Dry Sampling of Gas-Phase Isocyanates and Isocyanate Aerosols from Thermal Degradation of Polyurethane

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ABSTRACT

The performance of a dry sampler, with an impregnated denuder in series with a glass fibre filter, using di-\textit{n}-butylamine (DBA) for airborne isocyanates (200 ml min\textsuperscript{-1}) is investigated and compared with an impinger flask with a glass fibre filter in series (1 l min\textsuperscript{-1}). An exposure chamber containing 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and 2,4- and 2,6-toluene diisocyanate (TDI) in the concentration range of 5–205 μg m\textsuperscript{-3} [0.7–33 p.p.b.; relative humidity (RH) 50%], generated by gas- and liquid-phase permeation, was used for the investigation. The precision for the dry sampling for five series with eight samplers were in the range of 2.0–6.1% with an average of 3.8%. During 120-min sampling (\textit{n} = 4), no breakthrough was observed when analysing samplers in series. Sixty-four exposed samplers were analysed after storage for 0, 7, 14, and 21 days. No breakdown of isocyanate derivatives was observed. Twenty-eight samplers in groups of eight were collecting isocyanates during 0.5–32 h. Virtually linear relationships were obtained with regard to sampling time and collected isocyanates with correlation coefficients in the range of 0.998–0.999 with the intercept close to the origin. Pre- or post-exposure to ambient air did not affect the result.

Dry sampling (\textit{n} = 48) with impinger-filter sampling (\textit{n} = 48) of thermal decomposition product of polyurethane polymers, at RH 20, 40, 60, and 90%, was compared for 11 isocyanate compounds. The ratio between the different isocyanates collected with dry samplers and impinger-filter samplers was in the range of 0.80–1.14 for RH = 20%, 0.8–1.25 for RH = 40%, 0.76–1.4 for RH = 60%, and 0.72–3.7 for RH = 90%. Taking into account experimental errors, it seems clear that isocyanic acid DBA derivatives are found at higher levels in the dry samples compared with impinger-filter samplers at elevated humidity. The dry sampling using DBA as the reagent enables easy and robust sampling without the need of field extraction.

KEYWORDS: airborne isocyanates; dibutylamine derivatives; dry sampling; liquid chromatography–mass spectrometry; thermal decomposition
INTRODUCTION

Isocyanates are found in both gas and as a solid of liquid particles suspended in air. Isocyanates are highly reactive, and during sampling it is necessary to derivatize the isocyanate groups to avoid losses. One commonly used sampler for sampling of isocyanates is an impinger flask, followed by a filter for collection of particles that pass through the impinger flask (Henriks-Eckerman et al., 2000; Karlsson et al., 2000; White, 2006). The advantages of impinger flasks are that high reagent concentrations can be used and particles containing isocyanates are mixed with reagent during sampling, which gives an efficient derivatization. However, there are also several disadvantages using impinger sampling. For exposure measurements, it is often desirable that the sampler is attached on the worker. Impinger flasks are made of glass, usually contain a volatile and flammable solvent and are often not convenient to wear during work operations. In addition, the sampling time for an impinger can be limited, due to evaporation of the volatile solvent.

The alternatives to impinger flasks are dry samplers, e.g. impregnated filters. Several suggestions of air sampling of isocyanates using filters have been presented (Andersson et al., 1983; Purnell and Walker, 1985; Huynh et al., 1992; Lesage et al., 1992; Bello et al., 2002), but filters have several disadvantages compared with impinger flasks for isocyanate sampling. The absence of solvent on an impregnated filter makes the collection more affected by interferences and there is a risk of reagent depletion on the filters if the particle load is high. This may result in losses of isocyanates during sampling and underestimation of air concentrations (Hardy, 1984; Myer et al., 1993; Rudzinski et al., 1995; Maître et al., 1996; Sennbro et al., 2004; Mattsson et al., 2008).

A dry sampler for isocyanates has been presented, using di-n-butyl amine (DBA) as derivatization reagent (Marand et al., 2005).

DBA is a volatile compound, so dry samplers cannot be impregnated with DBA alone. Instead, DBA is mixed with acetic acid, forming an ion-pair to reduce the volatility. By this procedure, the volatility of the reagent is reduced, and it is possible to use as reagent in dry samplers. The air enters the sampler through a denuder tube, which collects gaseous isocyanates. After the denuder, an impregnated filter is connected to collect particles. Since a high concentration of a volatile reagent is used in the denuder, the filter is continuously flushed with DBA during sampling. Particles are collected on the filter, but the transport of reagent from the denuder minimizes the risk of reagent depletion. The same derivatization technique, impregnation with DBA and acetic acid, has also been used in a denuder-cascade impactor sampler. The sampler enabled size-separated sampling and analysis of isocyanates (Dahlin et al., 2008a,b).

The gas-phase diffusion efficiency for a cylindrical denuder has earlier been described by Zulfiqur et al. (1989). The diffusion efficiency for isocyanate in gas phase is first of all dependent of a stable and laminar gas flow and the viscosity and temperature are distributed homogeneously in the gas flow. A flow subduction zone can be applied prior to the filters to achieve a laminar flow (Zulfiqur et al., 1989). Another important factor is the isocyanates diffusion coefficient. To enhance the diffusion efficiency for analytes in gas phase, the sample flow rate should be decreased and the length of the cylindrical denuder tube should be increased. A denuder tube can only be increased to a certain length otherwise there will be loss of particles at the denuder walls. The particle penetration has shown to be unaffected by the diameter of cylindrical tubes for a given volumetric flow, which is opposite to the diffusion efficiency for analytes in gas phase (Zulfiqur et al., 1989; Hinds, 1999).

The aim of the present study is to investigate the robustness of the dry DBA sampler with regard to precision, storage, exposure of sampler to ambient air, influence from air humidity, and passive sampling, and how different sampling times and flow rates affect the sampling efficiency.

The sampling of thermal decomposition products is one of the most challenging tasks for isocyanate sampling and results from dry sampling and impinger-filter sampling were investigated.

EXPERIMENTAL

Chemicals

For a complete list of used chemicals see Appendix 1.

Instrumentation

For determining isocyanate-DBA derivatives in air samples, a liquid chromatography-tandem mass spectrometry (LC-MS/MS) system was used. For direct
reading measurements of isocyanates in the exposure chamber, a proton transfer reaction-mass spectrometer (PTR-MS) was used. For detailed information, see Appendix 2.

Isocyanate generation

Liquid membrane permeation

An isocyanate atmosphere containing 1,6-hexamethylene diisocyanate (HDI), isomers of isophorone diisocyanate (IPDI), and 2,4- and 2,6-toluene diisocyanate (TDI) was generated by liquid membrane permeation (Tinnerberg et al., 1995). Partially filled permeation tubes of silicon rubber (length 11.5 cm; inner diameter (ID) 8 mm, thickness 2 mm, VWR International AB, Stockholm, Sweden) containing varied volumes of isocyanates were placed inside a permeation chamber with a volume of 0.77 l.

The temperature of the permeation chamber was controlled by placing the permeation chamber in a temperature-controlled water bath (35–40°C). To the permeation chamber, an inlet flow of nitrogen was introduced at a flow rate of 2.5 l min⁻¹. The flow rates were regulated using constant flow regulator Brooks PC 8902 series and SHO-RATE GT1355 flow controller (Brooks automation, Inc., Chelmsford, MA, USA). The generated concentrations were controlled by varying the flow rate through the permeation chamber and varying the temperature of the permeation chamber. The generated gas-phase isocyanates were further diluted in the exposure chamber to constant concentrations, during the tests, in the average range of 5–205 μg m⁻³ (0.7–33 p.p.b.).

Thermal decomposition of polyurethane

Isocyanates were generated by heating different types of polyurethane (PUR) coating and PUR foam simultaneously. The studied PUR samples were placed in a glass tube between two glass wool plugs. Hot air (about 250–350°C) was blown through the tube and the formed decomposition products were introduced into the exposure chamber.

Exposure chamber

An exposure chamber with a total volume of 0.85 m³ was used. The chamber consisted of stainless steel with manipulative gloves. Inside the chamber, an LPKB 125 B mixing fan unit was mounted with flow rate range of 0–90 l s⁻¹ (Östberg Group AB, Avesta, Sweden). The chamber was connected to exhaust ventilation propelled by an EKB HB 4520-220T high-power fan (EKB-produkter AB, Mölletofta, Sweden). The air pressure was kept slightly lower in the chamber compared with the ambient pressure. A conditioning system is used for tempering and humidifying of the influent air. In the first step, the air was heated and humidified. A dosage pump was used to add the correct amount of water.

In the second step, the air was cooled to the desired temperature. Inlet air to the exposure chamber was passed through the air conditioner, in order to control and maintain a constant humidity of 50%.

A Bürkert 8626 mass flow controller with an air flow of 200 l min⁻¹ was used to regulate the influent air (Bürkert, Ingelfingen, Germany). The experiments were performed at 20°C. The relative humidity (RH) was monitored by a Testo 645 (Testo GmbH & Co, Lenzkirch, Germany).

Dry sampler

Sampler description

The sampler consisted of a polypropylene tube (length = 7 cm, ID = 0.8 cm) coupled in series with a 13-mm polypropylene filter holder (Swinnex 13 mm; Millipore, Bedford, MA, USA). To hold the reagent in the polypropylene tube, the inside of the tube is lined with a glass fibre filter (2.5 × 5.7 cm, 0.3 μm binder-free glass fibre filter; Munktell, Grycksbo, Sweden).

In addition to the sampler previously described by Marand et al. (2005), a glass fibre filter strip of the same type (1.4 cm × 5.7 cm) was folded as a ‘V’ and placed inside the tube to increase the denuder surface resulting in enhanced collection efficiency (the V filter divides the denuder into three channels). The total flow rate through the sampler was 0.21 min⁻¹.

Sampler impregnation

The dry sampler was then impregnated with 1.5 ml of impregnation solution B, by dropwise adding the solution to the filters at the top of the tube. After impregnation, the tube was dried by blowing nitrogen through the tube.

The end filter (diameter 13 mm) was impregnated with 100 μl of impregnation solution A. The impregnated end filters were stored in a nitrogen atmosphere.
in open cassettes and when the evaporation of the solvent was complete, the end filters were mounted to the denuder tubes. The complete sampler was then sealed at both ends.

Impregnation and drying of the filters were performed in a container filled with nitrogen to avoid contamination. The samplers were stored in a refrigerator prior to air sampling.

**Work-up**

After air sampling, the filters were carefully removed from the denuder and filter cassette using tweezers. The filters were folded and placed in test tubes with screw caps. To the test tubes, 3 ml of $1 \times 10^{-3}$ mol l$^{-1}$ H$_2$SO$_4$, 3 ml of methanol, 5.5 ml of toluene (that is used to rinse the empty denuder tube), and 100 μl of internal standard solution (see Appendix 3) are added.

The test tubes were then shaken for 5 min, sonicated for 10 min in an ultrasonic bath, and again shaken for 20 min to extract the isocyanate-DBA derivatives to the organic phase. After centrifugation for 10 min at 3000 r.p.m., the toluene solution was separated and transferred to a new test tube. To the tubes containing the filter and remaining mixture of methanol and acid, another aliquot of 5.5 ml of toluene was added, and the extraction procedure was repeated. The toluene was separated and transferred to the test tube containing toluene from the first extraction, giving a toluene solution with a total volume of ~11 ml. The toluene solution was then evaporated to dryness using a vacuum centrifuge (model SC210A; Savant Instruments Inc., Holbrook, NY, USA). To the dry residue, 0.5 ml of acetonitrile was added and the DBA derivatives were dissolved during sonication and then manually shaken. A volume of 0.1 ml of acetonitrile solution was transferred to a vial for LC-MS/MS analysis. Calibration standards (0.02–0.7 μg isocyanate) were prepared by adding different volumes of isocyanate-DBA standard stock solutions to test tubes containing 10 ml of 0.01 mol l$^{-1}$ DBA in toluene, followed by addition of 50 μl of the internal standard solution. The calibration standards were evaporated and dissolved in acetonitrile in the same way as the air samples.

**Impinger-filter sampler**

**Description**

An impinger-filter sampling system was used as a reference sampling method for the thermal decomposition studies (Karlsson et al., 2000, 2005). The midget impinger flasks (30 ml, Werner-Glas & Instruments AB, Stockholm, Sweden) contained 10 ml of 0.01 mol l$^{-1}$ DBA in toluene and a 13-mm glass fibre filter with a pore size of 0.3 μm (Munktell, Grycksbo, Sweden) in a polypropylene filter holder (Swinnex 13 mm, Millipore, Bedford, MA, USA) was connected in series after the impinger flask. The total flow rate through the sampler was 1.0 l min$^{-1}$.

**Work-up**

After sampling, the impinger solution and the glass fibre filter were transferred to a test tube. The test tubes were then sonicated for 10 min in an ultrasonic bath, and manually shaken and then centrifuged for 10 min at 3000 r.p.m. The solution was then transferred to new test tubes. To the new test tubes, a volume of 50 μl of internal standard solution (see Appendix 3) was added. The sample was evaporated to dryness using a vacuum centrifuge (model SC210A; Savant Instruments Inc., Holbrook, NY, USA). To the dry residue, 0.5 ml of acetonitrile was added and the DBA derivatives were dissolved during sonication and then manually shaken. A volume of 0.1 ml of acetonitrile solution was transferred to a vial for LC-MS/MS analysis. Calibration standards (0.02–0.7 μg isocyanate) were prepared by adding different volumes of isocyanate-DBA standard stock solutions to test tubes containing 10 ml of 0.01 mol l$^{-1}$ DBA in toluene, followed by addition of 50 μl of the internal standard stock solution. The calibration standards were evaporated and dissolved in acetonitrile in the same way as the air samples.

**Air sampling**

For the dry sampler tests, air sampling was performed utilizing novel air sampling pumps (Pump prototype, IFKAN, Hassleholm, Sweden) at flow rates in the range of 25–800 ml min$^{-1}$. Eight different pumps were simultaneously used for the experiments in the dry sampler tests. The flow rates of the pumps were designed to be ±2%. The air flow rate was checked before and after sampling using a TSI 4140 flow meter (TSI Inc., USA).

**Precision of the dry sampler**

The precision of the dry sampler was tested for eight dry samplers connected in parallel to the
exposure chamber using all glass connections. All samplers collected air volumes of the standard gas-phase atmospheres, at 50% RH, containing HDI, IPDI, and TDI during a sampling time of 30 min. A total of five tests were performed resulting in 40 air samples.

**Breakthrough of the dry sampler**

The potential of breakthrough of isocyanates from a standard atmosphere, at 50% RH, containing gas-phase HDI, IPDI, and TDI was tested. Air samples were collected from the exposure chamber with two samplers in series. Sampling for 30, 60, and 120 min was studied. Four sets of two dry samplers in series were connected in parallel using all glass connections. A total of three tests were performed resulting in 12 air samples of the first samplers in the series and 12 of the last in the series.

**Sampler efficiency**

Sampling, during five different flow rates (100–500 mL min⁻¹) for 30 min, in a standard atmosphere, at 50% RH, containing gas-phase HDI, IPDI, and TDI was investigated. Two sampler trains, each consisting of two dry samplers in series, were connected in parallel to the exposure chamber using all glass connections. Sampling was performed during 30 min. During work-up, the denuder filters and the end filter were analysed separately. The tests were repeated for flow rates of 100, 200, 300, 400, and 500 mL min⁻¹. A total of five tests were performed resulting in 10 air samples of the first samplers in the series and 10 of the last in the series.

**Storage of exposed samplers**

The stability of samplers exposed during 30 min to isocyanates from a standard atmosphere, at 50% RH, containing gas-phase HDI, IPDI, and TDI was tested. Eight dry samplers were connected in parallel to the exposure chamber using all glass connections. Sampling was performed for eight series of eight samplers each. From each of the series, two samplers were immediately worked up after sampling. Two samplers were worked up 7 days after sampling, two after 14 days after sampling, and two after 21 days after sampling. The samplers were stored in darkness in a refrigerator (+4°C) until work-up. The storage time tests generated 64 samples.

**Variation of sampling time**

Sampling with a sampling flow rate of 200 mL min⁻¹, during seven different sampling times (0.5–32 h), in a standard atmosphere, at 50% RH, containing gas-phase HDI, IPDI, and TDI was investigated. The concentrations of the different isocyanates were continuously monitored using the direct reading PTR-MS instrument. For each sampling time, four parallel samples were collected using all glass connections to the exposure chamber. The seven sampling time tests generated 28 samples.

**Variation of sampling flow**

Sampling, during four different sampling flows (200–800 mL min⁻¹), in a standard atmosphere, at 50% RH, containing gas-phase HDI, IPDI, and TDI was investigated. For each sampling flow, four parallel samples were collected using all glass connections to the exposure chamber, resulting in a total of 16 samples.

**Passive sampling**

The influence of passive diffusion sampling during active sampling was investigated by performing duplicate sampling of gas-phase HDI, IPDI, and TDI at 50% RH at different sampling flow rates (25, 50, 100, 150, and 200 mL min⁻¹) during a sampling period of 2 h (n = 10). The influence of passive diffusion sampling was also investigated during different exposure times (15, 30, 60, 90, and 120 min) without any mechanical air flow through the samplers (n = 20). Both tests were simultaneously performed inside an exposure chamber. The two passive sampling tests generated a total of 30 samples.

**Robustness of dry sampler**

Eight dry samplers were connected in parallel to the exposure chamber using all glass connections. All samplers were exposed to gas-phase HDI, IPDI, and TDI during a 30-min sampling time at a relative humidity of 50%. Two sample series and four samplers in each series were prior or after exposure exposed during 4 or 20 h to ambient air (sampling of clean air at 0.2 L min⁻¹ with no gas-phase isocyanates). The remaining four samplers in each exposure series were immediately worked-up and used as reference samples. A total of eight series were collected resulting in 64 samples.
Comparison of dry sampler with reference method

The dry sampler was tested for sampling of thermal degradation products from polyurethane polymers, at different relative humidity. The impinger-filter method was used as reference method. For comparison with the impinger-filter sampler, four dry samplers were used alongside with four impinger-filter samplers connected using all glass connections to the exposure chamber. For each test, the total sampling time was 15 min. In each test ~30 mg of a HDI/IPDI-based coating, 50 mg soft TDI-based foam, and 20 mg rigid MDI-based foam was used for isocyanate generation. Three tests were run at each level of the RH (20, 40, 60, and 90%). A total of 48 dry samplers and 48 impinger-filter samplers were compared.

The same sampling set-up was used to compare the dry sampler with the reference sampler when monitoring gas-phase HDI, TDI, and IPDI concentrations inside the exposure chamber. All samplers collected air volumes of the standard gas-phase atmosphere, generated by liquid membrane permeation, at 50% RH.

For each test, the total sampling time was 15 min. Three sampling series were performed (four dry samplers and four impinger samplers in each series), resulting in a total of 12 dry samplers and 12 impinger-filter samplers.

RESULTS

Generation of isocyanates

During generation of isocyanates by liquid membrane permeation, stable air concentrations (RH 50%) were obtained in the test chamber. The generated average concentrations for precision, robustness, breakthrough, storage, and sampling time studies were in the range of 52–205 µg m⁻³ for HDI, 11–118 µg m⁻³ for IPDI, and 5–154 µg m⁻³ for TDI. From PTR-MS data, the generated concentration varied <5% relative standard deviation (RSD) during a 24-h period and <2% RSD during a 6-h period.

Dry sampler—precision

The overall precision for collection of gas-phase HDI, IPDI, and TDI at 50% RH was investigated in five series of eight samplers during the studies with a 6-h sampling period. The sample time was 30 min for eight parallel samplers. The generated average concentrations for precision were 77 µg m⁻³ for HDI, 43 µg m⁻³ for IPDI, 20 µg m⁻³ for IPDI, 109 µg m⁻³ for 2,4-TDI, and 28 µg m⁻³ for 2,6-TDI. The RSDs for the air concentrations were in the range of 0.9–1.8%.

The precision for the isocyanate sampling for all the five series were in the range of 2.0–5.7% with an average of 3.6% (Table 1).

Breakthrough

The breakthrough was studied for 12 dry sampler pairs. The two samplers in each pair were connected in series. Four sampler pairs were in parallel exposed in three tests. The generated average concentrations were 125 µg m⁻³ for HDI, 83 µg m⁻³ for IPDI, 34 µg m⁻³ for IPDI, 154 µg m⁻³ for 2,4-TDI, and 37 µg m⁻³ for 2,6-TDI. No breakthrough was observed for any of the five isocyanates during sampling time (30, 60, and 120 min). Under the experimental conditions, the collection efficiencies for the dry sampler were for all the studied isocyanates >99.9% as calculated from the isocyanates collected in the first sampler and the detection limit under the experimental conditions.

Sampler efficiency

The sampler efficiency was studied using parallel sampling with two dry samplers in series. A total of 10 samplers in series were in parallel exposed over five tests. The generated concentrations were in the range of 148–173 µg m⁻³ for HDI, 22–27 µg m⁻³ for IPDI, 11–14 µg m⁻³ for IPDI, 31–59 µg m⁻³ for 2,4-TDI, and 13–20 µg m⁻³ for 2,6-TDI. The denuder collection efficiency was theoretically estimated. The dry sampler denuder efficiency has been calculated from the Gormley–Kennedy equation (Zulfiqur et al., 1989) and an altered cylindrical denuder efficiency formula from Dasgupta et al. (1997). All theoretical estimation was performed using the diffusion coefficients from Nordqvist (2004).

The ratio between experimentally determined denuder efficiency and the theoretically estimated denuder efficiency at the different flow rate for all five isocyanates was in the range of 96–100% for 100 ml min⁻¹, 86–91% for 200 ml min⁻¹, 80–86% for 300 ml min⁻¹, 81–89% for 400 ml min⁻¹, and 69–83% for 500 ml min⁻¹. The experimentally determined denuder collection efficiency is displayed in Table 2.

The increased sampling efficiency using the V-filter present in the denuder was studied by comparing the
Dry sampling of gas-phase isocyanates and isocyanate aerosols  

experimentally determined denuder efficiency for the dry sampler with the theoretical estimated denuder efficiency for a denuder without a V-filter. The increase in sampling efficiency was theoretically estimated to be 5–9% for 100 ml min$^{-1}$, 17–24% for 200 ml min$^{-1}$, 27–31% for 300 ml min$^{-1}$, 33–51% for 400 ml min$^{-1}$, and 21–51% for 500 ml min$^{-1}$.

Performing sampling with two samplers in series, no breakthrough onto backup dry sampler was observed for any of the five gas-phase isocyanates during any of tested flow rates (100, 200, 300, 400, and 500 ml min$^{-1}$). This indicates 100% collection efficiency using both denuder and the 13-mm end filter.

Storage of exposed dry samplers
During a period of 6 h, 64 dry samplers were exposed for 30 min in groups of eight. The generated average concentrations were 67 µg m$^{-3}$ for HDI, 48 µg m$^{-3}$ for IPDI$_1$, 24 µg m$^{-3}$ for IPDI$_2$, 72 µg m$^{-3}$ for 2,4-TDI, and 27 µg m$^{-3}$ for 2,6-TDI. The RSDs for the air concentrations were in the range of 4.1–8.8%. When storing the dry samplers for 1, 7, 14, and 21 days in a refrigerator, the ratio was calculated between stored samples and samples that were immediately worked up (day 1) (see Table 3).

The flow rates were in the range of 194–216 ml min$^{-1}$ and the RSD of the flow rates was <0.7% (average RSD 0.45%) for all eight series with eight pumps.

Within the experimental errors, the samplers were stable during storage up to 21 days and no trend in breakdown of the isocyanate derivatives was observed.

Sampling time
Different sampling times were investigated for collection of gas-phase HDI, IPDI, and TDI at 50% humidity in seven series of four samplers each during 3-day studies within 30 min to 32 h sampling periods. The generated mean concentrations, measured with the dry samplers, for the seven different sampling times

<table>
<thead>
<tr>
<th>Series</th>
<th>Average (µg m$^{-3}$); RSD (%)</th>
<th>HDI</th>
<th>IPDI$_1$</th>
<th>IPDI$_2$</th>
<th>2,4-TDI</th>
<th>2,6-TDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>77.3; 2.0</td>
<td>44.1; 2.9</td>
<td>20.1; 2.2</td>
<td>109.0; 3.3</td>
<td>28.3; 2.7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>77.4; 4.2</td>
<td>43.7; 4.7</td>
<td>19.9; 3.9</td>
<td>108.9; 3.5</td>
<td>28.0; 3.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>76.3; 3.8</td>
<td>43.1; 3.1</td>
<td>19.8; 3.0</td>
<td>106.7; 2.8</td>
<td>27.5; 4.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>77.2; 4.1</td>
<td>43.1; 5.2</td>
<td>19.8; 4.3</td>
<td>108.2; 5.0</td>
<td>27.7; 5.7</td>
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<tr>
<td>5</td>
<td>78.0; 3.0</td>
<td>42.9; 2.9</td>
<td>19.8; 3.5</td>
<td>110.6; 3.4</td>
<td>28.2; 4.3</td>
<td></td>
</tr>
<tr>
<td>Average RSD (%)</td>
<td>3.4</td>
<td>3.7</td>
<td>3.4</td>
<td>3.6</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Precision of samplers. Five series of samplers were exposed to gas-phase HDI, IPDI, and TDI during a 30-min sampling time at 50% RH in series of eight ($n = 40$)

<table>
<thead>
<tr>
<th>Collection efficiency of gas phase (%)</th>
<th>100 ml min$^{-1}$</th>
<th>200 ml min$^{-1}$</th>
<th>300 ml min$^{-1}$</th>
<th>400 ml min$^{-1}$</th>
<th>500 ml min$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>HDI</td>
<td>97.3</td>
<td>88.6</td>
<td>80.6</td>
<td>73.4</td>
<td>59.8</td>
</tr>
<tr>
<td>IPDI$_1$</td>
<td>95.6</td>
<td>83.7</td>
<td>73.8</td>
<td>75.0</td>
<td>63.5</td>
</tr>
<tr>
<td>IPDI$_2$</td>
<td>97.1</td>
<td>86.3</td>
<td>76.0</td>
<td>76.0</td>
<td>67.7</td>
</tr>
<tr>
<td>2,4-TDI</td>
<td>97.7</td>
<td>89.0</td>
<td>81.7</td>
<td>80.7</td>
<td>72.1</td>
</tr>
<tr>
<td>2,6-TDI</td>
<td>99.7</td>
<td>89.6</td>
<td>81.9</td>
<td>77.8</td>
<td>69.5</td>
</tr>
</tbody>
</table>

Table 2. Experimentally determined denuder collection efficiency of gas-phase HDI, IPDI, and TDI

Storage of exposed dry samplers
During a period of 6 h, 64 dry samplers were exposed for 30 min in groups of eight. The generated average concentrations were 67 µg m$^{-3}$ for HDI, 48 µg m$^{-3}$ for IPDI$_1$, 24 µg m$^{-3}$ for IPDI$_2$, 72 µg m$^{-3}$ for 2,4-TDI, and 27 µg m$^{-3}$ for 2,6-TDI.
were 205 µg m$^{-3}$ for HDI, 115 µg m$^{-3}$ for IPDI$_1$, 49 µg m$^{-3}$ for IPDI$_2$, 137 µg m$^{-3}$ for 2,4-TDI, and 32 µg m$^{-3}$ for 2,6-TDI. The RSD for the air concentrations was in the range of 8–14% for the five different isocyanates. The air concentrations in the exposure chamber, monitored by the PTR-MS, varied in the range of 8–15% during the experiments.

From the LC-MS data, the amount of the individual isocyanates in each of the samplers per sample volume was calculated. To present the relationship between the different sampling times and the sampler data, the sampler data needed to be adjusted with a correction factor for the variation in the air concentration. The correction factors (A) were calculated as follows: the average air concentration (PTR-MS) during the sampling period/the average air concentration (PTR-MS) during the 32-h experiments (equation 1).

$$\frac{C_{\text{Dry sampler}}}{A} = \text{Corrected air concentration for the dry sampler} \quad (1)$$

The amount of isocyanates was plotted against the duration of the sampling in the chamber (Fig. 1).

**Variation of sampling flow**

Different sampling flows (200–800 ml min$^{-1}$) were investigated for collection of gas-phase HDI, IPDI, and TDI at 50% humidity in four series of four samplers during a sampling period of 30 min. The generated concentrations, measured with the dry samplers, for the four different sampling flows were in the range of 73–82 µg m$^{-3}$ for HDI, 45–56 µg m$^{-3}$ for IPDI$_1$, 20–21 µg m$^{-3}$ for IPDI$_2$, 19–27 µg m$^{-3}$ for 2,4-TDI, and 4–6 µg m$^{-3}$ for 2,6-TDI (Table 4).

**Passive sampling**

The influence of diffusion flux during active sampling was investigated by performing duplicate sampling inside the exposure chamber at different sampling flow rates (25, 50, 100, 150, and 200 ml min$^{-1}$) of gas-phase HDI, IPDI, and TDI at 50% RH. The test was performed with a sampling period of 2 h. The generated mean concentrations, measured with the dry samplers, for the five different sampling flow rates were 100 µg m$^{-3}$ for HDI, 73 µg m$^{-3}$ for IPDI$_1$, 34 µg m$^{-3}$ for IPDI$_2$, 47 µg m$^{-3}$ for 2,4-TDI, and 11 µg m$^{-3}$ for 2,6-TDI (Fig. 2).

The influence of passive diffusion sampling investigated during different exposure periods (15–120 min) of passive diffusion for gas-phase HDI, IPDI, and TDI at 50% RH. The samplers were exposed without any active air flow rate in one series of four samplers per exposure period inside the exposure chamber. The generated mean concentrations, measured with the dry samplers inside the chamber (n = 2) with a sampling flow rate of 200 ml min$^{-1}$, for the five different sampling times were 73 µg m$^{-3}$ for HDI, 52 µg m$^{-3}$ for IPDI$_1$, 22 µg m$^{-3}$ for IPDI$_2$, 26 µg m$^{-3}$ for 2,4-TDI, and 6 µg m$^{-3}$ for 2,6-TDI. The RSD for the measured air concentrations was in the range of 5–11% for the five different isocyanates.

The passive diffusion for isocyanates during different exposure times (15–120 min) without any active
Dry sampling of gas-phase isocyanates and isocyanate aerosols

Air flow showed a passive diffusion sampling flow rate in the range of 29–45 ml min\(^{-1}\) with RSD in the range of 15–19% (\(n = 4\)) for the five different isocyanates (Fig. 3).

**Robustness**

Samplers were investigated with regard to pre-exposure to ambient air before sampling and post-exposure to ambient air after sampling (Tables 5 and 6).

The pre- and post-ambient air exposed samplers were compared with samplers that had only been exposed to air during sampling. The study proceeded during 2 days. Samplers were pre- and post-exposed to ambient air and the overall precision for collection of gas-phase HDI, IPDI, and TDI at 50% humidity was investigated in eight series with eight parallel samplers in each of the series. The air sampling times were 30 min for all of the samplers. Out of the eight samplers per series, four

---

Table 4. Average air concentrations of sampled isocyanates during sampling flow rate (200–800 ml min\(^{-1}\))

<table>
<thead>
<tr>
<th>Sampling flow rate (ml min(^{-1}))</th>
<th>Average µg m(^{-3}); RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,6-HDI</td>
</tr>
<tr>
<td>200</td>
<td>81.6; 6.7</td>
</tr>
<tr>
<td>400</td>
<td>72.9; 1.7</td>
</tr>
<tr>
<td>600</td>
<td>75.6; 8.5</td>
</tr>
<tr>
<td>800</td>
<td>75.1; 5.6</td>
</tr>
<tr>
<td>Average RSD (%)</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Four air samples were collected for each sampling flow rate from the exposure chamber containing a standard atmosphere.
Dry sampling of gas-phase isocyanates and isocyanate aerosols

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samplers were pre-exposed or post-exposed to ambient air during 4 or 20 h with a sample flow of 200 ml per min. The other four samplers in each series were reference samples that were not pre- or post-exposed to ambient air.

For samplers that were 4 h before or 4 h after exposed to ambient air, 30-min sampling was performed in air concentrations of 60 µg m⁻³ for HDI, 34 µg m⁻³ for IPDI₁, 16 µg m⁻³ for IPDI₂, 83 µg m⁻³ for 2,4-TDI, and 22 µg m⁻³ for 2,6-TDI. The RSDs for the air concentrations

2 The average (n = 2) air concentrations of isocyanates in the exposure chamber containing a standard atmosphere of HDI (●), IPDI₁ (■), IPDI₂ (▲), 2,4-TDI (×), and 2,6-TDI (○) determined by the dry sampler during different flow rates (25–200 ml min⁻¹). Duplicate sampling was performed for each flow rate with a sampling time of 2 h.

3 Passive sampling of isocyanates in the exposure chamber containing a standard atmosphere of HDI (●), IPDI₁ (■), IPDI₂ (▲), 2,4-TDI (×), and 2,6-TDI (○) using dry samplers during different exposure times (15–120 min).
Table 5. Stability of samplers—4 h pre- or post-exposed to ambient air. All samplers were exposed to gas-phase HDI, IPDI, and TDI during a 30-min sampling time at 50% RH (n = 32)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Average isocyanate concentration; RSD</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>4 h pre-exposed</td>
<td></td>
</tr>
<tr>
<td>HDI</td>
<td>1</td>
<td>41.7; 4.0</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>40.4; 6.6</td>
<td>1.11*</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>32.9; 5.7</td>
<td>0.97</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>33.0; 4.7</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>4 h post-exposed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HDI</td>
<td>1</td>
<td>34.0; 8.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
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<td></td>
<td>Reference</td>
<td>42.8; 3.6</td>
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<td></td>
<td>Reference</td>
<td>36.3; 3.0</td>
<td></td>
</tr>
<tr>
<td>IPDI₁</td>
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<td>22.5; 4.9</td>
<td>0.95</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>21.3; 8.9</td>
<td>1.06</td>
</tr>
<tr>
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<td>4 h post-exposed</td>
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<td></td>
</tr>
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<td>17.6; 4.4</td>
<td>1.00</td>
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<tr>
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<td></td>
<td>18.0; 4.0</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>20.1; 2.8</td>
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</tr>
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<td>1.01</td>
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<td>38.1; 3.2</td>
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<td></td>
<td>4 h post-exposed</td>
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<td></td>
</tr>
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<td>1.02</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>33.9; 2.5</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>37.7; 2.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>36.0; 2.1</td>
<td></td>
</tr>
<tr>
<td>2,4-TDI</td>
<td>1</td>
<td>64.4; 2.8</td>
<td>0.99</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>64.4; 6.6</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>4 h post-exposed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4-TDI</td>
<td>1</td>
<td>53.7; 5.2</td>
<td>0.96</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>54.1; 4.4</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>67.3; 1.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>57.7; 5.8</td>
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Table 5. Continued

<table>
<thead>
<tr>
<th>Series</th>
<th>Average isocyanate concentration; RSD</th>
<th>Ratio</th>
</tr>
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<tbody>
<tr>
<td>2,6-TDI</td>
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<td>12.3; 5.5</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>12.7; 2.1</td>
</tr>
<tr>
<td>2</td>
<td>4 h pre-exposed</td>
<td>11.9; 6.9</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>10.3; 2.8</td>
</tr>
<tr>
<td>1</td>
<td>4 h post-exposed</td>
<td>8.8; 7.5</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>9.9; 8.3</td>
</tr>
<tr>
<td>2</td>
<td>4 h post-exposed</td>
<td>9.3; 5.0</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>9.6; 3.5</td>
</tr>
</tbody>
</table>

*Significant differences between pre-/post-exposed dry samplers and reference dry samplers at the 95% level using Student’s t-test.

Table 6. Stability of samplers—20 h pre- or post-exposed to ambient air. All samplers were exposed to gas-phase HDI, IPDI, and TDI during a 30-min sampling time at a 50% RH (n = 32). No significant differences could be found in this test set

<table>
<thead>
<tr>
<th>Series</th>
<th>Average isocyanate concentration; RSD</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDI</td>
<td>1 20 h pre-exposed</td>
<td>90.1; 5.5</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>97.0; 5.5</td>
</tr>
<tr>
<td>2</td>
<td>20 h pre-exposed</td>
<td>95.2; 4.2</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>93.8; 3.0</td>
</tr>
<tr>
<td>1</td>
<td>20 h post-exposed</td>
<td>88.3; 2.9</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>94.6; 3.9</td>
</tr>
<tr>
<td>2</td>
<td>20 h post-exposed</td>
<td>88.4; 6.8</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>89.2; 5.7</td>
</tr>
<tr>
<td>IPDI₁</td>
<td>1 20 h pre-exposed</td>
<td>45.7; 5.0</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>48.4; 4.4</td>
</tr>
<tr>
<td>2</td>
<td>20 h pre-exposed</td>
<td>49.1; 1.7</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>48.9; 2.5</td>
</tr>
<tr>
<td>1</td>
<td>20 h post-exposed</td>
<td>46.9; 4.6</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>48.0; 0.8</td>
</tr>
<tr>
<td>2</td>
<td>20 h post-exposed</td>
<td>44.3; 7.1</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>44.6; 3.5</td>
</tr>
</tbody>
</table>
were in the range of 4.3–12% (Table 5). For samplers that were 20 h before or 20 h after exposed to ambient air, 30-min sampling was performed in air concentrations of 94 µg m⁻³ for HDI, 47 µg m⁻³ for IPDI₁, 21 µg m⁻³ for IPDI₂, 126 µg m⁻³ for 2,4-TDI, and 26 µg m⁻³ for 2,6-TDI. The RSDs for the air concentrations were in the range of 2.7–6.2% (Table 6). No significant difference was observed for pre- or post-exposure for up to 20 h (Student’s t-test at the 95% level).

### Table 6. Continued

<table>
<thead>
<tr>
<th>Series</th>
<th>Average isocyanate concentration; RSD</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPDI₂</td>
<td>20 h pre-exposed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>20 h pre-exposed</td>
<td>20.3; 8.1</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>21.3; 5.6</td>
</tr>
<tr>
<td></td>
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<td>21.6; 1.7</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>22.0; 5.2</td>
</tr>
<tr>
<td></td>
<td>20 h post-exposed</td>
<td>20.3; 7.0</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>20.2; 3.0</td>
</tr>
<tr>
<td>1</td>
<td>20 h pre-exposed</td>
<td>124.6; 6.2</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>132.1; 4.0</td>
</tr>
<tr>
<td>2</td>
<td>20 h pre-exposed</td>
<td>130.0; 2.9</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>125.3; 4.1</td>
</tr>
<tr>
<td>1</td>
<td>20 h post-exposed</td>
<td>128.4; 4.5</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>132.7; 1.5</td>
</tr>
<tr>
<td>2</td>
<td>20 h post-exposed</td>
<td>122.4; 4.7</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>122.0; 3.6</td>
</tr>
<tr>
<td>2,4-TDI</td>
<td>20 h pre-exposed</td>
<td>124.6; 6.2</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>132.1; 4.0</td>
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<td></td>
<td>20 h post-exposed</td>
<td>130.0; 2.9</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>125.3; 4.1</td>
</tr>
<tr>
<td>1</td>
<td>20 h post-exposed</td>
<td>128.4; 4.5</td>
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<tr>
<td></td>
<td>Reference</td>
<td>132.7; 1.5</td>
</tr>
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</tr>
<tr>
<td></td>
<td>Reference</td>
<td>122.0; 3.6</td>
</tr>
<tr>
<td>2,6-TDI</td>
<td>20 h pre-exposed</td>
<td>27.0; 5.9</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>26.0; 2.6</td>
</tr>
<tr>
<td></td>
<td>20 h post-exposed</td>
<td>26.5; 3.5</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>26.3; 2.5</td>
</tr>
<tr>
<td>1</td>
<td>20 h post-exposed</td>
<td>26.7; 4.2</td>
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<tr>
<td></td>
<td>Reference</td>
<td>27.7; 3.1</td>
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<tr>
<td>2</td>
<td>20 h post-exposed</td>
<td>25.9; 3.4</td>
</tr>
<tr>
<td></td>
<td>Reference</td>
<td>25.9; 3.2</td>
</tr>
</tbody>
</table>

Comparison between impinger-filter sampling and dry sampling

During generation of isocyanates by thermal decomposition, air concentrations were obtained in the test chamber during a short period, about 15 min. Comparison between the impinger-filter sampler and the dry sampler at different air humidity resulted in concentration ratios (dry sampler/impinger-filter sampler) of 0.80–1.14 for RH = 20%, 0.80–1.25 for
RH = 40%, 0.76–1.40 for RH = 60%, and 0.72–3.7 for RH = 90% (Table 7). Considerable significant differences were observed for ICA and TDI (Student’s t-test at the 95% level). ICA was found at higher levels in the dry sampler, especially at 90% RH. TDI was found at about 20% higher levels in the impinger flask.

Comparison between the impinger-filter sampler and the dry sampler at 50% air humidity, during generation of gas-phase HDI, TDI, and IPDI, using liquid membrane permeation resulted in concentrations ratios (dry sampler/impinger-filter sampler) of 1.03–1.44 (Table 8). Considerable significant differences between the different methods were observed for both the isomers of IPDI (Student’s t-test at the 95% level). IPDI was found at about 40% higher levels in the dry sampler.

**DISCUSSION**

When comparing sampling of isocyanates in gas phase, without the presence of thermal decomposition products, using the dry sampler and impinger-filter sampler, there was, with the exception for IPDI, a good agreement between the results. The relatively higher sampling recovery for IPDI in the dry sampler is most likely due to adsorption in the glass tubing in the impinger flask.

During thermal degradation of PUR, a complex mixture of mono- and diisocyanates in both gas and particle phase is formed and other interfering compounds present. The general agreement for MIC, EIC, PIC, Phi, HDI, IPDI, and MDI between the dry sampler and the reference method indicated efficient collection and derivatization of gas- and particle-phase isocyanates using the dry sampler. For TDI and ICA, there were considerable differences in the sampling. The derivatization chemistry for ICA was greatly affected by the humidity and ICA is possibly consumed by side reactions occurring in the impinger flask during sampling. TDI showed slightly higher levels (about 20%) in the impinger flask. The nature of TDI in the gas phase is not known in detail. This could indicate that there is a presence of TDI compounds that form TDI-DBA derivatives during sampling or storage of samples in toluene and that these reactions do not occur to the same extent in the dry sampler. IPDI showed about the same results for the dry sampler compared with impinger-filter sampling. This is most likely due to particle-borne IPDI that does not adsorb on the surfaces in the glass line in the impinger flask.

The advantage of a test atmosphere of thermal decomposition products of PUR is that it realistically reflects a worst-case situation, with regard to the chemical matrix, that can be expected during field measurements compared with studies of isocyanates in ‘clean’ atmospheres. It needs to be noted that there is a presence of many more compounds in thermal decompositions products of PUR other than isocyanates. To mention a few are aliphatic and aromatic amines, aminoisocyanates, polyols, and other ingredients present in the PUR polymer.

The actual sampling flow consists of an active flow and a passive flow. The passive sampling flow is greatly dependent on ventilation and great variations will occur when there are alterations in direction and strength of ventilation.

For the dry sampler, the contribution of passive sampling was considerable when using an active sampling flow of 25 and 50 ml min$^{-1}$ (Fig. 2). Increasing the active sampling flow, the contribution of passive sampling was drastically decreased.

In the present study, the sampling time and the robustness of the dry sampler were only studied for gas-phase isocyanates. Particle-borne isocyanates will be studied in more detail in a forthcoming paper.

Using the dry sampler for field sampling, there are great advantages compared with impinger-filter sampling. The dry sampler needs no field preparation except for removing sealing caps before sampling and putting them back after sampling. Impinger samplers must be loaded with reagent before sampling and after sampling the reagent shall be transferred back to test tubes before samples are shipped back to the laboratory for analysis.

The robustness of the dry sampler, demonstrated by the results presented in this article, enables long-time sampling (e.g. personal sampling for total isocyanate exposure). The impinger sampler can have limited sampling time due to solvent evaporation. Also the fragile glassware and presence of solvents such as toluene make the sampler not suitable for personal sampling.

**CONCLUSIONS**

For collection of gas-phase isocyanates and isocyanate aerosols generated during thermal degradation...
Table 7. Comparison of sampling using dry samplers and impinger-filter samplers for the collection of isocyanates generated during thermal degradation of polyurethane polymers. A total of 48 dry sampler and 48 impinger-filter samplers have been compared.

<table>
<thead>
<tr>
<th>Test</th>
<th>20% RH</th>
<th>40% RH</th>
<th>60% RH</th>
<th>90% RH</th>
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<tr>
<td></td>
<td>Average isocyanate concentration (µg m⁻³); RSD (%)</td>
<td>Ratio</td>
<td>Average isocyanate concentration (µg m⁻³); RSD (%)</td>
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<td></td>
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<td>Dry sampler</td>
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<td>397.1; 10</td>
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<td>Impinger-filter</td>
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<td>317.7; 3.2</td>
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<td>Dry sampler</td>
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<td>1.14*</td>
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<td>224.4; 3.7</td>
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*Significant differences between pre-/post-exposed dry samplers and reference dry samplers at the 95% level using Student's t-test.
Table 8. Comparison of sampling using dry samplers and impinger-filter samplers for the collection of isocyanates generated during generation of a standard atmosphere. A total of 12 dry sampler and 12 impinger-filter samplers have been compared

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of PUR, the dry sampler was demonstrated to be a superior alternative to impinger-filter sampling, allowing easy and precise sampling without the need of field extraction. The dry sampler was proven to enable sampling for up to 32 h and possibly longer time.

The robustness of the sampler was demonstrated by samplers that were pre- or post-exposed to ambient air that gave the same results as for samplers that had been exposed only to air during the sampling period. No breakthrough during sampling was observed. No breakdown of isocyanate derivatives were observed during storage.

FUNDING
Swedish government; Stockholm University.

APPENDIX 1. CHEMICALS
Di-n-butylamine (DBA), 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate, and toluene diisocyanate (80% 2,4-TDI, 20% 2,6-TDI) were obtained from Sigma–Aldrich (St Louis, MO, USA). Acetonitrile, acetic acid, formic acid, methanol, and toluene were obtained from Merck (Darmstadt, Germany). Ethyl isocyanate (EIC), propyl isocyanate (PIC), phenyl isocyanate (PhI), and 4,4′-MDI were obtained from Agros Organics (NJ, USA).

The DBA derivatives and the DBA-d9 derivatives of 1,6-hexamethylene diisocyanate (HDI), isocyanic acid (ICA), 1 and 2 isophorone diisocyanate (IPDI), 2,4- and 2,6-toluene diisocyanate (TDI), methyl isocyanate (MIC), and 4,4′-methylene diphenyl diisocyanate (MDI) have been synthesized in our laboratory (Karlsson et al., 2005). Deuterium-labelled DBA [NH(C₄H₉)(C₄D₉)] was obtained from Synthelec (Lund, Sweden) and was used for synthesis of internal standard. All solvent used were HPLC graded or higher.

APPENDIX 2. INSTRUMENTATION
Tandem mass spectrometry: For determining isocyanate-DBA derivatives, a Quattro Micro triple quadrupole mass spectrometer (Waters, Altrincham, Cheshire, UK) was used in the electrospray-mode monitoring positive ions (ESI⁺). The capillary voltage was 4.0 kV, the temperature of the ion source was 130°C, and the desolvation temperature was 200°C. Collision-induced dissociation was performed using argon as collision gas and the pressure of the collision cell was 4 × 10⁻³ mbar. For quantification, multiple-reaction monitoring (MRM) was performed, monitoring [M+H]+ ≥ [130]⁺ of the isocyanate-DBA derivatives and [M+H]+ ≥ [139]⁺ of the isocyanate-DBA-d9 derivatives. Cone voltage and collision energies for the different DBA derivatives were individually optimized and were set to 30 V and 28 eV for HDI, and 15 V and 20 eV for IPDI, and 35 V and 24 eV for 2,4- and 2,6-TDI (Karlsson et al., 2005). Six ions were monitored with a dwell time of 0.15 s.

Liquid chromatography system: The MS instrument was connected to a micro-LC pump (Shimadzu LC10ADV, Shimadzu Inc., Kyoto, Japan). Partially filled loop injections of 2.5 μl in a 20 μl loop volume

Table 8. Continued

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</table>

*Significant differences between pre-/post-exposed dry samplers and reference dry samplers at the 95% level using Student’s t-test.
containing 17.5 µl of a focus liquid of 5/95 (% v/v) acetonitrile/water solution were made with a CTC-pal autosampler (CTC Analytics AG, Zwingen, Switzerland). The flow rate was 70 µl min⁻¹, and the LC column was an Xbridge C18, 50 × 1.0 mm with 2.5 µm particles (Waters, Massachusetts, USA). The mobile phase was composed of A: 5/95/0.05 and B: 95/5/0.05 acetonitrile/water/formic acid (v/v/v). Gradient elution was performed from 40% B to 100% B in 10 min.

Proton transfer reaction mass spectrometer (PTR-MS): Measurements of gas-phase HDI, IPDI, and TDI in the test chamber were performed using a compact PTR-MS (Ionicon, Innsbruck, Austria). The instrument was equipped with a polyetheretherketone inlet capillary with a flow rate of 0.5 l min⁻¹ and heated to 90°C.

For TDI, the protonated molecular ion (m/z = 175) was monitored. For HDI and IPDI, the fragment ions m/z = 126 and m/z = 180 amu were monitored, respectively (Gylestam et al., 2011). The dwell time was 10 s; the pressure controller was set to 360 mbar and flow controller to 6.0 sccm. The source and source out voltages were 150 and 115 V, respectively. The drift tube, extraction lens, and nose cone voltages were 600, 158, and 6 V, respectively. The source current was set to 7 mA.

APPENDIX 3. SOLUTIONS

Internal standard stock solutions: Solutions containing d₉-DBA derivatives of 0.1 µg ml⁻¹ of ICA, MIC, EIC, PIC, PhI, HDI, 2,4-TDI, 2,6-TDI, IPDI, HMDI, and MDI in acetonitrile were prepared.

Standard stock solutions: Solutions containing DBA derivatives of 0.1 µg ml⁻¹ of ICA, MIC, EIC, PIC, PhI, HDI, 2,4-TDI, 2,6-TDI, IPDI, HMDI, and MDI in acetonitrile were also prepared.

Preparation of derivatives and characterization using LC-MS and LC-chemiluminescent nitrogen detection have been described previously (Karlsson et al., 2002).

Impregnation solution A (0.74 mol l⁻¹ DBA): Methanol (80 ml) and DBA (12.5 ml) were mixed in a 100-ml volumetric flask. Acetic acid (4.16 ml) was slowly added during stirring and finally methanol was added to the flask (up to the mark).

Impregnation solution B (1.5 mol l⁻¹ DBA): Methanol (60 ml) and DBA (25 ml) were mixed in a 100-ml volumetric flask. Acetic acid (8.32 ml) was slowly added during stirring and finally methanol was added to the flask (up to the mark).

REFERENCES


