World Applied Sciences Journal 6 (2): 242-247, 2009
ISSN 1818-4952

Indoor Air Pollution Study on Toluene Diisocyanate (TDI) and Biological Assessment of Toluene Diamine (TDA) in the Polyurethane Industries

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Abstract: One of the raw materials which are widely used in the polyurethane factories is diisocyanates. These compounds are widely used in surface coatings, polyurethane foams, adhesives, resins, elastomers, binders and sealants. The metabolite of toluene diisocyanate (TDI) is toluene diamine (TDA) which is found in worker's urine. One lot of 100 air samples was obtained using midget impingers. The impingers contained dimethyl sulfoxide (DMSO) absorbent as a solvent and tryptamine as reagent. High performance liquid chromatography (HPLC) with electrochemical (EC/UV) detector was used to analyze the samples using NIOSH 5522 method. Fifty urine samples were collected from the workers and analyzed by using William's biological analysis method. The results showed high maximum concentration of TDI (more than 75μg/m^3) when compared to the NIOSH standard (lowest feasible) and high concentration of TDA (4 μmol/mol creatinine) in the worker's urine. A statistical predictive model was obtained by correlation and regression test for TDA and TDI which can be useful for the prediction of diisocyanate pollution in the polyurethane factories.

Key words: Isocyanates · Polyurethane · TDI · TDA · Urine

INTRODUCTION

The lower molecular weight isocyanates tend to volatilize at room temperature, creating a vapor inhalation hazard. Conversely, the higher molecular weight isocyanates do not readily volatilize at ambient temperatures, but are still an inhalation hazard if aerosolized or heated in the work environment. The feature common to all diisocyanates (monomers) is the presence of two -N=C=O (isocyanate) functional groups attached to an aromatic or aliphatic parent compound [1].These compounds are widely used in surface coatings, polyurethane foams, adhesives, resins, elastomers, binders and sealants. In general, the types of exposures encountered during the use of isocyanates (i.e. monomers, prepolymers, polyisocyanates and oligomers) in the workplace are related to the vapor pressures of the individual compounds [2]. Isocyanates exist in many different physical forms in the workplace. The workers are potentially exposed to the unreacted monomer, prepolymer, polyisocyanate and/or oligomer species found in a given product formulation [3]. They can also be exposed to partial reaction of isocyanate-containing intermediates formed during polyurethane production [4]. The latter might be more hazardous as many reactions involving isocyanates are exothermic in nature and can provide the heat for their volatilization [5]. As exposure limits decrease, the volatility of solid materials becomes an issue. To reduce the vapor hazards associated with the lower molecular weight diisocyanates, prepolymer and polyisocyanate forms of these diisocyanates were developed and have replaced the monomers in many product formulations [6]. An example is toluene diisocyanate (TDI). Many prepolymer and polyisocyanate formulations contain a small fraction (usually less than 1%) of unreacted monomer [7].

Exposure to isocyanates is irritating to the skin, mucous membranes, eyes and respiratory tract. The most common adverse health outcome associated with isocyanate exposure is asthma due to sensitization. Less prevalent are contact dermatitis (both irritant and allergic forms) and hypersensitivity pneumonitis (HP) [8]. Contact dermatitis can result in symptoms such as rash, itching, hives and swelling of the extremities. A worker suspected

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of having isocyanate-induced asthma/sensitization will exhibit the traditional symptoms of acute airway obstruction, e.g., coughing, wheezing, shortness of breath, tightness in the chest and nocturnal awakening. An isocyanate-exposed worker may first develop an asthmatic condition (i.e., become sensitized) after a single (acute) exposure, but sensitization usually occurs after a few months to several years of exposure [9]. These are well documented in numerous studies where the aromatic diisocyanates will hydrolyze and react rapidly in both water and soil [10]. TDI reacts rapidly with water, thus if there are more moisturized in the TDI polyurethane factories, the TDI pollution will also be high. The psychrometric parameters such as indoor temperature and relative humidity also have relationship with isocyanates [11].

MATERIALS AND METHODS

The measurement of isocyanates in air is a challenging sampling and analytical problem for several reasons. Isocyanates can exist in air either as vapor, or as aerosol having a wide range of particle sizes. Isocyanates are very reactive and hence unstable and give many different chemical species, even in the same air sample, that need to be quantified. Pure analytical standards are not available for the vast majority of these isocyanate species and qualitative standards (bulk products) do not account for isocyanate species generated during polyurethane formation or breakdown. Finally, to measure isocyanates at levels corresponding to current exposure limits, analytical methods must be very sensitive. There are limitations to existing methods because of the complex problems associated with accurate sampling and analysis of total isocyanate group in air. To assess these limitations and to make rational decisions in choosing methodologies or making improvements to existing methodologies, it is useful to break down the sampling and analysis process, chronologically, into discrete steps. Another standard procedure to determine indoor isocyanate pollution in the polyurethane factories is biomonitoring using urine samples. Air sampling and biological sampling for isocyanates can be considered as a method for evaluation of isocyanate pollution in the polyurethane factories. A lot of five factories in Iran were selected. These factories produce foaming or polyurethane foams and the workers are exposed to TDI through indoor air pollution [5]. There were some workers who do not work full time. They work as officers and sometimes enter the workplace as unexposed worker. The

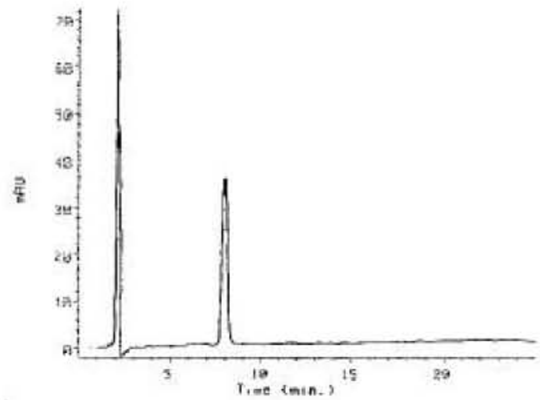

Fig. 1: TDI chromatogram by HPLC

air sampling and analyses of isocyanates from indoor air are divided into four steps: collection, derivatization, sample preparation, identification [5]. Samplers have been calibrated by using film flow meter. The Midget Impinger SKC personal inhalable sampler, with mini personal sampler pump SIBATA was used. All of the samplers with midget impinger wer connected to mini personal sampler pump fixed to work stations near the source of pollution. The air samples were collected in the third working time for 2 hours at a flow rate of 2 lit/min in impingers containing a solution of tryptamine reagent in dimethyl sulfoxide (DMSO) [5]. The air samples were collected throughout two hours of a work shift. After passing 120 liters of air the entire sample medium was transferred to the laboratory for analysis. Sample handling and preparation were done to make it compatible with the analytical procedure as per standard methods. The first step in the analysis of a solution is derivatization of isocyanates for the separation through High Performance Liquid Chromatography (HPLC) for their qualitative as well as quantitative analysis (Fig. 1).

The biological sampling was done by collecting worker's urine at the end of a working shift. Urine was collected into a polystyrene cup containing citric acid and transferred to the laboratory for analysis by Gas Chromatography Mass Spectrometry (GC. Mass) [9, 10].

The workers were divided into two groups; office personnel and factory workers. The first group was made up of one hundred persons and they had the least exposure. The other groups consist of 400 persons and were sufficiently exposed to TDI. A total of one hundred samples were collected randomly from working places inside the factory for the exposed persons. However, only five samples were collected from offices as blank samples for least exposed persons. All the air samples were analyzed in the laboratory for TDI using HPLC through standard method of analysis [5]. Biological samples were analyzed using GC Mass through method of Williams [12, 15]. Statistical analysis was carried out using ANOVA test and Regression through SPSS.

RESULTS AND DISCUSSION

Table 1 shows maximum concentration (=75 μg/m^3) of pollutant (TDI) at all factories. This is higher in comparison with the standard of The National Institute for Occupational Safety and Health (NIOSH) exposure limit value (lowest feasible). The result of analysis of the air samples by HPLC showed that the TDI concentration ranged from 53 to 81 μg/m^3. The relative humidity at the five factories ranged from 40 to 53% and dry bulb temperature was from 27 to 35°C. Workplace dimension for 5 polyurethane factories (T_1 - T_5) ranged from 4500 to 9900m^3. Altitude for five factories ranged from 135 to 1200m.

The relationship between multi factor scores and the TDI pollution were studied to understand the behavior of indoor air components with respect to different polyurethane factories. Regression analysis was used to assess the interactive behavior for TDI pollution and indoor air parameters.

As shown in Table 2 and Table 3, psychrometric parameters (relative humidity and dry bulb temperature) in the TDI polyurethane factories are significant predictors of TDI pollution concentration ($p < 0.001$). This indicates that increased psychometric parameters correspond to high levels of TDI.

According to Table 3 TDI concentration as a group the psychrometric factors together with the dimension of workplace and altitude in factories is significant ($p<0.001$).

A general regression model obtained from analysis of indoor air pollution factors and TDI pollution implies that there is a relationship between the increase of TDI concentration and psychrometric parameters. Based on Table 4 this prediction model at á level of 0.001 is significant for all of the parameters ($p < 0.0001$).

Possible relationship between the variables shown in Table 4 using multiple linear regression method which is appropriate in predicting the TDI concentration is given below:

$$Y = B_0 + B_1\,Rh + B_2\,Td - B_3\,D - B_4\,Alt \quad (1)$$

Where:

Y	= TDI concentration
$B_{0,\,1}$...	= Regression coefficients
Td	= Dry bulb temperature
D	= Dimension of workplace
Rh	= Relative humidity
Alt	= Altitude

The resultant predictive regression model with $r^2 = 0.979$ is:

$$TDI = 62.64 + 1.23\,Rh + 0.226\,Td - 0.0012\,D - 0.003\,Alt \quad (2)$$

The relative contribution of each variable to TDI concentration was directly measured by regression coefficient in the fitted model in Eq. 2. A positive sign for the regression coefficient in the fitted model indicates the direct relationship of the variables with TDI concentration, whilst the negative sign indicates the inverse relationship with TDI concentration in the polyurethane factories. This model may help to estimate

Table 1: Maximum and minimum reading of indoor air variables in the factories

Variables	Factories code T_1	T_2	T_3	T_4	T_5	Mean
TDI concentration (μg/m^3)						
Max	81.0	79.0	78.0	76.0	75.0	81.0
Min	59.0	58.0	57.0	55.0	53.0	53.0
Mean	69.5	68.2	67.1	66.0	64.3	67.0
Relative Humidity (%)						
Max	50.0	50.0	51.0	51.0	53.0	53.0
Min	40.0	40.0	40.0	41.0	43.0	40.0
Mean	43.8	43.8	45.6	46.2	48.0	45.6
Dry bulb temperature (C°)						
Max	35.0	35.0	33.0	33.0	33.0	35.0
Min	30.0	28.0	28.0	27.0	27.0	27.0
Mean	32.6	31.8	31.0	30.4	30.0	31.1
Mean Dimension of factory (m^3)	4500.0	5000.0	6700.0	8100.0	9900.0	
Altitude (m)	1200.0	1200.0	1100.0	850.0	135.0	

Max: Maximum, Min: Minimum

NIOSH guideline value: lowest feasible, carcinogenic

Table 2: Regression model summary

Model	R	r^2	Adjusted r^2	Std. Error of the Estimate
1	0.990	0.979	0.979	1.205

Predictors: (Constant), Altitude (m), Relative humidity (%), Dimension factory (m^3), Dry bulb temperature (°C)

Table 3: Result of analysis variance for psychrometric parameters and TDI Concentration

		Sum of Squares	Mean Square	F	p-value
TDI Pollution concentration (μg/m^3)	Regression	20098.31	5024.578	3457.655	<.0001(a)
	Residual	428.687	1.44		
	Total	20526.997			

(a) Predictors: (Constant), Altitude (m), Relative humidity (%), Dry bulb temperature (°C), Dimension factory (m^3), Altitude (m)

Dependent Variable: TDI Pollution concentration (μg/m^3)

Table 4: Descriptive of TDA concentration in different factories

TDA Factory code	Mean	Std. Deviation	Minimum	Maximum
T_1	3.20	0.624	2.0	4
T_2	3.15	0.580	2.0	4
T_3	3.10	0.550	2.0	4
T_4	3.00	0.643	2.0	4
T_5	2.95	0.632	2.5	4

Guideline value: 2 μmol/mol creatinine

Table 5 Relationship Test between TDI Results and TDA Results

Model		Sum of Squares	Mean Square	F	p-value
1	Regression	0.882	0.882	19.298	<.001
	Residual	0.594	0.0457		
	Total	1.477			

Predictors: (Constant), TDI Pollution, Dependent Variable: TDA Pollution

Table 6: Regression Model Coefficient for TDI and TDA

		Coefficients			
Model		B	Std. Error	t	p- Value
1	(Constant)	1.666	0.428	3.898	<0.002
	TDI Pollution	0.0281	0.006	4.393	<0.001

Dependent Variable: TDA Pollution

the pollution situation of TDI in the polyurethane workplaces based on the psychrometric parameters assessed.

All isocyanates inhaled by workers in the work places are metabolized or broken down in the body and eliminated in urine. The level of isocyanate metabolites in urine is an indicator of how much isocyanate has been absorbed and how well the controls are working. The levels of TDA are reported as 'μmol/mol creatinine'. Creatinine is found in everyone's urine and can be used to adjust the level of TDA to compensate for dilute or concentrated urine. The guideline value for TDA level is 2 μmol/mol creatinine samples above this value is considered contaminated [13-15].

Figure 2 showed that the maximum concentration of TDA obtained from worker's urine in all TDI polyurethane factories sampled was 4μmol/mol creatinine. This is higher than the guideline value by NIOSH (Table 4).

The regression statistical test was carried out for significant relationship between TDI air samples and urine samples from workers.

Table 5 shows that the statistical model for this group of data is significant and that the linear relationship between the two variables is significant ($p<0.001$) this mean that there is a strong relationship between TDI level in air samples and TDA level in urine samples. It implied that urine samples had high concentrations of the metabolite of TDI

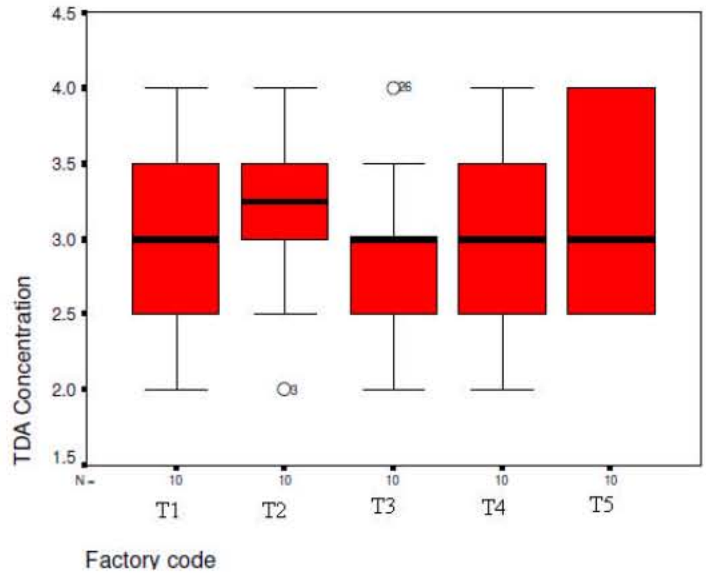

Fig. 2: Box-plot showing the concentration of TDA (μmol/mol creatinine) in different workplace area

(Toluenediamine) when the pollutant concentration in air samples is high.

The predictive statistical model for TDI pollution is extracted from Table 6, where the B coefficients were used to make the following model:

$$Y = a\,X + b \qquad (3)$$

Where:
Y is dependent variable (TDA)
b is model constant
a is model coefficient
X is independent variable (TDI)

$$Y = 0.028 + X + 1.666 \longrightarrow TDA = 0.028\ TDI + 1.666 \qquad (4)$$

Coefficients of this model (a and b) (Table 5) were significant ($p<0.001$) for both constant coefficient and TDI coefficient. This means that it can used for the prediction of TDA concentration in workers urine exposed to diisocyanates from the TDI concentration of polyurethane workplaces at a confidence level of 99.9%.

CONCLUSION

The indoor air quality evaluation in polyurethane factories showed that the level of TDI pollution is high at workplaces with high dry bulb temperature. This may be due to physicochemical processes of isocyanates which is thermophile. Similarly the pollution level is also high where the relative humidity is high. However, dimensions of workplace have opposite relation with pollution. Thus pollution can further be reduced by enhanced rate of ventilation, air flow and number of inlets and outlets which are responsible for dispersion of pollutant concentration in the workplaces [16]. The maintenance and correct use of injection sources and air-fed device as well as training in work practices are other key elements of minimizing isocyanate exposure. Besides that, use of personal protective equipment is also important for workers inside the factories to avoid health hazards. The result of this study showed that 54% of the samples exceeded 2μmol /mol creatinine TDA and 46% exceeded 3 μmol/mol creatinine. With regards to guideline value for TDA, the results obtained from the analysis of the worker's urine shows that all of the workers were infected with isocyanates in the workplace. This implies that the high level of metabolites concentration in the urine of the workers can be attributed to the polluted situation and workplaces. The concentrations of TDA detected in this study are similar to those found in other studies [17].

ACKNOWLEDGMENT

The authors gratefully acknowledge the research and financial support of Universiti Sains Malaysia (USM) [Grant No.304/PTEKIND/638063] and the technical support of the Ministry of Health and Medical Education of Iran, as well as Medical University of Mazandaran.

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