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 cyan reversed phase HPLC column and either UV or fluorescence detection. A SUPELCOSIL™ LC-CN cyan 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 0.5 µg/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

Table 1. Recovery of Isocyanate Derivatives from Spiked Filters

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

n=3

Ordering Information:

ORBO-80 Glass Fiber Filters
pkg. of 25
3-Piece Filter Cassette, pkg. of 100
37mm, w/ spacer ring (unassembled)
Support Pads
37mm, pkg. of 100
Sealing Bands for 37mm cassettes
pkg. of 100
ORBO-80 Kit
contains 25 each of coated filters, support pads, sealing bands, and cassettes (unassembled)
58231

Contact our Technical Service Department (phone 800-359-3041 or 814-359-3041, FAX 814-359-5468) for expert answers to your questions.

Detector responses for MDI and HDI derivatives were linear from 0.05 to 20 µg/mL (0.5-2000 ng on column), while responses for derivatives of both TDI isomers were only linear up to 5 µg/mL, using fluorescence detection. However, using UV detection, all compounds were linear in the range 0.5-20 µg/mL. Based on a 15-litter air volume, the detection limit standard for fluorescence detection is approximately 1/4 of the 20 µg/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 level standards specified by OSHA methods.

References
1. 1992-1993 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio.
2. Validated Organic Methods, Occupational Safety & Health Administration, Salt Lake Technical Center, Salt Lake City, Utah.

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Note 31

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