American Chemistry Council
Diisocyanates Panel
Considerations for Modifications to OSHA Method 47
Air Monitoring Method: Diphenylmethane Diisocyanate (MDI)

PURPOSE

The purpose of this document is to provide considerations for modifications to the Occupational Safety and Health Administration (OSHA) air sampling method for MDI: OSHA Method 47. These modifications can help improve the ability of the method to sample and derivatize MDI. 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 Analyte: 4,4'-Methylene diphenylisocyanate (MDI, Methylene di-*p*-phenyl diisocyanate); CAS [101-68-8]. (NOTE: this method may also be applied to the determination of 2,4'-MDI if appropriate reference material is obtained for preparing spiking solutions and calibration standards. Chromatographic conditions would have to be adjusted based upon the calibration standards.)

1.2 Matrix: Air

1.3 Limitations: This method should not be used in applications where an MDI-containing mixture is aerosolized by heat and pressure and forced through a spray nozzle (e.g. spray polyurethane foam and spray-on truck bed liner applications). (Ref 7.1)

1.4 Procedure: Adsorption on 13-mm glass fiber filters coated with 1-(2-pyridyl) piperazine (1, 2-PP) and diethyl phthalate (DEP) at a flow rate of 1 L/min for 0.25 to 4-hour time intervals; desorption into acetonitrile/DMSO and analysis using reverse-phase liquid chromatography with UV or fluorescence detection (HPLC/UV or FLD).

1.5 Basis and Validation: This method is an adaptation of OSHA Method 47 (Ref 7.2); the validation conducted for that method applies to this method. Several of these adaptations were made to improve the ability of the method to sample and derivatize MDI in both vapor and aerosol form; validation of the sampler for MDI aerosol/vapor mixtures has also been investigated (Ref. 7.3, 7.4). The areas of the method in which changes were made from OSHA 47 are:

The 37-mm filters and housings were replaced with a 13-mm filter and housing.

Diethyl phthalate was added to the filter coating.

Desorption of the sample in the field (Ref. 7.5).

A filter housing rinse during desorption.

Working standards and spiking solutions may be made using either MDI or a previously prepared sample of the 1,2-PP derivative of MDI (MDIP).

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 INLCUDE: MATERIAL 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 MDI 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 MDI (asthma or asthma-like symptoms) that may cause them to react to a later exposure to MDI at levels below the OEL. MDI can also cause irritation of the skin (upon direct skin contact) with symptoms of reddening, itching, and swelling. Direct splashing of liquid MDI into the eye can cause irritation with symptoms of reddening, tearing, stinging, and swelling. Refer to the MSDS 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 absorption 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 MSDS for more information including first aid measures.

3. APPARATUS

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

3.2 13-mm Glass fiber filters, P/N 225-16, obtained from SKC Inc. or equivalent.

3.3 13-mm Swinnex filter holders with polytetrafluoroethylene (PTFE) washers, P/N SX00-013-00, obtained from Millipore, P/N 4317 from Pall, or 225-32 from SKC or equivalent.

3.4 Luer Lock Plugs and Caps, P/N EW-45503-56 and EW-45500-28 from Cole-Parmer or equivalent.

3.5 PTFE Washer, P/N 225-3201, obtained from SKC Inc. or equivalent.

3.6 10-uL Syringe, blunt-tip, (Hamilton 702 SNR or equivalent).

3.7 Repipet dispenser, 2 mL.

3.8 Mechanical flatbed shaker capable of producing 160+ cycles per minute.

3.9 HPLC system equipped with pump, autosampler and detectors.

3.10 HPLC column, C18, 250mm x 4.6mm (I.D.) for conditions described in Section 5.7.3.

3.11 4 mL glass vials and PTFE-lined caps (Wheaton P/N 224742) or equivalent.

4. REAGENTS

4.1 4, 4'-Methylene diphenylisocyanate (MDI, Methylene di-*p*-phenyl diisocyanate) CAS [101-68-8], 99 %.

4.2 The 1,2-PP derivative of MDI (MDIP): N, N'-(Methylenediphenylene)bis[4-(2-pyridinyl)-1-piperazinecarboxyamide], available from Sigma-Aldrich (1 mg/mL in DMSO, Cat. No. 48147), or equivalent, or synthesized following the procedure in OSHA Method 47 (Ref 7.2).

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

4.4 1-(2-Pyridyl)piperazine (1,2-PP), CAS [34803-66-2], 99.5 + %, Cat No. 408166, obtained from the Sigma Aldrich Chemical Company, or equivalent.

4.5 Diethyl phthalate, CAS [84-66-2], 99%, Cat. No. D9,962-5, obtained from Sigma Aldrich Chemical Company, or equivalent.

4.6 Standard preparation solvent, 3mM 1,2-PP, CAS [34803-66-2] in acetonitrile (HPLC grade) prepared by diluting approximately 0.49 grams 1,2-PP into 1 liter of acetonitrile.

4.7 Ammonium Acetate, CAS [631-61-8], 98%, Cat. No. 15,852-6, obtained from Sigma Aldrich Chemical Company, or equivalent.

4.8 Glacial Acetic Acid, CAS [64-19-7], 99.7%, obtained from Fisher Scientific, or equivalent.

5. PROCEDURES

5.1 Preparation of Filter Coating Solution

5.1.1 Methylene Chloride or toluene can be used for the filter coating solution. Dissolve 2 grams of 1,2-PP into 95 mL of solvent; add 5 mL of diethyl phthalate to this solution (~20 µg/µL 1,2-PP).

5.1.2 Store the above solution (at ambient temperature) in a brown glass bottle.

5.1.3 Filter coating solution may be used for up to two months.

5.2 Coating of Glass Fiber Filters

5.2.1 Place the 13 mm glass fiber filters in a Petri dish so they are not in contact with each other.

5.2.2 Using an Eppendorf pipettor, apply 50 µL of filter coating solution to thoroughly wet each filter.

5.2.3 Allow the filters to air-dry in a laboratory hood until the solvent has evaporated (approximately 30 minutes) and then apply a second 50 µL of solution.

5.2.4 Allow the filters to dry for 1 hour.

5.2.5 Place the filters in a capped wide-mouth brown glass jar. Unused treated filters may be stored at freezer temperature (~ -10°C) for up to 2 months.

5.2.6 Filters should be prepared, handled, and stored in the dark as much as possible.

5.3 Assembly of Filter Housing

5.3.1 Place a PTFE washer into the inlet portion of the 13-mm polypropylene filter housing, then place the 13-mm coated glass fiber on top of it. A second PTFE washer can then be placed on top of the treated filter. (NOTE: the use of a second PTFE washer is optional; its use helps prevent the filter sticking to the cassette housing, facilitating removal of the filter from the cassette for analysis.)

5.3.2 Making sure that the filter is seated properly with no gaps or folds, screw the outlet portion of the 13-mm polypropylene filter housing onto the lower housing half containing the filter.

5.3.3 Cap the ends of the filter housing (red caps from 600-mg charcoal tubes work well).

5.4 Preparation of Spiked QC Samplers

5.4.1 For the low loading level (~ 2 µg) inject 1 µL of MDI spiking solution (~20 mg of MDI [or ~ 50 mg MDIP] in 10 mL of acetonitrile) directly onto the treated glass fiber filter (while it is in the filter housing) 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 housing or PTFE O-ring. The blunt tip syringe is used to avoid puncturing the filter. For the high loading level (~20 µg) inject 10 µL of MDI spiking solution.

5.4.2 Store the spiked samplers at freezer temperatures. Include a laboratory blank and the spiked samplers with samples for analysis.

5.5 Sampling Procedures

5.5.1 Use 13-mm glass fiber filters that have been coated and installed in filter housings. The caps to the housings must be removed before sampling.

5.5.2 Use an air sampling pump calibrated at a flow rate of approximately 1 L/min. Maximum sampling time should be limited to 4 hours. If the isocyanate level and/or amount of dust in the air are high, reduce the sample time to 2 hours. High ambient air temperatures and humidity will reduce the recommended sampling time due to potential loss of derivatizing agent.

5.5.3 Attach the pump to the filter cassette outlet with rubber tubing.

5.5.4 At the end of the sampling period, remove the sampling device and replace the caps over the ends of the cassette housings.

5.5.5 Measure and record air temperature, humidity, and pressure. Perform a post-sampling check of the pump flow rate.

5.5.6 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.

5.5.7 Desorb the sample immediately after sampling using the sample desorption procedure described below.

5.6 Field Desorption of Samples

5.6.1 Open the sample cassette, remove the 13-mm filter using tweezers, and place it in a glass vial which has been labeled with the sample identification.

5.6.2 Place the sample inlet portion of the top half of the cassette into the mouth of the vial (like a funnel). Place the PTFE washers and lower half of the cassette housing in a container for cleaning and reuse by the laboratory.

5.6.3 Using a pipettor or volumetric pipette, rinse the inside of the top half of the cassette into the glass vial with 4 mL of acetonitrile/DMSO desorbing solution. Following rinsing, place the top half of the cassette in the container with the rest of the cassette parts to be reused.

5.6.4 Cap the vial and store it at ambient lab or refrigerator temperatures until the rest of the set of samples has been processed.

5.6.5 Send the set of vials containing processed samples along with the container of cassette parts to the analysis laboratory. Cooling during shipment is not required. Ship according to DOT regulations. *See* Appendix A for general shipping guidance.

5.7 Analysis Conditions and Instrumentation

5.7.1 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 and a media blank may be used in place of those given here.

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

5.7.3

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, 100mm x 4.6mm, P/N 00D-4424-EO or equivalent C-18 column
Autosampler:	10µL injection volume
Eluent Program	A=Acetonitrile

B= 0.01M Ammonium Acetate, pH=6.0-6.2
Acetonitrile can be added at 5-20% to prevent microbial growth.

Time (min)	%A	%B	Flow (mL/min)
0	30	70	2.0
4.0	30	70	2.0
8.0	50	50	2.0
10.0	50	50	2.0
10.1	30	70	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.)

5.7.4 Retention time under these conditions: 4,4'-MDI: 8.6 min

5.7.5 Approximate limit of quantitation under these conditions: 0.1 µg per sample.

5.8 Preparation of Calibration Standards

5.8.1 Calibration standards may be prepared using MDI (as described below) or MDIP. (Note: A single stock solution may be used for calibration standards if a second stock solution is used for calibration verification.)

5.8.1.1 If MDIP is used, DMSO is a good solvent to use for making the concentrated stock solutions (5.8.2.1) for later dilution into acetonitrile.

5.8.1.2 The molecular weights of MDI (250.26) and MDIP (576.71) lead to a mass conversion factor of 0.4339 for expressing MDIP mass as MDI mass equivalent.

5.8.2 Prepare stock/standard solutions as follows:

5.8.2.1 Weigh ~15 mg (Stock A) and ~30 mg (Stock B) of solid MDI into separate 10-mL volumetric flasks and bring to volume with methylene chloride.

5.8.2.2 Allow the MDI to dissolve for ~ ½ hour with periodic agitation.

5.8.3 Prepare the following calibration standards from the stock standard solutions (Section 5.8.2.1)

5.8.3.1 Standard 1/100 A: inject 100 µL of Stock A (Section 5.8.2.1) into 9.9 mL of standard preparation solvent (concentrations = ~15 µg/mL).

5.8.3.2 Standard 1/1000 B: inject 10 µL of Stock B (Section 5.8.2.1) into 10 mL of standard preparation solvent (concentration= ~ 3 µg /mL).

5.8.3.3 Standard 1/1000 A: inject 10 µL of Stock A (Section 5.8.2.1) into 10 mL of standard preparation solvent (concentration= ~ 1.5 µg/mL).

5.8.3.4 Standard 1/10000 B: inject 1 µL of Stock B (Section 5.8.2.1) into 10 mL of standard preparation solvent (concentration= ~ 0.3 µg/mL).

5.8.3.5 Standard 1/10000 A: inject 1 µL of Stock A (Section 5.8.2.1) into 10 mL of standard preparation solvent (concentration= ~ 0.15 µg/mL).

5.8.3.6 Standard 1/100000 B: add 1 mL of Standard 1/10000 B (Section 5.8.3.4) into 9.0 mL of standard preparation solvent (concentration= ~0.03 µg/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

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7.2 Occupational Safety and Health Administration (OSHA), "OSHA Method 47: Methylene Bisphenyl Isocyanate," OSHA Analytical Laboratory, Organic Methods Development Branch, Salt Lake City, UT, 1985.

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7.4 Karoly WJ, Stability studies of diphenylmethane diisocyanate (MDI) on glass fiber filters, Amer.Ind.Hyg.Assoc.J., Vol.59, Sep., 1998, 645-647.

7.5 Schaeffer JW, Sargent LM, Sandfort DR; Brazile WJ, A Comparison of Two Sampling Methods for the Detection of Airborne Methylene Bisphenyl Diisocyanate, J.Occup.Environ.Hyg., May 2013, in press.

DISCLAIMER AND LEGAL NOTICE

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Appendix A – Shipping Guidance

Introduction

Since the procedure for the ACC Diisocyanates Panel Modification to OSHA Method 47 Air Monitoring Method: Diphenylmethane Diisocyanate (MDI) involves field desorption with an acetonitrile / dimethlysulfoxide solvent mixture, certain considerations apply for proper shipping of the solvent mixture to the field and the field-desorbed samples back to the laboratory. This guidance represents the best available summary of the practices employed by those experienced with the method in the United States of America (as of the date of publication) and is intended to give the user some ideas on practices that have been found to be effective***. The user of this method is advised to check current regulations and the advice of those responsible for shipping in their organization when establishing the practices they will use.***

Shipping Field Desorbed Samples to the Laboratory

As of the date of publication, field desorbed samples may be shipped to the laboratory for analysis without hazardous material boxes, labels or shipping documents according to the "small quantity exemption" in the US Department of Transportation regulations (49 CFR § 173.4). Below are some details for such shipments (current as of the date of publication of this Appendix), but always refer to 49 CFR § 173.4 for specific guidance:

- Shipment is by ground transport (highway or rail).
- Samples are desorbed in screw-cap glass vials which have a maximum solvent volume of 30mL (1 ounce).
    - Some headspace is left in the vials.
    - The cap of each vial is secured (for example, with tape or wire).
- The sample vials are packed in an inner container with cushioning and absorbent material sufficient to absorb the entire volume of solvent in the package.
- The inner packaging is contained in strong outer packaging that is marked with the statement, "This package conforms to 49 CFR 173.4 for domestic highway or rail transport only."
- The total weight of the package is no greater than 29 kg (64 pounds).

Examples of typical commercially-available packages meeting these characteristics are shown below:

Packaging must be appropriately labeled. Refer to 49 CFR § 173.4a for specific guidance.

Shipping Field Desorption Solvent to the Sampling Location

One option for shipping the field desorption solvent to the sampling location is to pre-fill the sample vials with the solvent in the lab and ship them to the sampling location following the guidance given above for shipping the field desorbed samples to the laboratory.

A second option is to ship the sample vials and packaging to the field empty and ship the desorption solvent separately in a bottle and shipping package designed for such shipping. In this case, the shipment would not meet the container volume requirements of the DOT "small quantity exemption" and so would need to be shipped as a "fully regulated" hazardous material shipment (requiring UN specification packaging, marks, and labels with the Bill of Lading, etc.). Any unused field desorption solvent would need to be properly disposed of at the sampling location or shipped back to the laboratory in sample vials as described above.