EVALUATION OF DIISOCYANATES AND THEIR METABOLITES IN SELECTED IRANIAN POLYURETHANE FACTORIES

by

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Abbreviations and glossary

ACGIH	The American conference of industrial hygienists
Diisocyanates	Isocyanates with two reactive groups (-NCO)
HDI	Hexamethylene diisocyanate
ICA	Isocyanic acid
IgE	Immunoglobulin E
IPDI	Isophorone diisocyanate
Isocyanate adducts	Isocyanates with low volatility and known structure eg. Biuret-, alofanate and isocyanurate adducts.
Isocyanates	Chemicals containing the highly unsaturated N-C-O group
LOAEL	Lowest Observed Adverse Effect Level
MDI	Methylene diphenyl diisocyanate, 4, 4´-methylenediphenyl diisocyanate
MIC	Methyl isocyanate
Monoisocyanates	Isocyanates with one reactive group (-NCO)
NDI	Naphthalene-1,5-diisocyanate
NIOSH	The National institute of occupational safety & health
NOAEL	No observed adverse effect level
OEL	Occupational Exposure Limit
OHS	Occupational Health and Safety
OSHA	The United States Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
PhI	Phenyl isocyanate
PIC	Propyl isocyanate
Polyisocyanates	Dimers and higher polymeric isocyanates
PPE	Personal Protective Equipment
Prepolymers	Isocyanates partly reacted with higher alcohols. Two kinds: 1. Isocyanates in excess reacted with alcohols

	and containing free, isocyanates.
	2. Isocyanates reacted in excess of alcohols and containing no free isocyantes
PU	Polyurethane
STEL	Short Term Exposure Level
TDI	Toluene diisocyanate
TLV	Threshold Limit Value
TWA	Time Weighted Average

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PENILAIAN DIISOSIANAT DAN METABOLITNYA DI DALAM KILANG-KILANG TERPILIH DI IRAN

Abstrak

Dalam tesis ini kepekatan diisosianat iaitu hekasametilena diisosianat (HDI), metilena difenil diisosianat (MDI), dan toluene diisosianat (TDI) dalam sampel udara dalaman dan kepekatan metabolit masing-masing iaitu heksanmetilena diamin (HAD), metilena dianiline (MDA) dan toluene diamin (TDA) yang ditemui dalam urin pekerja diukur di lima belas kilang poliuretan yang terletak di wilayah Tehran, bandar Karaj dan wilayah Mazandaran di Iran. Pengukuran kepekatan isosianat dilakukan dengan menggunakan kaedah NIOSH 5522. Pengukuran dilaksanakan untuk tiga syif kerja harian di lima belas buah kilang dengan jumlah tiga ratus sampel udara. Parameter psikometrik (suhu udara dalaman dan kelembapan relatif), dimensi dan altitud tempat kerja merupakan faktor-faktor yang dinilai untuk dikorelasikan dengan tahap pencemaran diisosianat. Hubungan antara diisosianat dengan kesan kesihatan dan sensitisasi khusus juga dikaji. Hasil kajian ini menunjukkan bahawa HDI, MDI dan TDI adalah dominan menurut frekuensi kejadian dan menunjukkan tahap pendedahan tertinggi berbanding dengan standard NIOSH, OSHA dan ACGIH dan beberapa kajian lain. Korelasi antara parameter psikometri dengan kepekatan diisosianat telah ditentukan dan hasilnya menunjukkan bahawa, kelembapan relatif dan suhu mentol kering mempunyai hubungan yang signifikan dan positif.

Dos dalaman sebenar yang diterima oleh pekerja dalam industri ini menurut kepekatan HDA, MDA dan TDA diukur dengan menggunakan sampel urin yang diperoleh dari 150 pekerja (50 sampel HDI, MDI dan TDI). Kepekatan tersebut adalah lebih tinggi nilainya dari standard NIOSH dan korelasi dengan tahap diisosianat dalaman adalah baik.

Hingga kini tiada kaedah yang disahkan boleh digunakan untuk penilaian kuantitatif pendeduhan kesihatan di Iran. Oleh itu sebuah kaedah pemantauan kesihatan digunakan untuk pekerja poliuretan. Dalam tesis ini jelas perkaitan antara pendeduhan kepada diisosianat dengan metabolit dan gejala pendeduhan telah ditunjukkan. Akhir sekali perkaitan yang telah diukur itu merupakan hasil kajian yang pertama sekali dibuat di Iran.

EVALUATION OF DIISOCYANATES AND THEIR METABOLITES IN SELECTED IRANIAN POLYURETHANE FACTORIES

ABSTRACT

In this thesis the concentration of diisocyanates namely hexamethylene diisocyanate (HDI), methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) in indoor air samples and their respective metabolites hexamethylene diamine (HDA), methylene dianiline (MDA) and toluene diamine (TDA) found in workers' urine were measured in fifteen polyurethane factories located in the Tehran province, Karaj city and Mazandaran province in Iran. Measurement of isocyanate concentration was performed using the NIOSH 5522 method. Measurement was conducted over three daily working shifts in fifteen factories with a total of three hundred air samples. Psychrometric parameters (indoor air temperature and relative humidity), workplace dimension and altitude factors were evaluated to correlate to the diisocyanate pollution level. The association between diisocyanates and health effects and specific sensitisation was also studied. The findings of this study demonstrated that HDI, MDI and TDI were dominant in frequency of occurrence and showed the highest exposure levels when compared to NIOSH, OSHA and ACGIH standards and some other studies. The correlation between psychrometric parameters and diisocyanate concentration was determined and the results showed that, relative humidity and dry bulb temperature have positive significant relationship.

Actual internal dose received by workers in these industries in terms of the concentration of HDA, MDA and TDA were assessed using urine samples collected from 150 workers (50 samples respectively per HDI, MDI and TDI factories). The concentrations were found to be higher than the NIOSH standard and correlated well with the indoor diisocyanates level.

To date no validated methods were available for quantitative health exposure assessment in Iran. Therefore a health surveillance method was used for the polyurethane workers. In this thesis clear associations between diisocyanate exposure and their metabolites and exposure symptoms were demonstrated. Finally this is the first study in which such associations were assessed in Iran.

CHAPTER 1

INTRODUCTION

1.1 Isocyanates

Isocyanates are chemicals that contain at least one isocyanate group in their structure. An isocyanate group, contains one nitrogen, one carbon and one oxygen atom. (Figure1.1)

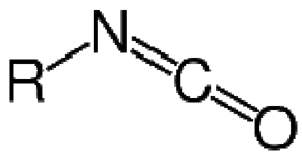

Figure 1.1 Isocyanates functional group

Diisocyanates such as hexamethylene diisocyanate (HDI), methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) are extensively used in the manufacture of polyurethane products. The main polyurethane products are flexible and rigid foams. Other applications include adhesives, resins, elastomers, binders, sealants and surface coatings (Tinnerberg and Sennbro, 2005; Streicher *et al*., 2002).

Kennedy and Brown (1992) reported that isocyanates are toxic to the sensory and respiratory system. The adverse effects of isocyanate have exposure range from irritation of mucous membranes, resulting in watering of the eyes, sneezing and coughing, to severe pulmonary disease, such as hypersensitivity pneumonitis or alveolitis and diisocyanates-induced asthma. Due to the widespread use, diisocyanates are known as a chemical cause of occupational asthma, necessitating strict controls on diisocyanate exposure (Malo *et al.,* 1997; Bernstein and Jolly, 1999; Raulf-Heimsoth and Baur, 1998).

The major route of occupational exposure to isocyanates is by inhalation of the vapor. Exposure may also occur through dermal contact during the handling of liquid isocyanates. Occupational exposure normally occurs during the production and use of them, particularly during the mixing and foaming processes in the polyurethane foam industry. Exposures to airborne isocyanates may also occur as a result of the melting or burning of polyurethane foams during firefighting (NIOSH, 2005).

1.2 Polyurethanes

Polyurethanes are produced by reacting diisocyanates with polyols and other chemicals. The range of polyurethane types are from flexible or rigid lightweight foams to tough, stiff elastomers and used in wide range by consumer and industrial applications.

Figure 1.2 shows the regional production of polyurethanes in the world (EPA, 2008). In terms of percentage of polyurethane production in the world, Asia Pacific region is in the third position. Figure 1.3 shows polyurethane production based on types of application (EPA, 2008).

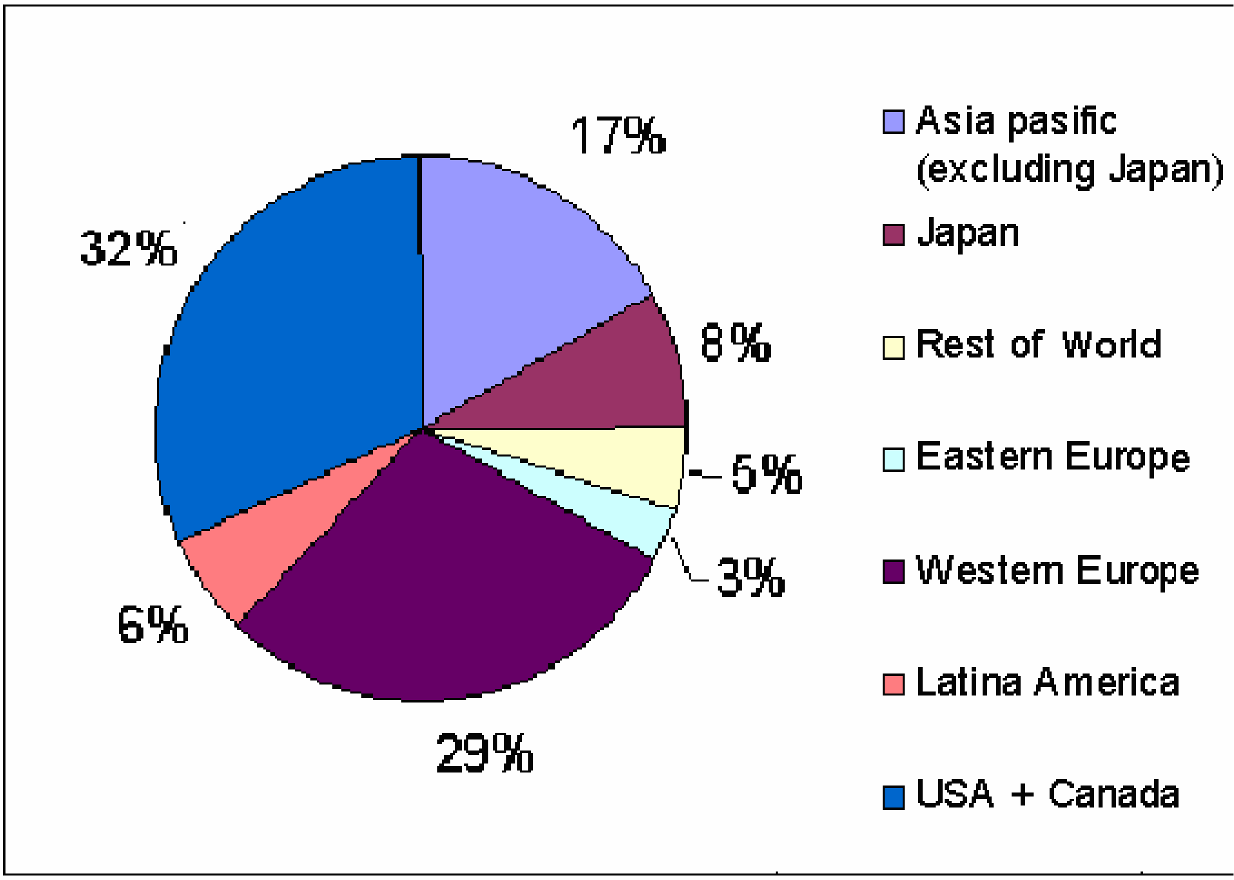

Figure 1.2 Regional productions of polyurethanes in the world by percentage (EPA, 2008)

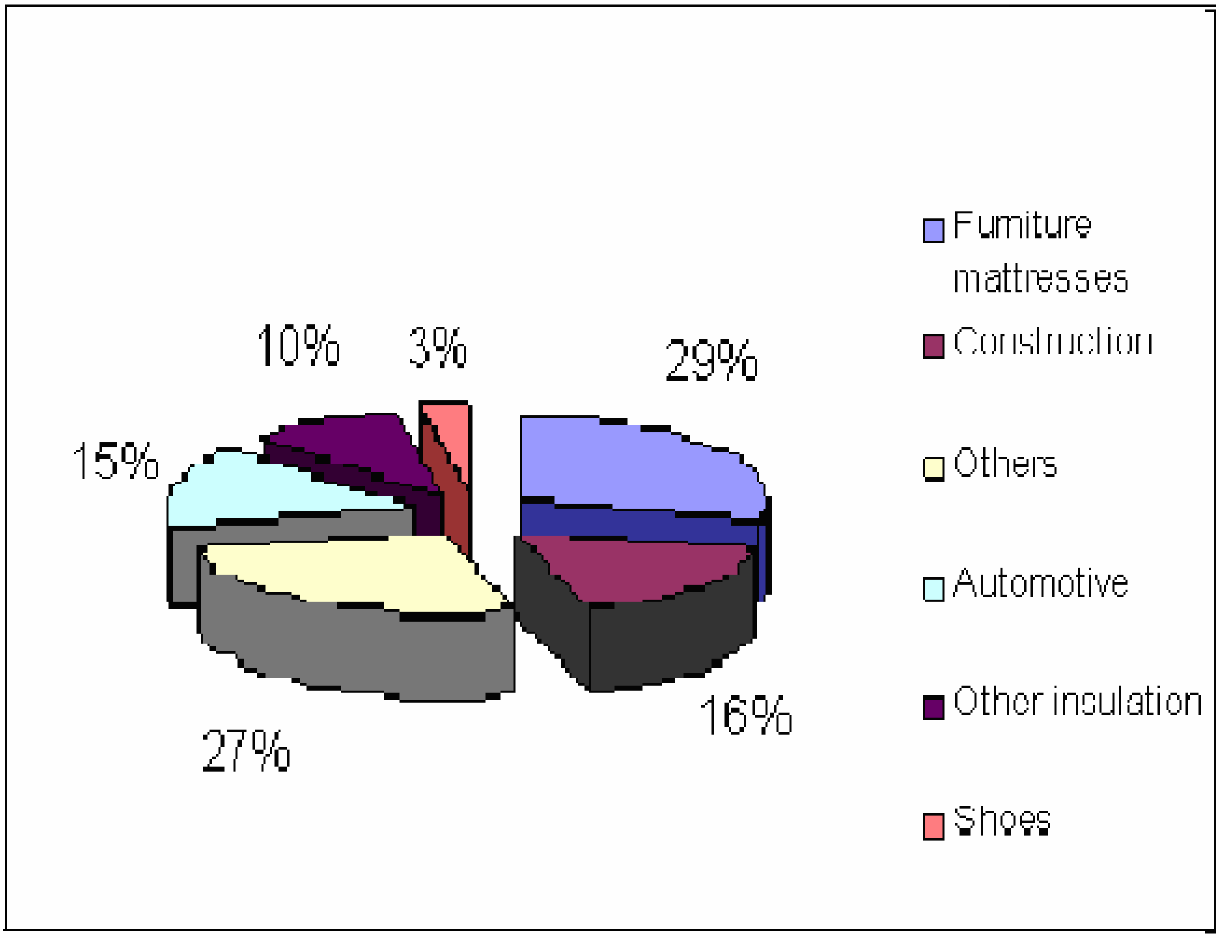

Figure 1.3 Polyurethane production based on type of application by percentage (EPA, 2008)

Environmental Protection Agency (EPA, 2008) has shown the percentage of polyurethane consumption according to the types of application. For example, furniture, mattresses and automotive seating are made predominantly from flexible foams and semi-rigid foams. Shoe applications relate to elastomers; construction and insulation are of rigid foams. Other applications include coatings, adhesives, artificial leather, fibers, and electronic applications. About 90% of the total isocyanate market is based on hexamethylene diisocyanate (HDI), methylene diphenyl diisocyanate

(MDI) and toluene diisocyanate (TDI) (Allport *et al.,* 2003). Furniture applications are predominantly related to TDI-based flexible foams while insulation and construction are almost entirely related to MDI-based rigid foams.

Global productions of MDI and TDI in tonnes are shown in Figure 1.4. MDI can be seen to be fast approaching to 4 million tonnes by 2010 and TDI is also following closely in terms of global tonnages.

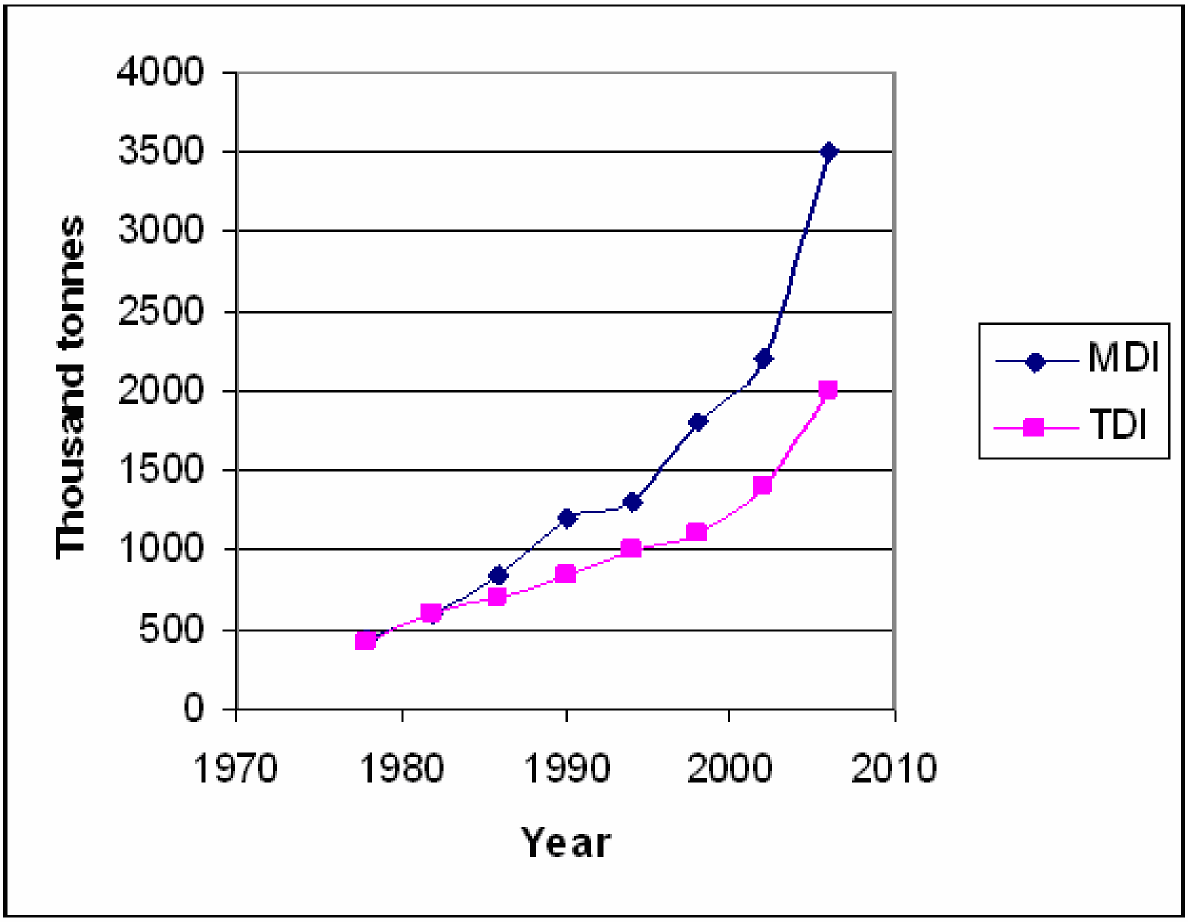

Figure 1.4 Global tonnages of MDI and TDI production from 1978 to 2007

(Allport *et al.*, 2003; Chemical Week, 2008)

The products of diisocyanates are extensively used in manufacture of polyurethane (PU). The global production of isocyanates had annual increasing trend (Tinnerberg and Sennbro, 2005). In Europe alone, it is estimated that there are more than 70,000 employees involved in manufacturing of isocyanates or PU products (Allport *et al.*, 2003).

Tinnerberg and Sennbro (2005) reported that in Sweden, after a long time of debate about concentration reduction of exposure and risk for adverse health effects to isocyanates, the occupational exposure limits has been decreased from 5 ppb to 2 ppb. Before employment, the requirements for all workers who will be exposed to diisocyanates are to go through a medical test and this case will be repeated in some intervals during isocyanates related to employment. Tinnerberg and Sennbro (2005) emphasized that such interest and rules imply the need for good and cheap methods to assess the exposure to isocyanates.

1.3 Air and Biological Monitoring of Isocyanate

The exposure to isocyanate is quite complex and different with respect to different applications. Exposure assessments are mainly conducted through air monitoring methods as well as biological monitoring of urine or plasma for isocyanate metabolites (Tinnerberg and Sennbro, 2005). However, all the methods used for the assessment of exposure to isocyanate have limitations. In the case of air monitoring the crucial point is that the isocyanate group is very reactive and need to be derivatised (protected) in the sampling step to prevent the isocyanate reacting with other reagents. Furthermore the isocyanate will in some industries appear mainly as a gas and in some other environments as particles.

The methods for air monitoring are mainly based on sampling with impingers or on impregnated filters, but some other sampling techniques have also been used (Tinnerberg ansd Sennbro, 2005). When using impingers, it is also known that small particles will not be efficiently collected and moreover the methods could be impractical in field studies.

Maitre *et al.* (1993b) in their work commented that the occupational exposure evaluation by air sampling yields only fragmentary information and may not be specific enough. Total avoidance of exposure may also be impossible as vapor or aerosol peaks may go unnoticed and percutaneous absorption cannot be avoided during routine work procedures. Skarping *et al.* (1991) in his work discussed that the TDI concentration in air and breathing zone give only partial information about the absorbed dose. And hence, biological monitoring of TDI would be an alternative of great interest.

Isocyanate if inhaled will be metabolised or broken down in the body and eliminated in urine where:

- hexamethylene diamine (HDA) is the metabolite of hexamethylene diisocyanate (HDI)
- methylene dianiline (MDA) is the metabolite of methylene diphenyl diisocyanate (MDI)
- toluene diamine (TDA) is the metabolite of toluene diisocyanate (TDI)

The level of isocyanate metabolites in urine can be used as an indicator of how much isocyanate has been absorbed and this forms the basis of biological monitoring. Maitre *et al.* (1993a) suggested that the biological monitoring is suitable to overcome the pitfalls of air monitoring. In the case of diisocyanates, the amines were derived from diisocyanates in human urine hydrolysis reaction which provides the necessary specificity (Berode *et al.,* 1996).

Skarping *et al.* (1991) cautioned that the biological monitoring requires highly sensitive methods for the determination of the chemical or its metabolites in biological media. Besides, the metabolism of the compound in humans must also be sufficiently known and inter-individual variations in biotransformation must be noted.

1.4 Determinants of Isocyanate Exposure

Indoor psychrometric parameters such as temperature and relative humidity are known to be related to isocyanate exposure. Denola *et al.* (2009) recently studied occupational exposure to airborne isocyanates in a tropical climate. In the work, it was discussed that the high ambient temperatures experienced in a tropical climate are likely to enhance vaporization of unreacted monomeric isocyanates during spray painting. Furthermore, the curing rate of the paint is likely to be accelerated by the elevated temperatures and high humidity. Studies regarding airborne isocyanate concentrations under tropical conditions are lacking. In a few known studies for example brush/roller applications in temperate climates showed that the isocyanate values are below the detection level (Coldwell and White, 2003) or at low concentrations (Pronk *et al.,* 2006).

In a related study on indoor air quality for a sustainable home, Palanivelraja and Manirathinem (2008) considered among others temperature and indoor relative humidity as important factors affecting indoor air pollution. In their study they also observed relationship between indoor and outdoor concentration of pollutants. Szycher (1999) illustrated that the most important psychrometric factors in the polyurethane factories affecting the diisocyanate level are humidity and indoor temperature.

Woskie *et al*. (2004) evaluated the determinants of isocyanate exposure in 33 auto body repair shops. The determinants identified include shop size, outdoor and indoor temperatures, indoor and outdoor relative humidity. Exposure determinants were identified using among others linear regression, tobit regression and logistic regression models. The identification of key exposure determinants was suggested to be useful in targeting exposure evaluation and control efforts to reduce isocyanate exposure.

1.5 Problem Statements

Isocyanate is widely used in Iranian polyurethane factories for making polyurethane (PU) products such as foams, paints, insulating materials, varnishes and rubber modifiers. Kakooi *et al.* (2006) evaluated the isocyanate personal inhalation exposure among employees working in the window fixation and window glue processes in an automobile manufacturing company in Iran. The number of workers in such polyurethane factories mentioned above can be more than 100 per factory. However, until now little or no work was done to evaluate the determinants of isocyanate exposure levels in the polyurethane factories in Iran. It will also be useful to conduct biological monitoring and air monitoring simultaneously because the correlations between biomarkers and air exposures are not yet well studied (Tinnerberg and Sennbro, 2005).

Kakooei *et al.* (2006) pointed to the importance of studying indoor air pollution in such industries for a developing country like Iran because the technology and the machinery used are normally imported from developed countries without the application of adequate engineering controls and proper safe work practice. These situations can cause great exposure to air pollutants resulting in more occupational health problems in developing countries than in developed countries.

The study in Iranian polyurethane factories is important for comparison as most previous work and models were done in temperate and developed countries whereas Iran is a developing country with different meteorological conditions, socioeconomic situations, and technological ability as well as different occupational health and safety culture.

A study carried out by Woskie *et al.* (2004) showed that the evaluation of exposure control has focused only on the effect of specific control to the exposure levels but neglected more generic questions like what worker activities or what process and environmental conditions which can increase the risk of isocyanate exposure. Environmental conditions can include the psychrometric parameters within factories such as the indoor temperature and relative humidity. The size of a factory might be related to contamination level. These factors were studied by Woskie *et al.* (2004) as determinants of isocyanate exposure but it was limited to auto body repair shops only. No specific and comprehensive study has been done about polyurethane factories in Iran. There is also no work that has been done to evaluate the effects of altitude at which a factory is located in relation to isocyanate exposure based on ideal gas law equation there is a adverse relationship between air pressure and altitude.

There is also a lack of data on inhalation exposure of workers to isocyanate using biological monitoring in large size factories. In a related study to assess understanding of workers in relation to the risks associated with using isocyanate, Jones *et al.* (2005) have seen that knowledge of isocyanate health risks was poor and some workers were not even aware of isocyanates. Biological monitoring showed that half of sprayers had detectable levels of isocyanate exposure and up to a third of bystanders also showed evidence of isocyanate exposure. Biological monitoring has the potential to measure a worker's body burden by all routes of exposure (Rosenberg *et al.,* 2002). The aim of this study was also to use urinalysis of diisocyanate-derived amine to evaluate workers exposure to isocyanate in the factories.

There are also no comprehensive studies on diisocyanates, metabolites of diisocyanates and risk assessment of exposed workers and bystanders in Iranian polyurethane factories. In Iran, there is a lack of data on assessment of diisocyanates as indoor air pollutants. The results of this study will be beneficial for benchmarking the isocyanate exposure level of exposed workers in Iranian polyurethane factories. Through this study the factors (relative humidity, dry bulb temperature, dimension of factory and altitude) affecting isocyanate as an indoor air pollutant and their relationships in the factories also will be determined. Hopefully, this study can be useful as an initial exploratory work to set guidelines in terms of process conditions and location of a polyurethane factory. Woskie *et al.* (2004) reported that identification of key exposure determinants will be useful in targeting exposure evaluation and control efforts to reduce isocyanate exposures. Implementation of effective control strategies is very important in reducing the incidence and prevalence of isocyanate asthma.

1.6 Limitation

This study involved fifteen selected polyurethane factories in Iran with a total of more than one thousand exposed workers. All of the polyurethane factories under this study were located in Tehran province, Karaj city and Mazandaran province. The factories were also located quite far from each other and posed challenges to sampling and transportation of the samples to the analytical laboratory. Sampling period was from September 2006 to August 2007.

For biological monitoring urine sampling is common. The reasons urine instead of blood sample was taken from the worker were simplicity and personal privacy. The urine samples are easily collected while blood sampling may create an atmosphere of searching for the addicted workers to drug or alcohols which is not acceptable to the worker. Hence therefore taking urine samples is quite customary for biological monitoring.

1.7 Objectives

Several objectives are put forward for this study:

1. To evaluate hexamethylene diisocyanate (HDI), methylene diphenyl diisocyanate (MDI) and evaluate toluene diisocyanate (TDI) as indoor air pollutants and biological assessment of hexamethylene diamine (HDA), methylene dianiline (MDA) and toluene diamine (TDA) in the polyurethane factories.
2. To evaluate the determinants of diisocyanates exposure with respect to HDI, MDI and TDI in the Iranian polyurethane factories.
3. To determine respectively the relationship between HDI, MDI and TDI concentration from air sampling and HDA, MDA and TDA concentration from biological sampling (worker's urine sample) in the polyurethane factories.
4. To assess health risk factors of diisocyanates (HDI, MDI and TDI) and their metabolites (HDA, MDA and TDA) in the Iranian polyurethane factories.

1.8 Outline of the Thesis

This thesis is arranged in seven chapters:

Chapter one – Introduction

The goals of this chapter are discussion on the importance of diisocyanates pollution, problem statements, limitations of study and objectives.

Chapter two – Literature Review

Chapter two is about previous work done by other scientists regarding diisocyanates air assessment, biological monitoring, indoor psychrometric factors and health risk assessment.

Chapter three – Materials and Methods

Chapter three relates materials and methods for diisocyanates air sampling and analysis in the polyurethane factories as well as biological sampling and analysis. This chapter also includes description about field sampling and sample size.

Chapters 4 to 6 are based on three published papers. These are the main results covered in the individual papers:

Chapter four - Paper 1 (Published in Environmental Monitoring Assessment Journal). "Evaluation of hexamethylene diisocyanate as an indoor air pollutant and biological assessment of hexamethylene diamine in the polyurethane factories". Environ Monit Assess (2010) 165:341–347. DOI 10.1007/s10661-009-0950-5.

Chapter five – Paper 2 (Published in Indian Journal of Occupational and Environmental Medicine). "Evaluation of methylene diphenyl diisocyanate as an indoor air pollutant and biological assessment of methylene diamine in the polyurethane factories". Indian journal of Occupational and Environmental Medicine- (2009) 13- (1): 38-42. DOI: 10.4103/0019-5278.50723.

Chapter six – Paper 3 (Published in World Applied Sciences Journal). "Evaluation of toluene diisocyanate as an indoor air pollutant and biological assessment of toluene diamine in the polyurethane factories". World Applied Sciences Journal (2009) 6 -(2): 242-247.

Chapter seven – Conclusion and Recommendations:

Conclusion summarises the main findings to answer the objectives of the study also some recommendations for future studies for diisocyanates.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Isocyanates are known as highly reactive chemicals. Isocyanates/ diisocyanates are often used as raw materials in production of polyurethane. The lower molecular weight isocyanates tend to vaporize at room temperature, and may create vaporized inhalation hazard. Conversely, the higher molecular weights isocyanates do not readily volatilize at ambient temperatures, but they may appear as aerosolized inhalation hazard in the working environment. The common feature of all diisocyanates (monomers) is the presence of two double bounds of isocyanate functional groups (−N=C=O) attached to an aromatic or aliphatic compounds which can generate toxic compounds as indoor pollutants (Seel *et al.,* 1999; Allport *et al.,* 2003). 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 workplace are related to vapor pressure of the individual chemical compounds (Bello *et al.,* 2002; Tury *et al.,* 2003; EPA, 2008).

Due to the highly unsaturated nature of the isocyanate functional group, the diisocyanates readily react with compounds containing active hydrogen atoms (electrophiles). Thus, the diisocyanates readily react with water (humidity), alcohols, amines, etc.; diisocyanates also react with themselves to form either dimmers or trimers (Randall and Lee, 2002). When a diisocyanate species reacts with a primary, secondary, or tertiary alcohol, a carbonate (NHCO-) group is formed, which is commonly referred to as a urethane, reactions involving a diisocyanate species and a polyol result in the formation of cross-linked polymers; i.e., polyurethanes. Hence, they are used in surface coatings, polyurethane foams, adhesives, resins, elastomers, binders, and sealants. Many material safety data sheets (MSDSs) use isocyanate-related terms interchangeably (Sparer *et al.,* 2004).

Isocyanates are used in the manufacture of many products, such as flexible and rigid polyurethane foams, polyurethane rubbers. Elastomers are to be found as cross linking agents in surface coatings, inks, adhesives and binders for foundry cores. They are used in a great variety of industries (Meredith *et al.,* 2000). About 1 million cars are discarded per year in Iran; each car has roughly 9 kg of polyurethane foam in the seats (Kakooei, *et al.,* 2006).

2.2 Isocyanates

Isocyanates exist in many physical forms in workplace. The workers are potentially exposed to unreacted monomer, prepolymer, polyisocyanate, and/or oligomer species found in a given product formulation (Rosa, 1994). They can also be exposed to partially reacted isocyanate containing intermediates formed in the course of polyurethane production (Woskie *et al.,* 2004; Tinnerberg and Sennbro, 2005). The second type of exposure might be more hazardous, as number of isocyanates reactions are exothermic in nature and also evolve sufficient heat for the volatilization isocyanate compounds (NIOSH, 1994).

The most widely used compounds are diisocyanates, categorized in two isocyanate and polyisocyanates groups. These compounds are usually derived from diisocyanates and may contain several isocyanate groups. The most commonly used diisocyanates include methylene bis (phenyl isocyanate) (MDI), toluene diisocyanate (TDI), and hexamethylene diisocyanate (HDI) (Tury *et al.,* 2003).

In general, Woskie *et al.* (2004) stated that the types of exposures encountered during the use of isocyanates (i.e., monomers, prepolymers, polyisocyanates, and oligomers) in the workplaces are related to the vapor pressures of the individual compounds. 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 (Woskie *et al.,* 2004). Vilhelm (2001) reported that polyurethane (PU) products are generated from part of a large number of products in daily use, such as foamed rubber, PU rubber, varnishes, adhesives, insulation foam, fillers, finishes on synthetic floorings, synthetic textile fibres, electronic circuit cards and a lot of other applications. Modern car windscreens are installed using PU adhesive. The world production rate at present is in capacity of 2-3 million tones per year (Vilhelm, 2001).

Henneken *et al.* (2006) identified that the MDI and TDI are high tonnage products, which comprise about 90% of the total diisocyanate market and 10% for HDI and other diisocyanates compounds. The range of polyurethane types started from flexible or rigid light weight of foams to tough, stiff elastomers allowing them to be used in a wide diversity of consumer and industrial applications (Allport *et al.,* 2003). Based on Woods (1990) reports some examples of the applications are:

Rigid foam

- thermal insulation of buildings, refrigerators, deep freeze equipment, pipelines and storage tanks;
- buoyancy aids in boats in boats and flotation equipment;
- packaging
- furniture
- housing equipments

Flexible foam

- household furniture including bedding;
- automotive seating;

- textile laminates.

Integral skin, semi-rigid and low density structural foams

- steering wells, headrests and other automotive interior trim components;
- furniture elements;
- sports goods such as skis and surf boards.

Elastomers

- shoe soles;
- vehicle body panel;
- rollers and gear wheels;
- conveyors;
- sealants for the construction and automotive industries;
- fibers.

2.2.1 Hexamethylene Diisocyanate (HDI)

Hexamethylene diisocyanate (HDI) is a colorless compound or may be slightly yellow liquid and is not much heavier than water (Adam *et al.,* 2002). This substance forms oily droplets in water and hydrolyses rapidly. HDI is an organic compound known as isocyanates. More specifically, it is an aliphatic diisocyanate. Hexamethylene diisocyanates (HDI) is widely used in Iranian polyurethane factories for manufacturing polyurethane (PU) products such as foams, paints, insulating materials, varnishes and rubber modifiers.

Information regarding the physical and chemical properties of HDI is presented in [Appendix. 1(a)]. HDI is a monomer used in the production of polyurethane foams and other related products, and is found in some industrial paints and spray painting operations. It has a vapor pressure of 0.5 mmHg at room temperature, but can be present in aerosol form allowing a potentially higher exposure to individuals. It would be expected to have a lower vapor pressure; however, the aerosol form can also be present, allowing potentially higher exposure of HDI to individuals. HDI reacts slowly with water to form carbon dioxide (HSDB, 2007). The chemical structure of HDI with two isocyanate functional groups is shown in Figure 2.1 (NIOSH, 2005). The base-catalyzed reaction of HDI with alcohols should be carried out in inert solvents.

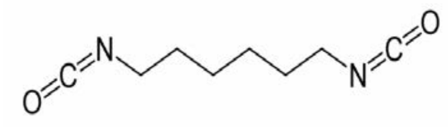

Figure 2.1 Structure of HDI. (NIOSH, 2005)

2.2.2 Methylene Diphenyl Diisocyanate (MDI)

Methylene diphenyl diisocyanate, most often abbreviated as MDI, is an aromatic diisocyanate. The MDI is most practically useful, and is also known as pure MDI. MDI is reacted with a polyol in the manufacturing of polyurethane. Among the PU products, the highest production rate in global market was devoted to MDI (61.3%) (Randall and Lee, 2002).

MDI is reacted with a polyol in the structure of polyurethane as shown in Figure 2.2. MDI which in the pure form is a light-yellow, fused solid. The primary hazard of this solution is the threat to the environment. Immediate steps should be taken to limit its spread to the environment. Since it is a liquid it can easily penetrate the soil and contaminate nearby streams or groundwater [See Appendix. 1(b)] (Allport *et al.*, 2003).

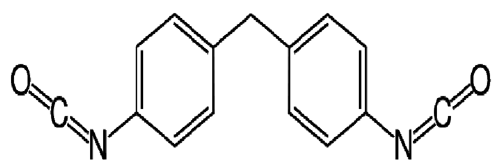

Figure 2.2 Structure of MDI (NIOSH, 2005)

Kakooei *et al.* (2006) have evaluated personal inhalation exposure to methylene diphenyl diisocyanate (MDI), among 39 employees working in window fixation and window glue processes in an automobile manufacturing company (Iran). Kakooei *et al.,*

(2006) reported that the workers exposed to MDI were affected by the chemical exposure of the contaminated air. They stated that the average concentration of MDI in both window fixation and window glue processes were 33.36 and 26.43 μg/m^3, respectively. The level of contamination was lower than the amount, recommended by American Conference of Governmental Industrial Hygiene (ACGIH), in which, the threshold limit value (TLV) is 51 μg/m^3 (Kakooei *et al.,* 2006).

2.2.3 Toluene Diisocyanate (TDI)

Toluene diisocyanate (TDI) is a colorless liquid and is not much heavier than water (Adam *et al.,* 2002). This substance forms oily droplets in water and hydrolyses rapidly. TDI is an organic compound and that is known as a class of isocyanates. More specifically, it is an aliphatic diisocyanate. TDI is insoluble in water. It is miscible with alcohol, diglycol, monoethyl ether, ether, acetone, carbon tetrachloride, benzene, chlorobenzene, kerosene, and olive oil (Budavari *et al.*, 1989). The properties of TDI and additional information are shown in Appendix 1(c). Furthermore, 2, 4-TDI is produced in the pure state, and it accounts for 34.1% of the global isocyanate market (Randall and Lee*,* 2002). TDI structure is shown in Figure 2.3.