1,6-Hexamethylene diisocyanate homopolymer

Method no.:	PV2125
Target concentration:	0.5 mg/m^3
Procedure:	Samples are collected by drawing a known volume of air through glass fiber filters coated with 1.0 mg of 1-(2-pyridyl) piperazine (1-2PP) which are sampled in open-face cassettes. Samples are extracted with 90/10 (v/v) acetonitrile/dimethyl sulfoxide (ACN/DMSO) and analyzed by liquid chromatography (LC) using an ultraviolet or fluorescence detector.
Recommended sampling time and sampling rate:	15 L at 1 L/min
Reliable quantitation limit:	0.023 mg/m^3
Special requirements:	It is recommended that coated glass fiber filters be stored at refrigerated temperature until used for sampling.
Status of method:	Partially evaluated method. This method has been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use.

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1. General Discussion

1.1 Background

1.1.1 History

Information on Hexamethylene diisocyanate homopolymer or HDI Homo (Desmodur 3300 manufactured by Bayer) was not available. It was decided to follow the OSHA Method 42[1] for Diisocyanates. HDI Homo is not available in pure form.

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

Recommended Manufacturer Guideline Level (MGL) is 0.5 mg/m³. This product is not listed by NTP, IRAC or regulated as a carcinogen by OSHA. Desmodur 3300 aerosols at concentrations above MGL can irritate (burning sensation). The mucus membranes in the respiratory tract (nose, throat, lungs) causing runny nose, sore throat, coughing, chest discomforts, shortness of breath and reduced lung function. Exposures well above MGL may lead to bronchitis, bronchial spasm and pulmonary edema (fluid in lungs). Chemical or hypersensitive pneumonitis, with flu like symptoms (e.g. fever, chills) has also been reported. Oral LD_{50} is >10000 mg/kg (rats), Dermal LD_{50} > 5000 mg/kg (rabbits)[2].

1.1.3 Workplace exposure

No exposure data is available at present, but this product is widely used in automobile industry in polyurethane paint.

1.1.4 Physical properties and other descriptive information[2]

CAS number:	28182-81-2	IMIS:	H130
molecular weight:	approx 500		
boiling point:	decomposes	Wavelength:	λmax - 254 nm
appearance:	yellowish liquid	molecular formula:	$C_{24}H_{36}N_6O_6$
odor:	odorless		
synonyms:	polymeric hexamethylene diisocyanate; HDI Homo		
solubility:	soluble in methylene chloride, decomposes in water and liberates carbon dioxide		

This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[3]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25°C and 101.3 kPa (760 mmHg).

1.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL):

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of 1,6 - Hexamethylene diisocyanate homopolymer such that the highest sampler loading was 0.375 µg/sample. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response for a sample blank. These spiked samplers and the sample blank were analyzed with the recommended

analytical parameters, and the data obtained used to calculate the required parameters (Standard Error of Estimate and Slope) for the calculation of the DLOP. Values of 4.65E04X-1.37E03 and 1570.14 were obtained for the slope and standard error of estimate respectively. DLOP was calculated to be 0.1 µg/sample (0.0066 mg/m³).

Table 1.2
Detection Limit of the Overall Procedure

mass per sample (µg)	area counts (µV-s)
0	0
0.15	5470
0.175	7356
0.200	7593
0.225	8312
0.250	8743
0.275	9976
0.300	11265
0.325	12413
0.350	17296
0.375	18444

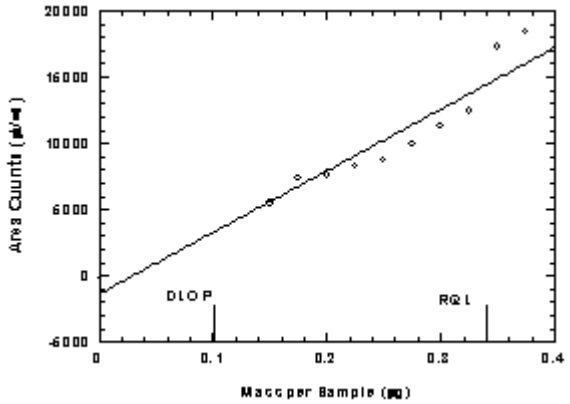

Figure 1.2.1 Plot of data to determine the DLOP/RQL. (Y = 4.65E04X - 1.37E03)

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The RQL is 0.34 µg per sample (0.023 mg/m³). Recovery at this concentration is 84.5%.

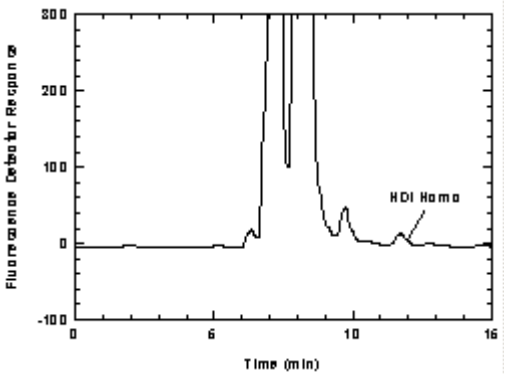

Figure 1.2.2 Chromatogram of the RQL for HDI Homo.

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

2.1.1 Samples are collected by use of a personal sampling pump that can be calibrated to within ±5% at 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 a backup pad. (Figure 2.1.2)

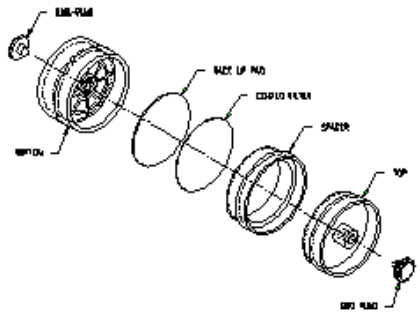

Figure 2.1.2 An illustration of the assembly of the filters in the cassette.

2.1.3 Coated filters are prepared by applying 0.5 ml of a solution of 0.2 mg/ml 1-2PP in methylene chloride to each glass fiber filter. The wet filters are allowed to air dry before placing them in a jar. Vacuum is applied to the jar to remove residual methylene chloride.

2.1.4 Coated filters should be stored at refrigerated temperature as a precaution.

2.2 Reagents

None required.

2.3 Technique

2.3.1 Immediately before sampling, remove the top piece and the end plug from the cassette.

2.3.2 Attach the cassette to the sampling pump so that it is in an approximately vertical position with the inlet facing down during sampling. Position the sampling pump, cassette and tubing so it does not impede work performance or safety.

2.3.3 Air being sampled should not pass through any hose or tubing before entering the cassette.

2.3.4 After sampling for the appropriate time, remove the sample, and replace the top piece and the end plugs. Wrap each sample end-to-end with a Form OSHA-21 seal.

2.3.5 Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.

2.3.6 Record sample volumes (in liters of air) for each sample, along with any potential interferences.

2.3.7 Ship any bulk samples separate from the air samples.

2.3.8 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator.

2.4 Extraction efficiency

The extraction efficiency of 1,6-hexamethylene diisocyanate homopolymer was determined by liquid-spiking glass fiber filter coated with 1.0 mg of 1-2PP with the analyte over the range of 0.5 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted with ACN/DMSO and analyzed. The mean extraction efficiency over the studied range was 98.3% for HDI Homopolymer.

Table 2.4
Extraction Efficiency of Hexamethylene diisocyanate homopolymer

level		sample number				
× target conc.	µg per sample	1	2	3	4	mean
0.1	0.75	96.7	103.3	101.2	96.5	99.4
0.2	1.50	105.7	102.1	102.2	92.5	100.6
0.5	3.75	99.2	95.3	96.6	96.9	97.0
1.0	7.50	99.0	98.6	100.9	91.3	97.5
2.0	15.0	99.5	97.6	97.5	94.2	97.2
average						98.3

2.5 Retention efficiency

Five glass fiber filter coated with 1.0 mg of 1-2PP were spiked with 15 µg 1,6-hexamethylene diisocyanate homopolymer, allowed to equilibrate for 6 h, and then had 15 L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2°C) pulled through them. The samples were extracted with ACN / DMSO and analyzed. The mean retention efficiency is 96.2 %.

Table 2.5
Retention Efficiency of Hexamethylene diisocyanate homopolymer

	sample number					
section	1	2	3	4	5	mean
	94.2	99.4	95.4	96.2	95.8	96.2

2.6 Sample storage

Nine glass fiber filters coated with 1.0 mg of 1-2PP were each spiked with 7.5 µg of 1,6-hexamethylene diisocyanate homopolymer. They had 15 L of air with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2°C) drawn through them. They were sealed and stored at room temperature. Three samples were analyzed immediately. Three more were analyzed after 7 days of storage and the remaining three after 18 days of storage. The amounts recovered, which are corrected for extraction efficiency, indicate good storage stability for the time period studied.

Table 2.6
Storage Test for Hexamethylene diisocyanate homopolymer

	sample		
time (days)	1	2	3
0	97.9	97.4	99.9
7	98.0	101.9	98.8
18	93.7	96.0	98.1

2.7 Recommended air volume and sampling rate

Based on the data collected in this evaluation, 15-L air samples should be collected at a sampling rate of 1.0 L/min.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan[4]. Avoid skin contact and inhalation of all chemicals.

3.1 Apparatus

3.1.1 A liquid chromatograph equipped with an ultraviolet and fluorescence detector. A Waters 600E controller,490E ultraviolet detector, spectra flow 980 fluorescence and 717 autosampler was used in this evaluation.

3.1.2 An LC column capable of separating the analyte from any interferences. The column used in this study was a Econosphere CN, 5-µm particle, 15-cm long with 4.6-mm i.d. An alternate column is Altech CN 5-µm particle, 25-cm long with 4.6-mm i.d.

3.1.3 An electronic integrator or some suitable method of measuring peak areas. A Waters Millennium[32] data system was used in this evaluation.

3.1.4 Four milliliter glass vials with PTFE-lined caps.

3.1.5 Volumetric flasks - 10-mL and other convenient sizes for preparing standards.

3.1.6 Pipets for dispensing the extracting solve.

3.2 Reagents

3.2.1 Methylene chloride, Fisher Scientific Optima lot # 964274.

3.2.2 Acetonitrile, Fisher Scientific HPLC grade lot # 964274.

3.2.3 Dimethyl sulfoxide, JT Baxter lot # BB 470.

3.2.4 Deionized water. A Millipore Milli-Q water purification system.

3.2.5 Phosphoric acid. JT Baker analyzed phosphoric acid 85.9%, (lot D25821).

3.2.6 1-(2-Pyridyl)piperazine, Aldrich, Milwaukee, WI.

3.2.7 Ammonium acetate, HPLC grade Fisher Scientific lot # 89784.

3.2.8 Glacial acetic acid, JT Baker analyzed lot # 18973.

3.2.9 Desmodur N 3300, Bayer lot # Bn 43671.

3.3 Standard preparation

The concentration of Desmodur N 3300 weighed out into a 10 mL flask was 15 mg, and methylene chloride was added to the mark. This stock standard was used to make working range standards by spiking on 1-2PP coated GFF, and extracting with 3 mL of 90/10 (v/v) ACN/DMSO.

3.4 Sample preparation

3.4.1 The polystyrene cassette is opened and the glass fiber filter is placed into a 4-mL vial so that the filter is flat against the inside surface of the vial, not folded or crumpled.

3.4.2 Three milliliters of the extracting solution, 90/10 (v/v) ACN/DMSO, are added.

3.4.3 A cap equipped with a Teflon liner is installed.

3.4.4 The vial is shaken to remove large air bubbles from between the filter and the glass. Let the vial set for 1 h.

3.5 Analysis

3.5.1 Reverse phase HPLC conditions

column:	Econosphere CN, 5-µm particle, 15-cm long with 4.6-mm i.d.
mobile phase:	0.01 M ammonium acetate in 60/ 40 ACN/water (v/v) adjusted to pH 6.0 with acetic acid
flow rate:	0.7 mL/min
UV detector:	254 nm
fluorescence detector:	240 nm excitation (370 nm emission)
injection size:	20 µL

3.5.2 Reverse phase HPLC conditions (alternate condition for general Diisocyanates)

column:	Altech CN, 5-µm particle, 25-cm long with 4.6-mm i.d.
mobile phase:	0.01 M ammonium acetate in 42/ 58 ACN/water (v/v) adjusted to pH 6.0 with acetic acid
flow rate:	1.0 mL/min
UV detector:	254 nm
fluorescence detector:	240 nm excitation (370 nm emission)
injection size:	20 µL
chromatogram:	Figure 3.5.1

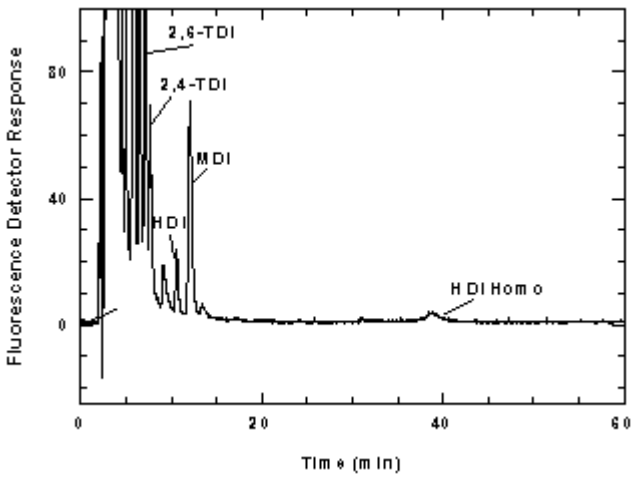

Figure 3.5.1 A chromatogram of an analytical standard at the target concentration.

3.5.2 An external standard procedure is used to prepare a calibration curve using at least 2 stock solutions from which dilutions are made. The calibration curve is prepared daily. The samples are bracketed with analytical standards.

3.6 Interferences (analytical)

3.6.1 Any compound having the same retention time as the analyte is a possible interference. Generally, chromatographic conditions can be altered to separate an interference.

3.6.2 Retention time on a single column is not proof of chemical identity. Analysis by an alternate column system, ratioing of wavelength response, and mass spectrometry are additional means of identity.

3.7 Calculation

$$C_M = \frac{M}{VE_E}$$

where

C_M is concentration by weight (mg/m^3)
M is micrograms per sample
V is liters of air sampled
E_E is extraction efficiency, in decimal form

4. Recommendations for Further Study

Collection and reproducibility study needs to be performed.

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1. Burright, D OSHA Method 42, DIISOCYANATES, http://www.osha.gov (02/02/2003 accessed).

2. Material safety data sheet, Desmodur N 3300, Bayer approval date: 04/06/200.

3. Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

4. Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 1998.