

Application

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Monitor Airborne Diisocyanates Using ORBO™-80 Coated Filters

Diisocyanates, the highly toxic compounds used in many manufacturing applications, are very reactive and require a means of stabilization when collected in air samples. Spiked ORBO-80 sampling filters were used in accordance with OSHA methodology. These filters demonstrated reproducibility and stability of the diisocyanates at concentrations below the OSHA-specified levels.

(ChromFax: 394031)

Key Words:

- diisocyanates
- ORBO glass fiber filters
- air samples

Diisocyanates are used extensively in the manufacture of polyurethane foams, coatings, and elastomers. The high toxicity of this group of compounds and the frequency of worker's potential exposure to them make monitoring of diisocyanates of great concern to industrial hygienists. Current threshold limit values established by the American Conference of Governmental Industrial Hygienists, Inc. (1) range from 34 to 51 µg/m³ for the four diisocyanates described here:

- 1,6-hexamethylene diisocyanate (HDI)
- toluene-2,6-diisocyanate (2,6-TDI)
- toluene-2,4-diisocyanate (2,4-TDI)
- methylene biphenyl isocyanate (MDI)

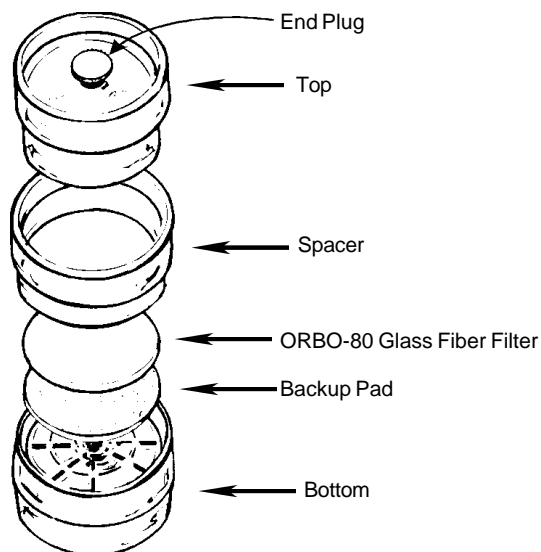
Because these compounds are very reactive, a derivatizing reagent is required to stabilize them as they are collected from an air sample. Currently used diisocyanate collection methods offer the alternatives of collecting the sample in a liquid impinger containing a derivatizing solution or on a glass fiber filter coated with a reagent (Figure A). Impingers are inconvenient to work with and present a safety hazard if the solution spills.

US Occupational Safety and Health Administration (OSHA) methods 42 and 47 describe the use of a glass fiber filter coated with 1 milligram of 1-(2-pyridyl)piperazine (1-2PP) as the derivatizing reagent for stabilizing the diisocyanates (2). When the sampling volume is 15 liters of air and the sampling rate is 1 liter/minute, the coated glass fiber filters are capable of collecting more than 200 micrograms of the four diisocyanates listed in these methods.

We evaluated our *ORBO-80 sampling filters* in accordance with OSHA methodology to demonstrate linearity, recovery, stability, and filter background levels (3). Because controlled test atmospheres of the isocyanates could not be sustained, due to their instability and toxicity, a mixture of the four isocyanate derivatives was spiked onto coated filters, then 15 liters of air was drawn through the assembled cassette.

The diisocyanate derivatives are analyzed by HPLC, using an octyl silyl or cyano reversed phase HPLC column and either UV or

Figure A. Summary of OSHA Methods 42 and 47



Filter Preparation:

37mm glass fiber filter coated with 1.0mg 1-(2-pyridyl) piperazine (in methylene chloride)

Sample Collection:

Filter assembled in three-piece cassette with back-up pad, sampled open-face
Recommended sample volume = 15 liters at 1 liter/min
Refrigerated storage of the filters (4°C) before and after sampling is recommended

Sample Preparation:

Filter extracted with 4.0mL acetonitrile:DMSO (9:1) for one hour
Extract filtered through 0.45µm filter

Standard Preparation:

Isocyanate urea derivatives prepared in DMSO/acetonitrile in the range of 0.05-20µg/mL

Analysis:

Reversed phase HPLC (C8 or cyano phase)

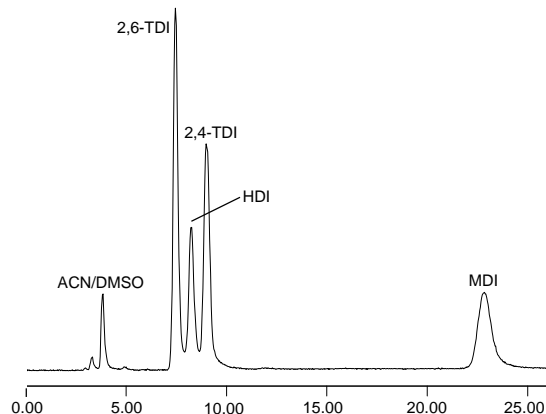
Detection:

Fluorescence (240nm excitation, 370nm emission) and UV (254nm) in series
711-0104

fluorescence detection. A SUPELCOSIL™ LC-CN cyano phase column, used with a fluorescence detector, completely separates the four derivatives. Figure B shows an analysis of the four compounds at an on-column concentration of 0.5µg/mL. This represents an air sample containing diisocyanates at a level well below the current OSHA action level of 20 micrograms per cubic meter. A ramped linear flow gradient provides optimum separation of all four isocyanate derivatives within 25 minutes. Analyses at levels lower than that shown in Figure B are affected by background from the residual, unreacted derivatizing agent in the extract.

Figure B. Isocyanate Derivatives Mixture

Column: **SUPELCOSIL™ LC-CN, 25cm x 4.6mm ID, 5µm particles**
 Cat. No.: **58231**
 Mobile Phase: 0.05M ammonium acetate in 70:30 water:acetonitrile adjusted to pH 6.0-6.2 with acetic acid
 Flow Rate: 0 min — 1mL/min
 15 min — 2mL/min, hold 10 min
 Det.: fluorescence, 240nm excitation, 370nm emission
 Inj.: 10µL of 0.5µg/mL



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Detector responses for MDI and HDI derivatives were linear from 0.05 - 20µg/mL (0.5-200ng on column), while responses for derivatives of both TDI isomers were only linear up to 5µg/mL, using fluorescence detection. However, using UV detection, all compounds were linear in the range 0.5-20µg/mL. Based on a 15-liter air volume, the detection limit standard for fluorescence detection is approximately 1/4 of the 20µg/m³ action level established by OSHA. Recovery values (Table 1) for the isocyanate derivatives, determined using fluorescence detection, were satisfactory for reliable monitoring of isocyanates below the OSHA action levels.

Blank coated filters stored in a sealed jar at 4°C for 6 months showed no signs of degradation or contamination. Spiked filters stored under the same conditions for 6 months yielded recoveries within the range of freshly prepared spiked filters.

ORBO-80 reagent coated glass fiber filters offer ease of use, reproducibility, and long-term stability for reliable assessment of isocyanates in air, at concentrations below action levels specified by OSHA methods.

References

- 1992-1993 *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio.
- Validated Organic Methods, Occupational Safety & Health Administration, Salt Lake Technical Center, Salt Lake City, Utah.
- 1992 Pittsburgh Conference poster, Commercialization of Coated Filters for Airborne Diisocyanate Collection.

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Table 1. Recovery of Isocyanate Derivatives from Spiked Filters

Isocyanate	Deriv. Spiked onto Filter (µg)	Avg.	Std. Dev.	%CV
1,6-Hexamethylene diisocyanate (HDI)	20	95.2	3.4	3.6
	2.0	72.8	9.6	13.1
	0.20	78.3	15.5	19.7
Methylene bisphenyl isocyanate (MDI)	20	89.8	4.2	4.7
	2.0	75.5	8.3	10.9
	0.20	78.3	2.4	3.0
Toluene-2,4-diisocyanate (2,4-TDI)	20	88.0	2.7	3.0
	2.0	70.0	8.9	12.7
	0.20	80.0	4.1	5.1
Toluene-2,6-diisocyanate (2,6-TDI)	20	99.7	6.2	6.2
	2.0	74.0	9.9	13.4
	0.20	65.0	7.1	10.9

n=3

Ordering Information:

ORBO-80 Glass Fiber Filters pkg. of 25	20811
3-Piece Filter Cassette, pkg. of 100 37mm, w/ spacer ring (unassembled)	23370
Support Pads 37mm, pkg. of 100	23385
Sealing Bands for 37mm cassettes pkg. of 100	23366
ORBO-80 Kit contains 25 each of coated filters, support pads, sealing bands, and cassettes (unassembled)	20812-U
SUPELCOSIL LC-CN HPLC Column 25cm x 4.6mm ID, 5µm particles	58231
Isocyanate Derivative Standards	
1-(2-Pyridyl)piperazine derivatives. Each solution consists of 1000µg/mL in 1mL dimethyl sulfoxide.	
2,6-TDI Derivative 2,6-bis(4-(2-Pyridyl)-1-piperazinylcarbonyl) toluene	48144
2,4-TDI Derivative 2,4-bis(4-(2-Pyridyl)-1-piperazinylcarbonyl) toluene	48145
1,6-HDI Derivative 1,6-bis(4-(2-Pyridyl)-1-piperazinylcarbonyl) hexane	48146
4,4'-MDI Derivative 4,4'-bis(4-(2-Pyridyl)-1-piperazinylcarbonyl) diphenyl methane	48147

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