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Original

Comparative Assessment of Carcinogenic Risk of Styrene Vapors Using Two Semi-Quantitative Methods in a Petrochemical Industry

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Abstract

Background: Styrene is one of the chemicals used in industries, especially the petrochemical industry, which affects health. Singaporean methods and the WHO use different parameters to assess the carcinogenic risk of the substance. Therefore, this study aimed to compare the level of carcinogenic risk due to exposure to styrene using the Singapore Department of Occupational Health with the risk levels provided using the WHO to achieve high-reliability results. **Methods**: In this study, 150 air samples were collected from the respiratory area of 50 employees by NIOSH1501 method, after identification of styrene emission units and preparation of identical exposure groups. The samples were analyzed by Varian-cp3800 gas chromatograph. Finally, the risk of styrene's health effects on petrochemical staff was calculated using the method of the Singapore Department of Occupational Health, and the results were compared with the risk levels of styrene presented by WHO. **Results**: The carcinogenicity of styrene was higher in polybutadiene latex (PBL) (2.3×10^{-4}) and the fire department (1.3×10^{-4}) in comparison with the other units. The World Health Organization-defined risk levels predicted 22% of staff to be a "definitive" carcinogenic risk. While the Singapore Department of Occupational Health approached a "low" risk rating. **Conclusion**: A "low" risk rating was obtained through the Singapore Department of Occupational Health. But the WHO method for 30 years of exposure to styrene predicted "probable risk" and "definitive risk." This showed a high difference in the results of the two semi-quantitative methods used.

Keywords: Health Risk Assessment; Styrene; Occupational exposure; Petrochemical

Introduction

Humans are exposed to various chemicals during their working life, some of which pose health risks. In particular, most of these health hazards arise in special chemical production processes.[1] Statistics show that 4 million people deal with chemicals based on their job in the world.[2, 3] One million people become ill or die from unprincipled exposure to chemicals annually.[4] Styrene with the formula C_8H_8 is found in the petrochemical industry and some other industries.[5] It is a single-ring aromatic hydrocarbon produced as a result of the dehydrogenation of ethylbenzene by cracking. This

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material is used in the plastics, rubber, and polyester resin industries.[6, 7] Based on human cancer and laboratory animal studies, styrene was listed as a carcinogen in the twelfth Report of the U.S. National Toxicology Program in 2011. There is, however, limited evidence of lymphoma cancer and genetic damage to white blood cells (lymphocytes) in workers treated with styrene.[8] The Office of Environmental Health Hazard Assessment (OEHHA) has identified it as carcinogenic in 2016.[9] Research has also shown that exposure to styrene alters DNA and eventually leads to cancer. Therefore, the International Agency for Research on Cancer (IARC) has placed this substance into group 2B (potential carcinogenicity for humans).[10]

To protect employees against the adverse effects of chemicals and appropriate control measures, chemical risk assessment is essential to make the right decision.[11] Health risk assessment is essential to identify high-risk locations and prioritize employee exposure control. If the risk assessment is not properly operated, it will waste cost and time for minor risks.[10] To assess the health risk of chemicals Qualitative (using risk assessment matrices) and quantitative methods are used.[1] The Singapore Health and Safety Association has introduced a semi-quantitative method for risk assessment.[11] This method controls the risk of chemicals by reducing the exposure index and the hazard degree of the compounds. Reducing the exposure index and degree of hazard is provided by removing or replacing the hazardous substance with a less hazardous substance.[2,12] Numerous studies have been performed using the Singapore Department of Occupational Health method.[10, 13, 14] Mousavifard et al. assessed the health risk of toluene diisocyanate and methylene diisocyanate using the Singapore Department of Occupational Health in car painting workshops in Alborz province in 2015. In this study, the toluene diisocyanate and methylene diisocyanate risk levels were high and medium, respectively.[2] Jahangiri et al. also investigated seven chemicals using the Singapore Department method in a polyurethane foam industry in 2011 and finally obtained a "high" risk level for toluene diisocyanate.[1] Chahak et al. used the Singapore Occupational Health Department's method to assess the semi-quantitative health risk of hazardous chemical compounds in the petrochemical industry in 2015. The study showed that 81% of the chemicals used had a "high" risk level.[4]

Some studies have compared the results of the carcinogenic risk assessment of the compounds with the risk level ranking provided by the World Health Organization (WHO) to determine the level of carcinogenic risk of volatile organic compounds.[15, 16, 17] WHO divided the risk of carcinogenicity of chemicals into four categories: definitive risk, probable risk, possible risk, and negligible risk.[17] Although these two methods were used to determine the level of carcinogenic risk of VOCs in numerous studies,[14, 18] in none of the studies, the carcinogenic risk of styrene has been studied simultaneously with these two methods. For the first time in the country, styrene carcinogenic risk was assessed by comparing the risk level by the Singapore Department of Occupational Health with the WHO risk rating in the petrochemical industry.

Methods

The petrochemical fact produces 36,000 tons of ABS annually and has 400 employees. Of these, 300 were working in production units at the time of the research. Sampling was performed in the studied units, including PBL, polymerization unit (SAN), compounding unit, bagging, unit 310, laboratory, fire department, and repairs. In the first step, the required sample size was estimated at 150 samples of respiratory air of 50 employees, according to the model proposed by the American National Institute of Occupational Safety and Health (NIOSH), as similar exposure groups (SEG). This number of workers were randomly selected from similar exposure groups to participate in

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the study. The second step was to determine the conditions for participating in the study, including having a full-time job in the study industry (full-time shift), not using hourly leave during the study, and having a job on production lines (excluding office workers). According to the health record, employees with a history of an underlying illness such as asthma or cancer themselves or first-degree relatives were excluded from the study. In the third step, sampling was performed based on the NIOSH1501 method. Three samples were taken from each of these workers (including two samples before rest and lunch and one sample after rest).

To reduce the sampling error, one blank sample was prepared for every ten main samples. Based on the NIOSH1501 method, the time of each sample was 90 minutes. Three environmental samples were also taken from the restaurant. For the initial estimate, ten environmental samples were taken before the main sampling to monitor the environment, which showed that the concentration of styrene in the restaurant was low. According to the NIOSH 1501 method, the sampling flow rate was two Lit/min. The average of environmental samples was considered as the concentration of exposure in the restaurant. In this study, an individual sampling pump model SKC Universal 44XR (flow rate 0.9 Lit/min) and a 150 mg activated charcoal tube of coconut skin origin (SKC Inc., PA, USA) were used to sample the workers' respiratory area. They were then placed in the cooling box and transferred to the laboratory at the end of the work shift and were ready in less than 72 hours to inject into the Gas Chromatograph (GC).

Analytical process

According to the NIOSH 1501 method, the sampler tube's front and back sorbent sections were poured into separate vials. 0.1 ml extraction solution (CS2) was added to each of them to desorb the contents. The vials were immediately capped and stirred for 30 minutes to extract the styrene from the absorbent as much as possible. A micro-syringe with a volume of 10 μl was washed with the sample to be prepared for injection. Afterward, 1μl of sample extract was injected into gas chromatography (Varian CP-3800). A flame ionization detector (FID) was used as the detector. The carrier gas was helium with a flow rate of 1.8 ml/min. The injection port temperature was 200 ° C. The column initial temperature was 40 °C for two minutes, then increased by 0.5 $°C.min^{-1}$ until the temperature reached 45 °C and was kept at this temperature for 10 minutes. The detector temperature was 220 ° C.

Semi-quantitative risk assessment method

According to the method provided by the Singapore Occupational Health Department, semi-quantitative health risk assessment of styrene was performed in four stages.

1- Determining the hazard rate (H.R.) based on one of the following methods (4):

A) Determination of the HR from lethal dose (LD50) and lethal concentration (LC50) of the chemical

B) Determination of the HR using International Agency for Research on Cancer (IARC) carcinogenicity classification

2- Determining the exposure rate (ER) using table 1 (2) that was completed using Eq. (1):[11]

$$E = \frac{M.D.F}{W} \qquad (1)$$

Where E is the weekly exposure (mg. m^{-3}), M is exposure (mg. m^{-3}), D is the average of time exposure (hr), F is the number of exposure in the week, and W is the weekly hours of work (hr.).

About table 1: the Permissible exposure limit (PEL) was corrected using the Brief &Scala relation for the three-day shift and the one-day break (Eq.2):[15]

$$RF = \frac{40}{H} \times \frac{168-H}{128} \qquad (2)$$

Where H is working hours per week, R.F. is the reduction factor. Then, the corrected permissible exposure limit (PEL_H) can be obtained using Eq.(3):[15]

$$PEL_H = RF \times PEL_8 \qquad (3)$$

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3- Calculating the risk level by Eq. (4):[11]

$$Risk\ level = \sqrt{HR + ER} \quad (4)$$

4- Risk ratings obtained based on risk ranking matrix table 2:2

Cancer risks assessment

Excess Lifetime Cancer Risk (ELCR) of styrene was calculated using Eq. (5),:[16]

ELCR=CDI×CSF (5)

Where the value of CSF (cancer slope factor) is 5.7×10^{-4} $((kg - day).mg^{-1})$ and CDI is chronic daily intake $(mg.(kg - day)^{-1})$ which can be calculated using Eq. (6):[19, 20, 21]

$$CDI = \frac{C \times IR \times ED \times EF}{AT \times BW} \quad (6)$$

Where C is the concentration of styrene in the air ($mg.m^{-3}$), IR is the inhalation rate ($m3.day^{-1}$), ED is exposure duration (year), AT is average lifetime (year), EF is exposure frequency ($days.year^{-1}$), BW is body weight (kg), and the numerical values of parameters can be seen in Table 3.[22, 23, 24] In this regard, the World Health Organization (WHO) has set defined limits for the ELCR: more than 10^{-4} as "definite risk," 10^{-5} to 10^{-4} as "probable risk," 10^{-6} to 10^{-5} as "possible risk" and less than 10^{-6} As "negligible risk".[16]

Statistical analysis

SPSS 25 software was employed for statistical analysis. The normality of the data was assessed by the Kolmogorov-Smirnov test. Kruskal-Wallis and Mann-Whitney tests were used to compare the health risks between different sections ($P < 0.05$).

Results

The demographic information of the participants in this study was collected, and its descriptive results can be seen in Table 4.

As can be seen in Table 5, the results showed that the highest mean TWA with a value of 4.6 mg/m3 was related to the PBL unit, and the lowest with an average of 0.27 mg/m3 was related to the laboratory unit in the studied petrochemical. The highest mean respiratory exposure to styrene was at the PBL unit ($4.06 \times 10^{-1}\ mg.(kg - day)^{-1}$) and the lowest was at the Dryer unit with a mean of $1.5 \times 10^{-3}\ mg.(kg - day)^{-1}$. The overall averages for CDI and ELCR are 1.16×10^{-1} and 6.6×10^{-5}, respectively.

Table 1. Exposure rate (ER)

ER	E/PEL_H
1	0.1<
2	0.1 – 0.5
3	0.5 – 1
4	1 – 2
5	2 ≤

Table 2. Risk ranking

Rank	Risk level
Little	1 – 1.7
Low	1.7 – 2.8
Average	2.8 – 3.5
High	3.5 – 4.5
Very high	4.5 - 5

Table 3. The parameters used to calculate CDI, EC, ELCR

parameter	Value	units	Reference
CSF	5.7×10^{-4}	$((kg - day).mg^{-1})$	(21)
IR	16	$m3.day^{-1}$	(22)
ED	30	year	(23)
EF	274	$days.year^{-1}$	(23)
AT	75 (year)×365(day)	day	(23,24)
AT	75×365×24	hr	(23,24)

Table 4. demographic information of employees working in the different operation units

units	NO. employees		Age			work experience			body weight		
	number	Frequency	Min	Mean(year)	Max	Min	Mean(year)	max	Min	Mean(Kg)	max
Total	50	100	29	37.04±4.80	52	1	10.82±4.45	17	52	75.84± 12.01	100

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Table 5. TWA, Average Respiratory Exposure and Carcinogenic Risk of Styrene

units	TWA		CDI		ELCR		
	Mean $mg.m^{-3}$	SD*	Mean $mg.(kg-day)^{-1}$	SD	Mean	SD	Carcinogenic Risk
310	0.57	0.4	1.57×10^{-2}	2.33×10^{-2}	1.5×10^{-5}	0.91×10^{-5}	unacceptable
bagging	0.97	0.54	2.60×10^{-2}	2.14×10^{-2}	1.4×10^{-5}	1.2×10^{-5}	unacceptable
Compound	0.95	0.96	6.6×10^{-2}	1.22×10^{-1}	3.8×10^{-5}	1.4×10^{-5}	unacceptable
Dryer	2.59	2.35	1.5×10^{-3}	0.8×10^{-3}	0.8×10^{-5}	0.5×10^{-6}	acceptable
SAN	0.30	0.29	1.37×10^{-1}	1.07×10^{-1}	0.7×10^{-4}	0.8×10^{-4}	unacceptable
laboratory	0.27	0.30	1.66×10^{-1}	1.45×10^{-1}	9.4×10^{-5}	1.3×10^{-5}	unacceptable
repairs unit	2.26	2.36	6.03×10^{-2}	5.51×10^{-2}	3.4×10^{-5}	3.1×10^{-5}	unacceptable
PBL	4.6	2.7	4.06×10^{-1}	1.74×10^{-1}	2.3×10^{-4}	0.9×10^{-4}	unacceptable
fire department	3.9	3.23	2.28×10^{-1}	1.19×10^{-1}	1.3×10^{-4}	1.2×10^{-4}	unacceptable
Total	1.94	2.28	1.16×10^{-1}	1.71×10^{-1}	6.6×10^{-5}	4.4×10^{-5}	unacceptable

* standard deviation

Table 6. Differences between different petrochemical departments in terms of respiratory exposure to styrene

	Unit 310	Bagging	Compound	Dryer	SAN	laboratory	repairs unit	PBL
Bagging	0.73							
Compound	0.2	0.6						
Dryer	0.25	0.15	* 0.01					
SAN	0.25	0.7	0.73	0.08				
laboratory	0.06	0.3	0.33	** 0.009	0.6			
repairs unit	0.2	0.42	0.48	* 0.02	0.7	0.49		
PBL	** 0.008	* 0.03	* 0.01	* 0.02	0.08	0.6	* 0.01	
fire department	* 0.03	0.15	0.30	* 0.02	0.2	0.38	0.18	0.53

*P-value < 0.05 ** P-value<0.01

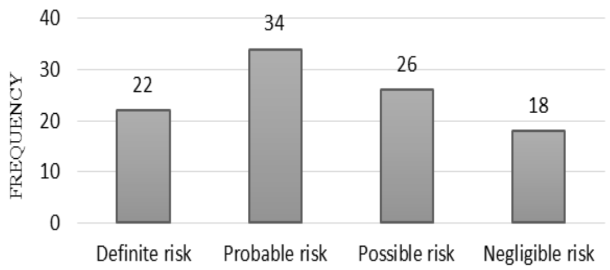

Figure 1. Cancer Risk Based on WHO Recommendation

Styrene carcinogenic risk according to WHO classification

As shown in Table 5. The results of styrene carcinogenicity calculations showed that the carcinogenicity of this substance in PBL (2.3×10^{-4}) and fire (1.3×10^{-4}) units were higher than other units. While the lowest carcinogenic effect of styrene was related to the dryer unit. According to the WHO recommendation, the prediction of carcinogenicity of styrene can be seen in Figure1, in the studied petrochemical.

The result of the Kolmogorov-Smirnov test for variables showed that the data are non-parametric (P <0.001). The results of the Kruskal-Wallis test showed that there was a significant difference between the units in the amount of exposure (P <0.05). Also, the results of the Mann-Whitney test (Table 6) showed that there is a significant difference between PBL units and others, including 310, Bagging, Compound, and Dryer units in terms of the amount of respiratory exposure to styrene. Significant differences between other sections are also shown in Table 6 so that the biggest statistical difference is related to PBL and 310 (P = 0.009).

The IARC places styrene in Group 2B. Therefore, in the semi-quantitative study of styrene's health risk level by the Singapore Department of Occupational Health, the hazard rate (HR)) for that value was considered to be 3.[2] Also, the exposure rate (ER) for all employees in different departments was one. Therefore, the numerical value 2 was calculated for the risk score, and then the "low" risk rating was extracted from Table 2.

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Discussion

Numerous studies have been performed to determine the health risk level of various chemicals using the semi-quantitative method of Singapore's occupational health department.[11] However, in this study, the results obtained from this method have been compared with the health risk levels provided by the World Health Organization. The daily rate of chronic exposure is calculated based on the concentration of pollutants in different units, but in some units, such as Dryer, the CDI rate was low despite the high TWA. The reason may be attributed to other parameters involved in calculating the CDI, such as the average body weight of employees working at this unit, which causes a change in the final values. Statistical analysis showed a significant difference between the units in terms of exposure to styrene. To examine the issue more closely, the Mann-Whitney test was used to determine which units are significantly different in terms of exposure. Finally, the sections that were significantly different in terms of exposure to styrene were provided in Table 6. The reason for the high exposure in the PBL unit in comparison with other units such as compound and 310, was the fact that the PBL unit was a three-story building with only natural ventilation (doors and windows), and this ventilation was limited due to lack of the area of windows and doors. The other units were in a semi-open environment due to the large area of the entrances and exits. Also, the number of PBL personnel was less than other units, so these people had to spend more time next to the production machines, but in other units, people worked in a rotating program and just left the restrooms to perform their assigned tasks, and they spent less time next to the production machines.

Besides, the production machines in the compound and 310 units were mostly automatic, which reduced the need for the presence of an operator. Firefighters also had a moderate to high exposure to styrene due to their constant visits and being near to production units. Also, when loading the tanks with raw materials due to the high risk of fire and explosion, several firefighters were present at the entire loading time of the tanks, which lasted several hours and was repeated almost every day. Therefore, these items can be considered reasons for the significant difference between the units in terms of styrene's carcinogenicity. Regarding the semi-quantitative evaluation of styrene's health effects, the results obtained from the Singapore method showed a "low" health risk level. While according to the WHO classification, the "definite risk" of carcinogenesis for 82% of workers was estimated to be 22%. The reason for this difference in the results of the WHO results and the Singapore department of occupational health method can be due to the further parameters in WHO Carcinogenic Risk Level. Having more than ten years of work experience is one of the reasons for the high values of cancer risk in the present study. Also, the high frequency of exposure and over 48 hours of work per week in all studied units are influential factors in the rate of daily respiratory absorption and, consequently, the increase in cancer risk level.

A study by Firoozi et al. was conducted to assess the risk of exposure to chemicals in the petrochemical industry using a semi-quantitative method (provided by the Occupational Safety and Health Association of Singapore) and calculated moderate and high-risk levels for 81% of cases. The results of their study show that the Singapore semi-quantitative method has a good reputation for assessing the risk of high-risk and high-exposure chemicals. However, for materials with low risk and exposure level, this method cannot be relied on.[4] As in the present study, a comparison of the results of the Singapore Department of Occupational Health method and the results of the WHO risk level proved this claim. Yari et al. Also assessed the health risk of exposure to several harmful chemical compounds by the Singapore Department of Occupational Health method. The results of their

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study indicated that for 82% of employees, the risk was moderate or low.[11] This result is consistent with the findings of the Singapore Department of Occupational Health risk assessment in this study. Bin Xu et al. compared the results of their study on the health risk assessment of exposure to volatile organic compounds in a subway in China with acceptable levels recommended by the World Health Organization. Finally, their studies showed that cancer risk was higher than the recommended level.[25] In fact, given that in order to maintain human health, the worst probabilities are always considered for planning in health and wellness issues, so it can be said that the risk rating provided by the WHO, at least for chemicals that has a lower risk rating according to Singapore's Department of Occupational Health, has higher reliability.

One of the limitations of this study was the lack of health risk assessment of other chemical compounds, which are suggested to be evaluated in future studies. Also, in this study, only WHO and Singaporean methods were used. Therefore, it is suggested that in future studies, the methods of the U.S. Environmental Protection Agency (USEPA) and the method of the American Conference of Governmental Industrial Hygienists (ACGIH) be used to assess the carcinogenic risk of styrene. One of the strengths of this study was the high number of samples collected (50 people participated in this study, of which three samples were collected from each person's respiratory area, and a total of 150 samples were collected) in a specific industry. Comparing the results of the health risk assessment of styrene using two semi-quantitative methods was the other strength.

Conclusion

The overall conclusion is that Styrene's health risk has been rated "low" according to the Singapore Department of Occupational Health method, but in the WHO rankings for 30 years of exposure to styrene, "probable risk" and "definite risk" were predicted, indicating a large difference in the results. Therefore, according to the results of this study, the WHO method is a more appropriate and accurate method for assessing the cancer risk of styrene.

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