Original Article

Quantitative and Semiquantitative Health Risk Assessment of Occupational Exposure to Styrene in a Petrochemical Industry

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Background: Styrene is one of the aromatic compounds used in acetonitrile–butadiene–styrene (ABS) producing petrochemicals, which has an impact on health of workers. Therefore, this study aimed to investigate the health risks of styrene emitted from the petrochemical industry in Iran.

Methods: Air samples were collected based on NIOSH 1501 method. The samples were analyzed by the Varian-cp3800 gas chromatograph. Finally, risk levels of styrene’s health effects on employees were assessed by the quantitative method of the U.S. Environmental Protection Agency (U.S. EPA) and the semiquantitative way by the Singapore Occupational Safety and Health Association.

Results: Based on the results, the employees had the highest average exposure to styrene vapors (4.06 × 10^−4 mg (kg − day)^−1) in the polybutadiene latex (PBL) unit. Therefore, the most top predictors of cancer and non-cancer risk were 2.3 × 10^−4 and 7.26 × 10^−1, respectively. Given that the lowest average exposure (1.5 × 10^−2 mg (kg − day)^−1) was in the dryer unit, the prediction showed a moderate risk of cancer (0.8 × 10^−6) and non-cancer (2.3 × 10^−3) for the employees. The EPA method also predicted that there would be a definite cancer risk in 16% and a probable risk in 76% of exposures. However, according to the semiquantitative approach, the rate of risk was at the “low” level for all staff. The results showed that there was a significant difference (p < 0.05) between the units in exposure and health risk of styrene (p < 0.05).

Conclusion: Given the high risk of styrene’s health effects, appropriate control measures are required to reduce the exposure level.

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1. Introduction

Petrochemical plants are large industries that their operating is associated with volatile organic compounds (VOCs) emission [1,2]. Exposure to VOCs can have a wide range of acute and chronic effects on human health, including carcinogenic effects, nervous system disorders, decreased pulmonary function, and others [3]. Thus, one million people get sick or die because of unsecured exposure to chemicals, annually [4].

Styrene is one of these organic chemicals that is widely used in the manufacture of acetonitrile–butadiene–styrene (ABS), plastics, rubber, polyester resin, fiberglass, toys, home appliances, and so on [5,6]. Styrene, with the chemical formula of C₈H₈ or CH₃CH=CH₂ or C₈H₈, is a benzene-derived aromatic hydrocarbon with a sweet smell, that is colorless and vaporizes quickly. Exposure to styrene causes toxic effects, including changes in the peripheral and central nervous system (such as drowsiness, headache, imbalance), irritation of the skin and respiratory system, and mild liver damage [6]. According to the evaluation, it is immediately absorbed through skin contact and via the lung, widely distributed in adipose tissue, and widely metabolized in the body. Epidemiological studies of cancer in large groups of occupations in the plastic injection industry have shown an increase in the incidence of leukaemia and lymphoma [7].

Based on studies of human cancer and animal laboratory studies, styrene was listed as a carcinogenic substance in the Twelfth Report of the U.S. National Toxicology Program in 2011. However, there is little evidence, which shows that lymphoma...
cancers and genetic damage to white blood cells (lymphocytes) are present in workers exposed to styrene [8]. The Office of Environmental Health Hazard Assessment (OEHHA) categorized styrene as a weak carcinogen in April 2016 [9]. The International Agency for Research on Cancer (IARC) has also designated Group 2B (probable carcinogen) for this substance [10].

There is a growing need to assess the risk of hazardous chemicals and their associated processes that affect the health of exposed individuals [4]. Chemical risk assessment enables us to make appropriate decisions regarding controlling measures and protect employees against adverse effects of chemicals [11]. Health risk assessment methods are carried out by either qualitatively (using the risk assessment matrix) or quantitatively methods [12].

In this regard, the U.S. Environmental Protection Agency (U.S. EPA) proposes the Integrated Risk Information System approach that can lead to quantitative risk prediction using exposure estimation [13]. Owing to the lack of epidemiological data and the long duration of quantitative methods, some studies use qualitative methods such as The Occupational Health Department of Singapore method to assess the risk of exposure to harmful chemical agents [4]. This method has also introduced a semiquantitative method for risk assessment [11]. This method evaluates and prioritizes health risk. In this method, the control of chemical risk is achievable by reducing the hazard rate (HR) and exposure rate (ER) (eliminating risk. In this method, the control of chemical risk is achievable by reducing the hazard rate (HR) and exposure rate (ER) (eliminating or replacing chemicals with a less hazardous substance) of the compounds [14]. Mohamadyan et al used the Singaporean and OEHHA methods to evaluate the health effects of styrene exposure on workers in the electronics industry. The results of the study showed that all workers are at definite risk of styrene carcinogenesis [10].

Some studies have been conducted to measure the exposure to styrene and its health effects on workers in industries such as shipbuilding, electronics, and plastics [10,15,16].

So far, few studies have been conducted to assess the carcinogenic risk of respiratory exposure to styrene in related industries. But, no study has been performed in the petrochemical industry producing ABS copolymers (owing to the high volume of styrene consumed in the production process). In addition, because of the different carcinogenic and health effects of each chemical compound in the petrochemical industry (considering the specific cancer slope factor [CSF] and HRs of each chemical compounds), conducting a study to assess the carcinogenic risk of occupational exposure to these chemical compounds and also comparing the results of two common quantitative and semiquantitative carcinogenic risk assessment methods for finding a best cancer and health risk assessment methodology (especially for respiratory exposure to styrene in high exposure industries) is very crucial in the working environments. Hence, the present study aimed to evaluate the exposure and health risk assessment of styrene using quantitative and semiquantitative methods in a petrochemical plant in the summer of 2019.

2. Materials and methods

The petrochemical plant is located in the west of Isfahan province. It produces 36,000 tons of ABS annually. The ratios of acrylonitrile, butadiene, and styrene in ABS products are 15–35, 5–30, and 40–60%, respectively. The number of employees in this industry was over 400, which 300 of them were working in production units.

2.1. Air sampling

Sampling was performed in eight units, including polybutadiene latex (PBL), styrene acrylonitrile (SAN) polymerization, compounding, bagging, 310, laboratory, fire department, and repairs unit, with the use of similar exposure groups. According to the NIOSH-1501 method [10], 150 air samples were collected from the respiratory area of workers (3 samples per person). As the workers spent most of their rest time in the restaurant and around, three environmental samples were also taken from this location to determine the concentration of styrene. One blank sample was taken for every 10 samples.

The sampling instrument consisted of an individual SKC sampling pump at a flow rate of 0.1 L min⁻¹ (sampling time ~90 min) and glass tube with 7 cm long, 6-mm O.D., 4-mm I.D., containing two sections of activated coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section, and a 3-mm urethane foam plug follows the back section (SKC Inc., PA, USA). The collected samples were kept in the refrigerator at a temperature below −4 °C during the shift. Then, they were 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).

2.1.1. Analytical process

According to the NIOSH 1501 method, the front and back sorbent sections of the sampler tube 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 were stirred for 30 minutes to extract the styrene from the absorbent as much as possible.

A microsyringe with a volume of 10 μl was washed with the sample to be prepared for injection. Afterward, 1 μl of sample extract was injected into the GC (Varian CP-3800). A flame ionization detector 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 initial temperature of the column was 40 °C for 2 minutes, then increased 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.

2.1.2. Quality control

The applied standard solutions were prepared at the concentrations of 0.5, 2, 5, 10, 50, 100, 400, and 1000 μg/ml and were injected into the GC. The R² value for the calibration curve was 0.998, the limit of detection (LOD) value was 0.2 μg/ml, and the limit of quantification (LOQ) value was 0.62 μg/ml.

2.1.3. Statistical analysis

SPSS version 25 (IBM in U.S) software was used for statistical analysis. Kruskal–Wallis and Mann–Whitney tests were used to compare the health risks between different sections (p < 0.05).

2.2. U.S. EPA health risk assessment method

2.2.1. Cancer risks assessment

Excess lifetime cancer risk (ELCR) of styrene was calculated using Eq. (1), [17]:

\[
ELCR = CDI \times CSF
\]

where the value of CSF (cancer slope factor) is 5.7 × 10⁻⁴ (kg − day⁻¹).mg⁻¹ and CDI is chronic daily intake (mg.(kg − day)⁻¹), which can be calculated using Eq. (2), [17]:

\[
CDI = \frac{C \times IR \times ED \times EF}{AT \times BW}
\]

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 1.

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” [18]. Also, EPA has recommended the value of ELCR to be less than 10⁻⁶ [19].

2.2.2. Non-cancer risk assessment

The non-cancerous hazard quotient (HQ) can be obtained using Eq. (3), according to exposure concentration (EC) and reference concentration (RFC) [17, 20].

\[
HQ = \frac{EC}{RFC}
\]  

(3)

where EC (measured in mg·m⁻³) was estimated using Eq. (4), [17, 20]:

\[
EC = \frac{C \times ET \times ED \times EF}{AT}
\]  

(4)

where ET is exposure time (hr·day⁻¹), the parameters of this equation are shown in Table 1. Employees had three days shifts and one day off, so their EF was counted at 274 days in year. Therefore, HQ < 1 indicates an acceptable hazard level, whereas HQ > 1 suggests that the potential risk can be severe and it will be unacceptable [17,21].

2.3. Singapore semiquantitative risk assessment method

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

1. Determining the HR based on one of the following methods [4]:
   ● Determination of the HR from lethal dose (LD50) and lethal concentration (LC50) of the chemical
   ● Determination of the HR using IARC carcinogenicity classification

2. Determining the ER using Table 2 [18] that was completed using Eq. (5), [11]:

\[
E = \frac{M.D.F}{W}
\]  

(5)

Table 2

| Parameter | Value | Units | Reference |
|-----------|-------|-------|-----------|
| ER        | 1     | >0.1  |           |
| 2         | 0.1–0.5 |       |           |
| 3         | 0.5–1 |       |           |
| 4         | 1–2   |       |           |
| 5         | 2     |       |           |

ER, exposure rate; PELₜₜₜ, corrected permissible exposure limit

where E is the weekly exposure (mg·m⁻³), M is exposure (mg·m⁻³), D is the average of exposure (h), F is the number of exposures in the week, and W is weekly hours of work (h).

About Table 2: the permissible exposure limit (PEL) was corrected using the Brief and Scala relation for the 3-day shift and the 1-day break (Eq. 6) [25]:

\[
RF = \frac{40}{H} \times \frac{168 - H}{128}
\]  

(6)

where H is working hours per week, RF is the reduction factor. Then, the corrected PEL (PELₜₜₜ) can be obtained using Eq. (7), [25]:

\[
PELₜₜₜ = RF \times PELₜₜₜ
\]  

(7)

3. Calculating the risk level by Eq. (8), [11]:

\[
Risk \ level = \sqrt{HR + ER}
\]  

(8)

4. Risk ratings obtained based on risk ranking matrix (Table 3) [14]:

Table 3

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

3. Results

This study involved 50 employees. Among the sections studied, as shown in Table 4, the lowest number of employees with three people was in the bagging unit (6%) and the laboratory had the most significant number of employees (18%). Also, according to Table 4, the highest and the lowest mean ages belonged to laboratory unit staff (40.8 ± 3.75 years) and unit 310 (33.57 ± 2.22 years), respectively. On the contrary, the highest mean of work experiences was in the Dryer unit (13.25 ± 2.87 years), and the lowest was in unit 310, with a mean of 7.28 ± 3.77 years because of hard physical work in unit 310.
3.1. Respiratory exposure to styrene

According to environmental prototypes, styrene was one of the highest concentrations in various segments of the ABS petrochemical industry. As presented in Table 5, the average concentration of styrene was $1.94 \pm 1.67 \text{mg m}^{-3}$. The average of its concentration was highest at compound ($4.60 \pm 2.7 \text{mg m}^{-3}$) and lowest at laboratory ($0.27 \pm 0.18 \text{mg m}^{-3}$). Table 5 presents that the highest and the lowest average respiratory exposure to styrene was in the PBL unit ($0.40 \pm 0.17 \text{mg (kg day)}^{-1}$) and dryer unit ($0.015 \pm 0.008 \text{mg (kg day)}^{-1}$), respectively. Firefighting unit personnel had the highest exposure to styrene after PBL personnel ($0.228 \pm 0.219 \text{mg (kg day)}^{-1}$).

3.1.1. Styrene cancer risk

The mean potential cancer risk of exposure to styrene through inhalation was evaluated using the U.S. EPA method. As shown in Table 5, styrene cancer risk for the PBL unit ($2.3 \times 10^{-4} \pm 9.0 \times 10^{-5}$) and the fire department ($1.3 \times 10^{-4} \pm 1.2 \times 10^{-4}$) was predicted higher than other units, whereas the dryer unit includes the lowest cancer risk ($0.8 \times 10^{-6} \pm 0.5 \times 10^{-6}$) of styrene exposure, according to predictors. Overall, Table 5 shows that according to the WHO recommendation, it was predicted that 16% of the calculated concentrations of styrene would lead to “definite risk” and 76% of exposure would lead to “probable risk” health effects after 30 years. Also, according to the EPA recommendation, unacceptable cancer risk was predicted for 92% of employees (the frequency of employees is presented in Table 4 by different sections).

3.1.2. Non-cancer risk

Similar to styrene carcinogenicity, non-cancer styrene risk was highest in PBL unit and fire department, with the mean values of 0.7265 and 0.3451, respectively (Table 5).

The results of the Kruskal–Wallis test showed that at a 95% confidence level, there was a significant difference between units on exposure and health risk of styrene ($p < 0.05$). The results of the Mann–Whitney test also showed a considerable difference between PBL and some units, including 310, bagging, compound, and dryer in terms of respiratory exposure to styrene, cancer risk, and non-cancer risk (Table 6). The most robust statistical difference was between the laboratory and the dryer units ($p = 0.009$).

3.2. Semiquantitative risk level

To calculate the health risk level of styrene using the Singapore Department of Occupational Health method (because the IARC placed styrene in Group 2B), the HR and ER were equal to three and two, respectively [14]. The rate of “low” risk was extracted from Table 3.

4. Discussion

In this study, the risk of exposure to styrene was assessed using two methods: the quantitative method of the U.S. EPA and the semiquantitative Singapore method in petrochemical plant. This study took place in a petrochemical industry because of its primary production materials (ABS), which styrene is one of them. At the

| Units       | No. of employees | Age | Work experience |
|-------------|------------------|-----|-----------------|
| Number      | Frequency        | Min | Mean (y) | Max | Min | Mean (y) | Max |
| 310         | 7                | 14  | 29        | 33.57 ± 2.22 | 36  | 3        | 7.28 ± 3.77 | 14 |
| Bagging     | 3                | 6   | 36        | 40.31 ± 1.78 | 43  | 8        | 12.45 ± 1.78 | 17 |
| Compound    | 8                | 16  | 30        | 35 ± 4.1    | 44  | 6        | 10 ± 4.1 | 16 |
| Dryer       | 4                | 8   | 33        | 36.5 ± 2.88 | 40  | 9        | 13.25 ± 2.87 | 15 |
| SAN         | 4                | 8   | 30        | 34.25 ± 5.31 | 42  | 8        | 10.5 ± 2.51 | 14 |
| Laboratory  | 9                | 18  | 33        | 40.8 ± 3.75 | 41  | 2        | 12.44 ± 4.41 | 16 |
| Repairs unit| 7                | 14  | 33        | 37.28 ± 2.81 | 41  | 6        | 11.58 ± 3.39 | 16 |
| PBL         | 4                | 8   | 30        | 39.5 ± 9.29 | 52  | 1        | 8.5 ± 7.04 | 15 |
| Fire department | 4            | 8   | 29        | 36.5 ± 5.25 | 41  | 4        | 12.5 ± 5.74 | 16 |
| Total       | 50               | 100 | 29        | 37.04 ± 4.80 | 52  | 1        | 10.82 ± 4.45 | 17 |

SAN, styrene acrylonitrile.
Table 6: Mann-Whitney test between different sections for respiratory exposure, cancer risk, and non-cancer risk of styrene.

| Unit          | 310 Bagging Compound Dryer | SAN Laboratory Repairs unit | PBL |
|---------------|-----------------------------|----------------------------|-----|
| R. Cancer risk | 0.73                        | 0.25                      | 0.008 |
| R. Non-Cancer risk | 0.06                    | 0.25                      | 0.08 |
| R. Cancer risk | 0.25                        | 0.006                     | 0.02 |
| R. Non-Cancer risk | 0.032                   | 0.008                     | 0.004 |

For respiratory exposure, cancer risk, and non-cancer risk.

P Value $< 0.05$.

PBL, polybutadiene latex; R. exposure, respiratory exposure; SAN, styrene acrylonitrile.

Table 6: Mann-Whitney test between different sections for respiratory exposure, cancer risk, and non-cancer risk of styrene.

Manufacturing process, styrene is combined with other chemicals at high temperature, which induces the release of styrene vapors into the environment. Several studies have shown that exposure to these fumes can have negative health effects [10,26].

Although the laboratory unit was not considered a production unit, its internal departments were very diverse in terms of staff duties. Among them, we can mention chemical agent units, ABS production modeling unit, paint materials quality testing unit, sample preparation unit, and their analysis with GC devices. Therefore, compared with other units, this unit had the most employees participating in the study.

The source of styrene release in PBL and dryer units included large storage tanks for styrene-containing chemicals. Results indicated that the most and the least level of respiratory exposure to styrene was in the PBL and the dryer units, respectively. As the dryer unit was the closest to the PBL unit, the significant difference of exposure to styrene between these units may be related to the following factors. First, the PBL was a three-story building with only natural ventilation (door and window) and low ventilation because of the small area of windows and doors, whereas the dryer unit was in an open environment. The second reason could be related to the type of work process which, the needed work time for the dryer was much less than the time the person had to spend in PBL. Firefighting personnel also had high exposure to styrene because of continuous patrols in production units and also because of the location of the fire station, which is next to the PBL unit.

Statistical analysis showed a significant difference between the sectors in terms of health risk and exposure to styrene.

PBL unit was significantly different from all units except SAN and firefighting units in terms of respiratory exposure, carcinogenic risk, and non-cancer risk. Compared with other units, SAN and fire departments were located near the PBL unit, which may be the reason for the similarity of the variables of these two units. The major difference in carcinogenic and non-cancerous risk was between PBL and 310 units. Although Unit 310 was a manufacturing unit, the lower risk in this unit can be attributed to two reasons. First, the amount of production volume and materials used in this unit were low. Second, most machines in this unit worked automatically and there was no need for the operator to be present near the machine full time.

In the present study, 16% of workers were at definite risk of carcinogenicity, whereas the study of Mohamadyan et al. indicated that all the workers of electronics industry are in definite risk [10]. The reason for this conflict can be explained by the difference in the equipment used (fully automatic, semiautomatic) and the amount of production.

Ruder and Bertke studied the cancer incidence of workers exposing to styrene in a boat-building industry. They obtained evidence of cancer due to styrene exposure that was significant because these workers had not reached the middle age (65 years), which is typical for cancer in the United States [7]. The results of their research are supporting the predictions of this study, which indicates that 92% of the employees were at risk for cancer.

The results of the non-cancer risk assessment indicated that HQ $/C_0 < 3$, which indicates that the risk of styrene was less than one [27]. However, Mohamadyan et al. stated that the difference in results is related to the direct relationship between the concentration of styrene and its non-cancerous effects [10].
The estimated health risk of exposure to styrene was higher in the EPA method than in the Singapore department. The similar result was also found in Bahrami et al.'s study. According to this study, in the EPA method, 25% of individuals were at definite risk, whereas the other 75% were categorized as possible risk level. The results of the Singapore method indicated that 50% were at probable risk level, whereas the other 50% were at possible risk level [28]. The reason for this difference in results of the two mentioned methods can be attributed to the inclusion of further parameters in study of the chemical risk level. EPA method includes parameters such as IR, AT, weight, which can provide more realistic results, but the Singapore method considers only the high concentrations as health risks.

One of the limitations of this study was to ignore the effects of wind speed and temperature as well as seasonal variations. Therefore, generalization should be done for annual caution. Also, the workers’ health (such as lung and liver problems, which according to the mentioned studies are directly related to exposure to styrene) and work experience in previous jobs, has not been considered. One of the strengths of this study is the high number of samples collected (150 samples) in a particular industry. The high number of samples naturally reduces the computational error and the results of the studies are close to the real values. It is important to note that in any environment, especially industrial environments that contain several different types of chemical compounds, the predictions about health disorders cannot be considered as the result of exposure to a particular substance. In this regard, it should be noted that this study only predicts the degree of health disorders caused by workers’ exposure to the calculated concentrations of styrene, but due to the presence of other chemicals in the environment, these disorders can be more severe, which requires further studies.

It can be concluded that styrene is a carcinogen, but as it is the primary raw material in this industry, it cannot be removed or replaced with another substance. Therefore, measures such as enclosing styrene leakage points, reducing exposure, improving the ventilation system and repairing, and updating machines to reduce styrene leakage may be useful to reduce workers’ exposure to this material.

5. Conclusion

The overall results of this study show that the carcinogenic risk and non-carcinogenic risk of styrene in some of the petrochemical sectors studied, especially in the PBL sector, were higher than the limits announced by the EPA. Also, 16% of the personnel surveyed in sectors studied, especially in the PBL sector, were higher than the limits announced by the EPA. Also, 16% of the personnel surveyed in some of the petrochemical plant. Toxicol Industrial Health 2020 Oct 27;0748233720962238,

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.shaw.2021.01.009.

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