Original Article

RISK ASSESSMENT OF HEXAMETHYLEN DIISOCYANATE AND HEXAMETHYLENE DIAMINE IN THE POLYURETHANE FACTORIES

Mirtaghi Mirmohammadi[1], M.H. Ibrahim[2], A. Ahmad[3], M.O. A. Kadir[4], M.Mohammadyan[5], S.B.Mirashrafi[6]

ABSTRACT

Objectives: To determine the risk assessment of diisocyanate for workers and HDI concentration in the indoor air.

Methodology: For air monitoring 100 air samples were obtained using National Institute of Occupational Safety and Health (NIOSH) 5522 and for biological monitoring 50 urine samples were collected from the workers and analyzed with using William's biological analysis method.

Results: The results showed high maximum concentration of hexamethylene diisocyanate (more than 88µg/m³) when compared to the NIOSH standard and high concentration of hexamethylene diamine in the worker's urine.

Conclusions: Multiple regression models were obtained to predict of HDI risk in the polyurethane factories.

KEY WORDS: ISO Cyanates, Polyurethane, Hexamethylene Diisocyanate, Hexamethylene Diamine, Occupational Health.

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1. Mirtaghi Mirmohammadi,
2. M.H. Ibrahim,
3. Ahmad A,
4. M.O. A. Kadir,
5. M.Mohammadyan,
6. S.B.Mirashrafi,

1-5: School of Industrial Technology, University Sains Malaysia, 11800, Pulau Pinang, Malaysia.

Correspondence

Dr. Mirtaghi Mirmohammadi,
Dept. of Occupational Health,
Faculty of Health,
Mazandaran University of Medical Sciences,
Mazandaran – Iran.
E-mail: mirtaghim@yahoo.com

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INTRODUCTION

The common feature of diisocyanates is the presence of two -N=C=O (isocyanate) functional groups attached to an aromatic or aliphatic parent compound.[1] Diisocyanates are used as a initial chemical material in different factories such as surface coatings, polyurethane foams, adhesives, resins, elastomers, binders, and sealants.[2] In the polyurethane workplace there are aerosols of diisocyanates which has important to effect on workers.[3] They can also be exposed to partial reaction of isocyanate-containing intermediates formed during polyurethane production.[4] The main thing for volatization of diisocyanate is exothermic reaction in the air which is most important in the workplace.[5] As exposure limits decrease, the volatility of solid materials

becomes an issue.[6] Many prepolymer and polyisocyanate formulations contain a small fraction (usually less than 1%) of un-reacted monomer.[7] Exposure to isocyanates is irritating to the skin, mucous membranes, eyes, and respiratory tract.[8] A worker suspected 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.[9] HDI reacts rapidly with water, thus if there are more moisture in the hexamethylene diisocyanate (HDI) polyurethane factories, the HDI pollution will also be high. The psychrometric parameters such as indoor temperature and relative humidity is also related with isocyanates.[10,11]

The objectives of this study was to determine the risk assessment of diisocyanate for workers and HDI concentration in the indoor air of polyurethane factories, and to determine of HDA level in worker's urine as a isocyanate biomarker. Another objective was to see whether the psychrometric parameters (relative humidity and dry bulb temperature) and other factors (dimension of factories and altitude) relevant to factory had any effect on HDI pollution concentration. These are important for two reasons: (i) better understanding of isocyanates pollution situation at different workplaces with variety psychrometric condition, (ii) recognition of concentration of HDI from hexamethylene diamine (HDA) results in worker's urine which is metabolite of HDI in urine.

METHODOLOGY

Regression tool was used to assess risk assessment for polyurethane factories. Data was obtained through questionnaires for health surveillance in relation to isocyanates. Health surveillance assessment was extended to all processes where significant exposure to isocyanates in the form of vapor or aerosol may occur. It was the employee's responsibility to fill up health surveillance questionnaire. This surveillance questionnaire was carried out under the supervision of an occupational hygienist. Statistical analysis was carried out using one multiple regression model through SPSS for both air and urine data.

$$Y = B_0 - B_1 D + B_2 RH + B_3 Td \quad (1)$$

Where:

Y = HDI concentration]

$B_{0,\ 1}$…= Regression coefficients

D= Dimension of workplace

RH= Relative humidity

Td= Dry bulb temperature

A lot of five polyurethane factories in Iran were selected which have about 500 workers, the factories producing foam or polyurethane foams and the workers are exposed to HDI through indoor air pollution. The air sampling and analysis of Isocyanates from indoor air were divided into four steps: collection, derivatization, sample preparation, identification.[5] Air sampling was performed according to US National Institute of Occupational Safety and Health (NIOSH) method 5522 for isocyanate in air. Air samples were collected at 2 l/min using a midget impinger sampler (SKC, Eighty Four, PA) and personal sampling pumps calibrated before and after sampling with a Dry Cal DC-Lite primary flow meter (Bios International Co., Pompton Plains, NJ). A KNAUER HPLC was used for air analysis, the HPLC equipment consisted of a high-pressure pump, a variable-wavelength UV detector and a loop injector, HPLC columns were made of stainless steel (200 mm long x 5 mm in inside diameter) packed with 5 m Nucleosil C 18.[5] The air concentrations of HDI was monitored continuously by the midget impinger instrument using a Dimethyl Sulfoxide with Tryptamine reagent and the sampling time for HPLC analyses was one hour at an air flow rate of 2 I/min. A GCMS-QP 1000 EI/CI equipped with a Shimadzu auto sampler (AOC-9) was used for metabolite analysis of Diisocyanates. For enrichment and evaporation of solvent, a vacuum desiccators connected to an aspirating pump was used the apparatus was equipped with an electrically heated oven that had been designed and manufactured at our laboratory for centrifugation of the samples.

All the factories used general ventilation in the workplaces and the air sampling of HDI was done using the midget impinger instrument (SKC). Calibration was performed as recommended by the manufacturer. For air sampling, SIBATA mini pumps were used; 25-ml midget impingers containing 20 ml of the sample medium (Dimethyl Sulfoxide with Tryptamine) were employed. Temperature and relative humidity was measured by an Asman hygrometer and thermometers. Fifty workers were studied; Williams' urine sampling method was used for the subjects.[9] All the subjects had been exposed to isocyanates before ending work shift (after 4 hour work was started) a urine sample was poured into a test cap (Polystyrene). The urine samples were made acidic by the addition of 0.5 g Citric acid to urine samples 30 cc caps before sampling. The samples were frozen at -20 °C until analysis HDA were assayed using a GC.MS technique.[12-16] A capillary GC method using selected ion monitoring (SIM) was applied for the analysis of MDA in urine,[16] for all of the samples, 100µl of heptanediamine 1ìM and ethylenedianiline 5µM was added to urine (2ml) acidified with concentrated sulphuric acid (200µl). Tubes were capped and incubated at 100 °C for 90 minutes. hydroxide (2ml, 10M) and diethyl ether (4ml) were added after cooling and mixed for 20 minutes. Then samples were centrifuged and removed 3ml of each ether layer to a clean tube and was removed the solvent under nitrogen. Samples medium was derivatised in toluene (500µl) in closed tubes at 55°C for 1h, then the mediums were cooled and removed the derivatizing reagent under nitrogen and reconstitute in toluene (100µl). Finally, the samples were injected (1µl) splitless (350°C, 30 sec) into a capillary column (30m x 0.3 mm BP5 1µm).

RESULTS

Regression analysis was used to assess health surveillance for isocyanates. The individual factors depend on workers health surveillance which has shown that it is clear that some of the evaluated factors associated with diisocyanates pollution are well defined.

The predictive regression model was obtained from Table-I for comparison between health surveillance factors and HDA, MDA and TDA risk of absorption by workers. In all cases only weight and symptoms of disease were significant. The predictive statistical modeling equations are as follows:

Regression model (R^2= 0.931) for HDA risk assessment was:

HDA Risk = 79.534 + 4.271 wt + 2.755 Disease symptoms

Air monitoring results showed that (Table-II) the mean concentration of HDI is 96µg/m³ at all factories. The relative humidity at the five factories ranged from 34 to 40.5% and dry bulb temperature was from 27.1 to 29.3ÚC. Workplace dimension for 5 polyurethane factories (H_1 – H_5) ranged from 5000 to 9900m³. Altitude for five factories ranged from 22 to 1200m.

A multiple regression model obtained from analysis of indoor air pollution factors and HDI pollution implies that there is a relationship between the increase of HDI concentration and

Table-I: Coefficients of regression model for isocyanates risk assessment

Model		*Coefficients*	*Std. Error*	*T*	*p - value*
	(Constant)	79.534	1.428	55.692	< 0.0001
	Age	0.0051	0.284	0.183	< 0.856
	Smoking	0.765	0.815	0.939	< 0.353
	Weight	4.271	0.775	5.512	< 0.0001
	Work history	-0.207	0.334	-.620	< 0.539
	Symptoms of disease	2.755	1.036	2.660	< 0.011

Dependent Variables: HDA concentration (%)

Table-II: Maximum and Minimum Reading of Indoor Air Variables in the Factories

Factories code Variables	H_1	H_2	H_3	H_4	H_5	*Mean*
Max HDI Pollution concentration (μg/m³)	96	95	90	90	88	96
Min	67	66	66	64	61	61
Mean	82.2	79.8	78.7	77	76.7	78.8
Max Relative Humidity (%)	40	45	45	52	52	52
Min	31	31	31	31	31	31
Mean	34	37	37	40	40.5	37.5
Max Dry bulb temperature (CÚ)	33	32	32	32	30	33
Min	25	24	24	24	23	23
Mean	29.3	27.8	28.7	28.7	27.1	28.1
Mean Dimension of factory (m³)	5000	6100	7400	9000	9800	
Mean Altitude (m)	1200	1200	1100	890	22	

Max: Maximum, Min: Minimum NIOSH guideline value: 35(μg/m³)

psychrometric parameters. Based on Table-IV this prediction model at á level of .001 is significant for all of the parameters (p <.0001).

The resultant predictive regression model obtained from Table 3 with $R^2 = 0.976$ is:

HDI = 20.13 – 0.0001 D + 0.1 RH + 2.61 Td (2)

A positive sign for the regression coefficient in the fitted model indicates the direct relationship of the variables with HDI concentration, whilst the negative sign indicates the inverse relationship with HDI concentration in the polyurethane factories.

The level of isocyanate metabolites in urine is an indicator of how much isocyanate has been absorbed and how well the controls are working. Creatinine is found in everyone's urine and can be used to adjust the level of HDA to compensate for dilute or concentrated urine. The guideline value for HDA level is 2 μmol/mol creatinine samples above this value is considered contaminated.[13-15]

There is a strong relationship between HDI and HDA (Fig-2). The regression statistical test was carried out for significant relationship between HDI air samples and urine samples from workers.

The biomonitoring predictive model was extracted from Table-IV (R^2= 0.999):

Y = 0.028 + X

HDA = 0.0536 HDI (3)

DISCUSSION

When comparing the present study with other studies where present conditions have been described, this study contributes on personal and hygiene conditions.[15] Isocyanates operation is usually done in a spray and molding process, with basic exhausts ventilation. Surprisingly, exposure levels during polyurethane operation and other task related isocyanates do not seem to be lower than those reported in the other studies. In addition, there was significant relationship in exposure levels between workers health surveillance factors (weight of workers and symptoms of disease) and concentration of absorbed isocyanates

Table-III: Coefficients of Regression Model for HDI Pollutant and Polyurethane Indoor Air Parameters

Model	*Coefficients*		*T*	*P-value.*
	B	*Std. Error*		
(Constant)	20.13	9.027	2.230	< 0.027
Dimension of factory (m³)	-0.0001	.000	-6.348	< 0.000
Relative humidity (%)	0.1	.032	3.108	< 0.002
Dry temperature (ÚC)	2.61	.106	24.606	< 0.000

Dependent Variable: HDI concentration (μg/m³)

Table-IV: Regression model coefficient for HDI and HDA

Model	*Coefficients*		*t*	*p- value*
	B	*Std. Error*		
(Constant)	-.83	0.696	-1.190	0.255
HDI Pollution	.0536	0.009	5.935	0.000

Dependent Variable: HDA Pollution

metabolite by workers, where hygiene conditions were also less controlled, which could be demonstrated. In this study mean concentration of HDA was 3.24µmol/mol creatinine, and this value was slightly close to that biological result of car repair shop but with small number of participants,[12] and this value was almost lesser than those found in other studies,[15] whereas Maitre[17] measured a value of 12µmol/mol creatinine for HDI exposure at this concentration from a survey of workers. The mean concentration of HDA was 3.24µmol/mol creatinine, and this value was slightly close to that biological result of car repair shop in Sweden but with small number of participants,[14] and this value was almost lesser than to those found in other studies, whereas Maitre measured a value of 12µmol/mol creatinine for HDI exposure at this concentration from a survey of workers.[17]

CONCLUSION

Among five individual risk factors, two of them (weight of workers and symptoms of disease) had relationship with absorbed isocyanates metabolites. However, compared to other factors (age of workers, history of work and smoking situation), no significance was observed. The models also showed that there is a strong relation ship between weight of workers in the polyurethane factories and appearance of symptoms of disease relevant to isocyanates on workers. Surprisingly, no significant effect was seen for the age of workers, smoking or non smoking and history of work.

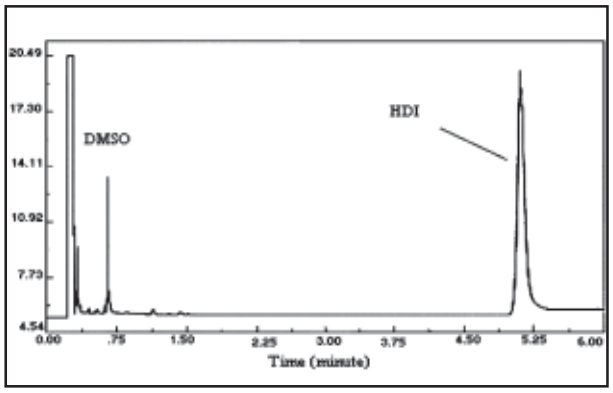

Fig-1: HDI chromatogram by HPLC

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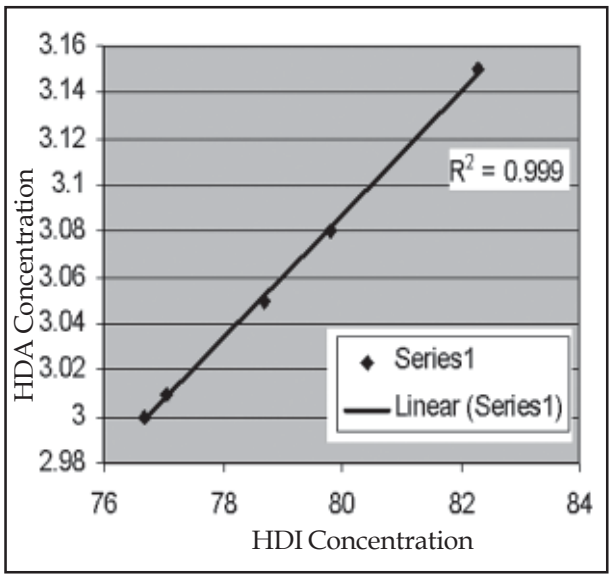

Fig-2: Relationships between HDI (µg/m³) and HDA (µmol/mol creatinine)

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