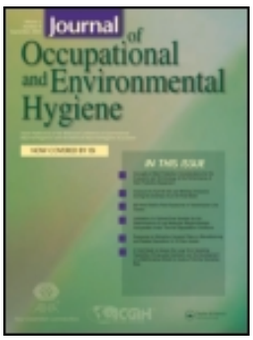

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A Comparison of Two Sampling Methods for the Detection of Airborne Methylene Bisphenyl Diisocyanate

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The purpose of this study was to determine if there was a significant difference between two readily available sampling methodologies for airborne methylene bisphenyl diisocyanate (MDI), which is an essential precursor in the spray-on truck bed lining industry. Seventy-two personal airborne samples of MDI were collected and analyzed from nine spray-on truck bed liner businesses in northern Colorado. Wide ranges of exposure concentrations were encountered during the spray-on application, including concentrations that exceeded the OSHA permissible exposure limit. The highest airborne MDI concentration measured was 690 ppb. A statistically significant difference between field-desorbed and laboratory-desorbed methods was determined. The field-desorbed sampling methodology yielded consistently higher MDI concentrations than the laboratory-desorbed sampling methodology, which suggests that immediate desorption minimizes isocyanate loss and potential underestimations. Results from the analysis of variance also indicated that different facility factors and environmental conditions within each company, such as the use of ventilation or humidity level, affected the MDI concentrations, indicating the potential for better mitigation of exposures using the hierarchy of controls.

Keywords field desorbed, laboratory desorbed, MDI, spray-on truck bed liner

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INTRODUCTION

Monomeric diisocyanates are a group of inherently reactive, bi-functional chemical species characterized by the presence of two NCO functional groups in varying positions on the parent compound.[1–5] Both aliphatic and aromatic moieties readily react with di- and poly-functional hydroxyl compounds (polyols and polyureas) in a typical two-component system resulting in the formation of polyurethanes.[1,5,6–10]

Polyols are compounds with multiple hydroxyl groups that serve as nucleophilic agents, which promote addition across the N=C double bonds.[8] As a result, repeat units of NHCOO groups are generated, which are characteristic of polyurethane (PUR) products that can be produced with varying degrees of mechanical strength, rigidity, or flexibility.[6–8,11–13] The functionality, moiety, and isomeric species of both the isocyanate and polyol help determine these properties to meet the needs for specific applications and emerging technologies.[6–8]

One industrial process involving a two-component spray application of isocyanate-containing materials is spray-on truck bed liners (STBLs), and the primary isocyanate used in this process is 4,4′-diphenylmethane diisocyanate, or monomeric MDI.[6] STBLs have gained popularity in the past 6 to 7 years and are estimated to involve 10,000 workers in over 2000 franchises nationwide.[14,15]

MDI is also used extensively in the synthesis of other rigid polyurethanes, which includes protective coatings for walls, decks, boats, as well as insulation materials for construction and industrial applications, such as refrigerators, freezers, piping, tanks, and shipbuilding.[13,16,17] The morphology of these foams typically exhibits a closed cell structure with superior mechanical properties (e.g., high compression strength, high strength-to-weight ratio, and low moisture permeability) and thermal stability (e.g., low thermal conductivity).

Domestic production capacity grew at a rate of 2.1% per year through 2004, and the trend is likely to continue at a high level as new markets and applications continue to develop.[6,18] As a result, the number of workers at risk for overexposures to MDI and toluene diisocyanate (TDI) will also increase.[9] According to a National Occupational Exposure Survey, approximately 280,000 U.S. workers are potentially exposed to MDI and TDI.[19]

Occupational exposure to MDI presents serious worker health concerns as it may lead to either short- or long-term health effects such as asthma, airway irritation, hypersensitivity pneumonitis, and irritation of skin and mucous membranes.[14,20] Inhalation is the most significant route of exposure due to the chemical and physical properties of MDI,

specifically, heating and spraying the two-component STBL product promotes volatilization and mechanical aerosolization of the MDI. For some sensitized individuals, acute exposure may prove fatal.[16] Contact dermatitis and irritation to mucous membranes are less common but may result in symptoms such as a rash, itching, hives, swelling of extremities, and irritation or serious burns to the eyes.[14,20]

To control monomeric MDI airborne exposures, the Occupational Safety and Health Administration (OSHA) mandates a ceiling permissible exposure limit (PEL) for monomeric MDI of 0.2 mg/m^3, which is equivalent to 20 ppb.[21] OSHA defines a ceiling value as an exposure limit that shall not be exceeded at any time during the working day for a particular substance. The ACGIH® recommends a threshold limit value (TLV®), 8-hr time-weighted average (TWA) of 0.051 mg/m^3 (5 ppb);[22] and the National Institute for Occupational Safety and Health (NIOSH) published a recommended exposure limit (REL) of 0.05 mg/m^3 (5 ppb) and a ceiling limit of 20 ppb for up to a 10-hr workday during a 40-hr workweek.[23] OSHA does not mandate an 8-hr TWA exposure limit as recommended by ACGIH and NIOSH.

Isocyanate sampling and analysis is challenging due to their chemical and physical properties that permit MDI to exist as a vapor or aerosol with a wide range of particle sizes.[5,6,24] While MDI does not readily volatilize at room temperature, certain processes may heat the isocyanate creating a vapor inhalation hazard. In addition, the reaction between MDI and a polyol is exothermic, consequently providing the heat necessary for volatilization.[5] Therefore, end users who spray MDI-based systems may encounter aerosol exposures from mechanical atomization of the material, as well as vapor exposures during exothermic reactions.

Other factors that must be considered when sampling isocyanates are the half-life, or cure rate, and particle size.[24] There are also different chemical species of isocyanates (e.g., monomeric, oligomeric, prepolymeric, and polyisocyanate forms) that may be present in any one sample. Depending on the form of isocyanate and physicochemical properties of the co-reactant (e.g., catalysis), a continuum of cure rates may range from seconds to hours.[24] Once sprayed, two-component STBL systems are considered to have a fast cure rate (i.e., less than a few minutes). These characteristics led to the development of a compilation of methods for sampling MDI based on specific derivatizing agents and timing of desorption.

NIOSH recommends an impinger method for airborne sampling during work operations that spray fast-curing isocyanates, especially when sampling times are not adjusted to the product half-life.[5,24,25] Consequently, loss of isocyanates to curing reactions can occur between collection and post-collection sample preparation. The impinger method uses a solvent medium to trap, dissolve, and derivatize the isocyanate aerosols to help prevent an underestimation of isocyanates.[5] Impinger methods are also recommended for processes that generate particles greater than 2 μm.[5,24] Impingers prevent the passage and allow dissolution of isocyanate particles greater than 2 μm; however, the use of an impinger is inconvenient and may prove to be unsuitable for certain conditions. For instance, the use of volatile solvents requires the impinger to be refilled due to evaporation. In addition, impingers are inherently hazardous, potentially exposing workers to solvents such as toluene and dimethyl sulfoxide. Furthermore, impinger solvents are potentially flammable.

Isocyanate personal samples are usually collected on filters by drawing a known volume of air through a glass fiber filter (GFF) coated with a derivatizing agent. The purpose of the derivatizing agent is two-fold: (1) a stable urea derivative is formed on reaction with isocyanates, and (2) analytical detection of the isocyanate is improved by strong molar absorptivities that increase sensitivity, or the limit of detection.[5,22]

Derivatizing agents are typically primary or secondary aliphatic amines.[5] Common derivatizing agents include tryptamine, 1-(2-methoxyphenyl) piperazine (MOPP), and 1-(9-anthracenylmethyl) piperazine (MAP) as listed in the *NIOSH Manual of Analytical Methods* for isocyanates; 9-(methylaminomethyl) anthracene (MAMA), which is used in the SKC Inc. Iso-Chek method; and, 1-(2-pyridyl) piperzine (1-2PP) as used in OSHA Method 47 for MDI.[26–29]

Tremblay et al.[30] investigated competitive rates of derivatization of several secondary amines and isocyanates. Relative differences were observed in MDI reactivity. The differences in reactivity were as follows (in decreasing order): dibutyl amine, MAP, MOPP, and MAMA. Steric hindrance was attributed to the observed differences in MDI reactivity. While slight differences in the reactivity of the reagents were reported, efficient mixing of MDI aerosols with the derivatizing agent is an essential step in the methodology.[5,25,31] Furthermore, inherent stability and high molar absorptivity of certain derivatizing agents may provide lower limits of detection when coupled with appropriate instrumentation.[6,32]

On reaction with the derivatizing agent, the isocyanate forms a urea derivative that is typically analyzed by isocratic reversed-phase high performance liquid chromatography (HPLC) in combination with a fluorescence detector.[32] HPLC separates the desired isocyanate-urea derivative from other compounds to accurately identify and quantify the isocyanate.

Airborne dust or particulate matter may physically hinder isocyanate groups from reacting with the derivatizing agent on the filter media.[33,34] For instance, MDI may be used as a binder in the manufacturing of engineered wood (e.g., medium-density fiberboard). Dust generated in wood mills during this application can impact the collection media and prevent contact of the isocyanate with the derivatizing agent. The isocyanate can be adsorbed onto the surface of the dust or particulate and undergo a curing reaction before a urea derivative is formed.[34] Consequently, the MDI in the sample is lost, and quantitative determinations of airborne concentrations underestimate exposure. These underestimations put the worker at potential risk for a recurring overexposure.

Isocyanate accessibility to the derivatizing agent is an important feature of reagent-coated GFFs, especially in two-component spray applications that consist of an isocyanate and

polyol mixture.[24,34] These PUR products rapidly cure with a half-life of less than 2 min. Micrographs of GFFs containing samples taken during spray applications show minimal contact with the reagent-coated fibers.[35] As a result, dispersal of the aerosol and mixing between isocyanate and reagent on the filter is negligible. In addition, the larger the aerosol, the greater the potential deficiency of reagent accessibility to the isocyanate group.[24] Unless the two components are separated, the curing reaction is disrupted and/or the two species are effectively brought together, then the MDI will not be preserved for quantitative analysis.[24] Instead, the MDI will be lost to a competitive reaction within the droplet despite its presence on the filter, and subsequently underestimated.[24]

To improve the performance of filter methods, the filter may be removed from the cassette in the field and desorbed immediately after sampling in a vial containing a solvent miscible with the reactants.[5,33] When the filter is desorbed, the extracting solvent will dissolve both the derivatizing reagent and any unreacted isocyanate, allowing the two to combine in solution and form a stable urea derivative. Streicher et al.[5] came to the general consensus that desorbing samples in the field immediately after sampling was a prudent practice. However, OSHA still prescribes filter desorption to occur at the analytical laboratory on receipt of sample shipment.

Currently, compliance officers use sampling method OSHA 47, which is based on a 37-mm GFF impregnated with the 1-(2-pyridyl) piperzine (1-2PP). The OSHA post-collection procedure assigns desorption of GFFs to the analytical laboratory, which uses a solution of 90% acetonitrile and 10% dimethyl sulfoxide (90/10 ACN/DMSO) to immerse the GFF. Alternatively, the Wisconsin Occupational Health Laboratory (WOHL) recommends field desorption of filters in their sampling method when using OSHA 47.

In an MDI stability study by Karoly,[33] samples were collected on 13-mm GFFs containing the derivatizing agent MOPP and 2% diethyl phthalate using a company-specific sampling and analytical method (ICI Polyurethanes Sampling and Analytical Method I 1024G, revision 1.7). Side-by-side samples were collected at four different wood mills from 1 to 3 hr, and sample preparation included one field desorbed (FD) and one laboratory desorbed (LD) filter within each sample set. Briefly, the FD filters were removed from the cassette, rinsed, and immersed in a vial containing derivatizing agent and toluene. LD samples were sealed in the cassette to be desorbed at the laboratory. Both sets of samples were sent to an analytical laboratory.

Field desorbed samples yielded statistically significant higher amounts of isocyanate as compared with LD samples. These results indicate that dusty environments have a negative impact on GFF methods used in isocyanate sampling. Most likely, FD samples promoted efficient mixing between MDI-coated dust particulates and MOPP.

While Karoly's study revealed limitations in using the LD method for GFF sampling in dusty environments, these results were based on proprietary methods (ICI Polyurethanes Sampling and Analytical Method I 1024G, revision 1.7) using the derivatizing agent MOPP. Our goal in this study was to ascertain if Karoly's results translated to those methods more readily used in the field for both consultation and compliance. We intend to narrow the gap in the understanding of sample collection for MDI in a fast reacting, two-component, spray-applied system.

Accordingly, we conducted side-by-side MDI sampling at STBL shops in northern Colorado to determine if there was a statistically significant difference between OSHA 47 and WOHL 48. We chose to monitor STBL environments because they generate aerosols that contain a mixture of isocyanate and polyol, as well as a wide range of particle sizes. These spray droplets and large particles have been conjectured as a limitation of the reagent-coated GFFs due to minimal contact between the isocyanate and the coated fibers. Our working hypothesis is that a significant difference exists between these two methods, and LD GFFs inherently underestimate MDI (as compared with FD GFFs) from significant loss to competitive reactions that cure the isocyanate before derivatization.

METHODS

This study was conducted according to written protocol approved by Colorado State University's (CSU) Research Integrity and Compliance Review Office. Subjects who performed STBL activities were recruited from nine STBL shops in Colorado. All shops employed the use of a two-component spray-on system that included MDI.

Sampling Methodology

The MDI sampling methodology for the FD and LD samples were based on drawing air through a 37-mm open-face cassette containing a glass fiber filter coated with 1.0 mg of 1-(2-pyridyl) piperazine (1-2PP) at a rate of 1.0 L/min for a maximum air volume of 15 L. However, post-sampling procedures were based on either the WOHL LC 48 FD method or the OSHA 47 LD method. Briefly, the OSHA 47 method dictates desorption of the sample filter at the analytical laboratory; the WOHL LC 48 method recommends immediate desorption of the filter after sampling in the field using a vial containing 2 mL of a 90/10 ACN/DMSO solution. All FD and LD samples were sent to the WOHL (an AIHA-accredited laboratory) for HPLC analysis.

We collected a total of 90 MDI paired samples; one sample was lost due to a collection error. The initial study design included an additional aim to evaluate inter-laboratory variability of analytical results by sending 17 LD-only samples to a second laboratory; however, this aim was abandoned due to attrition within the sample set as the 17 samples did not have detectable levels of derivatizing agent on the filters. Therefore, the total number of samples analyzed was 72 (46 FD and 26 LD). However, as presented in the next subsection, using the mixed procedure and analysis of variance approach,

appropriate inferences were still achieved for the unpaired FD samples.

Escort Electronic Laminar Flow (ELF) pumps (MSA, Pittsburgh, Pa.) were pre-calibrated at the sampling elevation to a flow rate of 1 L/min using an open-face cassette containing a 1-2PP treated filter with a backup pad connected in line to a DCLT-5K DC-Lite Primary Flow Meter (Bios International, Butler, N.J.). The MDI sampling cassettes and desorbing solution were stored in a refrigerator before use as prescribed by OSHA Method 47 and WOHL Method LC 48.

Two MSA pumps were attached to the applicator's waist, and Tygon tubing connected each pump to the sample cassettes. Cassettes were positioned so that one was on each shoulder, attached to the lapel of the worker's shirt as close to the breathing zone as possible, to perform side-by-side personal breathing zone air sampling. The medial or lateral placement of the LD and FD cassettes on the worker was chosen randomly. The sampling cassettes were changed every 15 min. If the spray-on process was completed in less than 15 min, the cassettes were removed on completion.

After the two sampling cassettes were removed from the applicator, the top cover and small plugs of the LD cassette were replaced and taped end to end. The FD filter was removed with forceps and placed into a glass vial containing 2 mL of 90/10 ACN/DMSO desorbing solution. The vial was gently agitated by the researcher, which ensured the filter was saturated with desorbing solution. The vial was sealed with the cap provided by WOHL and wrapped with tape around the top of the vial to prevent leaking. Field blanks were created using each method in their respective manners. Corresponding cassette and vial pairs were labeled with a specific sampling number that corresponded to the facility, date, sampling time, and air volume.

The sampling pumps were postcalibrated at the sampling elevation in the same manner as pre-calibration. None of the pre- and post-calibration values had a difference greater than 5%. All FD sample vials and LD cassettes were mailed overnight to WOHL.

Statistical Analysis

Because this was a pilot project, sample size and statistical power were not calculated a priori because variability was unknown for MDI sampling in this specific industry. Statistical Analysis System version 9.2 (SAS Institute, Cary, N.C.) was used to analyze all data using the MIXED procedure, with company and desorption method as fixed effects. Data were analyzed using analysis of variance (ANOVA) for a company fixed-model, and inferences were made only for the companies used in this study.

MDI sample concentrations reported in ppb were converted into 15-min TWAs to prevent bias from shorter sampling times. For example, ppb concentration was multiplied by time sampled and divided by 15. However, six samples exceeded the 15-min sampling time in four of the nine companies. While these samples could not be used for regulatory compliance, they were still normalized to a factor of 15 to make appropriate comparisons. Since the goal of this study was to determine if a significant difference exists between FD and LD methods in a side-by-side study, these normalized data were still valid to include.

Lower and upper confidence limits were calculated for samples only within a 15-min sampling time ($n = 66$) to show the wide range of airborne MDI concentrations that STBL workers encountered and while considering compliance with the OSHA ceiling PEL. The confidence limits were determined by calculating the standardized concentration (y) by dividing the 15-min TWA by the exposure limit of 20 ppb. Lower confidence limits (LCL) were calculated by subtracting the sampling and analytical error (SAE) from the standardized concentration, and upper confidence limits (UCL) were calculated by adding the SAE to the standardized concentration. If the UCL was less than 1, it was determined that an overexposure did not occur. If the LCL was less than 1 and the UCL was greater than 1, then a possible overexposure occurred. If the LCL was greater than 1, it was determined that overexposure occurred. To compare FD and LD results, data were $\log_{10}$ transformed subsequent to an observed normal distribution of the residuals with equal variance in a plot of residuals vs. predicted.

RESULTS AND DISCUSSION

A total of 72 samples were collected from nine STBL businesses in northern Colorado. As previously mentioned, paired sampling was not achieved in all nine companies. The data in Table I illustrate a wide range of airborne MDI concentrations that workers may encounter in a normal workweek. The standardized TWA was calculated for FD and LD results, as well as the lower and upper confidence limits using the reported SAE of 0.17. These results indicated that workers in Companies B (Sample 1), C (Samples 2 and 3), and H (Samples 1–6) encountered an overexposure.

Results from Companies B (Sample 2) and D (Samples 1 and 2) indicated that compliance with the OSHA ceiling PEL was a function of method selection. For instance, Sample 2 of Company B suggests an overexposure as reported by FD results (LCL $>$ 1), while the results from the other half of the side-by-side sample using the OSHA 47 LD method are consistent with a possible overexposure (LCL $<$ 1, UCL $>$ 1). FD results in Company D also reported an overexposure, but LD results suggested that a possible overexposure occurred.

Descriptive statistics of the data are presented in Table II. Due to the large standard deviation contrast between FD and LD samples, the coefficient of variation (CV) is reported for interpretations of the data. The CV indicates highly variable results (approximately two times the mean) within each method depending on the magnitude of the concentration reported between companies (221% for FD vs. 196% for LD). While the variability is constant between methods, higher concentrations, as seen in Company H, will experience larger deviations from the mean as opposed to those concentrations reported for Company E. Intra-company differences were also noted within

TABLE I. STBL Company Airborne MDI Data

Company	Sample	FD 15-Min TWA (ppb)	LD 15-Min TWA (ppb)	FD LCL	FD UCL	LD LCL	LD UCL
A	1	6.8	4.3	0.17	0.51	0.05	0.39
	2	10	6.2	0.33	0.67	0.14	0.48
	3[A]	3.1	2.0	NA	NA	NA	NA
	4	2.5	1.4	−0.05	0.29	−0.10	0.24
	5	2.3		−0.05	0.29		
	6	3.0		−0.02	0.32		
B	1[B]	50	49	2.3	2.7	2.3	2.6
	2[C]	41	22	1.9	2.2	0.93	1.3
	3	14	6	0.53	0.87	0.13	0.47
C	1[A]	83	52	NA	NA	NA	NA
	2[B]	81		3.9	4.2		
	3[B]	140		6.8	7.2		
D	1[C]	32	22	1.4	1.8	0.93	1.3
	2[C]	23	8.3	1	1.3	0.25	0.59
	3	12	15	0.42	0.76	0.6	0.94
	4	8.7		0.26	0.60		
	5	6.2		0.14	0.48		
	6[A]	16		NA	NA		
	7	6		0.13	0.47		
	8	8	1.4	0.23	0.57	−0.10	0.24
	9	17		0.70	1.0		
	10	17		0.68	1.0		
	11	16		0.60	0.94		
	12	17		0.67	1.0		
E	1	21	16	0.88	1.2	0.62	0.96
F	1	0.17		–0.16	0.18		
	2	0.13	0.12	–0.16	0.18	–0.16	0.18
	3	0.27	0.17	–0.16	0.18	–0.16	0.19
	4	0.18	0.13	–0.16	0.18	–0.16	0.18
	5	0.13		–0.16	0.18		
	6	0.13		–0.16	0.18		
	7	0.13		–0.16	0.18		
G	1[A]	0.45		NA	NA		
	2	0.13		−0.16	0.18		
	3	0.32	0.12	−0.15	0.19	−0.16	0.18
	4	0.29	0.12	−0.16	0.18	−0.16	0.18
H	1[B]	300	48	15	15	2.2	2.6
	2[B]	100	96	5.0	5.4	4.6	5.0
	3[B]	690	58	34	35	2.7	3.1
	4[B]	380	46	19	19	2.1	2.5
	5[B]	330	350	16	17	17	18
	6[B]	230	150	11	12	7.3	7.7
I	1	9.4	7.6	0.3	0.64	0.21	0.55
	2	3.4	4.2	0	0.34	0.04	0.38
	3	13		0.48	0.82		
	4	5.2		0.09	0.43		

[A]Samples that exceed 15 min (Company A, Sample 1: 18 min; Company B, Sample 1: 17 min; Company C, Sample 1: 16 min; Company E, Sample 1: 16 min).
[B]Samples that exceed the OSHA PEL (as indicated by the upper confidence limit).
[C]Samples that reported an overexposure by FD and a possible overexposure by LD.

TABLE II. MDI Field Desorbed Samples vs. Laboratory Desorbed Samples

	Mean (ppb)	Standard Deviation (ppb)	Coefficient of Variation	Range (ppb)
Field desorbed	58.8	130.5	2.22	0.13–690
Lab desorbed	37.2	72.9	1.96	0.12–350

each method. For instance, in Company C there was a two-fold difference between FD Sample 1 and FD Sample 6. FD samples from Company G and Company H reveal an approximately four- and six-fold company difference, respectively.

Statistical analyses were conducted using an alpha of 0.05. Results from the post-hoc analysis (Type 3 Tests of Fixed Effects) indicate that: (1) the effect of company is statistically significant ($p = <0.001$), and (2) the effect of methods is statistically significant ($p = 0.0038$). The interaction effect of company by desorption method was not statistically significant ($p = 0.5171$). An effect size of 0.22 between FD and LD was concluded as significant (mean FD = 0.93, SE = 0.050; mean LD = 0.71, SE = 0.62).

The statistically significant inter-company effect is obvious in that each company differs in their range of MDI concentrations (shown in Table III), which can be attributed to company-specific factors and environmental variables such as ventilation and humidity, respectively. These inter-company differences are illustrated in Figure 1 using error bars that represent a ± 1.4 SE confidence interval.

TABLE III. Log $_{10}$ Transformed MDI Estimates

Company	MDI Estimate
A	0.51
B	1.4
C	1.9
D	0.98
E	1.3
F	−0.85
G	−0.76
H	2.2
I	0.81

Concurrent with this study, the investigators evaluated certain variables believed to affect airborne MDI concentrations. The investigators collected personal MDI air samples while measuring the following variables: percentage MDI in bed liner product, process temperature and pressure, temperature and humidity of the paint booth during application, quantity of

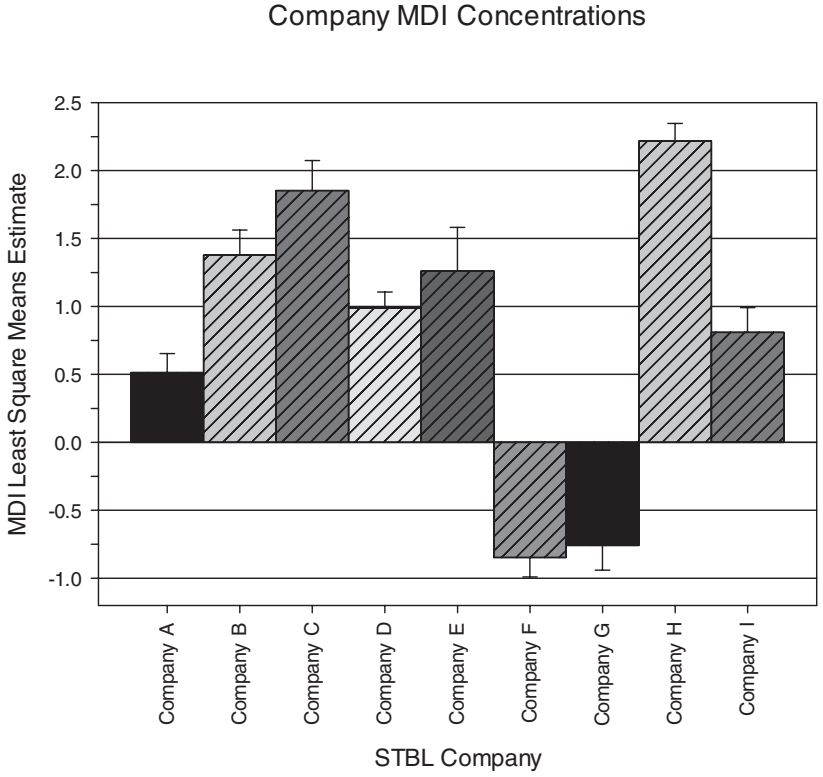

FIGURE 1. Inter-company differences among nine STBL shops in Colorado using a two-component spray-on system that included MDI (error bars are equal to ± 1.4 SE)

TABLE IV. Log $_{10}$ Transformed MDI Estimates for FD and LD Methods

Company	Desorption Method	MDI Estimate
A	FD	0.60
	LD	0.43
B	FD	1.5
	LD	1.3
C	FD	2.0
	LD	1.7
D	FD	1.1
	LD	0.86
E	FD	1.3
	LD	1.2
F	FD	–0.81
	LD	–0.89
G	FD	–0.58
	LD	–0.94
H	FD	2.5
	LD	1.9
I	FD	0.83
	LD	0.79

product used per truck, flow rate of the ventilation system, face velocity, capture velocity, air changes per minute, vehicle orientation in the paint booth, booth volume, and truck bed size.

Final conclusions of the data have not been made; however, percentage of MDI in product, process temperature, capture velocity, and air changes per minute are putative candidates that may affect personal airborne exposures to MDI. The percentage of MDI likely explains the similar MDI estimates in Companies A and I, B and C, and F and G. Comparable process temperatures between Companies D and E may account for the estimates observed in Figure 1. The ceiling location of the ventilation system in the spray booth of Company H may have pulled MDI through the applicator's breathing zone, which increased the applicator's exposure and inflated the MDI sample concentrations, as seen in Figure 1.

The least square means estimate of MDI concentrations are presented in Table IV for both FD and LD sampling methods. Relative measures of difference (based on log transformation) were used to compare FD and LD methods to ensure accurate interpretation of the results. The effect of desorption method remained fairly consistent across all nine STBL companies. However, intra-company comparisons of desorption methods did not show statistically significant differences, which could be attributed to lack of sample size collected at each company.

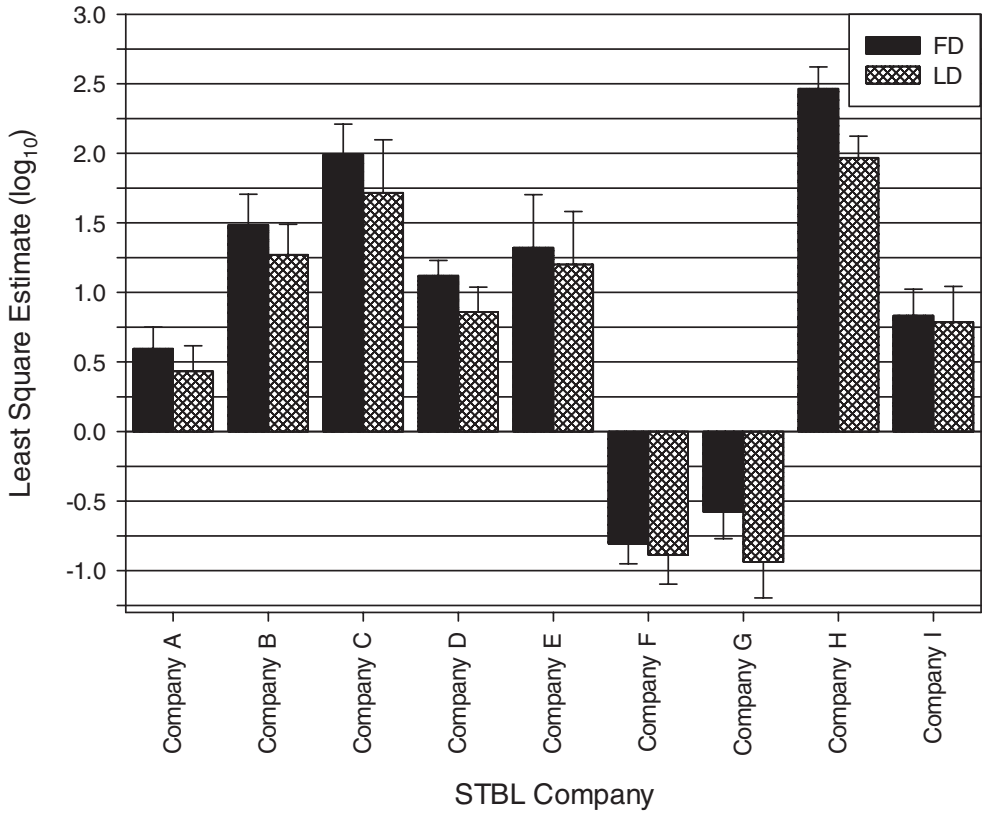

FIGURE 2. Overall difference between FD and LD methods across all nine companies (error bars are equal to ± 1.4 SE)

The overall difference observed between FD and LD methods across all nine companies was statistically significant and was unlikely due to chance alone. The FD least square estimate in each company demonstrated a greater recovery of MDI when compared with LD methods (Figure 2), which indicates potential underestimation of MDI concentrations when using LD methods. This difference was in agreement with Karoly's study;[33] however, dust putatively obstructed derivatization of the isocyanate on the filter in Karoly's study. Immediate desorption of the filter in the FD method rendered the isocyanate into an HPLC-ready derivative instead of reacting with the wood dust, moisture, or itself. These competitive reactions most likely explain the smaller amounts of MDI observed in the LD results in Karoly's study.

The STBL trend of higher values of MDI observed in the FD results can most likely be attributed to the generation of large MDI aerosols that prevent complete contact with 1-2PP, since dusty environments were not encountered. Contact between isocyanate in a large droplet and reagent coated on the fiber is probably minimal, allowing MDI to react within the droplet or other nucleophilic agents present in the workplace. Lesage et al.[25] investigated MDI particle size in the application of polyurethane spray foam (a two-component system) in residential construction while comparing results from filter and impinger samples collected in the breathing zone of a spray foam applicator.

Using a Marple 8-stage impactor (BGI, Waltham, Mass.), the majority of the spray foam particles were greater than 10 μm, and approximately 20% of the fractions collected were respirable. Filter sampling methods reported airborne MDI concentrations that were 6% to 40% lower than impinger determined concentrations. We attributed this difference to the observed particle size distribution. More research is needed to narrow the gap in understanding the effects of particle size on quantitative determinations of MDI.

Study Limitations

This field study was conducted at different STBL businesses in northern Colorado and, as a result, suffered limitations that are inherent with field investigations. Not all variables were controlled, such as ventilation system characteristics, percentage MDI in bed liner products, temperature, and humidity; these variables may have impacted sampling results. For instance, ventilation system characteristics such as capture velocities and air changes per minute may have been significantly different between companies. Therefore, airborne MDI concentrations may have been affected. In addition, percentage MDI in products can play a pivotal role in the airborne concentration. If one company uses a smaller percentage of MDI for their end product as compared with another company with a higher percentage of MDI, the airborne concentration may be significantly different between companies.

There was not adequate statistical power to determine within each company if a significant difference existed between FD and LD as a result of sample attrition that was experienced from attempting to evaluate inter-laboratory variance.

CONCLUSION

Over one-third of the breathing zone samples collected by both FD and LD methods in STBL applicators exceeded the OSHA-PEL-C, as seen in Table I. However, according to LD results from Companies B and D, worker exposures were below the PEL, whereas FD results generated an LCL consistent with an overexposure to MDI.

Results from the side-by-side comparison of the OSHA and WOHL methods for airborne MDI were significantly different. MDI estimates presented in Table III illustrate the impact company differences have on the amount of monomeric MDI present in the breathing zones.

The overall FD results presented in Table IV generated higher airborne MDI results than those observed for LD. Immediate desorption of the filter may have minimized the loss of unreacted MDI to competing reactions and, ultimately, an underestimation of the airborne concentration collected in the breathing zone of the worker. GFFs used in both the FD and LD methods have been recommended for particles less than 2 μm due to greater likelihood of dispersion and mixing between fiber and isocyanate.[24,35] More research is needed to determine if aerosols generated during the STBL process were greater than 2 μm, which may have affected the derivatization efficiency of the filter. This raises a concerning question regarding the accuracy of both the FD and LD methods and the interpretation of their results for protecting worker health, especially since the preferred sampling method for two-component spray applications is the use of an impinger method.

Since this study was conducted in the field, the true concentration of MDI present during sampling was unknown. Without having a true concentration against which to compare sample results, true accuracy of each method could not be determined, only that a difference between the two methods existed.

RECOMMENDATIONS

Although numerous methods exist to quantify airborne MDI, there is greater incentive to use method OSHA 47 to comply with the only enforceable occupational exposure limit. While LD filters can result in lower quantification of airborne MDI when compared to FD filters, further research is needed to determine which MDI sampling method (OSHA 47 or WOHL 48) is more accurate to ensure worker health; however, impinger methods remain as the preferred method for monitoring worker exposure to isocyanates. The authors are currently developing an MDI aerosol delivery system to mimic the spray technique in STBL facilities. The aim is to deliver and collect known MDI concentrations using serial dilutions of an acquired STBL bulk sample in a controlled setting to minimize typical environmental variables, which may otherwise interfere in field studies. The experimental results will be compared with theoretical results, which can be calculated from each MDI working solution concentration, the flow rate of MDI delivery, and sampling time. By comparing observed to

theoretical, the accuracy and consistency of each diisocyanate field sampling method can be determined.

Particle size effects of MDI aerosols should be determined to comprehensively evaluate the accuracy of the OSHA and WOHL sampling methods over a wide range of diameters, especially since particle sizes from spray-on applications largely fluctuate.

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REFERENCES

1. **Woolrich, P.F.:** Toxicology, industrial hygiene and medical control of TDI, MDI and PMPPI. *Am. Ind. Hyg. Assoc. J. 43*:89–98 (1982).
2. **Weyel, D.A., and R.B. Schaffer:** Pulmonary and sensory irritation of diphenylmethane-4,4′- and dicyclohexylmethane-4,4′-diisocyanate. *Toxicol. Appl. Pharmacol. 77*:427–433 (1985).
3. **Nakashima, K., T. Takeshita, and K. Morimoto:** Review of the occupational exposures to isocyanates: Mechanisms of action. *Environ. Health Prev. Med. 7*:1–6 (2002).
4. **Deschamps, F., A. Prevost, F. Lavaud, and S. Kochman:** Mechanisms of occupational asthma induced by isocyanates. *Ann. Occup. Hyg. 42*:33–36 (1998).
5. **Streicher, R., C. Reh, R. Key-Schwartz, P. Schlecht, M. Cassinelli, and P. Connor:** Determination of airborne isocyanate exposure: Considerations in method selection. *Am. Ind. Hyg. Assoc. J. 61*:544–556 (2000).
6. **Allport, D., D. Gilbert, and S. Outterside:** *MDI & TDI: Safety, Health, and the Environment*. Chichester, U.K.: John Wiley & Sons Ltd., 2003.
7. **Ashida, K.:** *Polyurethane and Related Foams (Chemistry and Technology)*. Boca Raton, Fla.: Taylor & Francis Group, 2007.
8. **Ulrich, H.:** *Chemistry and Technology of Isocyanates*. Chichester, U.K.: John Wiley & Sons Ltd., 1996.
9. **Henneken, H., M. Vogel, and U. Karst:** Determination of airborne isocyanates. *Bioanal. Chem. 387(1)*:219–236 (2007).
10. **Bello, D., S.R. Woskie, R.P. Streicher, et al.:** Isocyanates in occupational environments: A critical review of exposure limits and metrics. *Am. J. Ind. Med. 46(5)*:480–491 (2004).
11. **Raulf-Heimsoth, M., and X. Baur:** Pathomechanisms and pathophysiology of isocyanate-induced diseases—Summary of present knowledge. *Am. J. Ind. Med. 34(2)*:137–143 (1998).
12. **Cummings, B.J., and K.S. Booth:** Industrial hygiene sampling for airborne TDI in six flexible slabstock foam manufacturing facilities in the United States: A comparison of the short-term and long-term sampling data. *Appl. Occup. Environ. Hyg. 17*:863–871 (2002).
13. **Kim, S.H., B.K. Kim, and H. Lim:** Effect of isocyanate Index on the Properties of Rigid Polyurethane Foams by HFC 365mfc. *Macromolec. Res. 16(5)*:467–472 (2008).
14. **Chester, D., E. Hanna, B. Pickelman, et al.:** Asthma death after spraying polyeurethane truck bedliner. *Am. J. Ind. Med. 48*:78–84 (2005).
15. **Brooks, E.:** OSHA Compliance Issues—Isocyanate exposure in an autobody repair and collision center. *J. Occup. Environ. Hyg. 3*:D24–D27 (2006).
16. **Lofgren, D., T. Walley, P. Peters, and M. Weis:** MDI exposure for spray-on truck bed lining. *Appl. Occup. Environ. Hyg. 18*:772–779 (2003).
17. **Kang, M.J., Y.H. Kim, G.P. Park, M.S. Han, W.N. Kim, and S.D. Park:** Liquid nucleating additives for improving thermal insulating properties and mechanical strength of polyisocyanurate foams. *J. Mater. Sci. 45*:5412–5419 (2010).
18. "Toluene Diisocyanates." Available at http://ntp.niehs.nih.gov/ntp/roc/twelfth/profiles/Toluenediisocyanates.pdf (accessed September 12, 2012).
19. **Pronk, A., L. Preller, M. Raulf-Heimsoth, et al.:** Respiratory symptoms, sensitization, and exposure response relationships in spray painters exposed to isocyanates. *Am. J. Respir. Crit. Care Med. 176(11)*:1090–1097 (2007).
20. **Lushniak, B., C. Reh, D. Bernstein, and J. Gallagher:** Indirect assessment of 4,4′-diphenylmethane diisocyanate (MDI) exposure by evaluation of specific humoral immune responses to MDI conjugated to human serum albumin. *Am. J. Ind. Med. 33*:471–477 (1998).
21. "Toxic and Hazardous Substances," *Code of Federal Regulations Title 29*, Part 1910. Subpart Z.
22. **ACGIH:** *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*. Cincinnati, Ohio**:** ACGIH, 2006.
23. **National Institute for Occupational Safety and Health (NIOSH):** *NIOSH Pocket Guide to Chemical Hazards*. Pub. No. 2005-149. Cincinnati, Ohio**:** NIOSH, 2005.
24. **Streicher, R.P., C.M. Reh, R.J. Key-Schwartz, P.C. Schlecht, and M.E. Cassinelli:** Determination of airborne isocyanates. In *NIOSH Manual of Analytical Methods*. DHHS (NIOSH) Pub. 94-113. P.C. Schlecht and P.F. O'Connor (eds.). Cincinnati, Ohio**:** DHHS, NIOSH, 1994.
25. **Lesage, J., J. Stanley, W. Karoly, and F.W. Lichtenberg:** Airborne methylene diphenyl diisocyanate (MDI) concentrations associated with the application of polyurethane spray foam in residential construction. *J. Occup. Environ. Hyg. 4*:145–155 (2007).
26. "Total Isocyanates, Method 5525." Available at http://www.cdc.gov/niosh/docs/2003-154/pdfs/5525.pdf (accessed September 12, 2012).
27. "ISO-CHEK. Simultaneous and Separate Collection of Isocyanate." Available at http://www.skcinc.com/prod/225-9022.asp (accessed September 12, 2012).
28. "Isocyanates (Organic Methods #47)." Available at http://www.osha.gov/dts/sltc/methods/organic/org047/org047.html (accessed September 12, 2012).
29. "Isocyanates (Organic Methods #42)." Available at http://www.osha.gov/dts/sltc/methods/organic/org042/org042.html (accessed September 12, 2012).
30. **Tremblay, P., J. Lesage, C. Ostiguy, and H.V. Tra:** Investigation of the competitive rate of derivatization of several secondary amines with phenylisocyanate (PHI), hexamethylene-1,6-diisocyanate (HDI), 4,4′-methylenebis(phenyl isocyanate) (MDI) and toluene diisocyanate (TDI) in liquid medium. *Analyst 128(2)*:142–149 (2003).
31. **Streicher, R.P., J.E. Arnold, M.K. Ernst, and C.V. Cooper:** Development of a novel derivatization reagent for the sampling and analysis of total isocyanate group in air and comparison of its performance with that of several established reagents. *Am. Ind. Hyg. Assoc. J. 57*:905–913 (1996).
32. **Levine, S.P., K.J.D. Hillig, V. Dharmarajan, M.W. Spence, and M.D. Baker:** Critical review of methods of sampling, analysis, and monitoring for TDI and MDI. *Am. Ind. Hyg. Assoc. J. 56*:581–589 (1995).
33. **Karoly, W.J.:** Stability of diphenylmethane diisocyanate (MDI) on glass fiber filters. *Am. Ind. Hyg. Assoc. J. 59*:645–647 (1998).
34. **Booth, K., B. Cummings, W.J. Karoly, et al.:** Measurements of airborne methylene diphenyl diisocyanate (MDI) concentration in the U.S. workplace. *J. Occup. Environ. Hyg. 6***:** 228–238 (2009).
35. **Bell, J.:** "Evaluation of the OSHA 42 and NIOSH 5521 Methods in Determining the Free Isocyanate Concentration in Aerosols and Vapor Phases During Application of Two Component 1, 6-Hexamethylene Diisocyanate Paints." Master's thesis, Texas A&M University, College Station, Texas, 1994.