A Comparison of Surface Sampling Wipe Media for Isocyanate Sampling in the Auto Repair Industry

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Abstract

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Objective: Many opportunities exist for dermal exposure to isocyanates in the auto repair industry. Contaminated work surfaces may be of particular concern as surfaces sprayed with isocyanates have been shown to represent a source of exposure long after paints and clear coats have dried. Improvement upon currently used surface sampling methods may be important in evaluating work surfaces as a potential source of isocyanate exposure. In order to initiate these improvements, this study aims to compare multiple wipe media to find a material effective in recovering isocyanates.

Methods: Percent recovery of isocyanates was compared among 3 different wipe media composed of the following materials: PVDF, quartz fiber, and polypropylene. In addition, each wipe material was sampled from 3 surface types, including glass, ceramic, and aluminum. All wipe samples were analyzed using a quantitative HPLC assay at the Industrial Hygiene lab at the Washington State Department of Labor and Industries. Statistical analysis was used to determine whether differences in recovery of hexamethylene diisocyanates (HDI) could be attributed to differences in wipe media or surface type.

Results: Comparison of PVDF and quartz fiber media found that differences in recovered isocyanate species could not be explained by differences in the wipes. In contrast, a significant decline in mean recovery was observed when comparing polypropylene wipes to PVDF and quartz media. Surface type was also found to be a significant factor in determining isocyanate recovery. Samples taken from aluminum surfaces yielded the highest recovery of HDI.

Conclusion: Although PVDF and quartz media appeared to be associated with similar recovery of HDI, quartz wipes are not recommended for surface sampling due to durability issues. Since HDI recovery when using PVDF wipes is significantly higher compared to that of polypropylene media, PVDF may be an effective material for surface sampling.

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Introduction and Background

The use of isocyanates is widespread and steadily growing across multiple industries in the United States. Consumption of just two different types of the chemical amounted to 3 billion pounds in the U.S. during 2003, and demand for these products continues to rise.[22] The use of isocyanates as a spray-on coating product has led to the chemical becoming a common component of hardeners in coating systems in the automobile and auto repair industries. In addition to inhalation exposures, which have historically remained at the forefront of exposure research, dermal exposure is also of great concern for workers in these industries. The potential for exposure to the skin is further intensified by the improper use of dermal personal protective equipment among some members of the industry. As strong irritants and sensitizers, isocyanates pose a great health risk to frequently exposed workers.[21] In Washington State, as well as worldwide, work related asthma has been strongly associated with the auto repair industry, especially for vehicle spray painters.[2,15,36,37]

Isocyanates are a group of highly reactive chemicals, containing the functional group (-NCO), used in a number of consumer products as well as in the automobile industry, auto repair, and construction industries.[20] They are often required for the manufacture of polyurethane products, including foams, fibers, coatings, and paints. In particular, various forms of isocyanate chemicals can be found in clear coating systems as the hardening catalysts used in the final stage of automobile painting. They may also be found in primers and basecoats. The two-part coating systems are primarily composed of hexamethylene diisocyanate oligomers (HDI) with only 1% of the total isocyanate functional groups provided by the monomeric form of HDI.[25,26] Due to the high volatility of HDI monomers they are used in much lower quantities than that of oligomers. Oligomeric forms of HDI include Uritidone, isocyanurate, Biuret, and Diisocyanurate. Such use of HDI oligomers in greater concentrations than that of monomers may have potential health impacts as HDI oligomers have been shown to have a greater association with asthmatic reactions than monomers.[36]

Routes of exposure and opportunities for exposure

Previous studies of isocyanate exposure in the auto body repair industry have focused primarily on exposures directly related to spraying tasks.[18,29,32] However, many opportunities for dermal exposure still remain for tasks other than painting. Most auto repair shops perform painting and coating tasks in spray booths containing exhaust ventilation systems, which serve as a means of controlling isocyanate exposure.[32] However, even with the presence of controls, such as painting booths, painting frequently takes place outside of these booths allowing for overspray from the painting guns to contaminate other surfaces in the shop.[32,37,38] This may create opportunities for the painter and other shop workers to be exposed dermally. Spilling of paints and clear coat mixtures while mixing and gun cleaning are also likely to occur and may contaminate work surfaces as well. Since personal protective equipment, including gloves, are not likely to be used while not directly handling isocyanate containing paints and coatings, workers may be more susceptible to exposure when contacting potentially contaminated surfaces. These opportunities could include preparations of coatings, or other mixing activities, and contact with contaminated equipment or work surfaces. Additionally, for workers that do not wear gloves while painting, dermal contact with contaminated surfaces could increase overall exposure to isocyanates.

Much like the use of spray booths, personal protective equipment is often used improperly and inconsistently. Multiple studies have found that the majority of auto repair shop workers continue to wear latex gloves despite the poor protective qualities of the material.[4,10,33,38] Of those surveyed, 85% of workers reported wearing gloves while spraying clear coats, suggesting that a significant number of painters do not wear gloves during daily job tasks.[38] Still, for those who wear gloves regularly, dermal exposure to isocyanates may remain a concern. Glove permeation by isocyanates has been observed for many job activities. Isocyanates have been found beneath gloves and other types of personal protective equipment (PPE) following clear coating, mixing, and gun cleaning.[18,25] While relevant to activities associated with dermal isocyanate exposure, these studies fail to consider many other tasks that were originally believed to be free of isocyanate exposure. Tasks that involve dried paints and clear coats may still require the use of PPE as unbound isocyanate species have been quantitatively measured from sprayed vehicle parts as long as 273 hours after drying.[6] The Colorimetric SWYPE method was able to qualify the presence of unbound isocyanate species for up to 120 hours following drying of sprayed vehicle parts for most paint formulations used for spraying.[6] Unbound isocyanate species were qualitatively detected even up to 1 month after drying for other paint formulations. Evidence of such slow curing time for clear coats and paints has implications for other surfaces exposed to overspray during coating processes and spilling that might occur during paint mixing. Aside from sprayed parts, many work surfaces found in auto shops may also be contaminated with isocyanates hours or days after spraying events or spills. Qualitative assessments of multiple painting and mixing surfaces in auto repair shops have found numerous positive samples of isocyanates.[18] Little is known regarding the work practices while performing other job tasks that don't involve spraying, mixing, or gun cleaning. For this reason, it may be important to evaluate available isocyanate species on those surfaces that may provide opportunities for dermal exposure to workers.

Work related asthma rates in the auto repair industry

The Bureau of Labor Statistics estimates that a total of 44,730 workers were employed as painters of transportation equipment, such as automobiles, buses, trucks, boats, and other vehicles in 2011.[8] This is in addition to the other automotive repair workers that may also be exposed to isocyanates during the process of repairing and refinishing. Approximately 170,900 automotive body and glass repairers were employed in 2010.[9] The potential for exposure among these groups represents a great health concern, as isocyanates remain one of the most commonly reported causes of work-related asthma (WRA) in the United States and the UK.[2,15,38] Between 2000 and 2005 a total of 12 cases of work related asthma were reported through the Washington State Department of Labor and Industries. Of these 12 workers, 8 were believed to be associated with isocyanate exposures.[38] Despite recommendations for increased use of PPE and proper handling of the "clear coat", workers continue to report WRA as a result of isocyanate exposure. In addition to the risk of developing respiratory problems, there have also been reports of death associated with work related asthma caused by isocyanate exposure.[21]

Historically, these work-related asthma cases and other respiratory disorders associated with isocyanate exposure have been attributed to inhalation exposures. However, there is significant evidence to suggest that dermal exposure may play a role in the development of respiratory sensitization. Animal studies have found that isocyanate contact with skin may represent a route of exposure that results in respiratory sensitization and eventually asthma.[16,17,28,39] It was first suggested that dermal exposures might be linked to respiratory health effects in 1981.[17] Despite this early discovery, awareness of this issue remains low for many industries. Dermal exposure to isocyanates and related respiratory health effects remain a great concern among industries using isocyanates.

Human studies have also confirmed that exposure to isocyanates is strongly associated with an increased risk of asthma among various industries.[4,13,24,28,36,40] In particular, MDI, TDI, and HDI have been identified as the chemicals responsible for sensitization.[4,13,25,26] For auto shop workers, prepolymers of HDI may be the primary cause of respiratory sensitization as opposed to monomeric forms.[36] In addition, dermal exposures are also associated with skin irritation and dermatitis.[1,13] As a main component of polyurethane coating systems, isocyanates are widely used in the automotive and collision repair industry. Due to their presence in these products, there is a significant risk of occupational exposure by both inhalation and dermal pathways. Handling of “clear coat” solutions, from mixing and spraying to cleaning, provides many opportunities for exposures as a result of improper handling techniques, failure to use recommended PPE, as well as inadequate protective characteristics of the PPE. Bello et al. found various levels of the chemicals beneath both gloves and respirators suggesting an inability to provide a barrier to such exposures.[5]

Current regulations

Currently, NIOSH recommends 8-hour TWA exposure levels of 5 ppb (NIOSH REL) and a ceiling value of 20 ppb for HDI, TDI, and MDI. Exposure to isocyanates in various industries has been associated with dermatitis and occupational asthma.[1,13,24,28,40] Such health endpoints can prevent workers from continuing to work in industries involving isocycanates. Although solely identified as air contaminants by most agencies, it has been suggested that isocyanates also permeate the skin to induce sensitization and asthma. OSHA and other regulatory agencies do not currently have standards for surface contaminants, but certain chemicals have been designated as skin contaminants. MDI and TDI are the only diisocyanates included in OSHA regulations and have not yet been designated as skin contaminants. Both are regulated at air concentration ceiling values of 0.02 ppm. ACGIH has set RELs for MDI, TDI, and HDI at the same concentrations as those set by NIOSH. However, these values only include an 8-hour TWA and not a ceiling value. Despite extensive research conducted by Washington State Department of Labor and Industries (SHARP), there are currently no standards specific to isocyanate exposure in Washington State. Additional research of isocyanate surface contamination could be used to develop regulations for HDI and other forms of isocyanates, specific to skin exposure.

Current surface sampling methods

Quantifying dermal exposures to isocyanates is complicated by the chemical properties of the compound. The highly reactive nature of these chemicals often results in poor recovery after sampling. This creates many challenges for surface sampling methods. Most surface contamination assessments have included only qualitative methods.[11,18] Colorimetric SWYPEs are frequently used to indicate the presence of isocyanates on surfaces and skin. For this method, color intensity is correlated with a higher concentration of contaminants. While potentially having a wide margin of error, qualitative measurements yield fast and convenient results. SWYPE indicators may be used to quickly determine which surfaces require decontamination or additional curing time. Colorimetric SWYPEs have also been used to semi-quantitatively measure isocyanates on surfaces.[11] Using computerized imaging tools, the color changing pads were evaluated to estimate isocyanate surface loading. As a rapid method of analyzing isocyanate concentrations, the SWYPE method is useful in obtaining results quickly. While timely, the results may be less accurate than quantitative assessments. Also, the method is based on the analysis of a color change reaction. This analysis relies on both the quality of image that a photo scanner may provide as well as the accuracy of the color changing reaction in the prediction of isocyanate loading. In the case that either factor is inaccurate, the resulting recovery estimates may be greatly influenced. Such inaccuracies have been reflected in previous studies showing high specificity for isocyanates (100%), but relatively low sensitivity (55%).[18]

Other studies have used a quantitative approach to surface sampling.[5,6,18] In particular, a surface decontamination study involving a polypropylene glycol (PPG) solution and other decontaminating solutions was performed using aluminum sampling surfaces.[7] The study obtained recovery results ranging from 27% to 76% of total isocyanate species depending on the applied solution. Surface decontaminants used in the study served to increase physical removal of isocyanates and, thus, increase recovery of the samples. The major limitation of each of the decontaminant solutions was reactivity with isocyanates. Each of the decontaminants was able to react with the spiked isocyanates resulting in percent reacted isocyanates ranging from 5% - 100%. Therefore, use of decontaminants or wetting solutions may also contribute to large losses of isocyanates. Sampling of contaminated work surfaces have used similar methods and utilized the same PPG solution.[5,18] However, the primary objective of taking quantitative measurements was to provide comparison results to calibrate qualitative measurements. The accuracy of quantitative samples was not analyzed, so the effectiveness of the surface sampling method was not determined. Both studies obtained many positive results for the presence of isocyanates; however, without an established standard method for the purpose of comparison, it may be difficult to determine the accuracy of the methods. The development of a standard wipe method is necessary to determine the recovery of isocyanate species from inert surfaces prior to quantifying from surfaces that may readily react with isocyanates.

Although not frequently used in studies, an OSHA method exists for isocyanate surface sampling. The current OSHA W4002 method uses Ghost Wipes (polyvinyl alcohol copolymers) and includes a wetting solution of isopropanol and water made up in a 1:1 ratio.[23] Since the reactivity of isocyanates with alcohol and water has been observed, the presence of both may greatly increase the risk of those reactions.[27,31] A reaction rate experiment was conducted by OSHA to compare isocyanate loss to reaction for specific time intervals.[11] High recoveries of HDI were obtained ≥ 90% for samples immediately placed into derivatizing solutions. While the method includes a reaction time study comparing average recovery of HDI to specific time intervals following exposure to the wetting solution, wipes were not included in this experiment. Instead, HDI was spiked directly into vials containing the alcohol solution. This does not accurately reflect the conditions of the surface sampling method since both the Ghost Wipes and sampling surfaces are excluded. Therefore, it is difficult to determine the effects of the wetting solution on recovery for surface sampling specific to this method.

Average recovery of HDI was approximately 58% using Ghost Wipes to sample from spiked glass surfaces. Additionally, the target spiked concentration for this method was 340µg/100cm^2. This value is likely very high compared to surface concentrations found in auto shops. Qualitative assessment studies have estimated surface contamination to be closer to 4.2µg/100cm^2.[18] The water in the Ghost Wipes and wetting solution may also repel the isocyanates and prevent recovery of the chemical since HDIs are not very soluble in water due to polarity differences.[20] In addition to each of these concerns, the Ghost Wipes are large in terms of surface area, which creates challenges for laboratory analysis. Ghost Wipe media have been known to be difficult in digestion of the material and extraction of the sample.[12] An improved surface sampling method would take these issues into consideration and utilize materials that were both effective in recovering the chemical of interest as well as practical for laboratory analysis.

Current study

A lack of a reliable, standardized surface wipe method necessitates the development of an improved method. The overall goal of this study is to further develop the sampling procedures described by the OSHA method number W4002. An ideal wipe method would be able to improve recovery while eliminating the elements of the OSHA method that may cause problems with HDI sampling. One of the greatest problems associated with a wipe sampling method is the wetting solution used to improve recovery of isocyanate species. Some of the most commonly used wetting solutions include water and alcohols, which are both capable of reacting with isocyanates. A new wipe method would either eliminate the use of a wetting solution or would utilize a wetting solution that would neither react with isocyanates nor pose a hazard for auto shop workers that might result in adverse health outcomes. An additional concern associated with the use of a wetting solution involves the perception of the auto repair workers. It is possible that wetting solutions may be regarded with concern in terms of the potential effect of the solution on paints, clear coats, or painted parts. An auto shop owner may not allow anything believed to compromise the quality of work to be used on painting and mixing surfaces. Also, the wipe material used for sampling must not be capable of reacting with isocyanates and should not attract water. The material should also be durable enough to sample on multiple surface types. Although factors that affect surface sampling will be important for the development of a wipe method, laboratory analysis also greatly affects the recovery results. An ideal method would also work well for laboratory analysis in terms of digestion of the wipe material and extraction of the sample. Recent evidence of slow curing times for various paints and clear coats suggest that quantifiable amounts of unbound isocyanate species may remain on painted surfaces hours or even a week after sprayed parts have dried.[6] Improvement upon currently used methods will be necessary to evaluate the potential hazard presented by surfaces contaminated with slow curing paints or clear coats.

Specific Aims

1. Compare surface sampling wipe media using a standardized surface sampling procedure for hexamethylene diisocyanates that may be used in the auto repair industry.
2. Compare HDI percent recovery among polypropylene, quartz fiber, and polyvinylidene fluoride wipe media sampling from glass, ceramic, and aluminum surface types.
    a. Determine recovery differences among polypropylene, quartz fiber, and polyvinylidene fluoride wipe materials.
    b. Determine recovery differences when sampling from glass, ceramic, and aluminum surface types.
3. Analyze the variance of mean recovery of HDI to determine precision of the method for each wipe material as well as to assess the differences in mean recovery.

Methods and Materials

While necessary for improvement upon currently used methods, all of the previously described characteristics have not been evaluated in this project. An attempt was made to address as many concerns with previously used wipe methods; however, this study is limited in scope and serves, primarily, to identify elements in current surface sampling methods that are problematic in terms of obtaining accurate recovery results. The focus of this current study includes comparison of multiple media types, hydrophobicity of the wipe material, recovery from multiple surface types, and efficiency for laboratory analysis. By evaluating the HDI recoveries for different wipe media as an initial step in developing a surface sampling method for isocyanates, an element can be addressed that is central to sample recovery. Wipe media used in the sampling method can affect laboratory analysis results as well as removal of isocyanates from spiked surfaces. It will be important to evaluate wipe media performance before considering the effects of other materials, including wetting solutions, on recovery of HDI species. Additionally, time constraints of the study did not allow for the full development of a novel surface sampling method.

Three different wipe materials were compared using a standardized wipe method. Media of a wide range of hydrophobicity were chosen to determine differences in recovery based on this property. An HDI standard (N3300) containing three different HDI oligomers was used to spike aluminum, ceramic, and glass surface types with concentrations ranging from 0 – 180μg. Recovery was calculated based on the spike values and the quantity measured from sample wipes. Wipes were placed in vials containing 1-(2-methoxyphenyl)piperazine to optimize recovery of isocyanate species immediately following sampling. All samples were transported to the Washington State Division of Occupational Safety and Health Industrial Hygiene Laboratory for analysis.

Selection of media

Wipe materials were selected based on the chemical properties and presumed reactivity of HDI. Since isocyanates are known to react with water, materials of varying hydrophobic properties were used to determine the effect of this property on recovery. Polyvinylidene fluoride air filters, 25 mm in diameter, (Millipore, Billerica, MA) were used for HDI sampling, specifically, for the hydrophobic properties of the material. PVDF wipe media were found to be the most hydrophobic of all the wipe media used. Kimtech polypropylene wipes (Kimberly-Clark, Neenah, WI) were cut to 25 mm diameter sized wipes and used for HDI sampling. The Kimtech wipes are less hydrophobic than the PVDF filters, but also more absorptive. The least hydrophobic material used for collecting HDI was the SKC 25 mm diameter quartz filter (SKC, Fullerton, CA).

Wipe media size was limited to a diameter of 25 mm mostly for reasons of practicality. In order to accurately compare recovery for all wipe media, the size of each should be the same. In addition, of the sizes offered by manufacturers, media of this size (25 mm) were likely to fit well into vials used for sample collection. Larger media might necessitate folding to fit into vials. Folding may minimize the contact between media and derivatizing solution. In addition, two of the media used for the study were manufactured as air filters and intended for measuring air concentrations of contaminants. These were selected in consideration of laboratory analysis procedures. Since these materials are likely dissolved for sample extraction, they may be a practical choice for surface sampling media in terms of laboratory analysis. The polypropylene media was manufactured as an industrial wipe rather than an air filter. It was selected due to its use as a wipe material in anticipation that the media might improve removal of HDI.

Selection of surfaces

Inert, low porosity materials were selected in order to reduce analyte loss due to reactions between the surfaces and HDI. The three different surfaces included glass, ceramic, and aluminum and were used to indicate that the wipe methods are capable of collecting HDI from multiple surfaces and materials. Surface types were also standardized in terms of size. Each surface area was limited to 100 cm^2. Surfaces of this area were used to provide results comparable to previous surface sampling studies. A semi-quantitative surface sampling method and the OSHA method (W4002) have both used a surface area of 100 cm^2.[11,23] While these selected surfaces are not generally used in the auto shop industry as work surfaces, it will be important to sample from inert materials that are also of low porosity. This will aid in identifying which wipe material is able to recover the greatest amount of spiked standard. Determining recovery from these “best case” surfaces is necessary prior to attempting field sampling in order to reduce the effects of sampling from porous, reactive materials that may contribute to low recovery of isocyanates. Without understanding the recovery abilities of each wipe media when used on inert, low porosity surfaces, it will be difficult to accurately quantify HDI present on more reactive work surfaces.

Selection of standard

Standards were prepared using Desmodur N3300 (Bayer MaterialScience LLC, Pittsburgh, PA.) and reagent grade toluene. Desmodur N3300 was selected for its composition of HDI trimers, containing three HDI oligomers. A variety of hardeners containing isocyanates are available from the same manufacturer, but based on its frequency of use in the auto repair industry, N3300 was favored over other hardeners. This product will also best represent isocyanate exposure as HDI isocyanurates are typically found in greater quantities than other forms of HDI and are highly associated with exposure.[29,32] Sparer et al found that 79% of all bulk samples of paints or clear coat products contained some isocyanurate and 19% only contained isocyanurate as a hardening catalyst.[32] Another study determined that 67% of isocyanate air concentrations in excess of $1000\mu g/m^3$ were HDI isocyanurate species. Desmodur N3300 is an HDI homopolymer product containing greater than or equal to 95% HDI homopolymer by weight.

Selection of derivatizing solution

1-(2-Methoxyphenyl)piperazine (MPP) was used as a derivatizing solution to improve recovery of isocyanate species. By binding to MPP, the isocyanates are unable to undergo reactions to form ureas or other reaction products, which helps to stabilize the chemical of interest. The use of a derivatizing solution could also improve detection of HDI since detection will only include MPP-HDI derivatives. All MPP solutions were dissolved in reagent grade toluene. After sampling, all wipe samples were placed in glass vials containing 5 ml MPP in concentrations of 1.0 mg MPP/ml Toluene (Sigma-Aldrich, Saint Louis, MO). Exposing samples to the derivatizing solution immediately following isocyanate collection will improve recovery of the chemicals.[34,35]

Surface sampling procedure

Prior to sampling, all surfaces were thoroughly cleaned using acetone and Kimwipes then allowed to air dry. Forceps were also cleaned with acetone and allowed to air dry. In addition to decontamination of surfaces and forceps between sample collection, gloves were also changed every 30 minutes to decrease cross-contamination and to prevent dermal exposure for the researcher due to glove permeation. To prepare isocyanate standards, 100 mg of Desmodur N3300 was dissolved in 10 ml of Toluene.

Serial dilutions were made from the solution of 10 mg/ml N3300 in Toluene in the following concentrations: 5mg/ml, 1mg/ml, and 0.05mg/ml. Volumes ranging from 20µl - 100µl were spiked onto each of the three surfaces to yield the following spiked amounts of HDI: 4µg, 40µg, 80µg, and 180µg. Although these quantities are not identical to the spiked concentration used in the OSHA method W4002 (340µg/100cm^2 HDI), they may be more representative of measurements found on auto repair shop surfaces. Qualitative assessment of auto repair shop surfaces found measurements closer to 4µg/100cm^2 HDI.[18] In the case that the qualitative sampling method failed to remove the total HDI bound to surfaces, it is possible that a greater concentration was present. Since the standardized OSHA method (W4002) does not specify drying time of the spiked standard prior to surface sampling, surface sampling procedures used in a SWYPE sampling study were used.[11] Each spiked volume was given 2 minutes to air dry before wiping. Once dry, forceps were used to wipe the spiked surface in a circular motion over the entire surface area ($100cm^2$). Starting from the outermost part of the surface, media was wiped in decreasing concentric movements in order to cover the entire area. The wipe sample was immediately placed into a vial containing the derivatizing solution, 1-(2-Methoxyphenyl)piperazine to prevent degradation of recovered isocyanates. All sample containers were labeled and stored at -20°C to prevent evaporation of the MPP solution. The vials were kept in cooled containers with internal temperatures of approximately 0°C while transporting the samples to the laboratory for analysis to minimize loss of toluene due to evaporation. Following each surface sampling, surfaces were rinsed with acetone and wiped with clean Kimwipes in order to remove residual HDI. All experimental procedures were performed in a chemical hood while wearing nitrile gloves, a laboratory coat, and safety glasses.

Randomization of sample collection

The order in which samples were collected was randomized so that all samples were treated independently of one another. That is, the way in which one sample was handled would be identical the way the following sample would be handled. This was done in order to perform a balanced experiment, such that HDI loading on surfaces would not affect average recovery of HDI. Random selection was performed using Microsoft

Excel. A list of all the samples was sorted according to a list of randomly generated numbers. A total of 108 wipe samples were taken, with 36 taken for each surface type and 36 taken for each media type (Table 1). An equal number of samples were also taken for each spiked amount of HDI (Table 2). These sample numbers include replicates. A total of 3 repeated samples were taken for each spiked HDI mass for each media type taken from each surface type.

Table 1. Sample size by media and surface type

Sample type	Number of samples (n)
Media	108
Quartz	36
Polypropylene	36
PVDF	36
Surface	108
Ceramic	36
Glass	36
Aluminum	36
Total	**108**

Table 2. Distribution and summary of sample size for HDI loading by media and surface type

	Media type			Surface type		
HDI loading (µg)	Quartz	Polypropylene	PVDF	Ceramic	Glass	Aluminum
4	9	9	9	9	9	9
40	9	9	9	9	9	9
80	9	9	9	9	9	9
180	9	9	9	9	9	9
Total samples	**36**	**36**	**36**	**36**	**36**	**36**

Quality control and field blanks

Prior to any sample collection, lab blank media were analyzed for evidence of contaminants present on the materials that might cause interference in laboratory analysis. These lab blanks were taken directly from the packaged materials and were not exposed to HDI during sampling. Field blanks were also used to account for background levels of HDI present on ceramic, aluminum, and glass surfaces. These field blanks were treated in a manner identical to that of collected samples; however, these wipes were not exposed to the isocyanate standard. Once wiped on the un-spiked surface, field blank wipes were placed into vials containing the MPP derivatizing agent and placed into a cooler. Surfaces used for field blanks were not spiked with N3300.

In order to evaluate matrix effects associated with the wipe media and laboratory analysis procedures that might affect recovery, quality control samples were spiked with 27µg of an N3300 solution. Matrix spiking was performed at the DOSH IH laboratory in Olympia, WA.

Data analysis

After receiving quantitative measurements of HDI detected on the wipe media, percent recovery of HDI was calculated using the following equation:

$$\%\, Recovery\ of\ HDI = \frac{Observed\ HDI - Blank}{Spiked\ value} x\ 100$$

Percent recovery values were used to calculate arithmetic means for each surface type, wipe media type, and spiked HDI mass. Mean values were used to describe the central tendency of recovery as well as to present differences between wipe media and surface type in terms of recovery. Mean percent recovery of HDI was calculated for each media and surface type, as well as for each HDI loading value. Blank values were estimated based on the detected HDI. Since HDI was not detected on blank media, except in one case, all measurements of HDI for blanks were reported as “none detected”, or <0.87μg HDI. The stated limit of detection (LOD) for the Department of Occupational Safety and Health Industrial Hygiene Laboratory is 0.87μg HDI. The blank value used to calculate recovery of HDI was a value ½ of the LOD: (0.87μg HDI)/2 = 0.44μg HDI.

Standard error values were also calculated for mean recovery values according to the following equation: $Standard\ error = s/\sqrt{n}$

Where ‘s’ is equivalent to the standard deviation of the mean and ‘n’ equals the number of samples included in the calculation of the mean.

Additional statistical testing was used to further investigate differences in HDI recovery for different surface types and wipe media types. All statistical analysis was performed with STATA version 11. A Kruskal-Wallis test was conducted to compare HDI recovery according to wipe media type. The statistical test is a non-parametric, rank-sum test that is frequently used to compare categorical and continuous variables.[30] Recovery has shown to increase at higher masses of spiked HDI, and the data is not normally distributed. In order to perform the Kruskal-Wallis the data must be sorted and ranked. The mean rank sums are compared to determine differences in the populations. Comparisons may be made for 2 or more datasets using the Kruskal-Wallis test. In this case, since sample distributions are all non-normal and similarly asymmetric in shape, this is an acceptable test to compare mean or median values of recovery.[30]

Since the Kruskal-Wallis test is only able to determine whether all population means are identical or different, additional analysis was required to determine which groups were significantly different. The Mann-Whitney Rank-Sum test was used to perform pairwise comparisons of the wipe media. Similar to the Kruskal-Wallis test, the Mann-Whitney is also a non-parametric test used when normality cannot be assumed for the dataset.[14] Like the Kruskal-Wallis test, all recovery values, categorized by surface type or wipe media, were ranked and sorted. The test is used to evaluate the whether a randomly chosen value from one group is greater than a randomly chosen value from the comparison group. The results of this test will indicate which groups are associated with significantly higher, or lower, recovery of HDI.

Results

Standard solutions

The HDI standard solutions used in surface spiking were analyzed, and summarized (Table 3). Differences between expected values of the standard solutions and observed values tend to be small except when concentrations are less than 1 µg/µl. Concentrations below this value greatly exceed theoretical values and may be associated with error. Since the 'observed' spike quantities were calculated based on the observed N3300 concentrations, the error associated with the observed quantity of 12.8µg of N3300 is dependent upon the measured concentration of 0.16µg/µl N3300. This high value greatly influenced percent recovery calculations.

Table 3. HDI standards and spike quantities

Expected N3300 (µg/µl)	Observed N3300 (µg/µl)	Spike quantity expected (µg)	Spike quantity Observed (µg)
10	11.2	180	195.12
5	5.42	80	69.6
1	0.87	40	34.8
0.05	0.16	4	12.8
0	0.22	0	NA*

*NA = Not applicable. Toluene not used to spike sampling surfaces.

Comparison of the observed and expected values for HDI concentrations (Figure 1) shows a linear correlation of $r^2=0.99$ suggesting strong correlation between observed and expected concentrations. Laboratory analysis of the expected standard concentration value 0.05μg/μl HDI presented challenges in obtaining accurate results. The observed concentration was reported as 0.16μg/μl HDI, which is 3 times the expected value. For all standard concentrations, it was assumed that the hardener dissolved and mixed uniformly in the toluene solution..

Standard concentrations of N3300 were compared to peak areas to plot a calibration curve (Figure 2). A linear relationship was observed between peak area and N3300 concentrations ranging from $8.71\text{x}10^{-1}$μg/ml to 44.44μg/ml HDI with a correlation coefficient of 0.99969. The Washington State Division of Occupational Safety and Health Industrial Hygiene Lab (DOSH IH lab) used this calibration curve in analyzing HDI samples. Comparison of the standard solution, 0.05μg/μl HDI, to this calibration curve indicates that this concentration is not within the limit of detection of the instrument. Spiked masses produced from the standard concentration, 0.05μg/μl HDI, could not be reliably measured. The limit of detection was reported as $8.71\text{x}10^{-1}$μg/μl HDI.

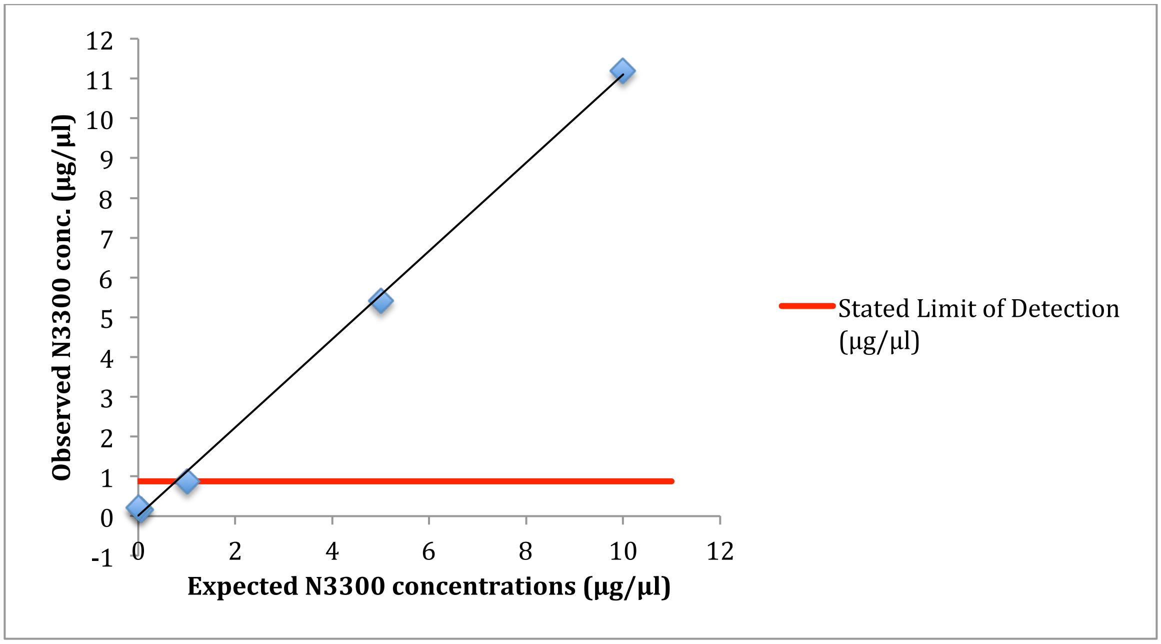

Figure 1. Comparison of expected and observed concentrations of N3300 standards show good agreement between expected and observed concentrations of N3300 above values of 1µg/µl. A line representing the stated detection limit of 0.87µg/µl is shown.

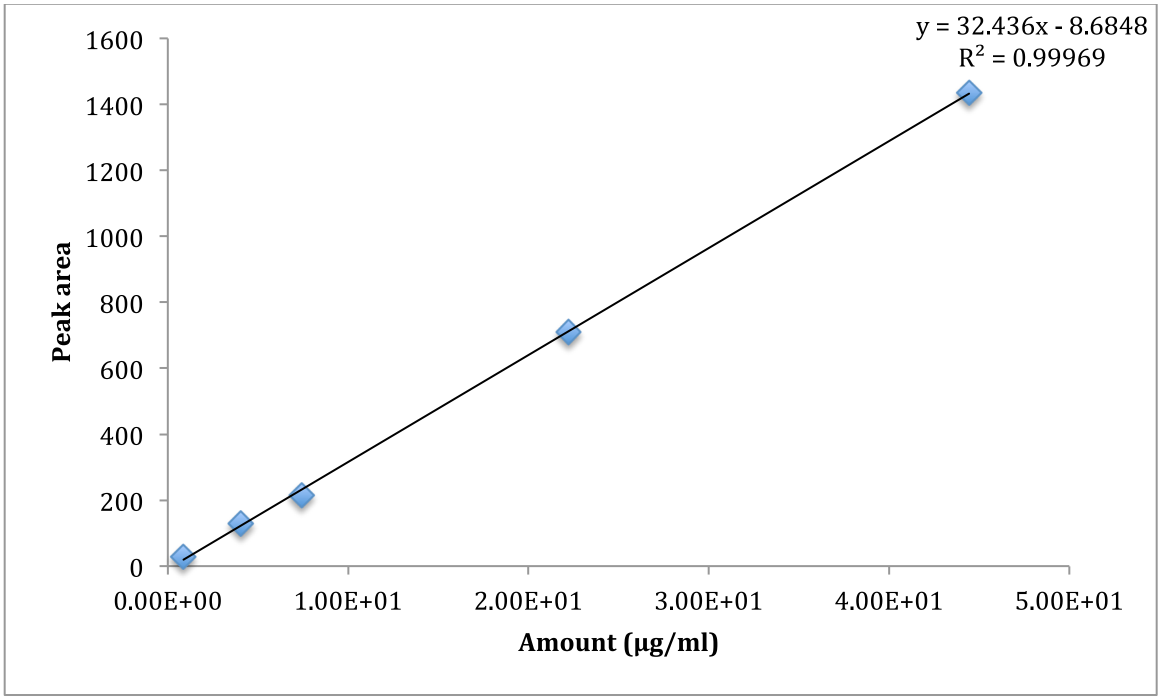

Figure 2. Calibration curve describing the relationship between the concentrations of the N3300 standards and the instrumental response (peak area) used to estimate HDI samples by the Washington State DOSH lab.

Quality control

Media previously unexposed to isocyanates were spiked with known quantities of the N3300 standard, performed by the Industrial Hygiene laboratory of the Division of Occupational Safety and Health in Olympia, WA. Matrix spiking is often conducted to assess sample preparation procedures that may lead to issues of matrix effects or interference.[41] Additionally, prior to sampling, blank wipe materials were submitted to the DOSH laboratory in order to evaluate the effects of the untreated materials and laboratory procedures as well as to test for background levels of HDI species on unexposed media. No detectable levels of HDI species or other elements known to interfere with analysis were found on any of the blank media.

Matrix spike results indicate very high levels of recovery for all wipe media ≥96.8% (Table 4). Mean recoveries showed very little difference when comparing polypropylene, quartz, and PVDF wipe materials (Table 4). There appears to be no indication of matrix effects or interference associated with the wipe media or laboratory analysis procedures that could potentially influence mean recovery of HDI.

Table 4. Summary of mean recovery and standard deviation for matrix spikes

Wipe material	No. of observations	Mean Recovery (%)	Standard Deviation (%)	Min (%)	Max (%)
Polypropylene	6	98.8	8.7	92.2	114.5
Quartz	5	96.8	3.7	92.9	102.8
PVDF	5	97.0	1.6	94.7	98.5

Percent recovery: Wipe media

Recovery of HDI was calculated according to the wipe media used. These values represent recovery of HDI for all surface types used (aluminum, ceramic, and glass). In general, mean percent recovery tends to increase with larger masses of spiked N3300 (Table 5). For all wipe materials, mean recoveries are relatively low as none exceed 53.5%. Polypropylene media may be the least effective for surface sampling as the material recovered the smallest quantity of detected HDI (28%). Quartz and PVDF media achieved higher recoveries with similar quantities detected on both wipes (49.5% and 53.5%, respectively).

Table 5. Summary of mean HDI recovery for polypropylene, quartz, and PVDF media taken from all surface types

Wipe	Observed Spike N3300 (µg)	Mean Percent Recovered (%)	Min (%)	Max (%)	Standard Error
Polypropylene	12.8	11.3	0.0	25.3	3.1
Polypropylene	34.8	14.1	0.0	28.9	3.3
Polypropylene	69.6	28.2	1.6	66.9	7.7
Polypropylene	195.1	52.6	22.5	106.9	8.6
Total		**26.5**	**0.0**	**106.9**	**4.0**
Quartz	12.8	10.9	0.0	29.6	3.6
Quartz	34.8	62.1	16.9	87.3	7.4
Quartz	69.6	68.4	51.4	88.9	3.5
Quartz	195.1	50.8	11.3	86.2	8.0
Total		**48.1**	**0.0**	**86.2**	**4.7**
PVDF	12.8	16.7	0.0	41.0	4.2
PVDF	34.8	45.6	32.9	74.6	4.2
PVDF	69.6	48.4	23.7	78.0	7.2
PVDF	195.1	94.6	62.3	176.6	12.9
Total		**51.3**	**0.0**	**176.6**	**12.1**

Recoveries for each wipe media show increasingly larger mean recovery at higher spike levels of standard solution (Figure 3). Differences between media indicate poor recovery of isocyanates for polypropylene media compared to quartz and PVDF. For almost all spike levels, quartz and PVDF media were able to obtain higher recovery of the sample than polypropylene. Both quartz and PVDF media mean recoveries do not significantly differ from one another. Although the overall mean recoveries are similar for these two wipe media, quartz media recovery does not consistently increase at higher spike levels. There is an estimated 18% decrease in mean recovery for the 195.1μg spike level for quartz compared to the preceding spike value of 69.6μg. This inconsistency can be attributed to durability issues associated with the media. During sampling procedures quartz media quickly deteriorated leaving small fibrous material on sampling surfaces. These pieces of material were difficult to collect and likely contributed to loss of HDI.

Statistical analysis of HDI recovery for each media type was performed using a Kruskal-Wallis test. Results of the test suggested that median recovery of HDI for quartz, PVDF, and polypropylene media were significantly different when compared together ($X^2(2)=14.962$, $p<0.001$). An additional pairwise comparison of polypropylene, and PVDF media was also performed to determine significant differences between media. A Mann-Whitney test was performed for the pairwise comparison of polypropylene and PVDF media. Quartz media results were not included in pairwise comparisons due to the associated durability issues. This media is not a recommended media for use in surface sampling methods. Instead, a greater focus was placed on PVDF and polypropylene as media used for a surface sampling method. Since PVDF is more durable and less likely to deteriorate, it is a more practical wipe material. Moreover, after eliminating quartz media as a potential wipe material, comparison of the two remaining media by ranked values indicates that PVDF is much more likely to obtain higher recovery of HDI than polypropylene (Figure 4). A Mann-Whitney test confirmed this finding ($Z=-3.99$, $p<0.001$).

The distributions of all percent recovery values for polypropylene, quartz, and PVDF media were represented in a boxplot graph. Recovery of HDI was limited to values calculated using 40μg-180μg expected spike values. Results indicate higher variance within the polypropylene media dataset compared to PVDF and quartz media (Figure 5). Values calculated using the expected spike mass of 4μg HDI were eliminated from the figure due to potential error associated with laboratory analysis of the standard solution used for the 4μg HDI spike.

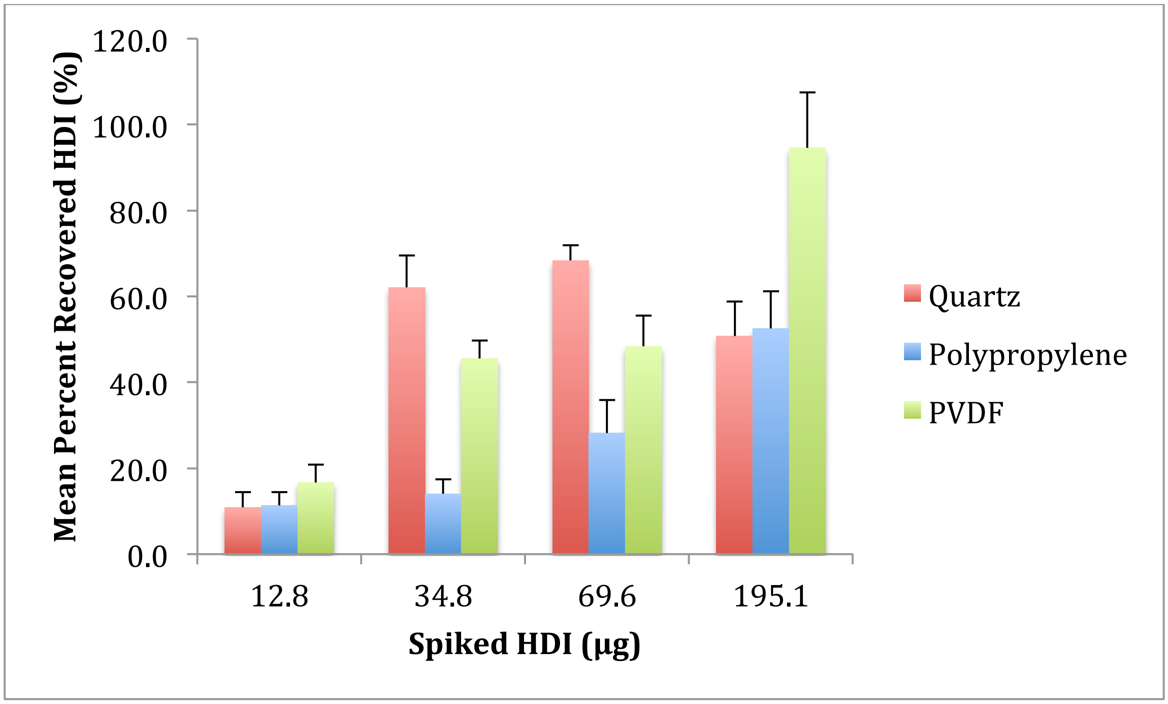

Figure 3. Comparison of mean percent recovery of HDI for polypropylene, quartz, and PVDF media shows greater recovery for greater spiked masses of HDI. Error bars represent standard errors.

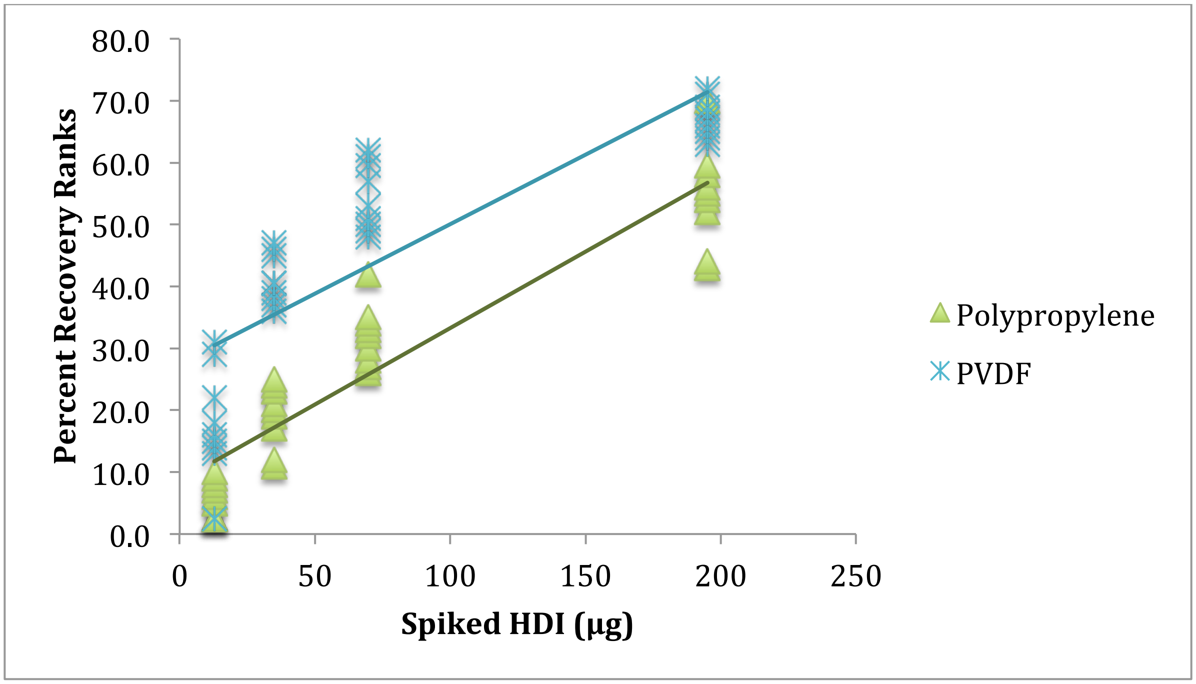

Figure 4. Comparison of percent recovery ranks for polypropylene and PVDF media based on Mann-Whitney pairwise test shows a significant difference in HDI recovery.

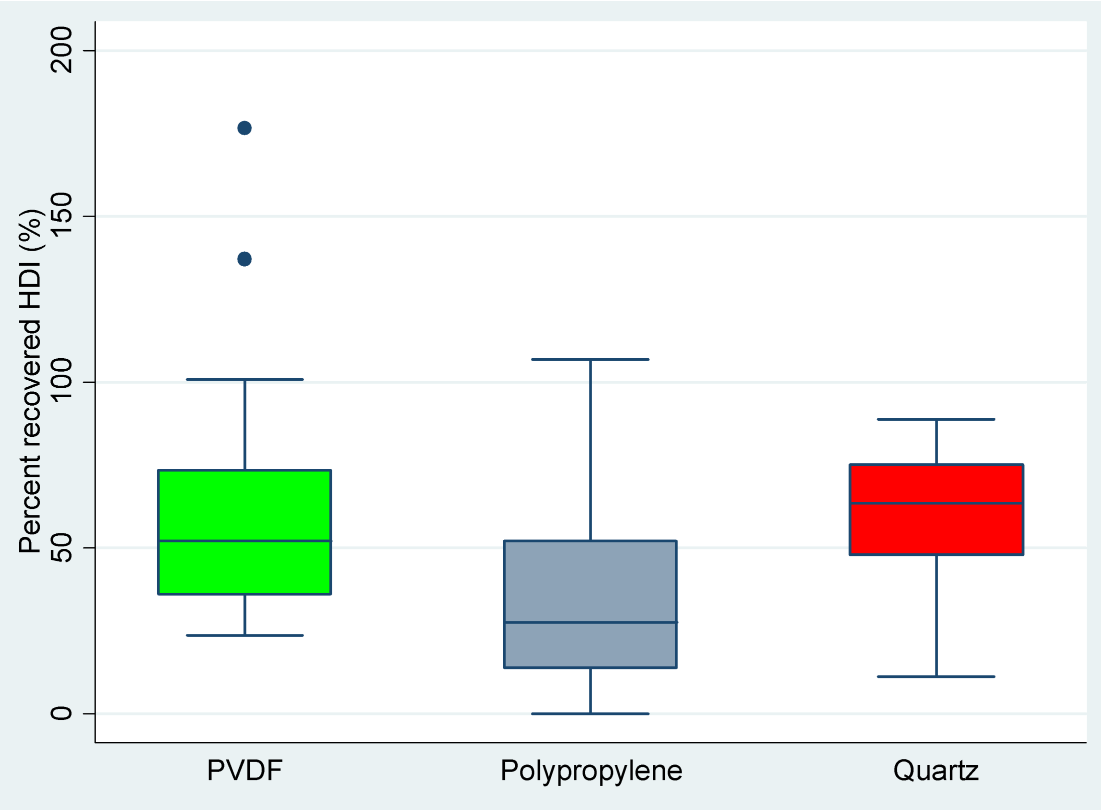

Figure 5. Comparison of the distribution of percent recovery values among PVDF, polypropylene, and quartz media. Percent recoveries included in the figure are limited to values calculated using expected spike values ranging from 40µg-180µg HDI

Percent recovery: Surfaces

Recoveries for wipe materials were also analyzed based on surface type. Recovery values were calculated by including data for all media types. Mean recoveries include samples taken for each surface type using PVDF, quartz, and polypropylene media. Ceramic stands out among the 3 surface types as having the lowest mean percent recovered HDI at 33.7% recovery (Table 6). Aluminum and glass surfaces are associated with greater recoveries and a small difference in values (52.3% and 45% recovery, respectively).

Table 6. Summary of mean HDI recovery for aluminum, ceramic, and glass surfaces for all media types

Surface	Observed Spike N3300 (μg)	Mean Percent Recovered (%)	Min (%)	Max(%)	Standard Error
Aluminum	12.8	19.5	5.7	41.0	3.5
Aluminum	34.8	44.3	0.0	75.8	8.4
Aluminum	69.6	59.7	23.7	78.0	5.8
Aluminum	195.1	75.5	36.7	176.6	14.0
Total Average		**49.8**	**0.0**	**176.6**	**5.5**
Ceramic	12.8	7.7	0.0	20.0	2.6
Ceramic	34.8	32.7	3.7	80.4	8.6
Ceramic	69.6	37.3	1.6	88.9	10.3
Ceramic	195.1	53.0	11.3	137.1	12.8
Total Average		**32.7**	**0.0**	**137.1**	**5.2**
Glass	12.8	11.7	0.0	33.0	3.7
Glass	34.8	44.7	13.8	87.3	8.7
Glass	69.6	48.0	17.1	75.2	7.3
Glass	195.1	69.5	36.3	106.9	8.0
Total Average		**43.5**	**0.0**	**106.9**	**9.8**

Similar linearity, as observed in comparisons according to media type, is evident in increasingly higher recoveries at higher spike levels of HDI (Figure 6). Samples taken from ceramic surfaces resulted in the lowest recoveries of isocyanates. HDI may be most effectively recovered from aluminum surfaces, as recovery is highest for this surface type.

A Kruskal-Wallis rank sum test was used to evaluate percent recovery of HDI by surface type. Results suggest a significant difference in median values of recovery for aluminum, ceramic, and glass surfaces ($X^2(2)=6.705$, $p<0.05$). After determining whether median recovery of HDI for the surface types were equal, Mann-Whitney tests were performed to compare pairs of data. Mean percent recovery of HDI was compared for the following pairs: aluminum and glass, glass and ceramic, and aluminum and ceramic. Although different mean recoveries were obtained for each surface type, the tests indicated that there is no significant difference in mean rank sums of HDI recovery when comparing aluminum and glass surfaces ($Z=1.477$, $p=0.1397$). A comparison of glass and ceramic surfaces suggested a significant difference in mean recovery of HDI ($Z=-2.954$, $p<0.01$). A significant difference in mean rank recovery was also observed when comparing aluminum and ceramic surfaces ($Z=2.922$, $p<0.01$).

Boxplots comparing distribution of percent recovery for aluminum, ceramic, and glass surface types indicate that the spread of data for each surface is similar (Figure 7). With the exception of 2 outliers, there is very little difference between boxplots. Medians and variance are not significantly different between surface types with the exception of ceramic surfaces. Median recovery of HDI obtained from ceramic surfaces is notably lower than for glass and aluminum surfaces in agreement with Mann-Whitney test results.

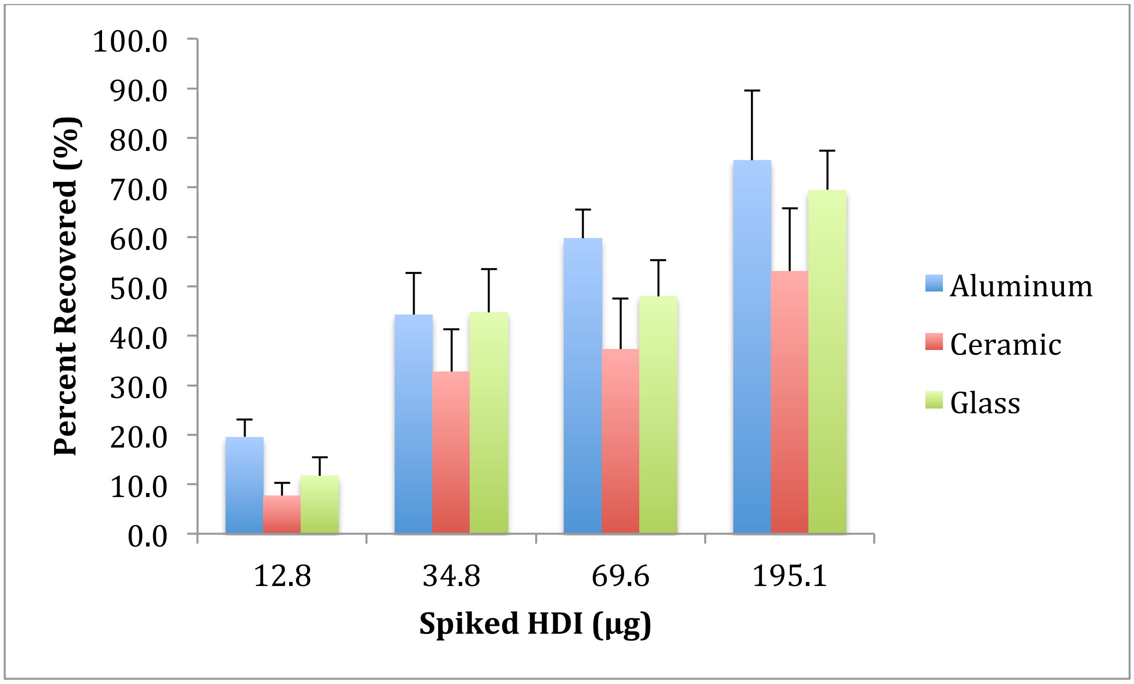

Figure 6. Comparison of mean percent recovered HDI for aluminum, ceramic, and glass surfaces indicate that differences in recovery are dependent upon surface type ($X^2(2)=8.14$, $p<0.05$). Error bars represent standard errors.

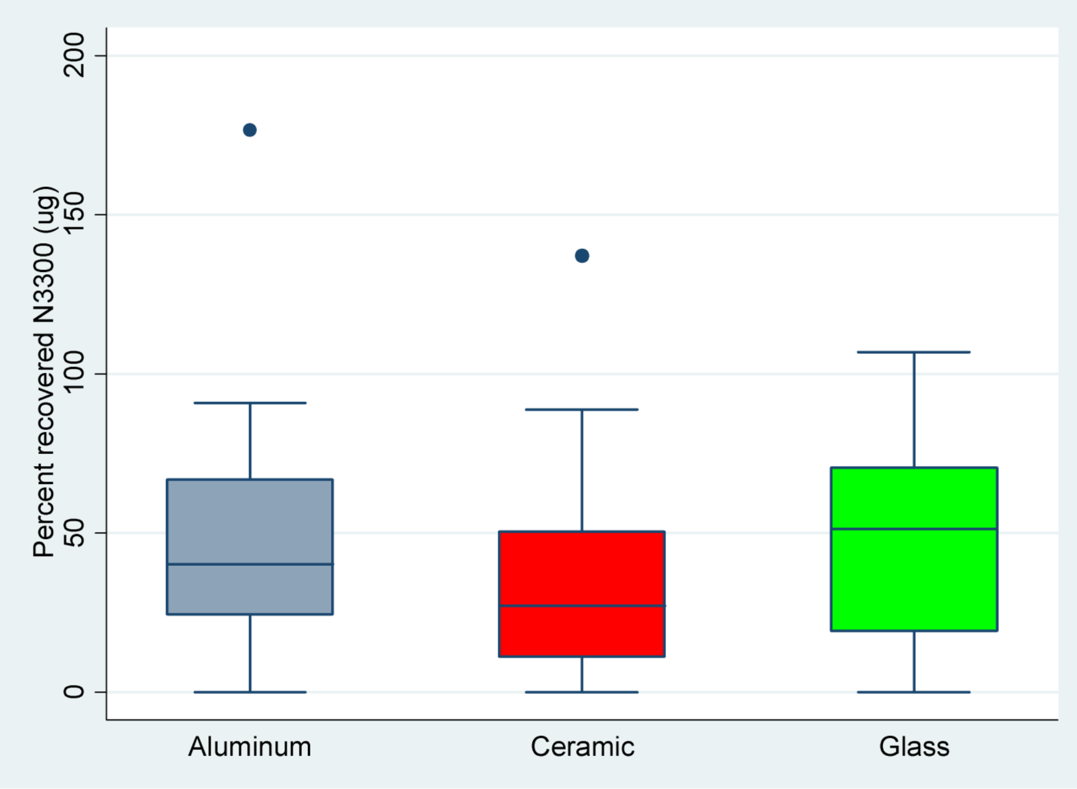

Figure 7. Boxplot comparing percent recovery by aluminum, ceramic, and glass surfaces shows little difference in the distribution of the data.

Blanks and data censorship

HDI was not detected on field blanks, as expected, since field blank media were not intentionally exposed to HDI standards (Table 7). However, one exception was discovered among the blank measurements, which was reported as 1.18 µg HDI. It was assumed that this high value was related to cross-contamination as no other samples were similarly affected. Due to this contamination, this value was not included in previous calculations or statistical analysis. All other detected values were reported as "none detected" for field blanks, or <0.87µg HDI. The stated limit of detection (LOD) for laboratory analysis is 0.87µg HDI. All blank sample measurements were replaced with ½ of the detection limit (50% of 0.87µg = 0.435µg).[41] This value was used to calculate all recovery values of HDI.

From the recovery results, it was observed that about 5.5% of all samples were below the detection limit of 0.87 µg HDI. When the number of censored values does not exceed 15% of the total samples, the values are usually replaced with ½ LOD or some small value (Zhang).[41] All censored data was replaced with 0.435 µg HDI, representing a value that is 50% of the detection limit.

Table 7. Observed and expected measurements of HDI for media

Wipe	Expected Spike N3300 (µg)	Observed Spike N3300 (µg)	HDI Detected (µg)	Number of samples (n)
Polypropylene	0	<0.87	0.435	9
Quartz	0	<0.87	0.435	9
PVDF	0	<0.87	0.435	9

Discussion and Interpretation of Results

The primary objective of this project was to observe the differences in recovery of HDI among three different wipe media. By choosing materials vastly different from those included in currently used methods, it was hoped that recovery might be improved. The factors of greatest concern when comparing wipe media included hydrophobicity of the materials, consistency of recovery when sampling from multiple surface types, elimination of a wetting solution that might negatively impact recovery, and precision of the surface sampling method. Each of these factors was assessed using STATA data and analysis statistical software and by comparing mean recoveries.

Major differences in wipe materials and surface type

In general, the PVDF media, also the most hydrophobic of the three materials, was found to recover the highest quantities of HDI when compared to those composed of polypropylene and quartz. Mean percent recoveries were highest for PVDF overall and in general when comparing the various media according to spiked HDI mass. One of the primary factors involved in selecting the wipe materials included hydrophobicity. When considering this factor in correlation with isocyanate sampling, it was originally expected that a material with a greater tendency to repel water molecules would be more effective in collecting isocyanate species since water is thought to repel isocyanates.[32]

However, hydrophobicity is likely not the most important factor to consider when comparing sampling media. Unlike for PVDF, this factor was not reflected in the results for quartz samples. The manufacturer of the quartz fiber media used in the study described the product as having hydrophilic properties (SKC, Fullerton, CA). Despite expectations of low HDI recovery, it was reported that the quartz media also produced high recoveries of HDI with a mean recovery very similar to that of the PVDF samples. There was not sufficient evidence to suggest any significant difference of percent recovery of HDI between the wipe media. The strong hydrophilic tendencies of quartz media are likely to attract water molecules that would repel HDI and decrease recovery. Greater recovery of HDI compared to other media is also surprising when considering the fibrous structure of the filters. While performing the wipe sampling procedures, the quartz media readily deteriorated. It was often not possible to collect all lost pieces of the quartz media. Due to such loss, it was expected that recovery might be negatively affected.

For these reasons of expected loss and hydrophobic properties of the materials, polypropylene media were also expected to perform better than quartz media in terms of percent recovery of HDI species. Polypropylene products are known to have hydrophobic properties.[19] However, the opposite effect was observed as polypropylene achieved the lowest mean recovery when comparing the three media. After eliminating quartz media for durability related issues, pairwise comparison of polypropylene and PVDF materials suggested that recoveries obtained using PVDF media were significantly higher.

Matrix spikes performed in the Washington State DOSH laboratory also produced results in opposition of the expected outcomes. Statistical tests found no significant difference in recovery between each of the three media. Since there were no discernable differences between the materials in terms of laboratory analysis and overall percent recovery, other factors may be more important in optimizing HDI sampling other than media type. Reductions in recovery are not likely caused by matrix effects between the chemical and wipe material. Instead, the primary concerns of HDI recovery from surfaces include isocyanate-surface binding, the ability of surface sampling media to physically remove HDI from surfaces, or isocyanate reactions prior to derivatizing solution exposure.

Comparisons of recovery by surface type may provide evidence to suggest that surface binding is an important factor in HDI sampling. Distinct differences were observed in mean recoveries for each HDI spike level. Samples taken from aluminum surfaces achieved highest percent recoveries among the surface types, while ceramic surfaces were associated with approximately 20% lower recovery values in comparison. The physical properties of the ceramic surfaces might result in greater binding of isocyanates compared to glass and aluminum. In contrast, it is possible that unrecovered HDI may be unbound and remaining on sampling surfaces as a result of the inability of the media to completely remove the sample.

Comparison to previous wipe studies

In terms of mean recovery of isocyanate species, few studies have measured recovery capabilities of wipe media based on a known spike quantity of an isocyanate standard. Liu et al included quantitative surface sampling in a study evaluating the accuracy of qualitative SWYPE indicators.[18] Surface sampling was conducted in the field, so the total mass of isocyanates present on those surfaces was unknown, and results were used only to confirm positive and negative results for the SWYPEs. Another study found recoveries of up to 79% using PPG and other solutions to improve removal of total isocyanates from an aluminum foil surface.[7] However, the aim of that study was to decontaminate surfaces, and all decontaminating solutions used in the experiment reacted with the spiked isocyanate standards. Despite the elimination of a wetting solution in this study, frequently used to improve recovery, mean recoveries from three different surfaces was estimated to be 51% compared to the decontamination study. A wetting solution was not included in this experiment due to the ability of most solutions to react readily with isocyanates.

The current OSHA method (W4002) recommends a 50% mixture of isopropanol in water, both of which have been known to react with isocyanates. The wetting solution used in the method is included in the sampling procedures based on the belief that it would improve recovery. Consequently, there does not appear to be a significant difference between percent recoveries of HDI for the OSHA method and the results of the current study. Mean recovery of HDI for the highest spiked amount (195.1μg/100cm^2 HDI) was 50.8%, 52.6%, and 94.6% for quartz, polypropylene, and PVDF media, respectively. Mean recovery of HDI, as reported by OSHA, was approximately 58.1% for a spiked mass of 340µg/cm^2 HDI. Furthermore, the recovery value for PVDF media was significantly higher compared to the W4002 method.

The target concentration for the method is 340µg/100cm^2 and no other spike values were used to estimate recovery efficiency. For this reason, recovery estimates may not accurately reflect the ability of the surface sampling method to recover HDI. In comparison, the current study included multiple spiked amounts of HDI. Results suggested that higher spiked masses of HDI were associated with higher recovery values. Compared to recoveries for quartz and polypropylene, the values obtained by the two methods are comparable, especially considering the spiked mass and lack of a wetting solution for the current study. Since recovery seems to increase with larger spikes of HDI, it is likely that recovery would match or exceed the results obtained by the OSHA method for a spiked value of 340µg HDI. However, this spiked mass is not likely representative of HDI concentrations found on surfaces in auto shops. According to a qualitative assessment, isocyanates collected from auto shop surfaces may be closer to 4µg/100cm^2.[18]

When comparing this quantitative method to the qualitative SWYPE method, the proposed procedures including any of the PVDF, polypropylene, or quartz media may not be an improvement upon semi-quantitative methods as recovery with SWYPEs has been comparable to the W4002 method.[11] However, qualitative methods fall short of expectations in terms of sensitivity. Colorimetric SWYPEs have been shown to have an estimated sensitivity of 55% for isocyanates compared to the qualitative method proposed in this study (93.5%).[18]

Limitations of the study

Standard dilutions of N3300 dissolved in different volumes of toluene were submitted to the DOSH IH laboratory for analysis to quantitatively measure the concentrations used for spiking surfaces. After receiving the results, it was discovered that the standard solutions of HDI of concentrations less than 1µg/µl were were excessively high compared to the expected value. The lowest concentration used for spiking was expected to be 0.05µg/µl HDI. A volume of 80µl of this concentration of N3300 standard was spiked onto each of the three surfaces for sampling. Unfortunately, since the concentration of 0.05µg/µl HDI was measured as 0.16µg/µl HDI measurements at these low levels are inflated. The large measurements may be attributed to interference or other issues with laboratory analysis. As a result, the theoretical mass of spiked HDI was increased from 4µg to 12.8µg. It is possible that the true spiked values were closer to 4µg; however, since the original concentration is likely inaccurate it is not possible to determine the true value. Based on this data, it is possible that either the standard solution submitted for analysis was incorrectly diluted, or laboratory analysis procedures and handling of the standard may have resulted in poor detection of HDI. In either case, it may be that HDI detection estimates and calculated recovery values based on the 0.05µg/µl HDI standard are associated with a wide margin of error and do not represent reliable values. However, it is likely that these inaccuracies were limited to the 0.05μg/μl HDI standard since there was good agreement between expected and observed concentrations of HDI standards of greater concentrations.

Other areas of concern likely to influence recovery include blanks, or a lack of blanks taken on surfaces. Since the blank samples included in the experiment were only exposed to surfaces that were not spiked with HDI standard solutions, background levels could not be adequately established for surfaces that had been spiked with N3300. Although surfaces were thoroughly cleaned with acetone between samples, but not tested, it is possible that some HDI species remained. Unfortunately, samples were not taken between spiked samples. It is unknown whether background levels of HDI were present on surfaces prior to sampling. This may have inflated recovered HDI species detected on the wipe media. However, as mean recoveries for wipe materials were not particularly high it is not likely that background levels of HDI were present while sampling, or that any residual quantities greatly influenced results. The only strong evidence of contamination includes extremely large outliers resulting from PVDF sampling. Two outliers amounting to 137% and 176% recovery can either be attributed to cross contamination or poor decontamination of surfaces between sampling.

Another limitation to the study is a failure to include matrix spikes to evaluate matrix effects. Quality control samples were spiked with known quantities of HDI by the DOSH IH laboratory, but a similar procedure was not conducted when collecting wipe samples.

The quality control samples were able to determine whether there was a matrix effect between the standard and the wipe media, but these controls were only spiked in the DOSH laboratory. They would not be able to account for any sampling procedures that could affect recovery, but instead could only explain differences in laboratory analysis procedures.

Recommendations for Future Work

This study aimed to evaluate wipe media in order to find materials that are more effective in recovering isocyanates and more practical for laboratory analysis compared to currently used quantitative surface sampling methods. In particular, the current study attempted to improve upon Ghost Wipe media used in the OSHA method number W4002. Large differences were observed when comparing matrix spike recovery values to HDI recovery from spike surfaces. Since matrix spike recoveries were ≥96.8%, it has been assumed that loss of HDI was caused by isocyanate reactivity, isocyanate binding to surfaces, or that media was incapable of removing the entire spiked sample.

Additional research is required to further develop the methods used in this study. The use of a derivatizing solution to impregnate sampling media may aid in improving percent recovery results. A wetting solution was intentionally left out of the experiment in an attempt to improve recovery; however, observed recoveries were comparable to results obtained with the OSHA W4002 Method. It is possible that an added wetting solution, such as a derivatizing solution, might improve recovery. The challenge in utilizing these types of solutions involves finding a non-toxic chemical that will react with isocyanates to form reactants that can be analyzed with currently used quantitative analysis methods. The derivatizing solution used in this study, MPP, is dissolved in the solvent, toluene. Exposure to the solvent is associated with cardiovascular and neurological health effects.[3]

Compared to the W4002 method, spiked concentrations of HDI were closer to concentrations found on auto repair shop surfaces for this study. However, a future study should include lower concentrations that may be more representative of HDI concentrations found on auto repair shop surfaces. This would likely require concentrations ranging from approximately 200ng/100cm^2 to 4μg/100cm^2 HDI based on previous quantitative assessments of auto repair shop surfaces.[18] This would provide greater insight into the effectiveness of the surface sampling method for lower concentrations.

In order to draw direct comparisons between the W4002 method and an improved method, a future study would need to include the Ghost Wipe media used in the OSHA method. Since this study did not include a wetting solution and used a different spike concentration of HDI, it is difficult to compare the methods beyond speculation. Inclusion of both media would also allow for side-by-side comparison of durability and practicality in addition to HDI recovery.

Other elements that this study failed to address include blanks and matrix spikes. Future studies would need to include blank samples taken from spiked surfaces following acetone cleaning. This would confirm whether any isocyanate standard remained prior to taking another sample. However, in order to measure the total remaining HDI, surfaces would also need to be rinsed with a derivatizing solution. Collection of the rinse liquid would be necessary to quantify the HDI. A blank collected following the rinse would be used to confirm that no residual HDI was still bound to the sampling surface. This information would be helpful in determining the amount of HDI lost to reactions or bound to surfaces. Matrix spikes taken in the same laboratory in which sampling took place may also account for recovery differences related to sampling procedures. This would confirm that laboratory equipment and sampling were not adversely affecting HDI recovery. In the case that laboratory procedures did not influence recovery results, then the likelihood that HDI was lost to reactions and surface binding would be increased.

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