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Methylene bis-(4-Cyclohexylisocyanate) (HMDI)

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Method number: PV2092

Target Concentration: 0.055 mg/m<sup>3</sup> or 0.005 ppm (ACGIH TLV).

Procedure: Samples are collected by drawing a known volume of air through an open-faced cassette containing glass fiber filters coated with 1.0 mg of 1-(2-pyridyl) piperazine (1-2PP). Samples are extracted with 90/10 (V/V) acetonitrile/dimethyl sulfoxide (ACN/DMSO) and analyzed by high performance liquid chromatography (HPLC) using an ultraviolet (UV) or fluorescence detector.

Recommended air volume and sampling rate: 60 minutes at 1 L/min (60 L)

Detection limit of the overall procedure: 0.4 µg/m<sup>3</sup> (based on the recommended air volume):

Special requirements: If the coated glass fiber filters are to be stored for any length of time, before sampling, they should be kept in a refrigerator.

Status of method: Partially validated method. This method has been only partially evaluated and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

This evaluation was undertaken to determine the effectiveness of a 1-2PP coated glass fiber filter as a sampling device for HMDI. It follows the procedure developed for methylene bisphenyl isocyanate (MDI). (Ref. 5.1)

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy).

HMDI has a low oral toxicity with an LD<sub>50</sub> in rats of 9.9 g/kg. In addition, the chemical is a strong eye and skin irritant. Several other animal studies are capsulized in the ACGIH document. (Ref. 5.2)

Exposure of humans to HMDI has resulted in skin sensitization, but only rarely in pulmonary sensitization. In this respect, it differs from other isocyanates (i.e., TDI and IPDI). However, it depresses respiration by producing pulmonary irritation. (Ref. 5.2)

The ACGIH has suggested a change from a ceiling value of 0.01 ppm to a TLV value of 0.005 ppm, the same as TDI. This level will continue to prevent pulmonary irritation. (Ref. 5.2)

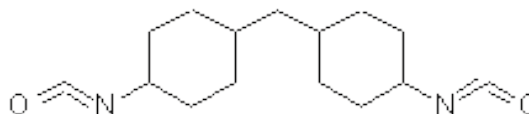
1.1.3 Potential workplace exposure

No estimate of worker exposure to HMDI could be found. HMDI is used primarily to produce urethane products which will not yellow on exposure to light. (Ref. 5.2.)

1.1.4 Physical properties (Ref. 5.2.)

CAS#:	5124-30-1
Molecular weight:	262.35
Molecular formula:	C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>
Melting point:	< -10 °C
Specific gravity:	1.07
Vapor pressure:	0.4 mmHg at 150 °C
Appearance:	colorless liquid
Solubility:	soluble in acetone.
Synonyms:	Desmodur W, HMDI, hydrogenated, MDI
Chemical name:	Methylene bis-(4-cyclohexylisocyanate)

Structure:



(Mixture of several stereoisomers which elute as one major peak)

1.2 Limit defining parameters

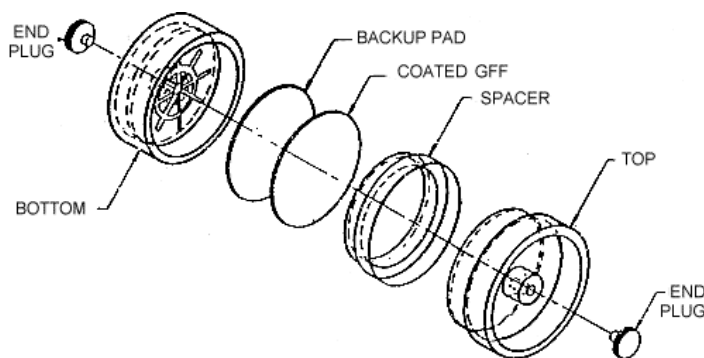
The detection limit of the analytical procedure is 0.055 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

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## 2 Sampling procedure

### 2.1 Apparatus

- 2.1.1 A personal sampling pump that can be calibrated to within  $\pm 5\%$  of the recommended flow rate with the sampling device in line.
- 2.1.2 A three-piece styrene cassette containing a glass fiber filter coated with 1.0 mg of 1-2PP and an untreated backup pad.



### 2.2 Glass fiber filter coating procedure

Prepare a solution of 2 mg/mL of 1-2PP in methylene chloride. Spike the glass fiber filters with 0.5 mL of this solution. Allow the filters to air dry, and then dry them in a 40 °C vacuum oven for an additional 2 hours.

Store coated glass fiber filters in a closed jar at reduced temperature as a precaution to prevent decomposition of the 1-2PP. Avoid exposure to strong sunlight.

### 2.3 Sampling technique

- 2.3.1 Perform open-faced sampling by removing the top cover (with small plug in place) from the three-piece cassette and the small plug from the exit port.
- 2.3.2 Attach the cassette to the sampling pump with flexible, plastic tubing such that the open face is vertically downward in the worker's breathing zone and in such a manner that it does not impede work performance.
- 2.3.3 After sampling for the appropriate time, remove the sampling device and replace the small exit plug and the top cover.
- 2.3.4 Wrap each sample end-to-end with a Form OSHA-21 seal.
- 2.3.5 Submit at least one blank with each set of samples. Handle the blanks the same as the other samples except draw no air through them.
- 2.3.6 Submit any bulk samples in a separate container. Do not ship them with the air samples.

### 2.4 Extraction efficiency

Nine 1-2PP coated glass fiber filters were each liquid spiked with 12  $\mu\text{L}$  of a DMSO solution of HMDI 1-2PP derivative equivalent to 273  $\mu\text{g/mL}$  HMDI. Three of these filters, along with a blank

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filter, were extracted with 4.0 mL 90/10 (V/V) ACN/DMSO and then analyzed. The remaining six filters were used in the retention and storage studies.

Table 2.4  
Class Fiber Filter Extraction Study

filter #	µg spiked	µg recovered	% recovered
1	3.276	3.203	97.8
2	3.276	3.242	99.0
3	3.276	3.262	99.6
blank	0.00	0.00	blank

average recovery = 98.8%

## 2.5 Retention efficiency

The remaining six spiked filters each had 60 liters of humid air (65% relative humidity) drawn through them. Three of these filters were extracted with 4.0 mL 90/10, (V/V) ACN/DMSO and analyzed immediately. The remaining three filters were stored at room temperature in a drawer for the storage study.

Table 2.5  
Retention Efficiency Study

filter #	µg spiked	µg recovered	% recovered
1	3.276	3.260	99.5
2	3.276	3.153	96.2
3	3.276	3.147	96.1

average recovery = 97.3%

## 2.6 Sample storage

The remaining three spiked filters were stored for a total of 7 days in a drawer at room temperature. They were then extracted with 4.0 mL 90/10 (V/V) ACN/DMSO and analyzed.

Table 2.6  
Storage Study

filter #	µg spiked	µg recovered	% recovered
1	3.276	3.217	98.2
2	3.276	3.234	98.7
3	3.276	3.133	95.6

average recovery = 97.5%

## 2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 60 L.

2.7.2 The recommended flow rate is 1 L/min.

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2.8 Interferences

Compounds such as acid chlorides, anhydrides, and other isocyanates that react with the 1-2PP may compete for the derivatizing agent on the glass fiber filter and diminish the latter's effectiveness.

Suspected interferences should be reported to the laboratory with submitted samples.

2.9 Safety precautions

2.9.1 Attach the sampling equipment in such a manner that it will not interfere with work performance or employee safety.

2.9.2 Follow all safety practices that apply to the work area being sampled.

3 Analytical procedure

3.1 Apparatus

3.1.1 A high performance liquid chromatograph equipped with a UV or fluorescence detector, and manual or automatic injector. A Waters M6000A pump, Waters 712 autosampler, Kratos Spectroflow 980 fluorescence detector, and a Waters 440 dual wavelength UV detector were used in this evaluation.

3.1.2 An HPLC column capable of separating IPDI from any interference. A 25-cm × 4.6-mm i.d. Chromagabond 5- $\mu$ m TMS column was used in this evaluation.

3.1.3 An electronic integrator or other suitable means of measuring detector response. A Hewlett-Packard 3357 data system was used in this evaluation.

3.1.4 Vials, 4-mL glass with polytetrafluoroethylene (PTFE)-lined septa.

3.1.5 Volumetric flasks, pipettes, and syringes for preparing standards, making dilutions, and performing injections.

3.2 Reagents

3.2.1 HPLC grade ACN.

3.2.2 HPLC grade water. A Millipore Milli-OQ system was used to prepare the water in this evaluation.

3.2.3 HPLC grade DMSO

3.2.4 HMDI 1-2PP derivative prepared by D. Burrig.

3.3 Standard preparation

Prepare stock standard solutions by adding DMSO to preweighed amounts of HMDI 1-2PP derivative. Prepare working range standard solutions by diluting stock solutions with 90/10 (V/V) ACN/DMSO.

Apply a correction factor of 0.446 (F.W. of HMDI, 262.35 /F.W. of the 1-2PP derivative, 588.23) to express concentrations in terms of HMDI. Store stock and dilute standards in a freezer.

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3.4 Sample preparation

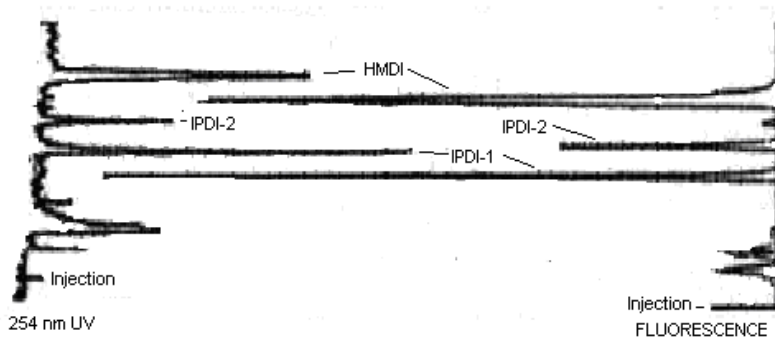
- 3.4.1 Open the styrene cassette and place the coated glass fiber filter in a 4-mL vial so that the filter is flat against the inside of the vial. Do not fold or crumple it.
- 3.4.2 Add 4.0 mL of 90/10 (V/V) ACN/DMSO to each vial.
- 3.4.3 Seal the vials with PTFE-lined septa and allow them to extract for one hour. Shake the vials by hand periodically during this extraction time.

3.5 Analysis

3.5.1 Instrument conditions

Column:	25-cm × 4.6-mm i.d. Chromegabond 5- $\mu$ m TMS
Mobile Phase:	49.5:50.5 ACN/water, with 0.045 M Ammonium acetate buffer adjusted to pH 5.9
Flow rate:	1 mL/minute
Fluorescence Detector:	excitation = 240 nm, emission = 370 nm
UV Detector:	254 nm
Retention time:	11.5 minutes
Injection volume:	10 $\mu$ L

3.5.2 Chromatogram



3.6 Interferences

- 3.6.1 Any compound having a similar retention time to the analyte is a potential interference. Generally, chromatographic conditions can be altered to separate interference from the analyte.
- 3.6.2 Retention time on a single column is not proof of chemical identity. Analysis by an alternate HPLC column, detection at another wavelength, comparison of absorbance response ratios (or comparison of UV to fluorescence response ratios), and confirmation by mass spectrometry are additional means of identification.

3.7 Calculations

- 3.7.1 A calibration curve is constructed by plotting detector response versus standard concentration.
- 3.7.2 The concentration of HMDI in a sample is determined from the calibration curve.
- 3.7.3 The total HMDI concentration is then determined by the following formula:

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$$\text{mg} / \text{m}^3 = \frac{(\mu\text{g} / \text{mL, blank corrected})(\text{desorption volume, mL})}{(\text{air volume, L})(\text{desorption efficiency, decimal})}$$

3.8 Safety precautions

3.8.1 Avoid exposure to all standards.

3.8.2 Avoid exposure to all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendations for further study

This method should be fully validated.

5 References

5.1 "OSHA Analytical Methods Manual," U.S. Department of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory: Salt Lake City, UT, Method 47, American Conference of Governmental Industrial Hygienists (ACGIH): Cincinnati, OH, 1985, ISBN: 0-936712-X.

5.2 "Documentation of the Threshold Limit Values and Biological Exposure Indices," American Conference of Governmental Industrial Hygienists Inc., fifth edition, 1986.