**Supplemental Materials**

**Overview of evaluation methods used in the study**

The ASSET-EZ4-NCO sampler was developed by the InstitutetförKemisk- AnalysNorden AB (IFKAN) in Hasselholm, Sweden(Marand et al. 2005; Skarping and Dalene 2010). The evaluation method exists as a standard under International Organization for Standardization (ISO) 17734-1(ISO 2008). This sampler is made of two parts, a denuder and a final filter, retaining vapor phase and particulate phases of isocyanate respectively. The denuder is a tube in which two filters are placed: one to cover the inner wall and the second, V-shaped, is inserted into the tube. The tube is connected to a final filter. All filters are made of fiber-glass and are impregnated with dibutylamine (DBA) (Brown and Halpenny 2013). The analyte, 4,4'-methylene diphenyl diisocyanate-2 (di-n-butylamine) (4,4'-MDI-2(DBA)) is desorbed with toluene, and the analyte is prepared in the lab and quantified using either an Liquid Chromatograph - Mass Spectrometer (LC-MS) or LC - tandem Mass Spectrometer (LC-MS/MS).

The ISO-Chek sampler was developed by the IRSST in Montreal, Quebec, Canada (Lesage et al. 1992) (Lesage and Perrault 1990) and has also been published by ISO under ISO 17736 (ISO 2010) and by ASTM International under D5932 (ASTM International 2008) . This device consists of two filters in series. The first, made of polytetrafluoroethylene (PTFE), has no derivatizing agent while the second, of fiberglass, is impregnated with 9-(methyaminomethyl)anthracene (MAMA). The first step captures any aerosols present while the second traps any TDI vapors. One of the advantages of this dual filter system is the possibility of quantifying vapor phase separately from particulate phase isocyanates. Since no derivatizing agent is present on the first filter, this sampler should not be run for more than 15 min in the presence of isocyanate particles (International Organization for Standardization (ISO) 2010). Nonetheless, if only vapor is present, it can be run for a longer period of time since the second filter, impregnated with MAMA, captures and stabilizes isocyanates. Immediately upon sampling, the first filter is immersed in a solution of MP in toluene, producing TDI-MP, while the second filter, containing TDI-MAMA, do not require field desorption. These anthracene compounds are photosensitive and must be protected from light(Sangö and Zimerson 1980). Analysis in the lab is carried out using a HPLC equipped with an ultraviolet (UV).

The Occupational Safety and Health Administration (OSHA) regulates workplace hazards and testing methods in the USA. It developed the OSHA method 42 which uses an open-faced sampler with a 37-mm fiberglass filter impregnated with 1-(2-pyridyl)piperazine (PP) (OSHA 1989).The American Chemical Council (ACC) suggested a modified version of the original OSHA method 42 which uses a larger amount of PP on the filter (minimum of 2 mg per filter)(ACC 2014). This method has also been published under ISO 14382 (ISO 2012).

Finally, the *Capteur Individuel de Polluants* (CIP10) was developed by the Institut national de recherche et de sécurité (INRS) in Vandoeuvre-lès-Nancy, France, for the air sampling of coal and other industrial dusts. A variation on the CIP10, the CIP10M, is used to quantify microbial spores. The IRSST in Quebec successfully adapted this sampler to the collection of isocyanate aerosols in spray applications (Puscasu et al. 2014; Puscasu et al. 2015). The CIP10M has an auto-propelled rotating cup at the bottom of the sampler instead of an attached pump. The cup is filled with a solution of MP in tributyl phosphate (TBP) and the MDI species pulled in by the rotation of the cup reacts to give MDI-MP. As for the dissolved derivative from the first filter of the ISO-CHEK sampler, the solution containing MDI-MP, is transferred to a vial and quantified in the lab by HPLC with a UV detector.

**Standard and Analyte Preparation and Analysis**

*ASSET EZ4-NCO*

The ASSET EZ4-NCO standards and samples were prepared following the protocol provided by Supelco(Brown and Halpenny 2013). The prepared solutions were injected (10 µL) into the UPLC-MS via its autosampler set at 15°C. The mobile phase was composed of ACN + 0.1% FA (eluant A) and water + 0.1% FA (eluant B). The run started with a gradient of 70% eluant A (0.5 min.), ramped to 90% eluant A (2.5 min.), held at 90% eluant A (2 min.), ramped to 100% eluant A (3 min.) and finally equilibrated at 70% eluant A (2 min.). The flow rate in the column was 0.6 mL/min. and the temperature was maintained at 50°C. The Xevo TQ was used in positive mode with the capillary voltage set at 2 kV and the source temperature at 150°C. The desolvation temperature and flow were 500°C and 1000 L/hr, respectively; while the collision gas flow was set at 0.15 mL/min. The [M+H]+for TDI-DBA is m/z 433.2 and that of the internal standard, TDI-DBA-d18, is m/z 451.2. The data was acquired in multiple reaction monitoring (MRM) mode (Table S1). Manual adjustments were made on the integrations to ensure that the entire peak was covered before the data was recorded. The results were used to create a regression calibration curve with linear fit.

**Table S1** SMS-MRM species calculated and measured.

|  |  |  |
| --- | --- | --- |
| **MS parameters** | **Substance** | **MRM transitions** |
| Cone voltage : 30V  Collision Energy : 25eV | 2,4 TDI-DBA  2,6 TDI-DBA | 433.2 – 130.1 |
| TDI-DBA-d18 | 451.2-139.1 |

**Laboratory sampler performance evaluation for DAN and CIP10**

All the sampling devices had been used in the field previously except the DAN coated filters for TDI and the CIP10/MP device for TDI, so field use of these devices was preceded by laboratory evaluations to characterize their performances.

All the analytical parameters were evaluated as in Puscasu et al(Puscasu et al. 2015). As can be seen in Table S2, the analytical performances are in the same range as those obtained when the CIP10/MP evaluation for MDI was performed(Puscasu et al. 2015). In addition, as was done with CIP10/MP with MDI, sample loss was evaluated for CIP10/MP with TDI. Known free 2,4- and 2,6-TDI concentrations were spiked in the CIP10/MP in duplicate and the CIP10 was operated as it would be during a normal sampling period. No loss of TDI derivatives was observed after 1h. These performances were judged satisfactory to conduct formal air sampling evaluation with this approach.

**Table S2.** Analytical performances of TDI CIP10/MP

|  |  |  |
| --- | --- | --- |
| **Analytical parameters** | **2,4TDI** | **2,6TDI** |
| Estimated LOD (µg/sample) | 0.008 | 0.008 |
| Estimated LOQ (µg/sample) | 0.026 | 0.026 |
| Dynamic range (µg/mL) | 0.025 – 0.490 | 0.025 – 0.490 |
| R2 | >0.990 | >0.990 |
| Intra-day precision (%) | 1 | 1 |
| Inter-day precision (%) | 2 | 1 |
| Accuracy (%) | 95 ± 5 | 100 ± 0.2 |
| Recovery and matrix effect (%) | 101 ± 7 | 95 ± 12 |
| LOD: limit of detection, LOQ: limit of quantification | | |

The mass spectrometer parameters used to analyzed primidone are presented in table S3. Perimidone recovery was determined by spiking known concentrations of 2,4- and 2,6-TDI on DAN impregnated filter (Table S4). Each spiked filter had sufficient time to dry at room temperature in order to simulate the filter desorption of an air collection. Spiked filters provide a good estimation of the recovery, but do not replace a formal air sampling comparison. The recovery was judged reasonable and the evaluation was continued. No correction of the measured values in the field was done as it would have had a minimal impact on the measured concentration.

**Table S3.** MS analytical parameters for Perimidone (DAN method)

|  |  |  |
| --- | --- | --- |
| **Substance** | **Calculated**  **[M+H]+** | **MRM transition** |
| Perimidone | 185 | 185 - 115 |
| 185 - 130 |
| Perimidone-d6 | 191 | 191 - 121 |
| 191 - 136 |

**Table S4.** Perimidone recovery for DAN coated filters spiked with free TDI

|  |  |  |
| --- | --- | --- |
| **Perimidone level (ng/mL)** | **Recovery (%)A** | |
| **2,4-TDI** | **2,6-TDI** |
| 500 | 87 ± 7 | 76 ± 8 |
| 1000 | 82 ± 9 | 78 ± 3 |
| 2000 | 74 ± 10 | 77 ± 3 |
| A n = 5 for each level |  |  |

**Determinants of measured TDI concentration**



**Figure S1.** Particle concentration vs TDI index (A) and TDI emission vs TDI index (B)

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