

ABSTRACT

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LABORATORY AND FIELD COMPARISONS OF AIR SAMPLING METHODS FOR 1,6-HEXAMETHYLENE DIISOCYANATE (Under the direction of Dr. Leena A. Nylander-French)

The published literature on evaluation of sampling devices and methods for determining workers' exposure to diisocyanate-containing compounds is conflicting and most of the methods have not been tested in both a laboratory and occupational setting. The objective of this study was to evaluate the performance of commonly used sampling devices for 1,6-hexamethylene diisocyanate (HDI) in both the laboratory and occupational field setting. Polystyrene (PS) and polypropylene (PP) cassettes with treated filters, IOM cassettes, OSHA Method 42 cassettes, and IsoChek[®] cassettes were evaluated in the laboratory setting. Recovery of HDI mass using either toluene (HDI/TOL) or acetonitrile (HDI/ACN) as solvents was determined. In the laboratory, the IOM and 25-mm PP cassette types recovered the most HDI mass (>77%) while the IsoChek[®] performed the worst recovering <16% of HDI mass. The reactivity of HDI with different filter housings and sampling materials was determined by spiking pure HDI, HDI/TOL, or HDI/ACN onto filter housings and sampling materials. Pure HDI and HDI/TOL were most reactive with PS and the reaction of HDI with sampling materials was amplified by the presence of a non-polar solvent (i.e., TOL). The sampling efficiencies of 1- and 2-stage PP and PS cassettes were compared to an impinger in

the occupational setting by spraying fast- or slow-drying clear coat containing HDI polyisocyanates above the samplers. No significant difference was observed in HDI monomer recovery between PP and PS samplers. However, significant difference ($p < 0.05$) was observed in the recovery of HDI oligomers between 1- and 2-stage cassettes and between fast- and slow-drying clear coats. The 1-stage cassettes recovered more HDI monomer and oligomer when a fast-drying clear coat was applied. In summary, this study provides evidence that sampling losses may occur due to the reactivity of HDI with sampling materials or with polyols in automotive paint overspray. We also demonstrate the importance of performing experiments in both the laboratory and occupational setting. Experiments performed in the occupational setting indicate that the type of clear coat used during spray-painting activities should be considered when selecting a sampler for monitoring exposure to HDI.

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LIST OF ABBREVIATIONS

1-2PP	1-(2-pyridyl)-piperazine
ACN	Acetonitrile
DMF	<i>N,N</i> -Dimethylformamide
GFF	Glass fiber filter
HDI	1,6-hexamethylene diisocyanate
HPLC	High pressure liquid chromatography
IOM	Institute of Occupational Medicine
LC-MS	Liquid chromatography – mass spectrometry
MAMA	9-(<i>N</i> -methylaminomethyl) anthracene
MAP	1-(9-anthracenylmethyl)-piperazine
MDI	Methylene bisphenyl diisocyanate
MPP	1-(2-methoxyphenyl)-piperazine
N	Sample number
NDI	Naphthalene diisocyanate
NIOSH	National Institute for Occupational Safety and Health
ODIU	Octamethylene diisocyanate urea derivative

OSHA	Occupational Safety and Health Administration
PP	Polypropylene
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
TDI	Toluene diisocyanate
TOL	Toluene
UV	Ultraviolet

CHAPTER I

INTRODUCTION

According to the National Institute for Occupational Safety and Health (NIOSH), isocyanates are highly reactive, low molecular weight chemicals (NIOSH 2006). They are used in the manufacturing of foams, fibers, coatings, and elastomers. They are also increasingly used in the auto industry, auto-body repair, and building insulation materials. Isocyanates are known powerful irritants to the mucous membranes of the eyes and gastrointestinal and respiratory tracts (NIOSH 2006). The most widely used compounds are diisocyanates, which contain two isocyanate groups, and polyisocyanates, which are usually derived from diisocyanates and may contain several isocyanate groups. The most commonly used diisocyanates include methylene bis-phenyl diisocyanate (MDI), toluene diisocyanate (TDI), and 1,6-hexamethylene diisocyanate (HDI). Other common diisocyanates include naphthalene diisocyanate (NDI), methylene bis-cyclohexylisocyanate (HMDI) (hydrogenated MDI), and isophorone diisocyanate (IPDI). Examples of widely used polyisocyanates include HDI biuret and HDI isocyanurate (NIOSH 2006).

Most paints used for automobile finishing consist of polyisocyanates based on HDI, which contain trace amounts of HDI-monomer (NIOSH 1983; Science-Applications-International-Corp. 1997). The measurement of airborne isocyanate-containing compounds continues to be a challenge in the industrial hygiene field. Sampling is difficult because, in

the spray-painting environment, HDI monomer and HDI-based oligomers are present in both aerosol and vapor phases (England et al. 2000). According to Streicher et al. (1994), isocyanates are very reactive and, therefore, unstable after collection and cannot simply be collected on a filter. The isocyanates can be lost through reaction with other compounds in the aerosol particle or simultaneously collected on the filter. Therefore, it is necessary to derivatize the isocyanate species rapidly upon collection. Filters and sorbents impregnated with derivatizing reagent as well as an impinger or a bubbler containing solution of derivatizing reagent have been used for the collection of isocyanate aerosol. However, neither filters nor impingers appear to adequately sample for the entire range of isocyanate aerosol likely to be encountered in the workplace (Streicher et al. 1994). Particles smaller than 2 μm in diameter are not efficiently collected by an impinger and isocyanate species present in large particles are not efficiently derivatized when collected on reagent-coated filters (Nordqvist et al. 2005, Streicher et al. 1994, Spanne et al. 1999).

There are several methods for the measurement and analysis of HDI monomer and HDI-based oligomer present in both the aerosol and vapor phase. Some common sampling devices include a variety of cassettes with treated filters, Institute of Medicine (IOM) cassettes, Occupational Safety and Health Administration (OSHA) Method 42, and IsoChek[®] cassettes.

The IOM sampler is a 25-mm inhalable sampler developed by the IOM. The IOM sampler, which meets the sampling criteria for inhalable particulate mass set by American Conference of Governmental Industrial Hygienists (ACGIH), is a conductive plastic sampling head that houses a reusable 25-mm filter cassette with specified filter for the collection of inhalable airborne particles. When attached to a personal sampling pump

operating at 2 L/min and clipped near a worker's breathing zone, the IOM effectively traps particles up to 100 μm in aerodynamic diameter and closely simulates the manner in which airborne workplace particles are inhaled through the nose and mouth (SKC 2007). Bello et al. (2002) compared stainless steel IOM samplers loaded with 25-mm quartz fiber filters impregnated with 500 μg of 1-(9-anthracenylmethyl)piperazine (MAP) with MAP impinger samples. They found that impingers and treated filter IOMs perform equally well with respect to collection efficiency for the monomer and total oligomeric HDI.

OSHA Method 42 is the most widely used and represents the current state-of-the-art against which all other methods must be measured (Levine 2002). Since this method is used by OSHA, there is a great incentive for US companies to use it. The method uses 1-(2-pyridyl) piperazine (1-2PP) on a glass fiber filter (GFF), with solvent desorption in the laboratory and high-performance liquid chromatography (HPLC) analysis using ultraviolet (UV) or fluorescence detector. Samples are collected by drawing a known volume of air through a GFF coated with 0.1 mg of 1-2PP that are contained in open-face 37-mm polystyrene (PS) cassettes. A limitation of the OSHA Method 42 is that it only identifies and quantitates the isocyanate monomer (Rando et al. 2002). It has also been reported that the OSHA Method 42 may underestimate isocyanate in aerosol form when sampling for extended periods (Podlak et al. 1987). In a comparison study of isocyanate sampling methods for HDI monomer and HDI oligomer in spray-painting environments OSHA Method 42 appeared to have the greatest variability when compared to other methods (England et al. 2000).

The IsoChek® sampler consists of a three-piece cassette containing an untreated polytetrafluoroethylene (PTFE) filter to collect aerosol and/or particulate and a treated GFF

to collect vapor phase isocyanates (SKC 2006). The GFF is impregnated with 9-(N-methylaminomethyl) anthracene (MAMA) for the collection of vapor phase isocyanates. IsoChek[®] samples are analyzed using HPLC/UV detection. There have been several criticisms of the IsoChek[®] sampler in the literature (Nordqvist et al. 2005, Rando et al. 2002). In a controlled laboratory study, the IsoChek[®] sampler significantly underestimated TDI and MDI monomer concentrations and inaccurately apportioned them into vapor and aerosol phases (Rando et al. 2002). The two-stage filter sampling system may produce biased results due to evaporation of aerosol off the PTFE filter and adsorption of vapor onto the PTFE filter (Nordqvist et al. 2005). However, in a field study performed by England et al. (2000), the IsoChek[®] sampler collected HDI monomer concentrations that did not differ significantly from four other commonly used sampling methods (NIOSH 5521, NIOSH 5522, MAP (proposed NIOSH method), and OSHA Method 42). However, for HDI-based polyisocyanates, England et al. (2000) found that NIOSH 5522, NIOSH 5521, IsoChek[®], and the Total Aerosol Mass Method (TAMM) were significantly different from one another.

A two-stage filter cassette system developed in our laboratory has been used for sampling HDI in auto-body shops. This 2-stage filter system is similar to the IsoChek[®], however, the impregnation solution and analysis methods are different. The first stage of the cassette is a PTFE filter for the collection of aerosol followed by a GFF coated with 400 μ L of 1-(2-methoxyphenyl)-piperazine (MPP) to collect vapor. The same criticisms of the IsoChek[®] may apply to this sampler.

It is important to perform experiments in the laboratory and the field because the occupational environment differs greatly from a controlled laboratory setting. According to Streicher et al. (1994), in laboratory-generated isocyanate atmospheres, water is likely the

only species competing with the derivatizing reagent for the available isocyanate. In the occupational environment, particles contain isocyanate, polyol, and catalysts and, therefore, the lifetime of isocyanate species in such particles may be very short. They also state that in the absence of solvent, isocyanate-polyol mixtures are not readily dispersed and reagent may not readily be transported to the isocyanate, therefore allowing time for the isocyanate to be lost through reaction with polyol.

Sennbro et al. (2004) compared two different devices for sampling phenyl isocyanate: (1) a PS cassette with single impregnated GFF, and (2) a polypropylene (PP) cassette with two impregnated GFFs. The methods collected approximately 30 and 55% of phenyl isocyanate, respectively. Because phenyl isocyanate has similar physical properties to HDI, the observations made in this study and by Sennbro et al. (2004) may indicate that isocyanate vapor is reacting or adhering to certain types of plastics.

The objective of this study was to evaluate the performance of commonly used air sampling devices for HDI in both the laboratory and occupational field setting. A variety of sampler types were evaluated and compared in the laboratory and occupational environments. The recovery of HDI vapor generated in the laboratory for several sampling devices was determined. The reactivity of HDI with different cassettes and sampling materials was determined in the laboratory setting. Collection efficiencies of several sampler types were investigated in a spray-painting facility during application of clear coat.

CHAPTER II

MATERIALS & METHODS

I. Laboratory Experiments

The objective of these experiments was to determine the recovery of HDI vapor generated in the laboratory using several sampling devices. The following sampling devices were tested and are summarized in **Table 1**:

- A) 1-stage 37-mm PS and 1-stage 37-mm PP cassettes,
- B) IOM and 25-mm PP cassettes, and
- C) OSHA Method 42, IsoChek[®], and 2-stage 37-mm PS cassettes

A) Experiment using 1-Stage 37-mm PS and PP Cassettes

The recovery of HDI vapor using 1-stage 37-mm open-face PS cassettes as well as open and closed-face 37-mm PP cassettes was determined in this experiment. The objective of this experiment was to compare polypropylene and polystyrene cassettes as well as different flow rates and open- vs. closed-face sampling methods. GFF (Type AE, SKC, Eighty Four, PA) were impregnated with 400 μ L of MPP impregnation solution and allowed to dry for 15 min and then placed in the cassette housing. The MPP impregnation solution was made by dissolving 1.1 mL of MPP (192.3 g/mol; 1.09 g/mL; 98%; Sigma-Aldrich Co., St. Louis, MO) in 100 mL of toluene (TOL, 92.14 g/mol, \geq 99.9%, Sigma-Aldrich).

Two HDI spiking solutions were made using acetonitrile (ACN, 41.05 g/mol, \geq 99.9%, Sigma-Aldrich) and TOL. Twenty-five μ L of HDI (168.2 g/mol; 1.05 g/mL; 99%; Sigma-

Aldrich) was dissolved in either 100 mL of TOL or 100 mL of ACN. The spiking solution concentrations generated were 1,550 pmol/ μ L HDI/TOL and 1,550 pmol/ μ L HDI/ACN.

The GFFs were housed in 37-mm PS cassettes (SKC) and 37-mm PP cassettes (SKC) with stainless steel support pads (SKC). An additional GFF was placed in the cassette before the impregnated GFF. This GFF was not impregnated but spiked with 40 μ L of the spiking solution (either HDI/ACN or HDI/TOL).

The PS cassettes were attached to sampling pumps (Aircheck Model 224-PCXR4, SKC) operated at 1 L/min for 15 min. The open- and closed-face PP cassettes were attached to sampling pumps (Aircheck Model 224-PCXR4, SKC) operated at 1 or 2 L/min for 15 min. As air was drawn over the spiked filters HDI vapor was generated. Fritted-glass impingers (SKC) containing 15 mL of 2 g/L MPP in 30% *N,N*-dimethylformamide (DMF, 73.09 g/mol, \geq 99.9%, Sigma-Aldrich)/ACN derivatizing solution were attached after the filter housing to investigate breakthrough. Sets of three samples were collected using either HDI/ACN or HDI/TOL as the spiking solution for each cassette type. Three samples were collected open-face using PS cassettes. Three samples were collected for both open- and closed-face at each flow rate using the PP cassettes.

Table 1. Summary of Laboratory Experiments.

EXPERIMENT A											
Cassette Type	1-stage 37-mm PS				1-stage 37-mm PP						
Face	Open-Face		Open-Face				Closed-Face				
Spiking Solution	HDI/ACN	HDI/TOL	HDI/ACN		HDI/TOL		HDI/ACN		HDI/TOL		
Flow Rate	1L/min	1 L/min	1 L/min	2 L/min	1 L/min	2 L/min	1 L/min	2 L/min	1 L/min	2 L/min	
Breakthrough	Impinger	Impinger	Impinger	ND	Impinger	ND	Impinger	ND	Impinger	ND	
Sample Size	N=3	N=3	N=3	N=3	N=3	N=3	N=3	N=3	N=3	N=3	
Filters	GFF	GFF	GFF	GFF	GFF	GFF	GFF	GFF	GFF	GFF	
Sample Time	15 min	15 min	15 min	15 min	15 min	15 min	15 min	15 min	15 min	15 min	
Analytical Method	LC-MS	LC-MS	LC-MS	LC-MS	LC-MS	LC-MS	LC-MS	LC-MS	LC-MS	LC-MS	
EXPERIMENT B											
Cassette Type	1-stage 25-mm IOM Steel			1-stage 25-mm IOM Plastic			1-stage 25-mm PP				
Face	Open-Face			Open-Face			Open-Face				
Spiking Solution	HDI/ACN		HDI/TOL	HDI/ACN		HDI/TOL	HDI/ACN		HDI/TOL		
Flow Rate	2 L/min		2 L/min	2 L/min		2 L/min	2 L/min		2 L/min		
Breakthrough	ND		ND	ND		ND	Impregnated QF		Impregnated QF		
Sample Size	N=3		N=3	N=3		N=3	N=3		N=3		
Filters	QF		QF	QF		QF	QF		QF		
Sample Time	15 min		15 min	15 min		15 min	15 min		15 min		
Analytical Method	LC-MS		LC-MS	LC-MS		LC-MS	LC-MS		LC-MS		
EXPERIMENT C											
Cassette Type	2-stage 37-mm IsoChek [®]			1-stage 37-mm OSHA Method 42				2-stage 37-mm PS			
Face	Closed-Face			Open-Face				Closed-Face			
Spiking Solution	HDI/ACN		HDI/TOL	HDI/ACN		HDI/TOL		HDI/ACN		HDI/TOL	
Flow Rate	1 L/min		1 L/min	1 L/min		1 L/min		1 L/min		1 L/min	
Breakthrough	Impinger		Impinger	Impinger		Impinger		Impinger		Impinger	
Sample Size	N=3		N=3	N=3		N=3		N=3		N=3	
Filters	PTFE, GFF		PTFE, GFF	GFF		GFF		PTFE, GFF		PTFE, GFF	
Sample Time	15 min		15 min	15 min		15 min		15 min		15 min	
Analytical Method	HPLC/UV followed by fluorescence LC-MS (Spiked GFF only)		HPLC/UV followed by fluorescence LC-MS (Spiked GFF only)	HPLC/UV LC-MS (Spiked GFF only)		HPLC/UV LC-MS (Spiked GFF only)		LC-MS		LC-MS	

ND=not determined, PS=polystyrene, PP=polypropylene, HDI=1,6-hexamethylene diisocyanate, ACN=acetonitrile, TOL=toluene, N=sample size, GFF=glass fiber filter, LC-MS=liquid chromatography – mass spectrometry, QF=quartz filter, PTFE=polytetrafluoroethylene, HPLC/UV=high-pressure liquid chromatography/ultraviolet

The spiked filter, impregnated filter, impinger, and reference samples were analyzed for HDI monomer to determine the mass balance. After sample collection, the filters were removed from the cassette housing and placed in 4.8 mL of 2 g/L MPP in 30% DMF/ACN derivatizing solution. Samples were processed by adding 100 μ L of acetic anhydride and 100 μ L of the internal standard octamethylene diisocyanate (50 pmol/ μ L ODIU). A 400 μ L aliquot of the sample was transferred to a 2-mL glass vial and the sample was analyzed using a published liquid chromatograph-mass spectrometry (LC-MS) method (Fent et al. 2006).

Reference samples were collected to establish a comparison of HDI mass recovered without passing air through the sampling device. Reference samples were collected by spiking a GFF housed in a 37-mm PS or PP cassette. After the spiking, the filter was placed in 4.9 mL of 2 g/L MPP in 30% DMF/ACN derivatizing solution and 100 μ L of acetic anhydride was then added to the sample. A 200 μ L aliquot of the sample and 200 μ L of 2 pmol/ μ L ODIU (internal standard) were added to a 2-mL glass vial and the sample analyzed using LC-MS (Fent et al. 2006).

The impinger was processed by removing 9.8 mL of the sample from the impinger into a 20-mL glass vial and then acetic anhydride (200 μ L) was added to the vial. A 200 μ L aliquot of this sample and 200 μ L of 2 pmol/ μ L ODIU (internal standard) were added to a 2-mL glass vial and the sample analyzed using LC-MS (Fent et al. 2006).

B) Experiment using IOM and 1-Stage 25-mm Open-Face PP Cassettes

The recovery of HDI vapor using IOM (SKC) steel and plastic samplers as well as 1-stage 25-mm open-face PP cassettes (SKC) was determined in this experiment. The objective of this experiment was to compare the IOM steel with IOM plastic cassettes and to also compare the IOM plastic with the 25-mm PP cassettes. NIOSH Method 5525 calls for

an IOM sampler with steel cassette operated at 2 L/min. Quartz filters were selected for use based on the work of Woskie et al. (2004). Quartz filters (37-mm, Type R-100, SKC) were cut to 25-mm diameter and impregnated with a total of 400 μ L of the MPP impregnation solution described previously (I-A, p. 6). This was performed by applying first 200 μ L of impregnation solution to the filter and allowing 15 min to dry and then applying an additional 200 μ L of impregnation solution and allowing 15 min to dry prior to being placed in the housings of the IOM or 25-mm PP cassettes. Two impregnated quartz filters were housed in the 25-mm PP cassettes. The second impregnated quartz filter was used instead of an impinger to investigate breakthrough. Breakthrough was not investigated for the IOM cassette samples.

SKC did not provide information about the type of plastic used in the IOM cassettes; but they stated that the plastic is very similar to PP. A 37-mm quartz filter was placed over top of the IOM or 25-mm PP cassette inlet and spiked with 40 μ L of the spiking solutions. The IOM and 25-mm PP cassettes were attached to sampling pumps (Aircheck Model 224-PCXR4, SKC) operated at a flow rate of 2 L/min for 15 min. As air passed over the spiked filters, HDI vapor was generated. A glass funnel (Pyrex[®], Germany) was placed over top of the spiked filter of the 25-mm PP cassette following the spike to prevent evaporation of HDI off the spiked quartz filter. Three samples were collected using HDI/ACN and HDI/TOL as the spiking solution for both IOM steel and IOM plastic as well as 25-mm PP cassettes. Reference samples were collected by spiking a quartz filter housed in an IOM or 25-mm PP cassette as previously described (I-A, p. 7).

The spiked filter, impregnated filter, and reference samples were analyzed for HDI monomer. The samples were processed and analyzed as described previously (I-A, p. 9) using LC-MS.

C) Experiment using IsoChek®, OSHA Method 42, and 2-Stage PS Cassettes

The recovery of HDI vapor using IsoChek®, OSHA Method 42, and 2-stage PS cassettes was determined in this experiment. The IsoChek® sampler, purchased from Galson Laboratories (East Syracuse, New York), consists of a three-piece 37-mm PS cassette containing two stages, an untreated PTFE filter to collect aerosol and/or particulate and a treated GFF to collect vapor phase isocyanates. The treated GFF is impregnated with MAMA. The IsoChek sampler is used closed-face.

OSHA Method 42 calls for open-face sampling at a flow rate of 1 L/min for at least 15 min. OSHA Method 42 cassettes were purchased from Galson Laboratories. OSHA Method 42 cassettes consist of one GFF coated with 0.1 mg of 1-2PP and housed in a 37-mm PS cassette.

The closed-face 37-mm two-stage PS filter cassettes (SKC) designed to separate isocyanate vapor and aerosol were comprised of a first-stage untreated PTFE filter (SKC) and a second-stage impregnated GFF. The GFF was impregnated with 400 μ L of the MPP impregnation solution described previously (I-A, p. 6). A cellulose support pad (SKC) followed the impregnated GFF. In addition to sample recovery, this experiment allowed us to investigate how much HDI vapor absorbs to the PTFE filter during sample collection. The PTFE filter should, theoretically, collect HDI aerosol only, and since we are generating vapor alone we should not detect any HDI on the PTFE.

An additional GFF was placed before the IsoChek[®], OSHA Method 42, and 2-stage PS cassettes. This GFF was not impregnated, but spiked with 40 μ L of the spiking solution (either HDI/ACN or HDI/TOL). The IsoChek[®], OSHA Method 42, and 2-stage PS cassettes were attached to sampling pumps (Aircheck Model 224-PCXR4, SKC) operated at a flow rate of 1 L/min for 15 min. As air passed over the spiked filters, HDI vapor was generated. A glass funnel (Pyrex[®]) was placed over the top of the spiked filter of the OSHA Method 42 cassettes following the spike to inhibit evaporation of HDI off the spiked GFF. Fritted-glass impingers were used to investigate breakthrough. The impingers were prepared and analyzed as described previously (I-A, p. 9). Three samples were collected using HDI/ACN or HDI/TOL as the spiking solution. Reference samples as described previously (I-A, p. 7) were collected by spiking a GFF housed in a 37-mm PS cassette.

The OSHA Method 42 and IsoChek[®] spiked filter, impregnated filter, impinger, and reference samples were analyzed for HDI monomer. The spiked filters, impingers and reference samples were processed and analyzed in our laboratory using LC-MS as described previously (I-A, p. 9). The impregnated OSHA Method 42 GFFs were analyzed by Galson Laboratories using a reverse phase HPLC column with a UV detector and fluorescence detector in series. Following the sampling with IsoChek[®] cassettes, the PTFE filter was derivatized by placing it in a jar supplied by Galson Laboratories containing methoxy-2-phenyl-1-piperazine reagent (MOPIP). The PTFE filters in solution and cassettes with GFF in place were sealed and stored at -40°C until shipment to Galson Laboratories for analysis.

The spiked filter, PTFE filter, impregnated GFF, impinger, and reference samples from the 2-stage PS cassettes were analyzed for HDI monomer. The samples were processed and analyzed using LC-MS as described previously (I-A, p. 9).

II. HDI Reaction with Different Material Types

Reactivity of HDI with different cassettes and sampling materials was determined in the laboratory. This experiment was performed to determine if HDI was more reactive with certain material types as indicated by the findings in Experiments A-C. PS cassettes, PP cassettes, polyvinyl chloride (PVC) cassettes, PVC tubing, and Tygon tubing were tested. In addition, PTFE and GFFs were tested during this experiment. Pieces of each material were placed in 100 mL glass jars (Pyrex®). Each material was spiked with 10 μL of pure HDI and allowed 15 min for reaction. After 15 min, the samples were processed and analyzed as described below. Three samples were collected for each material type.

Samples were processed by adding 100 mL of 2 g/L MPP in 30% DMF/methanol derivatizing solution. This sample was then diluted by 1/100 with methanol. A 200 μL aliquot of this dilution and 200 μL of the internal standard (2 pmol/ μL ODIU) were placed into a 2-mL glass vial and analyzed using LC-MS (Fent et. al., 2006).

Additional samples were collected using the same materials and spiking them with 10 μL of 1,550 pmol/ μL solution of HDI/TOL or HDI/ACN as described previously (I-A, p. 6). Three samples were collected for each material type and HDI spiking solution. Samples were processed and analyzed as described above. Reference samples were collected to determine what was actually recovered using this method. The reference samples were collected by spiking 10 μL of pure HDI, HDI/TOL, and HDI/ACN solutions in an empty glass jar and processing and analyzing as described above.

III. Field Experiments

The collection efficiencies of 1- and 2-stage 37-mm PS cassettes, 1- and 2-stage 37-mm PP cassettes, and impingers were investigated in a spray-painting facility. This experiment was performed to determine how the samplers behave in the field setting compared to the laboratory setting. Two different samplers, three cassettes of each sampler type, were compared at any given time by attaching them to a cardboard cutout and placed in alternating order. A fritted-glass impinger filled with 15 mL of 2 g/L MPP in 30% DMF/ACN derivatizing solution was placed in the center. Only the two sampling cassettes closest to the impinger were compared to the impinger. The cardboard cutout with sampling cassettes attached to sampling pumps (Aircheck Model 224-PCXR4) were hung inside the paint booth. The painter sprayed HDI containing clear coat directly above the samplers, producing overspray that deposited over the cassettes and impinger. This was performed for approximately 10 s at 5 min intervals over a span of approximately 10 min. All samplers were processed and analyzed as previously described using LC-MS (I-A, p. 6-9). Table 2 summarizes the experiments performed in the field.

Table 2. Summary of Field Experiments.

Experiment	Cassette Types	Flow Rate (L/min)	Time (min)	Face	Clear coat
D	2-stage PS vs. 2-stage PP	1	8.5-11	Closed	Slow
E	1-stage PS vs. 1-stage PP	1	10-13	Open	Fast
F	1-stage PS vs. 2-stage PS	1	10-13	Open (1-stage) Closed (2-stage)	Fast

PS=polystyrene, PP=polypropylene

IV. Data Analysis

In the laboratory experiments A-C, a percent recovery was calculated for each cassette type and spiking solution (HDI/ACN or HDI/TOL). The amount of HDI mass left on the spiked filter was subtracted from the reference samples as an adjusted mass generated. Mass collected on backup devices such as impingers or additional GFF, were subtracted from the amount recovered as well as HDI mass collected on the first stage of cassette types such as IsoChek[®] and 2-stage PS. This procedure normalized the data and allowed comparison of the HDI vapor recovered by each cassette type.

For the determination of the HDI reactivity with different plastics, the concentration of HDI in each sample was calculated in pmol/ μ L. The percent recovery for the mean recovery for each material was calculated as a percent of the mean of the reference sample concentrations.

In the field experiments D-F, samples that could be compared to the impinger were used in this data analysis. Air concentrations (μ g/ m^3) were calculated based on the volume and flow rate of each sample and the data was normalized as a percentage of the impinger by dividing the air concentration of the cassette by the air concentration of the impinger sample for that trial.

Statistical analyses of the data were performed using SAS Version 9.1.3 (Cary, NC). PROC MEANS was used to determine the mean, 95% confidence interval, and standard deviation for the percent of HDI mass recovered as compared to the reference samples for each group (experiments A-C). Microsoft Excel was used to calculate the mean, 95% confidence interval, and standard deviation for the HDI reaction with plastics and field experiments (D-F). PROC TTEST (SAS) was used to test for significant differences in the

recovery of HDI based on spiking solution (HDI/ACN or HDI/TOL) and cassette types. The Student's *t*-test was used as the test statistic and significance was determined at the $\alpha = 0.05$ level. The folded form of the F-statistic was used to test the hypothesis that the variances are equal. If the variances were determined to be equal, a pooled *t*-test was used in determining the significance while the Satterthwaite *t*-test was used for unequal variances.

CHAPTER III

RESULTS

I. Laboratory Experiments

A) Experiment using 1-Stage 37-mm PS and PP Cassettes

Significantly ($p = 0.014$) more HDI vapor was recovered using 1-stage 37-mm open-face PS cassettes when HDI/ACN solution was used as the spiking solution than HDI/TOL (**Table 3**). The PS cassettes recovered 53% of the spiked HDI mass when HDI was dissolved into ACN compared to a recovery of 32% when dissolved into TOL. Breakthrough was not observed with either spiking solution.

The recoveries of HDI vapor using 1-stage open- and closed-face 37-mm PP cassettes at different flow rates are also presented in **Table 3**. Significant difference ($p = 0.044$) was observed for samples collected with open-face PP cassettes at 2 L/min when using ACN (75%) as a spiking solution compared to TOL (46%). Samples collected with open-face PP cassettes at 1 L/min using ACN (77%) as solvent performed better than when using TOL (45%) as a solvent. Using ACN as a solvent with closed-face PP cassettes at 1 L/min (53%) and 2 L/min (75%) recovered more than when using TOL at 1 L/min (37%) or 2 L/min (36%). However, significant difference ($p < 0.05$) was not observed between 1 and 2 L/min flow rate or open- vs. closed-face sampling. The impinger analysis indicated small (<1%) breakthrough during sample collection using 1-stage open-face 37-mm PP at a flow rate of 1 L/min with HDI/ACN spiking solution and when using 1-stage closed-face 37-mm PP at a

flow rate of 1 L/min with HDI/TOL spiking solution. Breakthrough was not observed during sample collection with the other samplers.

The results of the 1-stage 37-mm open-face PS and PP cassettes (Experiment A) are presented in **Figure 1**. Although the PP cassettes recovered 13-24% more HDI mass than the PS cassettes, this difference was not statistically significant ($p < 0.05$).

Table 3. Results of Experiment A (1-stage 37-mm PP and PS cassettes).

Cassette Type	Solvent	N	Flow Rate (L/min)	Mean \pm STD (%)	95% Confidence Interval	p-value
Open-Face PS	ACN	3	1	53.04 \pm 1.14	51.98 – 54.25	0.014
	TOL	3		31.84 \pm 8.64	26.61 – 41.80	
Open-Face PP	ACN	3	1	77.48 \pm 19.9	54.64 – 91.13	0.086*
	TOL	3		44.79 \pm 10.29	36.98 – 56.45	
Open-Face PP	ACN	3	2	74.75 \pm 12.29	61.12 – 84.99	0.044*
	TOL	3		46.43 \pm 4.49	42.77 – 51.43	
Closed-Face PP	ACN	3	1	53.10 \pm 12.03	39.91 – 63.45	0.137*
	TOL	3		37.13 \pm 4.07	34.01 – 41.74	
Closed-Face PP	ACN	3	2	74.68 \pm 8.98	64.83 – 82.43	0.084*
	TOL	3		36.44 \pm 22.64	16.07 – 60.81	

PS=polystyrene, PP=polypropylene, ACN=acetonitrile, TOL=toluene, N=sample size

*Using Satterthwaite Unequal variance instead of Pooled Equal variance

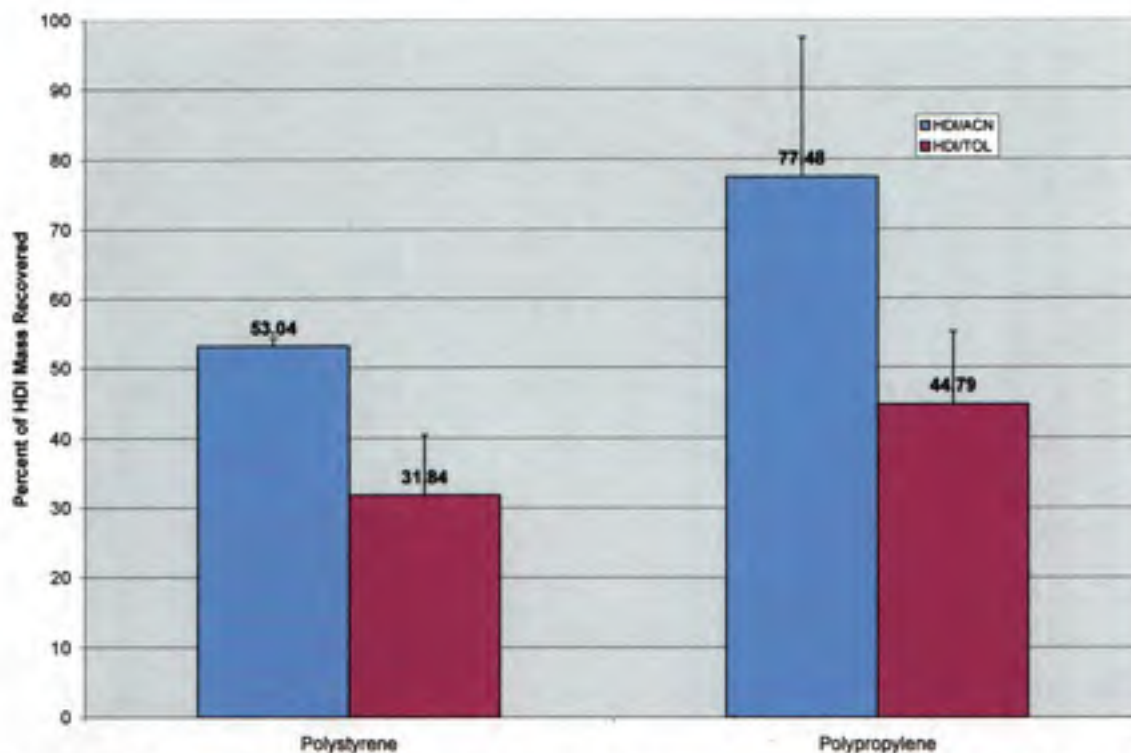


Figure 1. 1-Stage 37-mm Open-Face PS vs. PP Cassettes run at a flow rate of 1 L/min for 15 min.

B) Experiment using IOM and 1-Stage 25-mm Open-Face PP Cassettes

The results of the recovery of HDI vapor using IOM steel and IOM plastic cassettes are summarized in **Table 4**. Both the IOM steel and IOM plastic recovered more than 80% of the HDI vapor generated. Significant difference ($p = 0.017$) was observed between ACN (83%) and TOL (88%) as a solvent for the spiking solution when sampling with the IOM plastic cassette. Significant difference ($p = 0.034$) was observed between the IOM plastic (82%) and IOM steel (88%) cassette when using HDI/ACN as a spiking solution but not when using HDI/TOL as a spiking solution. IOM steel cassette recovered 87% while IOM plastic cassette recovered 88% when HDI/TOL was used as a spiking solution.

The results of the recovery of HDI vapor using 1-stage open-face 25-mm PP cassettes at a flow rate of 2 L/min for 15 min are summarized in **Table 4**. Significant difference ($p =$

0.037) between ACN (91.5%) and TOL (77%) as a solvent for the spiking solutions were observed when using this sampler. Breakthrough was not observed on the backup impregnated quartz filters.

The results of the 25-mm PP cassettes were compared to the IOM plastic cassettes since the cassette materials are similar and both samplers were used open-face at a flow rate of 2 L/min for 15 min. Significant difference ($p = 0.0002$) was observed between the 25-mm PP cassette (77%) and IOM plastic cassette (88%) when using HDI/TOL as a spiking solution (**Figure 2**) but not when using HDI/ACN as a spiking solution. Recovery was 91.5% with 25-mm PP cassette and 83% with IOM plastic cassette when using HDI/ACN as a spiking solution.

Table 4. Results of Experiment B (IOM and 25-mm PP cassettes).

Type	Solvent	N	Mean \pm STD (%)	95% Confidence Interval	p-value
IOM Steel	ACN	3	88.81 \pm 2.57	86.23 – 91.36	0.444*
	TOL	3	86.91 \pm 2.90	84.25 – 89.99	
IOM Plastic	ACN	3	82.75 \pm 1.74	80.74 – 83.81	0.017*
	TOL	3	88.22 \pm 0.86	87.70 – 89.21	
1-Stage 25-mm PP	ACN	3	91.49 \pm 5.32	87.20 – 97.43	0.037*
	TOL	3	76.95 \pm 1.08	75.79 – 77.92	

PP=polypropylene, ACN=acetonitrile, TOL=toluene, N=sample size

*Using Satterthwaite unequal variance instead of pooled equal variance.

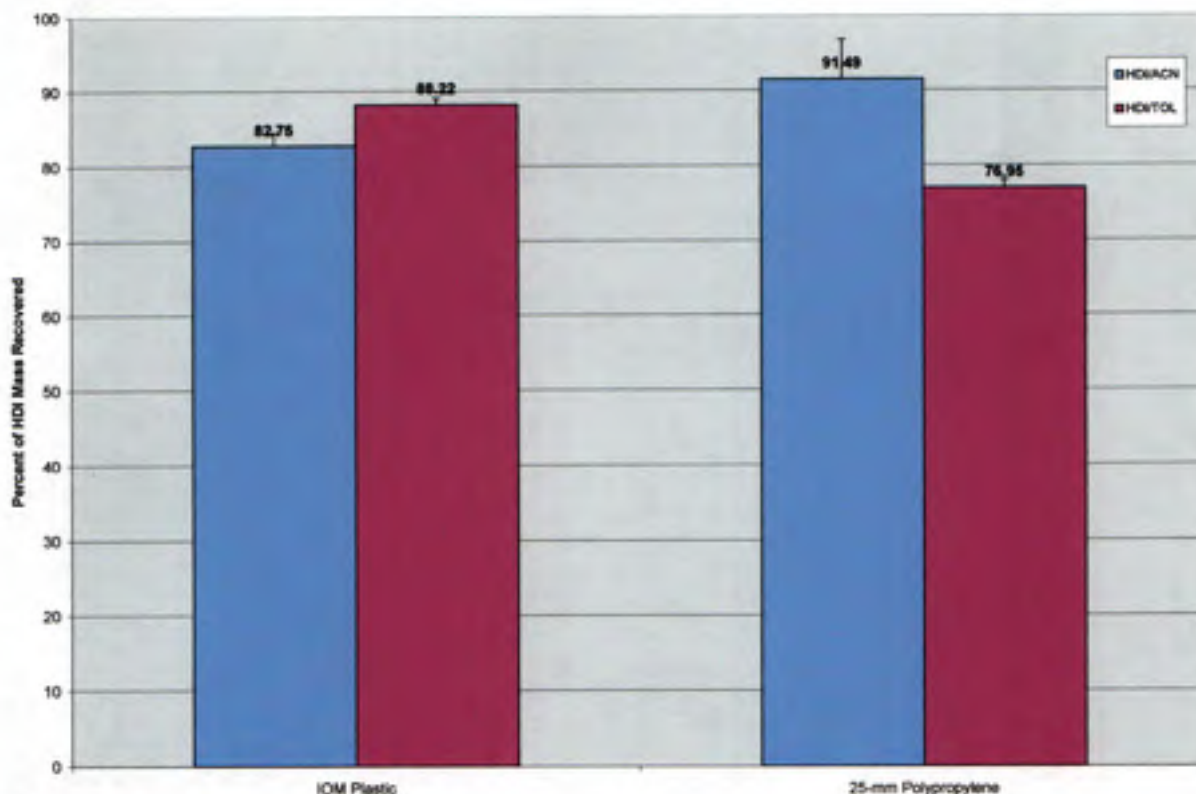


Figure 2. IOM Plastic vs. 25-mm PP Cassette.

C) Experiment using IsoChek[®], OSHA Method 42, and 2-Stage PS Cassettes

The results of the IsoChek[®] cassette experiment are summarized in **Table 5**. The IsoChek[®] performed the worst of all samplers recovering 16% and 10% of the adjusted mean reference using HDI/ACN and HDI/TOL as spiking solutions, respectively. The results of the PTFE filter analysis performed by Galson Laboratories for this experiment showed HDI levels below the limit of detection (0.03 µg).

The results of the OSHA Method 42 cassettes experiment are summarized in **Table 5**. Significant difference ($p = 0.038$) was observed between the HDI/ACN (55%) and HDI/TOL (35%) spiking solution. Breakthrough was not observed.

The results of the closed-face 2-stage 37-mm PS cassettes experiment are summarized in **Table 5**. Significant difference ($p = 0.893$) was not observed between the HDI/ACN (27%) and HDI/TOL (29%).

The comparison of IsoChek[®], OSHA Method 42, and 2-stage PS samplers are summarized in **Figure 3**. Significant difference ($p = 0.002$) was observed between OSHA Method 42 (55%) and 2-stage PS (27%) when using HDI/ACN as a spiking solution. Significant difference ($p = 0.007$) was also observed between IsoChek[®] (16%) and 2-stage PS (27%) with the HDI/ACN spiking solution. Significant difference ($p < 0.005$) was observed between IsoChek[®] and OSHA Method 42 for both the HDI/ACN (16% and 55%, respectively) and HDI/TOL (10% and 29%, respectively) spiking solutions.

Table 5. Results of Experiment C (IsoChek[®], OSHA 42, 2-Stage PS Cassettes)

Type	Solvent	N	Mean \pm STD (%)	95% Confidence Interval	p-value
IsoChek [®] Closed-Face	ACN	3	15.63 \pm 2.51	13.34 – 18.33	0.046*
	TOL	3	9.78 \pm 0.75	9.35 – 10.64	
OSHA 42 Open-Face	ACN	3	54.59 \pm 1.98	52.60 – 56.57	0.038*
	TOL	3	35.17 \pm 7.41	26.64 – 39.95	
2-Stage PS Closed-Face	ACN	3	27.31 \pm 1.06	26.58 – 28.53	0.893
	TOL	3	28.71 \pm 16.96	9.50 – 41.61	

PS=polystyrene, ACN=acetonitrile, TOL=toluene, N=sample size

*Using Satterthwaite unequal variance instead of pooled equal variance.

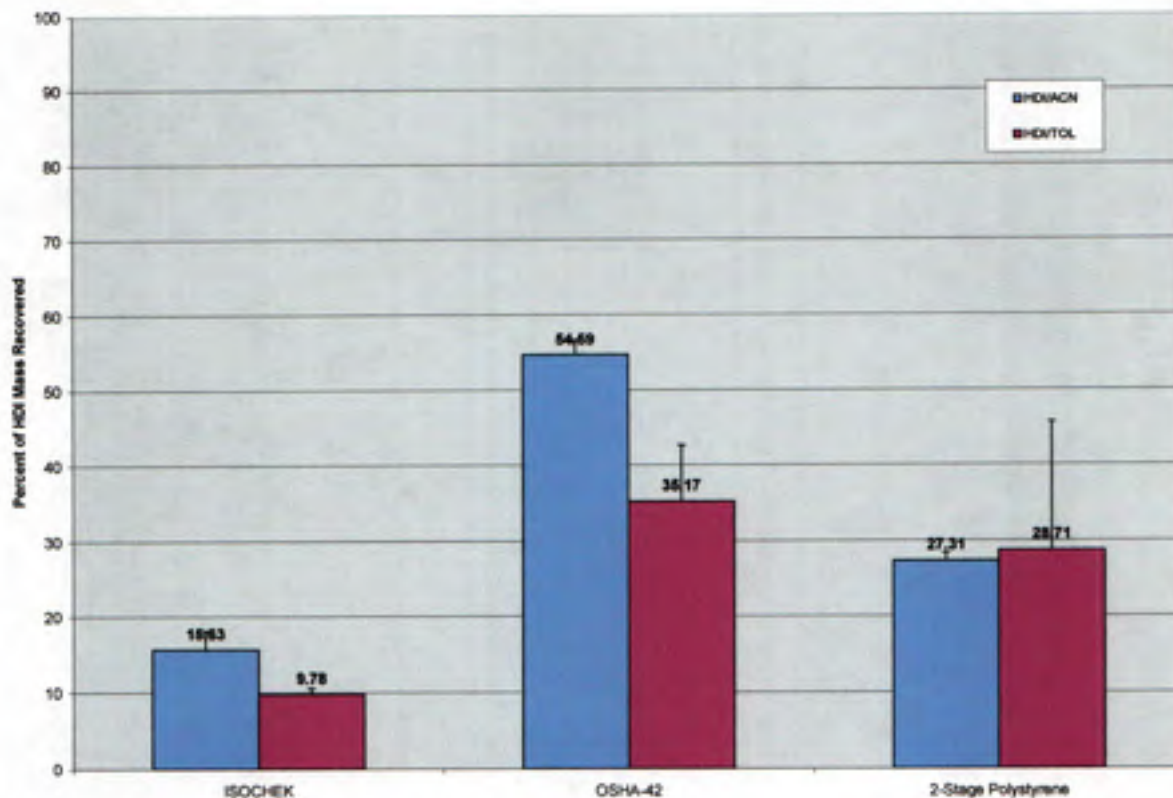


Figure 3. Comparison of IsoChek[®], OSHA Method 42, and 2-Stage PS Samplers.

II. HDI Reaction with Different Material Types

The results of the laboratory experiments to determine if HDI is reacting with a variety of cassette materials are summarized in **Table 6**. Based on the 95% confidence intervals, when compared to the reference samples, HDI without solvent reacted with PS, PVC, and Tygon. From the 95% confidence intervals, HDI in toluene reacted with PS, PVC, and Tygon, and HDI in ACN reacted with PVC and Tygon.

Table 6. Summary of HDI Reaction with Different Material Types (N=3).

Solvent	Material	Mean \pm STD (pmol/ μ L)	95% Confidence Interval	Percent of Theoretical	Recovery (% of Reference)
None	Reference	3.28 \pm 0.32	2.91 – 3.64	106	100
	Polystyrene	1.92 \pm 0.44	1.43 – 2.42	62*	59*
	PVC	2.16 \pm 0.07	2.08 – 2.23	70*	66*
	PVC tubing	2.39 \pm 0.50	1.82 – 2.96	77*	73*
	Tygon tubing	2.46 \pm 0.47	1.93 – 3.00	79*	75*
	Polypropylene	3.15 \pm 0.08	3.06 – 3.24	101	96
	Teflon	3.13 \pm 0.04	3.08 – 3.17	101	95
	GFF	2.98 \pm 0.07	2.90 – 3.06	96	91
Toluene	Reference	2.99 \pm 0.08	2.90 – 3.08	93	100
	Polystyrene	0.87 \pm 0.13	0.72 – 1.02	27*	29*
	PVC	1.69 \pm 0.03	1.66 – 1.72	53*	56*
	PVC tubing	1.67 \pm 0.22	1.41 – 1.92	52*	56*
	Tygon tubing	1.65 \pm 0.20	1.42 – 1.88	51*	55*
	Polypropylene	2.98 \pm 0.07	2.90 – 3.06	93	100
	Teflon	3.02 \pm 0.01	3.01 – 3.04	94	101
	GFF	2.88 \pm 0.01	2.87 – 2.89	90	96
Acetonitrile	Reference	3.15 \pm 0.08	3.06 – 3.24	98	100
	Polystyrene	2.88 \pm 0.27	2.57 – 3.19	90	91
	PVC	2.47 \pm 0.21	2.24 – 2.71	77*	79*
	PVC tubing	2.36 \pm 0.030	2.33 – 2.40	74*	75*
	Tygon tubing	2.11 \pm 0.34	1.72 – 2.49	66*	67*
	Polypropylene	3.23 \pm 0.11	3.11 – 3.35	101	103
	Teflon	3.22 \pm 0.05	3.16 – 3.29	101	102
	GFF	3.12 \pm 0.09	3.02 – 3.22	97	99

Note: Theoretical concentration is 3.1 pmol/ μ L when HDI was not dissolved in solvent and 3.2 pmol/ μ L when HDI was dissolved in either ACN or TOL.

*indicates material is reacting with HDI and associated solvent.

III. Field Sampling Experiments

The results of the field sampling experiments are summarized in **Figure 4** and **Table 7**. The results show that the closed-face 2-stage PP and 2-stage PS cassettes performed similarly when the slow drying clear coat was used.

Table 8 provides a summary of the statistical analysis of the field sampling results. Significant difference ($p < 0.05$) was not observed for any of the comparisons for the HDI monomer analysis. Significant difference was observed when comparing a slow- and fast-drying clear coat using a closed-face 2-stage PS cassette for HDI oligomer analysis (for all $p < 0.05$).

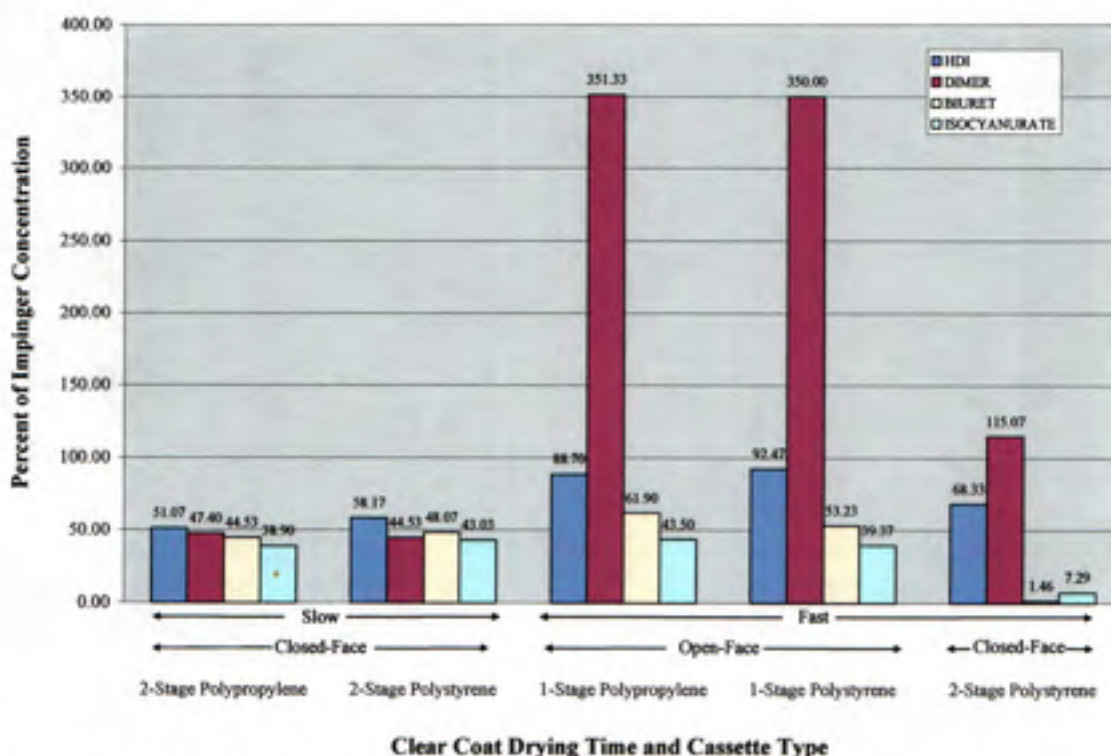


Figure 4. Summary of the Field Sampling Experiments.

Table 7. Summary of the Field Sampling Experiment Results.

Cassette Type	Clear Coat	N	Mean Recovery ± STD (% Impinger)		95% Confidence Interval
Closed-Face 2-Stage PP	Slow	3	HDI	21.1 ± 51.1	11.0 – 104
			Dimer	31.0 ± 47.4	16.1 – 124
			Biuret	1.95 ± 44.5	16.4 – 65.1
			Isocyanurate	3.82 ± 38.9	1.99 – 48.4
Closed-Face 2-Stage PS	Slow	3	HDI	16.7 ± 58.2	8.69 – 99.6
			Dimer	23.3 ± 44.5	12.2 – 103
			Biuret	0.67 ± 48.1	0.347 – 49.7
			Isocyanurate	3.32 ± 43.0	1.73 – 51.3
Open-Face 1-Stage PP	Fast	3	HDI	31.6 ± 88.7	16.4 – 167
			Dimer	226 ± 351	118 – 914
			Biuret	32.1 ± 61.9	16.7 – 142
			Isocyanurate	13.6 ± 43.5	7.09 – 77.3
Open-Face 1-Stage PS	Fast	3	HDI	38.5 ± 92.5	20.0 – 188
			Dimer	228 ± 350	119 – 918
			Biuret	10.0 ± 53.2	5.21 – 78.1
			Isocyanurate	6.00 ± 39.4	3.12 – 54.3
Closed-Face 2-Stage PS	Fast	3	HDI	19.8 ± 68.3	10.3 – 118
			Dimer	36.0 ± 115	18.7 – 204
			Biuret	0.79 ± 1.46	0.411 – 3.42
			Isocyanurate	2.60 ± 7.29	1.36 – 13.8

PS=polystyrene, PP=polypropylene N=sample size

Table 8. Summary of Statistical Analysis for Field Experiment Comparisons.

Cassette Type	Clear Coat Drying Time	p-value	
Closed-Face 2-Stage PS vs. Open-Face 1-Stage PS	Fast	HDI	0.389
		Dimer*	0.215
		Biuret*	0.012
		Isocyanurate	0.001
Open-Face 1-Stage PS vs. 1- Stage PP	Fast	HDI	0.902
		Dimer	0.995
		Biuret	0.678
		Isocyanurate	0.655
Closed-Face 2-Stage PP vs. 2-Stage PS	Slow	HDI	0.672
		Dimer	0.904
		Biuret*	0.041
		Isocyanurate	0.230
Closed-Face 2-Stage PS	Slow vs. Fast	HDI	0.534
		Dimer	0.046
		Biuret	<0.0001
		Isocyanurate	0.0001

PS=polystyrene, PP=polypropylene

*Using Satterthwaite unequal variance instead of pooled equal variance.

CHAPTER IV

DISCUSSION

The measurement of airborne isocyanate-containing compounds continues to be a challenge in the industrial hygiene field. Several different sampling devices are available for use in the field setting. Sampling is difficult because, in the spray-painting environment, HDI monomer and HDI-based oligomers are present in both aerosol and vapor phases (England 2000). Isocyanates are also very reactive and, therefore, unstable after collection adding to the sampling challenge.

Some of the available and common sampling devices for isocyanates are a variety of cassettes with treated filters, IOM cassettes, OSHA Method 42, and IsoChek[®] cassettes. A variety of cassettes were compared in a controlled and occupational environment. Both field and laboratory comparisons of isocyanate samplers are necessary to fully evaluate their performances because the occupational environment differs greatly from a controlled laboratory setting. Significant difference between HDI/ACN and HDI/TOL as a spiking solution were observed when sampling with the 1-stage 37-mm PS cassettes. Using the HDI/ACN as a spiking solution, the PS cassettes recovered an average of 53% HDI mass. These cassettes performed worse, recovering 32%, when spiked with HDI/TOL. The remaining 47% and 68% of the mass spiked cannot be accounted for and breakthrough was not observed. Losses may occur due to evaporation off the spiked filter; however, it is not reasonable to assume all

of the mass is lost this way since the cassettes were spiked with pumps running or pumps started immediately after spiking. We believe HDI is reacting with cassette materials and therefore creating sample losses. Significant difference was observed in HDI recovery between HDI/ACN (75%) and HDI/TOL (46%) when 1-stage 37-mm open-face PP cassettes were used at 2 L/min. When comparing PP to PS, PP recovered 13-24% more than PS. However, this difference was not statistically significant but may be due to the large variability within sampling groups.

The PP cassettes recovered approximately 53-77% when spiked with HDI/ACN and 36-46% when spiked with HDI/TOL. Flow rates and open- vs. closed-face sampling did not significantly influence the performance of the PP cassettes. The PP cassettes recovered more of the spiked HDI mass than the PS cassettes. Only 27% of the HDI/TOL spiked on the styrene cassette material could be recovered compared to 62% with pure HDI and 90% when using a HDI/ACN spiking solution. This finding is supported by the HDI reactivity experiment based on the observation that HDI and HDI/TOL are very reactive with styrene.

Significant difference was observed between HDI/ACN (83%) and HDI/TOL (88%) for IOM plastic cassettes (Experiment B) and when comparing IOM plastic (83%) to IOM steel (89%) for the HDI/ACN spiking solution. These results are not surprising since we observed that HDI is reacting with different cassette material types. The HDI reactivity experiment supports this finding based on the observation that HDI reacts with PS, PVC, and Tygon; HDI/TOL reacts with PS, PVC, and Tygon; and HDI/ACN reacts with PVC and Tygon. Brorson et al. (1989) investigated the influence of the material used for sampling connections on sampling losses. High losses, 35-65% for HDI, were caused by 150-mm tubings of

materials such as silicone rubber, latex, PVC or PP. Brorson et al. emphasized the necessity of using glass, stainless steel, or Teflon[®] connections when sampling diisocyanates.

The 25-mm PP cassettes performed the best, recovering 91.5% HDI when using HDI/ACN as a spiking solution compared to 77% recovered when using the HDI/TOL as a spiking solution ($p = 0.037$). When comparing the 25-mm PP cassette to the IOM plastic using HDI/TOL as a spiking solution, the difference was statistically significant ($p = 0.0002$) with the IOM plastic cassette recovering 88% of HDI mass. It is surprising that significant difference was observed between these two sampling devices since SKC stated that these plastics are very similar.

Significant difference was observed between HDI/ACN and HDI/TOL spiking solutions for OSHA Method 42 and IsoChek[®]. OSHA Method 42 and IsoChek[®] cassettes are both made of PS. When sampling with OSHA Method 42 cassettes, 55% and 35% of HDI mass were recovered using HDI/ACN and HDI/TOL spiking solutions, respectively. The IsoChek[®] recovered 16% and 10% of HDI mass when using HDI/ACN and HDI/TOL spiking solutions, respectively. OSHA Method 42 uses a single GFF as well as different analysis methods and different impregnation and derivatizing agents than the dual filter (PTFE and GFF) IsoChek[®]. This may account for the differences between these devices.

OSHA Method 42 performed the best compared to the 2-stage PS and IsoChek[®] cassettes, recovering 55% when using HDI/ACN as a spiking solution. Statistically significant differences were observed between OSHA Method 42 and the 2-stage PS (27%) as well as between the IsoChek[®] (16%) and 2-stage PS cassettes when using HDI/ACN as a spiking solution. Significant difference was observed between IsoChek[®] and OSHA Method 42 for HDI/ACN and HDI/TOL. All of these sampling devices are made of PS and IsoChek[®]

and the 2-stage PS cassettes contain an additional cassette piece providing more surface area of material. This may be the reason why these cassettes performed the worst in our controlled laboratory experiments. More HDI mass may be lost to reaction with the PS because of this additional cassette piece. Although significant difference was not observed for all of the comparisons in the controlled laboratory experiments, the recovery of HDI mass definitely varied among the different sampling devices.

In the occupational setting, significant difference in the recovery of HDI oligomers was observed between the fast- and the slow-drying clear coats when using 2-stage PS cassettes. A number of factors influence the ability of a sampler to effectively collect a reactive material like isocyanates. These factors include the distribution of isocyanates among vapor and aerosol phase, the relative collection efficiency of the sampler for these phases (aspiration efficiency, internal wall, or transmission losses), the relative derivatization kinetics of the derivatizing reagent on the filter versus in solution, sample preparation methods, the curing rate of isocyanates, and sampling time (Bello et al., 2002).

Sampling losses may occur due to the reactivity of HDI with sampling materials or with polyols in automotive paint overspray as evidenced by these experiments. The reaction of HDI with sampling materials is amplified by the presence of a non-polar solvent (i.e., TOL). HDI oligomers appear to possibly polymerize to the surface of the PTFE filter when atmospheres of fast drying clear coat are sampled.

In the field setting, the cassette material type did not impact the sampling efficiency as greatly as it did in the laboratory setting. In the laboratory setting, the HDI generated was in the vapor phase. Mixtures of monomers, oligomers, higher molecular weight prepolymers, and other intermediate products are typical in many isocyanate applications, especially in

auto-body repair shops (Bello et. al. 2002). Exposure to isocyanates in auto-body shops is predominantly as an aerosol (Bello et. al. 2002, Rudzinski et. al. 1995). This further confirms the necessity and utility of performing both field and laboratory comparisons of isocyanate samplers.

Based on these experiments, it is evident that all of these sampling devices perform differently and some may be undersampling. These findings demonstrate the importance of performing experiments both in the laboratory and occupational setting. The results also indicate that the type of clear coat used during spray-painting activities should be considered when selecting a sampler for monitoring exposure to HDI. Based on the results of these experiments I recommend using a 1-stage 37-mm PP or PS cassette when performing field sampling for HDI during spray-painting in the auto-body industry. Although the 25-mm PP cassette performed the best in the laboratory experiments, they were not tested in these field experiments. The field experiments show that the 2-stage sampling cassette may underestimate HDI monomer and oligomer concentrations when sampling spray-painting operations that use fast-drying clear coat because of polymerization of HDI on the PTFE filter. Using the 1-stage cassette with an impregnated GFF will allow collection of both the aerosol and vapor phases of the HDI monomer as well as aerosol phase oligomers and eliminate the possible polymerization from occurring on the filter. Separation of vapor and aerosol fractions is not possible when 1-stage cassette is used. However, in the spray-painting environment the predominant exposure is to aerosols (Bello et. al. 2002, Rudzinski et. al. 1995).

The laboratory environment is very different than the occupational field setting. The presence of other polyols and the way in which HDI is applied is very different in the field

versus laboratory setting. Also, only HDI monomer phase was investigated in the laboratory experiments. However, the laboratory experiments were important as we observed that HDI was reacting with cassette materials and that this reaction was amplified in the presence of a non-polar solvent. This phenomenon was not observed in the field experiments.

CHAPTER V

CONCLUSION

Exposure assessments focusing on the inhalation route of exposure in industries with potential diisocyanate exposures have been performed and documented. Many of the sampling devices used to measure diisocyanate exposures have been criticized as underestimating or inadequately sampling the entire range of isocyanate aerosols. These devices may be considered unreliable in certain situations. It is important that the air samples collected during exposure assessment accurately measure air concentration so that reliable predictive exposure models can be developed and to ensure worker protection as well as compliance with regulatory limits.

In this study, we observed that the cassette material had an influence on the collection of HDI. In the laboratory experiments (I and II), we provide evidence that the sampling losses may occur due to the reactivity of HDI with sampling materials. These results also indicate that the reaction of HDI with sampling materials is amplified by the presence of a non-polar solvent (i.e., TOL).

The results from the field experiments (III) indicated that the clear coat used during spray-painting activities affects the collection efficiency of the sampling device. These results also suggest that HDI oligomers may polymerize on the surface of the PTFE filter of 2-stage sampling cassettes. However, in the field setting, the cassette material was not observed to impact the sampling efficiency as greatly as it did in the laboratory setting.

Based on the results of these experiments I recommend using a 1-stage 37-mm PP or PS cassette when performing field sampling for HDI during spray-painting in the auto-body industry. Using the 2-stage sampler, HDI monomer and oligomers were observed to polymerize on the PTFE filter. Use of the 1-stage sampler will reduce the possibility of polymerization on a filter; however, aerosol and vapor phases cannot be separated. This study demonstrates the importance of performing both field and laboratory comparisons of diisocyanate samplers. Additional laboratory and occupational sampling experiments need to be performed with all sampling devices and different clear coats to fully evaluate their reliability.

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