenser, 4mL.

3.6 Mechanical flatbed shaker capable of producing 160+ cycles per minute available from Eberbach Corporation, or equivalent.

3.7 HPLC system.

3.8 HPLC column, Phenomenex Synergi™ 4 µm Fusion-RP 80Å, 100 mm x 4.6 mm , P/N 00D-4424-EO, or equivalent.

3.9 4 mL glass vials and PTFE-lined caps (Wheaton P/N 224742) or equivalent.

4. REAGENTS

4.1 2,4-TDI, CAS # 584-84-9, Sigma-Aldrich (Fluka) Catalog #33427, or equivalent.

4.2 The 2,4-TDIP derivative (2,4-Bis(4-(2-pyridyl)-1-piperazinylcarbamyl) toluene), CAS # 72375-21-4, can be purchased at 1 mg/mL in DMSO, Special Order Catalog # D-5836-01A-DER, AccuStandard, Inc., or equivalent.

4.3 2,6-TDI, CAS # 91-08-7, Sigma-Aldrich (Fluka) Catalog #33493, or equivalent.

4.4 The 2,6-TDIP derivative (2,6-Bis(4-(2-pyridyl)-1-piperazinylcarbamyl) toluene), CAS # 72375-21-4, can be purchased at 1 mg/mL in DMSO, Special Order Catalog # D-5836-02A-DER, AccuStandard, Inc., or equivalent.

4.5 Desorbing solution: 90/10 (v/v) Acetonitrile (HPLC grade)/Dimethyl sulfoxide (DMSO).

4.6 1-(2-Pyridyl)piperazine (PP), CAS# 34803-66-2, 99.5%, Cat. No. 408166, obtained from the Aldrich Chemical Company or equivalent.

4.7 Standard Preparation Solvent, 3mM 1,2-PP, CAS 34803-66-2 in acetonitrile (HPLC grade) prepared by diluting approximately 0.49 grams of 1,2-PP into 1 liter of 90/10 acetonitrile/DMSO.

4.8 Ammonium Acetate, CAS# 631-61-8, 98%, Cat. No. 15,852-6, obtained from Aldrich Chemical Company or equivalent.

4.9 Glacial Acetic Acid, CAS# 64-19-7, 99.7%, obtained from Fisher Scientific, or equivalent.

5. PROCEDURES

5.1 Preparation of Filter for TDI Monitoring

5.1.2 Use a 37-mm glass fiber filter that has been pre-coated with a minimum of 2 mg of PP. This media may be available commercially or made in-house according to the directions below.

5.1.3 Prepare a sufficient volume of a 4 mg/mL solution of PP in methylene chloride or toluene. One filter uses 0.5 mL of this solution. Store the coating solution in an amber bottle for up to 60 days at ambient temperature.

5.1.4 Place the 37-mm glass fiber filters in a Petri dish so they are not in contact with each other.

5.1.5 Using an Eppendorf pipettor, apply 500 µL of filter coating solution to thoroughly wet each filter. Allow filters to air-dry in a laboratory hood until the solvent has evaporated (approximately 30 minutes).

5.1.6 Place the filters in a capped wide-mouth brown glass jar. Unused treated filters may be stored in a freezer (~ -10°C) for up to 2 months. Filters should be prepared, handled, and stored in the dark as much as possible.

5.1.7 Assembly of filter cassettes: Place one PP-coated glass fiber filter, or one coated filter and a coated backup pad (see section 1.4) into the bottom section of the cassette. Assemble the remaining sections of the cassette and press together firmly to seal. Band the lower two sections of the cassette.

5.2 Preparation of Spiked Samplers and Reference Solution

5.2.1 Prepare a spiking stock solution by either weighing 23 mg of each TDIP isomer and dissolving in 4 mL of 90/10 acetonitrile/DMSO, or by weighing 8 mg of each TDI isomer and dissolving in 4 mL of methylene chloride. If using vendor-purchased stock standards (e.g., Accustandard or equivalent), adjust your procedures accordingly in order to duplicate the spike levels in 5.2.2.

5.2.2 For the low loading level (~2 µg of each TDI isomer) inject 1 µL of spiking solution directly onto the treated glass fiber filter (while it is in

the filter cassette) with a 10-µL blunt tipped syringe. The blunt tip of the syringe is placed directly on the treated glass fiber filter to assure that the spike is on the filter and not on the filter cassette. The blunt tip syringe is used to avoid puncturing the filter. For the high loading level (~20 µg of each TDI isomer) inject 10 µL of TDI spiking solution. Allow the filters to air-dry for approximately 10 minutes, then cap. Consider duplicate preparation at each level to determine lab precision.

5.2.3 Store the spiked samplers at freezer temperatures; include with samples for analysis.

5.3 Sampling Procedure

5.3.1 Use 37-mm glass fiber filters that have been coated with PP and placed in three-piece 37-mm cassettes.

5.3.2 Connect the 37-mm filter cassette to the sampling pump with tubing (i.e. Tygon®) and a Luer connector. Calibrate the air sampling pump with the sampler connected prior to sample collection to a flow rate of approximately 1L/min.

5.3.3 The maximum sampling time should be limited to 4 hours. If the isocyanate level and/or amount of dust in the air are expected to be high, reduce the sample time to 2 hours. High ambient air temperatures and humidity may reduce the recommended sampling time due to potential loss of derivatizing agent. Analytical confirmation of excess derivatizing agent can be used to confirm validity of the sample.

5.3.4 Place the cassette in the breathing zone of the worker to be monitored or in an appropriate location in the workplace area which is to be monitored. Immediately prior to the start of the sample period, remove the top level of the three-piece cassette to sample "open" face. All sample cassettes, whether attached to a worker's shirt lapel or placed in a specific work area, should be mounted so they are facing downward. Turn on the pump for sample collection and record the start time.

5.3.5 After the desired sampling period, turn off the pump and record the stop time. Proceed to a clean location (i.e., office area) to post-calibrate the pump. Calculate and use the average air sample pump flow rate to determine the total volume of air sampled (i.e., total sample time in minutes x the average sample pump flow rate = total sample air volume in liters).

5.3.6 Measure and record workplace air temperature and humidity.

5.3.7 Prepare the collected samples for shipment to the laboratory. Ensure the top section of the cassette and caps are secured in place prior to shipment to the lab. With each set of samples, at least one blank should be submitted and should be treated the same as the samples except without the air being drawn through it.

5.4 Desorption of Samples

5.4.1 Pry open the bottom of the cassette and remove the glass fiber filter.

5.4.2 Place the filters into separate vials and add 4 mL of 90/10 acetonitrile/ DMSO, and cap the vials.

5.4.3 Shake the sample vials for approximately 1 hour on a flatbed mechanical shaker or equivalent.

5.4.4 Transfer an aliquot of extract to an appropriate vial for analysis.

5.5 Analysis Conditions and Instrumentation

5.5.1 The conditions and instrumentation given below are known to work well for this analysis. Any other set of conditions and instrumentation that are demonstrated to work by analysis of the calibration standards may be used in place of those given here.

5.5.2 Prepare the mobile phase by dissolving 7.7 grams of ammonium acetate into 10 L of purified water (0.01 M Ammonium Acetate). Then adjust the pH of the solution to pH 6.0 - 6.2 by adding glacial acetic acid drop-wise.

5.5.3

Pump:	HPLC gradient pump
UV Detector:	254 nm (313 nm for confirmation wavelength)
Fluorescence Detector:	Excitation=240 nm Emission= 370 nm
Column:	Phenomenex Synergi™ 4µm Fusion-RP 80Å, 100 mm x 4.6 mm, P/N 00D-4424-EO
Injection Volume:	10 µL
Eluent Program:	A = Acetonitrile B = 0.01 M Ammonium Acetate, pH = 6.0 - 6.2

Acetonitrile can be added at 5-20% to prevent microbial growth; the gradient may need to be adjusted to compensate.

Time (min)	%A	%B	Flow (mL/min)
0	25	75	2.0
4.0	25	75	2.0
8.0	50	50	2.0
11.0	50	50	2.0
11.1	25	75	2.0

(Note: Running a higher concentration of acetonitrile after the end of each analytical run may be required if the derivatizing agents or other components tend to build up on the column. If changes in separation occur, this may be a possible reason.)

5.5.4 Retention time under these conditions:
2,6-TDI: 5.8 min
2,4-TDI: 6.9 min

5.5.5 Approximate limit of quantitation under these conditions: 0.1 μg of each isomer per sample.

5.6 Preparation of Calibration Standards

5.6.1 Calibration standards can be prepared using the TDI isomers or the PP derivatives of TDI (2,6-TDIP and 2,4-TDIP).

Notes:
A single stock solution may be used for calibration standards if a second stock solution is used for calibration verification.

If TDIP is used, DMSO is a good solvent to use for making the concentrated stock solutions for later dilution into acetonitrile.

If using vendor-purchased stock standards (e.g., Accustandard or equivalent), adjust the dilutions accordingly in order to duplicate the standard concentrations below.

The molecular weights of TDI (174.16) and TDIP (500.61) lead to a mass conversion factor of 0.3479 for expressing TDIP mass as TDI mass equivalent. Follow the same dilutions as below but divide the weights by 0.3479.

5.6.2 Prepare stock/standard solutions as follows: Weigh ~10.5 mg of each TDI isomer into a vial. Add 30 mL of methylene chloride to the vial, and then allow the TDI isomers to dissolve for ~1/2 hour with periodic agitation. This is Stock A.

5.6.3 Prepare the following calibration standards from Stock A.

5.6.3.1 Standard 1: inject 300 µL of Stock A into 9.70 mL of standard preparation solvent (concentration = ~10 µg of each TDI isomer/mL).

5.6.3.2 Standard 2: inject 60 µL of Stock A into 10 mL of standard preparation solvent (concentration = ~2 µg of each TDI isomer/mL).

5.6.3.3 Standard 3: inject 30 µL of Stock A into 10 mL of standard preparation solvent (concentration = ~1.0 µg of each TDI isomer/mL).

5.6.3.4 Standard 4: inject 6 µL of Stock A into 10 mL of standard preparation solvent (concentration = ~0.2 µg of each TDI isomer/mL).

5.6.3.5 Standard 5: inject 100 µL of Standard 1 into 9.9 mL of standard preparation solvent (concentration = ~0.1 µg of each TDI isomer/mL).

5.6.3.6 Standard 6: inject 200 µL of Standard 2 into 9.8 mL of standard preparation solvent (concentration = ~0.04 µg of each TDI isomer/mL).

5.6.3.7 Standard 7: inject 100 µL of Standard 2 into 9.9 mL of standard preparation solvent (concentration = ~0.02 µg of each TDI isomer/mL).

6. CALCULATIONS

6.1 Generate a calibration line from the standards.

6.2 Use the equation from the calibration to calculate the µg/sample for each sampler, correcting for the desorption volume (4 mL).

6.3 Correct the sample concentration based on the method recovery.
$M^1 = (M*100)/\%\ R$

where: M^1= corrected mass of the analyte

M= uncorrected mass of the analyte
% R= appropriate recovery value (expressed as a percent).

a. The average extraction efficiency given in OSHA Method 47 (96.3%),
   or
b. The mean percent recovery of the spiked samplers analyzed with the sample if that mean differs from the OSHA extraction efficiency by more than ± 15 %.

7. REFERENCES

Occupational Safety and Health Administration (OSHA), "OSHA Method 42: Diisocyanates", OSHA Analytical Laboratory, Organic Methods Development Branch, Salt Lake City, UT, 1989.

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