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CIP10 Optimization for 4,4-Methylene Diphenyl Diisocyanate Aerosol Sampling and Field Comparison With Impinger Method

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ABSTRACT

4,4-methylene diphenyl diisocyanate (MDI) aerosol exposure evaluation in spray foam insulation application is known as being a challenge because the spray foam application actually involves a fast-curing process. Available techniques are either not user-friendly or are inaccurate or not validated for this application. To address these issues, a new approach using a CIP10M was developed to appropriately collect MDI aerosol in spray foam insulation while being suitable for personal sampling. The CIP10M is a commercially available personal aerosol sampler that has been validated for the collection of microbial spores into a liquid medium. Tributylphosphate with 1-(2-methoxyphenyl)piperazine (MOPIP) was introduced into the CIP10M to collect and stabilize the MDI aerosols. The limit of detection and limit of quantification of the method were 0.007 and 0.024 μg ml^{-1}, respectively. The dynamic range was from 0.024 to 0.787 μg ml^{-1} (with $R^2 \geq 0.990$), which corresponds to concentrations in the air from 0.04 to 1.3 μg m^{-3}, assuming 60 min of sampling at 10 l min^{-1}. The intraday and interday analytical precisions were <2% for all of the concentration levels tested, and the accuracy was within an appropriate range of 98 ± 1%. No matrix effect was observed, and a total recovery of 99% was obtained. Parallel sampling was performed in a real MDI foam spraying environment with a CIP10M and impingers containing toluene/MOPIP (reference method). The results obtained show that the CIP10M provides levels of MDI monomer in the same range as the impingers, and higher levels of MDI oligomers. The negative bias observed for MDI monomer was between 2 and 26%, whereas the positive bias observed for MDI oligomers was between 76 and 113%, with both biases calculated with a confidence level of 95%. The CIP10M seems to be a promising approach for MDI aerosol exposure evaluation in spray foam applications.

KEYWORDS: aerosol; CIP10; MDI; oligomer; polyurethane foam

INTRODUCTION

4,4-methylene diphenyl diisocyanate (MDI) is used in many industrial applications involving polyurethane. MDI is known as a respiratory and cutaneous chemical sensitizer and irritant. The main work-related illness linked to MDI monomer and oligomer overexposure

is occupational asthma (Malo *et al.*, 1983; Banks *et al.*, 1986; Mapp *et al.*, 1988; Musk *et al.*, 1988; Vandenplas *et al.*, 1988; Mapp *et al.*, 1999). Most countries have established their occupational exposure limit (OEL) at 5 p.p.b. (OSHA, Occupational Safety and Health Administration: CFR: Code of Federal Regulations, 1992; NIOSH: National Institute for Occupational Safety and Health (NIOSH) Alert, 1996; SNBOSH: Swedish National Board of Occupational Safety and Health, 2000; Québec (Province), 2012; ACGIH: American Conference of Governmental Industrial Hygienists, 2013) for the MDI monomer. One application in which MDI is used is the spraying of insulation foam. Accurate evaluation of the air in workplaces where MDI-based insulation foam is applied is critical for adequately protecting workers against exposure. It has been reported that sampling of MDI in fast-curing applications could be a challenge when using existing filter sampling techniques (Streicher *et al.*, 1998, Lesage *et al.*, 2007; Puscasu *et al.*, 2014).

Isocyanates in air can be found in two different forms: vapor and aerosols. However, it has been shown that MDI in spray foam insulation industries is mainly present as an aerosol with a negligible vapor phase (Roberge *et al.*, 2009). To sample the MDI aerosols in these applications, the reference method for exposure evaluation is the impinger (MDHS 25/3, 1999; Lesage *et al.*, 2007; Puscasu *et al.*, 2014). An impinger collects the aerosol using an air flow impacting in a solvent containing a derivatization agent. The MDI aerosol is therefore solubilized rapidly by the solvent and stabilized rapidly by the derivatization agent. Because the collection and reaction occur rapidly in the liquid medium, the efficiency of the device has been thought to be optimal. The stable derivative formed can be analyzed in the laboratory using liquid chromatography techniques (Lesage *et al.*, 2007; Puscasu *et al.*, 2014). This being said, the impinger approach has severe limitations. Risk of explosion is associated with this sampling device when it is used with a volatile solvent. Potential leakages may occur during sampling in the personal breathing zone. Finally, the risk of flask breakage leading to solvent spill is an additional issue with this sampling device. For several decades, studies have investigated alternate sampling techniques that would avoid the limitations linked to the use of impingers, but offering the same sampling efficiency. Sampling devices such as filters (Streicher *et al.*, 1998; Marand *et al.*, 2005; Lesage *et al.*, 2007), denuders (ASSET EZ4-NCO; Sigma-Aldrich) (Marand *et al.*, 2005; Nordqvist *et al.*, 2005) and other equipments (Rudzinski *et al.*, 1998; Rando and Poovey, 1999) have been proposed, but so far, either limitations in term of efficiency or a lack of characterization for MDI during spray foam insulation application have been reported (Lesage *et al.*, 2007; Puscasu *et al.*, 2014).

The investigation of a new alternative based on the CIP10 for MDI sampling during spray foam insulation application has recently been published (Görner *et al.*, 2006; Puscasu *et al.*, 2014; www.tecora.com, June 2014). The CIP10 is designed to collect air samples at a high flow rate of 10 l min^{-1}. Multiple configurations could be used, but the configuration for microorganism (CIP10M) sampling has recently been adapted (Puscasu *et al.*, 2014) to MDI aerosols. It is reported that this configuration has aspiration efficiency slightly higher than the inhalable convention, thus making it an efficient sampler for relatively large particles (Görner *et al.*, 2006). Since this sampler uses the centrifugal force to collect particles, the collection efficiency differs from the aspiration efficiency. It was determined that the collection efficiency is ~20% for particles <1 μm and is >95% for aerosols having aerodynamic diameters >2.8 μm (Görner *et al.*, 2006). For use in sampling MDI aerosols, the aqueous medium normally used with the CIP10M has been replaced by a nonvolatile co-solvent in which the derivatization agent 1-(2-methoxyphenyl)piperazine (MOPIP) is introduced. When the CIP10M is operating, the air containing the MDI aerosol is aspirated through the CIP10M inlet and directed toward the rotating cup containing the co-solvent. Once the aerosols impact the co-solvent by centrifugal force, the MDI aerosols are dissolved in the co-solvent and stabilized rapidly by the MOPIP. The mixture is kept inside the cup by continuous centrifugation at high speed (~7000 r.p.m.) and the air is evacuated through slits on top of the rotating cup. No sampling pumps are needed as the CIP10M has its own motor, and the collected sample can be further analyzed in the laboratory by liquid chromatography techniques. It is believed that the sampling efficiency for MDI aerosol would be optimal, as most of the particles are >10 μm (Lesage *et al.*, 2007), which is within the efficient sampling range of the CIP10M.

Up to now, this technique for MDI aerosol sampling has been used only in the laboratory, and no field study has been reported. The objective of this paper is to describe the laboratory optimization of the CIP10M device for efficient MDI sampling and to compare the performance of a CIP10M for MDI aerosol sampling in real field operations of spray foam insulation application with the impinger reference technique.

MATERIALS AND METHODS

Chemicals

MDI (98% purity), MOPIP (98% purity), dimethylpolysiloxane (DMPS; viscosity 5cSt), tributylphosphate (TBP; >99%), dimethylsulfoxide (>99.9%), and acetic anhydride (AA; 98% purity) were obtained from Sigma-Aldrich (Milwaukee, WI, USA) and were used without any further purification. Mondur 541 polymeric MDI (pMDI) was obtained from Bayer Material Science (Leverkusen, Germany). Acetonitrile (ACN), water (H_2O), both optima grade, and sodium acetate (99.4% purity) were obtained from Fisher Scientific (St-Laurent, Québec, Canada). Glacial acetic acid was obtained from J.T. Baker. Toluene (99.9% purity) was obtained from EMD Millipore Corp. (Billerica, MA, USA). The in-house synthesis of MDI–MOPIP monomer derivative and the purity check were done using a known and reliable procedure (Tremblay *et al.*, 2003; Puscasu *et al.*, 2014). The in-house synthesis of MDI-MOPIP oligomers was done using the same protocol as for the MDI–MOPIP monomer, except that the MDI monomer was replaced by pMDI (Puscasu *et al.*, 2014).

Instruments and analytical conditions

Impinger analysis

The Ultra High Performance Liquid Chromatography (UHPLC) system coupled to a photodiode array detector (PDA) consisted of an Agilent series 1290 (Mississauga, Ontario, Canada). The analytical column used was a Zorbax Bonus RP, 3.5 µm, 4.6×150 mm from Agilent. The software used to operate the system and analyze the data was Chemstation. The calibration curve regression was linear fit.

The mobile phase was composed of ACN (eluent A), water + 152 mM sodium acetate adjusted to pH 6 with acetic acid (eluent B). The eluents were degassed with a 13-mm Acrodisc CR13 PTFE filter syringe, 0.2 µm from PALL Corporation Life Science (Ville St-Laurent, Quebec, Canada). UHPLC separation was achieved using an isocratic program of 62% eluent A for 40 min. The flow rate was 1.0 ml min^{-1} and the column was kept at room temperature. The injection volume was 20 µl. The PDA detector was operated between 200–400 nm and the quantification was done at 250 nm.

CIP10M analysis

The high-performance liquid chromatography (HPLC)-PDA system consisted of an Agilent series 1100 (Mississauga, Ontario, Canada). The analytical column used was a Luna C18 (2), 3 µm, 3×150 mm from Phenomenex (Torrance, CA, USA). The software used to operate the system and analyze the data was Chemstation. The calibration curve regression was linear fit.

For CIP10M/DMPS analysis, the mobile phase was composed of ACN (eluent A), water + 152 mM sodium acetate adjusted to pH 6 with acetic acid (eluent B). The eluents were degassed with a 13-mm Acrodisc CR13 PTFE filter syringe, 0.2 µm, from PALL Corporation Life Science (Ville St-Laurent, Quebec, Canada). HPLC separation was achieved using an isocratic program of 60% eluent A for 40 min. The flow rate was 0.6 ml min^{-1} and the column was kept at room temperature. The injection volume was 20 µl. The PDA detector was operated between 200–400 nm and the quantification was done at 250 nm. For the CIP10M/TBP analysis, the same conditions as above were used except that a gradient was used rather than an isocratic elution program. The gradient was 58% eluent A for 7 min at 0.5 ml min^{-1}, then ramped to 75% eluent A in 0.01 min and maintained for 11 min at 0.4 ml min^{-1}. Column equilibration was done at 58% eluent A for 7 min at 0.5 ml min^{-1}.

Sample and standard preparation

The impinger samples and standards were prepared using a well-established procedure (MDHS 25/3, 1999; Lesage *et al.*, 2007). The CIP10M/DMPS samples and standards were prepared using a protocol previously optimized and described (Puscasu *et al.*, 2014). The CIP10M/TBP samples were prepared by directly diluting the TBP from the CIP10M 1:9 in ACN + AA 0.5%. For the preparation of the MDI-MOPIP standards with TBP, the MDI–MOPIP monomer stock solution was prepared separately by dissolving 20 mg of the respective powder in 100 ml

of TBP. The calibration standards were prepared by spiking aliquots of the stock solutions into the 0.5 mg ml^{-1} TBP-MOPIP/ACN + AA 0.5% (1/9) liquid medium. Five calibration points were used for the MDI–MOPIP monomer. The concentrations of the calibration standards for the MDI–MOPIP monomer were 0.079, 0.118, 0.197, 0.394, and 0.787 μg ml^{-1}. The protocol used to prepare the standard was the same as the one used to prepare the samples. The MDI–MOPIP monomer stock solution was kept at 4°C. Results for the oligomers are calculated as the total peak area detected and quantified using the standard curve prepared with the MDI–MOPIP monomer since no individual pure MDI–MOPIP oligomer standards are available. When needed, the second peak after the MDI monomer, known as MDI triisocyanate, was quantified as a discreet compound using the standard curve prepared with the MDI–MOPIP monomer in order to provide explanations of the sampling results presented further.

Analytical performance evaluation

The impinger method (MDHS 25/3, 1999; Lesage *et al.*, 2007) and the CIP10M/DMPS method (Puscasu *et al.*, 2014) have been previously described.

The CIP10M/TBP method was validated as follows. The analytical parameters were evaluated for MDI–MOPIP monomer using the sample preparation procedure described above. The recovery and matrix effect were investigated by comparing six replicates at five concentration levels spiked in TBP + MOPIP (0.5 mg ml^{-1}) with replicates spiked into pure ACN. The concentrations of the replicates were identical to the ones used to build the calibration curve. The limit of detection (LOD) and the limit of quantification (LOQ) reported were based on signal-to-noise ratios of 3:1 and 10:1, respectively. The intraday precision was calculated from six separate measurements of five different concentrations in the desired dynamic range on a single day. The interday precision was calculated from five different concentrations distributed over the entire dynamic range and repeated six times for each measurement by the same person on the same instrument, but on six different days. The accuracy was evaluated by analyzing a known concentration of MDI-MOPIP prepared from a second stock solution in the dynamic range and quantified using a standard curve.

Air sample collection

Particle sizes were measured using 8-stage Marple Sierra 298 impactors from Thermo Scientific (Waltham, MA, USA). The mass collected by the impactors was corrected in relation to the median variation observed for a group of six blank substrates. The results were then corrected according to the curves supplied by the manufacturer to take into account wall deposition losses. The geometric standard deviations (GSDs) were calculated by assuming a log-normal distribution, therefore by drawing a regression line on the log probability graph of the particle size distribution. Only the most significant points were used, by giving less weight to the cumulative points <10% and >90%, as recommended in the literature (Lodge and Chan, 1986). Simpson's rule was applied during calculation and is described in the literature (Lodge and Chan, 1986). To be able to compare the samples, the histograms of the particle size distributions were normalized. The mass percentages for each particle diameter could thus be evaluated directly from the histograms.

MDI aerosols were sampled in parallel with impingers and the CIP10M. The 25-ml impingers were from SKC (Eighty Four, PA, USA). Impinger samples were collected at a flow rate of 1 l min^{-1} using an SKC pump model 224-PCXR4/8 (Eighty Four, PA, USA). The flow rate was calibrated using a TSI 4146 flowmeter (Shoreview, MN, USA); 15 ml of toluene containing 0.1 mg ml^{-1} of MOPIP was added to the impinger for aerosol sampling. No backup filter cassettes were used in series with the impingers because no small particles (<2 μm) were expected (Lesage *et al.*, 2007). The aspiration efficiency of the impinger was determined equivalent to an inhalable fraction sampler, the IOM sampler, for the collection of pMDI (Hext *et al.*, 2003) in the aerodynamic diameter range of 5–30 μm.

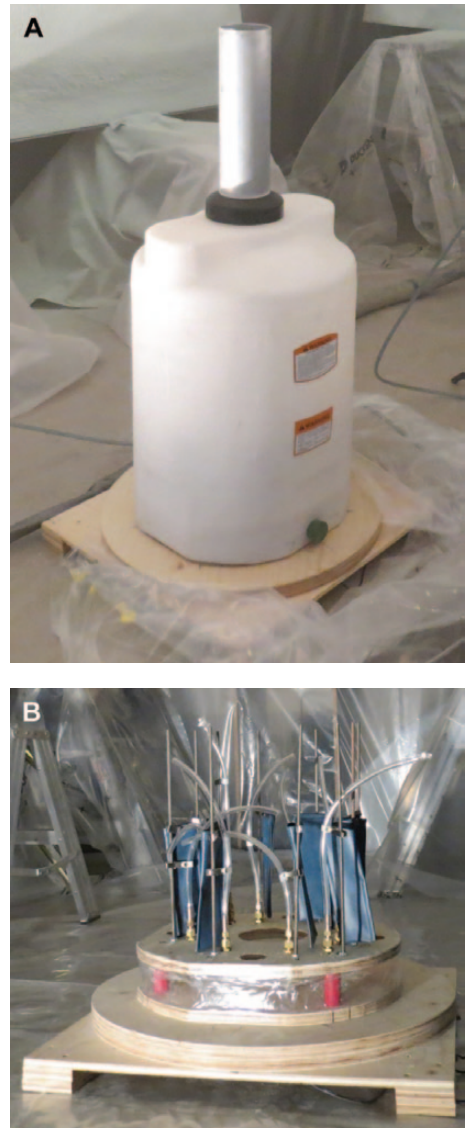
The CIP10Ms used were from Arelco (Fontenay-sous-Bois Cedex, France) and were run at 10 l min^{-1} as shown in the picture in Fig. 1. The initial CIP10M calibration was done using a TSI 4043 flowmeter (Shoreview, MN, USA) and a calibration device supplied by Arelco. The flow rate was then measured in the field using a 6236SI tachometer also supplied by Arelco; 2 ml of TBP containing 0.5 mg ml^{-1} of MOPIP were added to the cup for aerosol sampling. The CIP10M was kept in a vertical position when the cup was immobile to avoid leakage. The CIP10M can be

1 CIP10M configuration.

moved freely when the cup rotates at high speed since the liquid is kept inside the cup by centrifugal force.

Workplace setup and jar

Spraying of MDI-based polyurethane insulation foam was performed by a professional sprayer from Isolation Majeau et Frères (St-Esprit, Quebec, Canada). The isocyanate component of the sprayed foam was Isocyanate A100, CAS nos. 9016-87-9, 101-68-8, and 26447-40-5 from Demilec (Boisbriand, Quebec, Canada) with a ratio of monomer:oligomers of 40:60. The sprayer worked in a 3.1 × 4.0 × 2.3 m room with the ceiling and walls covered by a vinyl curtain. Two plywood panels (1.2 × 2.4 m) were placed in the room and the sprayer applied 2 cm of foam on each plywood panel every 5 min, using exactly the same procedure as in a normal working day. After each application, the sprayer was asked to leave the room. Each test consisted of this procedure repeated at least four or five times, which led to a test duration of ~30 min. Inside the room, a jar was positioned near the sprayer. The jar shown in Fig. 2A,B has a diameter of 45 cm, a height of 65 cm, and an inlet tube of 40 cm with an orifice diameter of 10 cm fixed on its top. Each sampler was



2 (A) Overall sampling jar; (B) Inside sampling jar.

fixed 40 cm from the inner bottom. A fan located at the bottom of the jar sucked air at a flow rate of 94 l min^{-1} through the inlet. The velocity of the air at the jar inlet was measured with an 8384-M-GB anemometer from TSI. The objective of using the jar was to create a homogenous environment in order to expose several samplers to the same concentration and thus avoid potential orientation effects. The jar was compatible with all the sampling devices used. Up to 10 sampling devices can be run in parallel inside the jar per test to accomplish intermethod comparison. The amount of

MDI-based foam sprayed per test allowed the concentration of MDI in the room to reach 50–150% of the typical OEL (0.051 mg m^{-3} MDI monomer)

Statistics

MDI concentrations were compared between the impinger and CIP10M sampling methods in a total of 12 different tests. Descriptive statistics (histograms, normal probability plots) were applied to determine MDI monomer and oligomer data distributions. Since preliminary investigation indicated a within-test correlation between MDI concentrations (monomer and oligomers), analyses were carried out using linear mixed effect models assuming a hierarchical structure of the data, with the MDI concentration results as the dependent variable. The MDI sampling method (impinger; CIP10M) was included in the models as a fixed effect, and the test number as a random effect. MDI concentrations were not log-transformed because the monomer and oligomer distributions were approximately normal. The following model was fit to the data:

$$C_{ij} = \alpha + \beta \times \text{method}_{ij} + a_i + \varepsilon_{ij}$$

MDI concentrations (C_{ij}) in mg m^{-3} were modeled as an intercept (a), plus a sampling method effect (method_{ij}), a random intercept a_i that is assumed to be normally distributed with mean 0 and variance σ_a^2, and residual error (ε_{ij}). The index i refers to tests ($i = 1, \ldots, 12$) and j to the observation within a test ($j = 1, \ldots, 6$). The term ε_{ij} is the within-test variation, and is assumed to be independently normally distributed with mean 0 and variance σ^2. The plot of residuals against fitted values showed some evidence of heterogeneity because the residual spreads were different between the two MDI sampling methods. The random structure was optimized by adding a different residual standard deviation for each level of the method variable.

All analyses were performed using R 2.14.2 statistical software (R Development Core Team, Vienna, Austria).

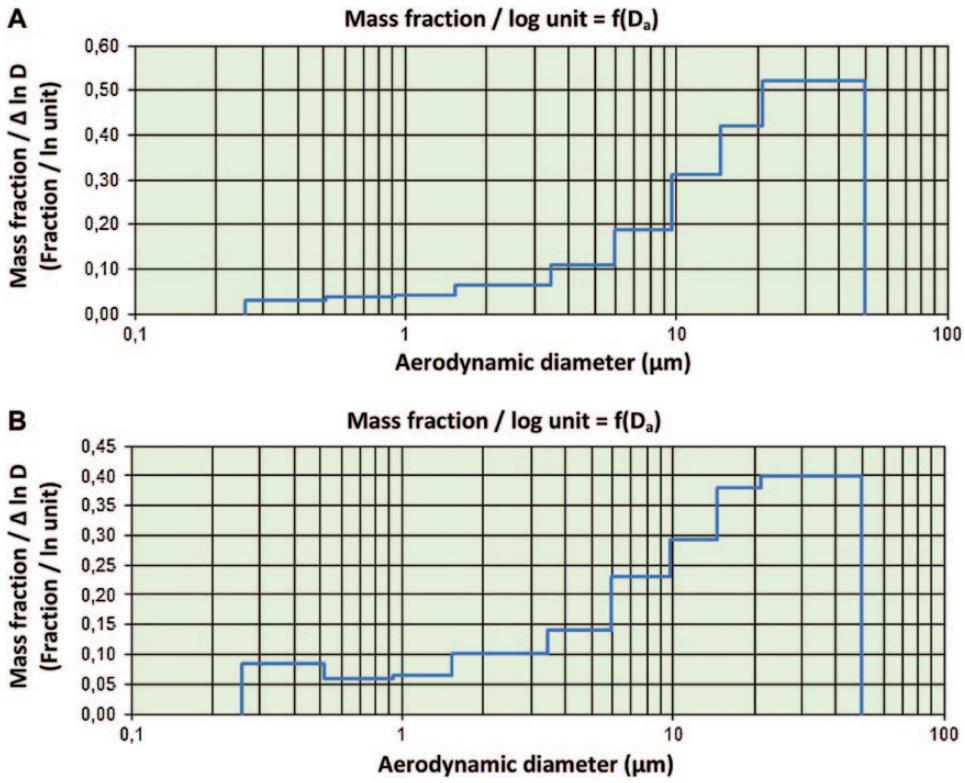
RESULTS AND DISCUSSION

Laboratory optimization

Before the formal comparison of the sampling devices was done, the experimental setup was characterized in order to determine whether it was suitable to perform an intermethod comparison. First, the particle size distribution of the MDI aerosols was evaluated inside and outside the jar to make sure that the jar had no significant effect on the particle size distribution of the aerosols emitted by the spray gun. Fig. 3A,B show the particle size histograms inside and outside the jar. The mass median aerodynamic diameter (MMAD) measured outside the jar was 20 μm with a GSD of 4 μm, and the MMAD inside the jar was 13 μm with a GSD of 7 μm. Since no significant particle size difference was measured inside and outside the jar, we concluded that the jar did not segregate the particles at its inlet. Moreover, the particle size distributions measured were similar to those obtained in another study (Lesage *et al.*, 2007). These results also supported the decision not to use backup filter cassettes with the impingers. Second, impingers ($n = 8$) were placed inside the jar to establish the MDI concentration variability inside the jar. Table 1 shows the monomer and oligomer concentrations obtained inside the jar after two different tests. As can be observed in Table 1, the variability is minimal and acceptable for all the samples collected with the impingers for the monomer (6–24%) and the oligomers (11–25%). Moreover, the same monomer/oligomer ratios were obtained inside and outside the jar (data not shown), confirming the absence of effect on the chemical form of MDI. It was therefore considered that the jar produced a homogenous and representative atmosphere of a typical workplace in which MDI-based insulation foam is applied.

As a final step in this initial attempt, the CIP10M ($n = 5$) with DMPS + MOPIP (Puscasu *et al.*, 2014) was used inside the jar under the same conditions as the impingers were used to assess MDI concentration variability. As can be seen in Table 1, the MDI concentration levels obtained with the CIP10M containing DMPS + MOPIP were below the LOQ for each sampler. From this experiment, it was obvious that the CIP10M with DMPS + MOPIP would have to be modified before any further sampling comparison could be performed since the device did not collect or retain any MDI.

Several hypotheses can be made to explain the results obtained in Table 1 with the CIP10M containing DMPS + MOPIP. However, the hypothesis that had more impact in addressing the issue was the sample loss evaluation. To evaluate the potential

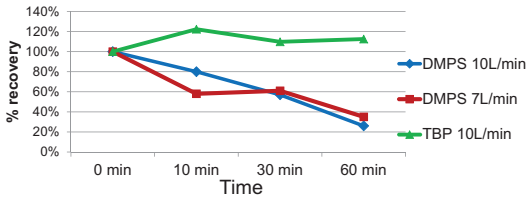


3 (A) Outside jar; (B) Inside jar.

Table 1. Homogeneity inside the jar.

Sampled MDI (mg m^{-3})				
Sampling time (min)	Impinger inside jar, $n = 8$ (1 l min^{-1})		CIP10M, $n = 5$ (10 l min^{-1})	
	Monomer	Oligomers	Monomer	Oligomers
45	0.17 ± 0.01	0.09 ± 0.01	X	X
54	0.17 ± 0.04	0.08 ± 0.02	X	X
31	X	X	<0.08	<0.08

sample loss, a known amount of MDI monomer was spiked inside the cup containing DMPS + MOPIP and the device was run for >1 h, and the residual MDI derivative was measured at several time points. The experiment was conducted at 10 and 7 l min^{-1}. The results are presented in Fig. 4. This figure shows that a significant amount of MDI monomer derivative is lost after 1 h. The experiment was also tried with MDI–MOPIP derivate and the same trend has been observed (data not shown). DMPS does not seem to be an efficient medium for MDI sampling with a CIP10M since sample loss occurs with this medium. DMPS was initially proposed because this substance is nonvolatile, nonflammable, and minimally toxic. At this point, the DMPS was replaced with TBP which is also nonvolatile, nonflammable and already used in some MDI sampling (Lesage *et al.*, 2007). As can be seen in Fig. 4, the replacement of DMPS with TBP addressed the sample loss issue. Since TBP is solvent-based, a solvation shell (Marcus, 1985) is



4 Sample loss evaluation.

Table 2. Analytical performances with TBP + MOPIP.

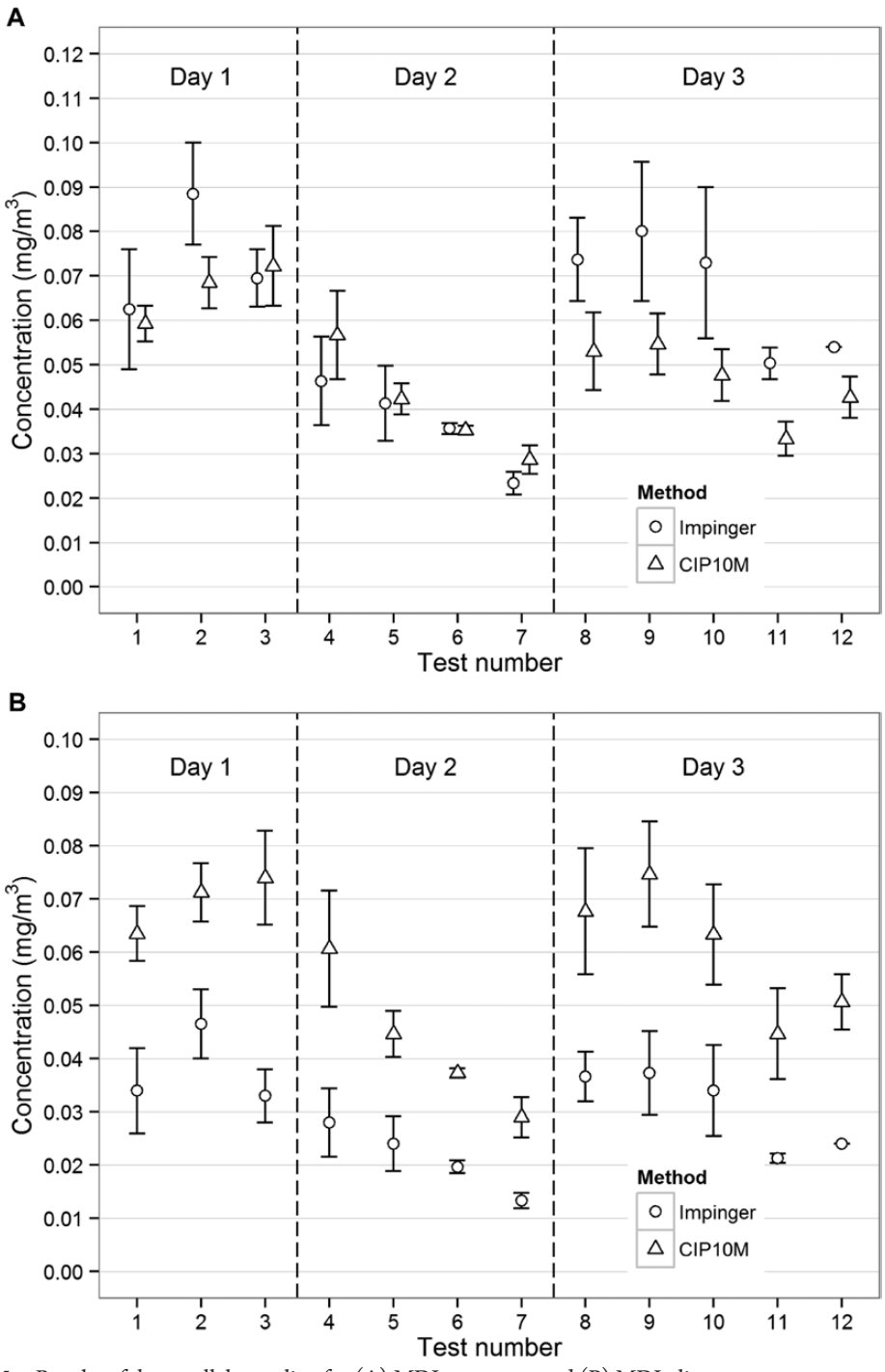
Analytical parameters	MDI-MOPIP
LOD	0.007 μg ml^{-1}
LOQ	0.024 μg ml^{-1}
Intraday precision	2%
Interday precision	1%
Recovery	99 ± 9%
Accuracy	98 ± 1%
Matrix effect	<5%

formed around the MDI derivative. This shell is not present with DMPS because this substance is polymer-based. The additional interaction offered by the TBP solvation shell seems to help retain the MDI derivative inside the CIP10M during centrifugation and avoid sample loss.

Some laboratory validation was conducted with the CIP10M containing TBP + MOPIP to establish the analytical performances. As was done with DMPS (Puscasu *et al.*, 2014), the reaction kinetics between the MDI and the MOPIP was measured (data not shown). Kinetics similar to the one obtained with an impinger was observed, as has been seen in the past for DMPS (Puscasu *et al.*, 2014). The use of TBP does not prevent the reaction between MDI and MOPIP, and a quantitative reaction is obtained. Analytical performances by HPLC-DAD have been previously described for DMPS (Puscasu *et al.*, 2014) and were re-established with TBP for the selectivity, specificity, recovery, matrix effect, carryover, dynamic range, LOD/LOQ, precision, and accuracy. Table 2 summarizes the analytical performances obtained with TBP. The analytical performances obtained were not different from the one obtained with DMPS and the method was ready to be tested in a field comparison.

Field comparison

The tests were conducted over three different days in order to obtain a sufficient number of samples to achieve statistical method reliability with a high level of confidence without overwhelming the workers. The three datasets are presented in Fig. 5A,B. One impinger had to be rejected for test 12 because of pump failure. As can be seen in Fig. 5A, the MDI monomer concentrations provided by the CIP10M sampling method were 14% (95% approximate confidence interval (CI): 2–26%) lower than the ones provided by the impingers. The CIP10M aspiration efficiency was not considered to be significantly different as compared to the impinger efficiency and thus cannot explain the difference observed in the results. However, a bias of 14% is considered very low compared to the typical environmental variability observed in exposure data in workplaces (Ignacio and Bullock, 2006). A closer look at Fig. 5A, Day 3 data, reveals a different trend as compared to Day 1 and 2 data between the impinger and CIP10M results, with a higher variability for the impinger results. When restricting the analysis to Days 1 and 2, the results show that the two sampling methods (i.e. CIP10M versus impingers) provided comparable results [difference of 0% (95% CI: −15 to 15%)]. Nevertheless, the authors were unable to explain the inconsistency observed in the MDI monomer results for Day 3. For oligomers, the CIP10M provided higher concentrations than the impingers as shown in Fig. 5B. The MDI oligomer concentrations provided by the CIP10M sampling method were approximately two times greater [difference of 94% (95% CI: 76–113%)] than the ones provided by the impingers as seen in Fig. 5B. This difference cannot be interpreted because even if the impinger were chosen as the reference method, the absolute recovery for MDI oligomers has never been formally established for this sampling technique. However, the amount of oligomers detected agrees with the formulation of the foams used. Moreover, the quantitation of the MDI triisocyanate as a discreet compound conducts to higher levels in the CIP10M as compared to the impinger. The CIP10M appears to be more efficient than the impingers for the collection and derivatization of MDI oligomers.



5 Results of the parallel sampling for (A) MDI monomer and (B) MDI oligomers.

Conclusion

CIP10M technology is promising for industrial hygienists who want to evaluate MDI levels when rapidly curing MDI-based products are sprayed. A CIP10M containing TBP + MOPIP provided MDI monomer concentrations with a negative bias between 2 and 26% as compared to the impinger reference method. However, the main portion of the

bias is due to inconsistent results obtained with the impingers on the third day of the evaluation since the first 2 days showed results without any statistical differences. Nevertheless, the inclusion of all the data represent a bias much lower than the typical environmental variability observed in an industrial hygiene context. The MDI monomer concentrations obtained with the CIP10M were therefore considered similar to those obtained with the reference impinger method. Moreover, MDI oligomer concentrations were sampled more efficiently with the CIP10M than with the impingers, as demonstrated by the positive bias obtained between 76 and 113%. This comparative study could be extended to other sampling devices available on the market for isocyanates, where formal comparison could be done using this study's setup.

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DISCLAIMER

The article contents, including any opinions and/or conclusions expressed, are those of the authors.

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