

Exposure Assessment to Benzene, Toluene, Ethyl Benzene and Xylene (BTEX) in Gas Stations in Central Region of Iran

Mehrzad Ebrahimzadih, Abolfazl Barkhordari Firooz Abadi¹,
Omid Giahhi and Nasim Tahmasebi^{1*}

Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran

¹Department of Occupational Health, School of Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran

✉ emhrzad@yahoo.com

Received September 8, 2015; revised and accepted December 28, 2015

Abstract: Benzene, toluene, ethyl benzene and xylene are among the volatile organic compounds with similar physical and chemical properties. BTEX present in gas enters the urban atmosphere through vapourization from the gas in gas stations. Hence, the gas station workers are exposed to these hazardous vapours. The purpose of this study was to optimize the conditions of BTEX extraction from air samples using the solid phase microextraction (SPME) and measure the rate of pollution in Yazd gas stations in central region of Iran. This was a descriptive, cross-sectional study in which 13 gas stations were selected randomly. Air sampling was done in 35 gas stations at the end of the morning shift. The air samples were collected with Tedlar gas sampling bags and analyzed using SPME fibre via gas chromatography with FID. The findings of the study showed that most of the area under curve belonged to the fibre polydimethyl cyclohexan-carboxen (PDMS/CAR) compared to other two types of fibre. Also, the extraction time and sample recycling time from the fibre were determined to be 1 and 3 min, respectively. The mean concentration of benzene, toluene, ethyl benzene and xylene were $1932 \pm 807 \mu\text{g}/\text{m}^3$, $667 \pm 405 \mu\text{g}/\text{m}^3$, $148 \pm 89 \mu\text{g}/\text{m}^3$ and $340 \pm 216 \mu\text{g}/\text{m}^3$, respectively. The mean concentration of air benzene was higher than the permissible standard rate recommended by the National Technical Committee of Occupational Health (0.5 PPM), while the concentrations of toluene, ethyl benzene and xylene were less than the permissible limits.

Key words: Volatile organic compounds, recycling and extraction time, solid phase microextraction, gas station.

Introduction

Volatile organic compounds are among the air pollutants that exist in the form of volatile liquids or solids. These compounds that contain organic carbon are produced through various processes and vapourize quickly (Keshavarzi Shirazi et al., 2004). Benzene, toluene, ethyl benzene and xylene (BTEX) are among the volatile organic compounds with similar physical and chemical properties. Of these, BTEX is more significant and is used extensively in pharmaceutical and chemical

industries. These substances are the basic constituents of petrol (Tang et al., 2000) and the most principal solvents used in industries (Harbison, 1998). BTEX present in the consumed gas (petrol) enters the urban atmosphere through car exhausts, engine and carburetor and also via vapourization in oil products distribution stations. Hence, gas station workers are exposed to these compounds (Harbison, 1998). The main feature of these compounds is the high speed of vapourization (Wexler, 1998).

*Corresponding Author

Individuals' exposure to toluene may lead to numerous complications such as changes in the central nervous system (CNS) including exhaustion, dizziness, lack of coordination, and latency in reaction time and comprehension speed (Wexler, 1998). Ethyl benzene has sometimes induced the irritation of eyes and the digestive tract. Direct contact of the skin with xylene has led to its irritation and induced dryness, dermal cracks, blistering and dermatitis (Wexler, 1998). Acute myelogenic leukemia, hematological disorders, damages to the immune system, menstrual disturbances, and changes in the size of the ovaries are among the complications of exposure to benzene (Boogaard et al., 1995; Lynge et al., 1997). The permissible limits for benzene, toluene, xylene and ethyl benzene are 0.5, 50, 100 and 100 PPM, respectively (Iran Occupational Health Committee, 2003). Gas chromatography is one of the methods of analyzing the pollutants and poisons (toxins). According to the standards of National Institute of Occupational Safety and Health (NIOSH), the measurement method of volatile organic compounds is the gaseous chromatography using flame ionization detector (FID) (Boyd-Boland et al., 1996; Chen et al., 1995; NIOSH Manual of Analytical Methods, 2003) in which the extraction method applies active coal and isolation via carbon disulphide.

Extraction with solvent is not only time-consuming, but also induces environmental pollution. Solid phase microextraction (SPME) is among the innovative methods of extraction. This method was developed and used by Pawlizyn for the first time and then its application spread to other environments by various researchers (Boyd-Boland et al., 1996; Chen et al., 1995; Arthur et al., 1990; Koziel et al., 2000; Almeida et al., 2004). One of the applications of SPME is in the rapid analysis of volatile organic compounds in the air (Arthur et al., 1990). This method does not need any solvent and introduces the analyte directly to the gas chromatography setup through absorbing it to the silicone surface of the fibre. Other advantages of this extraction method include removal of the sample preparation processes, shortening of extraction time, and high accuracy in the measurement of analytes (Namiesnik et al., 2000; Tumbiolo et al., 2004; Mosaddegh et al., 2001).

In the study by Lagorio et al. (1998) the mean concentrations of benzene and toluene in twelve service stations were 169 and 424 $\mu\text{g}/\text{m}^3$ of gas, respectively. Furthermore, in the studies by Egeghy et al. (2000)

and Ghittori et al. (1993) the benzene concentration was 2.9 and 0.736 mg/m^3 , respectively. In addition, Bahrami et al. (2002) studied exposure to benzene in gas stations of Hamedan, Iran. They reported the rate of the measured benzene to lie within 106.73 and 42.17 PPB. It should be noted that in Iran sampling of volatile organic compounds has so far been conducted only using activated carbon (Bahrami et al., 2002). The extraction of these compounds from charcoal is also carried out utilizing toxic solvents which requires high degree of expertise. Furthermore, the extraction process is often associated with health hazards of the exposure to these chemicals for the laboratory technicians (Keshavarzi Shirazi et al., 2004; Bahrami et al., 2002). Therefore regarding the advantages of the new extraction method of volatile organic compounds which is solid phase microextraction (SPME) and also noting the point that this method has not been yet employed in Iran for measuring the volatile organic compounds, the researchers decided to measure BTEX compounds using the solid phase microextraction and gas chromatography. The aim of this study was to optimize the conditions of BTEX extraction for air samples and measure the rate of pollution of gas stations in Yazd, central Iran.

Experimental

This was a descriptive, cross-sectional study conducted in the winter of 2010 in which 13 petrol stations were randomly selected and air sampling was done in 35 gas stations at the end of the morning shift. The SKC individual sampling pump, made in UK, was used for sampling. The 5-litre sampling bags, made by SKC Company of England were used to collect samples. All the chemical substances used in this study (benzene, ethyl benzene, toluene, methanol, xylene and acetonitrile) were purchased with appropriate purity (HPLC Grade) from the German Merck Company to be analyzed by gas chromatography setup. The gas chromatography setup used for sample analysis was Youglin model YL6100, made in Korea, with FID and DB5MS-J&W Scientific column (column length: 60 m, internal diameter of column: 0.125 mm, film thickness: 0.25 μm). The fibres polydimethyl cyclohexan-divinyl benzene PDMS-DVB (65 μm), polydimethyl cyclohexan-carboxen PDMS-CAR (75 μm), and polydimethyl cyclohexan PDMS (100 μm) were purchased from the Supelco Company of England for sample extraction.

Sample Extraction and Analysis

This study used three types of well-known fibres for volatile organic compounds including PDMS-DVB (65 μm), PDMS-CAR (75 μm), and PDMS (100 μm) (Ouyang et al., 2006) to investigate the effect of fibre type on the rate of benzene extraction. Regarding the gaseous type of the sample, the direct extraction method was applied. This method is performed on the basis of equilibrium of concentration between the two phases of the sample in the fibre. The extraction time was studied between the time range of 1-7 min and the sample recycling time from the fibre was investigated within the range of 20-180 (S). The fibres were directly placed within the sample so that the sample could be extracted by the fibre. Then, the fibre was separated from the injection site of the bag and injected into the gas chromatography setup (GC).

Standardization Procedure in Sampling Bags

At first, the mother standard solution (Analyte/ acetonitrile) with concentration 0.5:1000 (v/v) was prepared for each substance. Then, the working standards of BTEX were prepared in sampling bags with concentrations of 87, 438, 2630 and 5260 $\mu\text{g}/\text{m}^3$ for benzene, 86, 216, 432 and 1720 $\mu\text{g}/\text{m}^3$ for toluene, 43, 86, 214 and 430 $\mu\text{g}/\text{m}^3$ for ethyl benzene, and 43, 214, 430, and 860 $\mu\text{g}/\text{m}^3$ for xylene. After 30 min (Hippelein, 2006), the sample was extracted with fibre SPME and injected into gas chromatography setup. Thereafter, the area under curve corresponding to each concentration was determined. Methanol was used as the internal standard.

Sampling

All the samples were collected within the respiratory domain of the workers at the end of the morning shift (round). To do so, first the output of the pump was setup at 0.5 litre/min. Then, using a suitable hose, the pump connector was attached to the sampling bag. For each sampling, first the bag was filled and emptied three times with fresh air. Sampling continued for 8 min till the air volume reached 80% (5 L) of the capacity of the bag. The samples were subsequently transported to the laboratory quickly and extracted with SPME fibre and analyzed via gas chromatography setup. The gleaned data were analyzed using SPSS 16 (USA, I1, Chicago, Inc SPSS).

Results

Measurement of BTEX concentration using the Solid Phase Microextraction (SPME) and gas chromatography was investigated which is the first report of this type. Regarding the similar physicochemical properties of these substances, the optimal conditions such as fibre type, extraction time, and recycling time for benzene were investigated. The findings are displayed in Table 1.

Selection of Fibre Type

The findings of assessment of the fibres used for extraction demonstrated that the fibre PDMS/CAR had the greatest area under curve compared to other two types of fibres and that it had more efficiency and effectiveness in absorption and extraction of benzene (Figure 1).

Selection of Extraction Time

Extraction using SPME method was performed on the basis of equilibrium of concentration between the two phases of the sample and the fibre. According to previous reports, the extraction time was studied in the range of 1-7 min. As the findings show, most of the area under curve was obtained after 3 min of placing the fibre in the sampling bag. By the way, increasing the extraction time beyond 3 min did not cause any improvement in the rate of sample extraction and did not increase the area under curve (Figure 2).

Selection of Sample Recycling Time from the Fibre

All the samples extracted from the fibre at different times between 20 to 180 s were placed at the injection site of the device. The findings revealed that all the samples separated from the fibre during 60 s. In other words, placing the fibre for more than 60 s at the injection site of the device did not increase the area under curve. We should note that exposing the fibre to extreme heat for long periods of time may lead to decreased longevity of the fibre. Consequently, the time of 60 s was used for sample analysis (Figure 3).

The mean concentrations of benzene, toluene, ethyl benzene and xylene from analysis of samples were 1932 ± 807 , 667 ± 405 , 148 ± 89 and 340 ± 216 $\mu\text{g}/\text{m}^3$, respectively (Table 2).

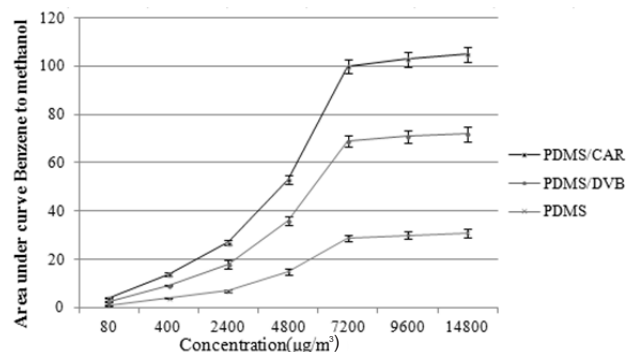
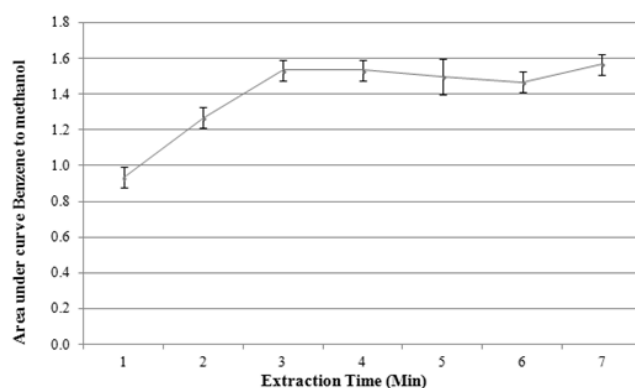
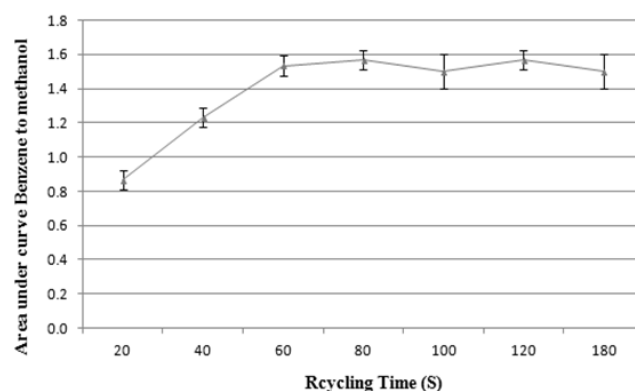
Comparison of BTEX Concentrations in the Samples

As can be observed, the mean concentrations of benzene and toluene are greater than those of ethyl benzene and

Table 1: BTEX concentration in the air for each gas station

Gasoline	Station number	Benzene ($\mu\text{g}/\text{m}^3$)	Toluene ($\mu\text{g}/\text{m}^3$)	Ethyl benzene ($\mu\text{g}/\text{m}^3$)	Xylene ($\mu\text{g}/\text{m}^3$)
1	1	736	298	183	735
	2	1280	321	100	233
	3	1440	300	80	400
2	1	2208	630	157	269
	2	1472	320	97	128
	3	1920	420	100	124
3	1	1818	596	153	313.5
	2	2880	310	79	134
	3	3040	299	87	164
4	1	2048	640	75	140
	2	2816	800	122	320
	3	3520	1618	240	668
5	1	1246	530	78	170
	2	1600	560	89	145
	3	1920	1005	207	565
6	1	1504	420	110	283
	2	3520	1226	226.5	615
	3	2016	740	110	140
7	1	2240	580	93	320
	2	2236	766	148	322
	3	1888	380	90	160
8	1	1600	325	70	210
	2	1760	940	230	430
9	1	2016	586	188	455
	2	1056	340	86	233
10	1	960	298	90	140
	2	2592	860	190	430
11	1	960	420	90	200
	2	1088	410	146	320
12	1	310	300	78	156
	2	1088	855	227	480
	3	2048	1600	253	765
13	1	2816	1486	543	754
	2	3520	1600	210	856
	3	2320	566	154	135

xylene. The value obtained for benzene is greater than the permissible limits of 0.5 PPM ($1600 \mu\text{g}/\text{m}^3$). The mean of toluene, ethyl benzene and xylene in the studied gas stations is lower than the permissible limits. The mean of air temperature has been $14.6 \pm 2.1^\circ\text{C}$ indicating that there is no correlation between the concentration of these compounds in the air and the rate of air temperature ($P < 0.05$).

**Figure 1: Rate of benzene extraction from the air by SPME.****Figure 2: Rate of benzene extraction from the air by PDMS/CAR fibre at different times.****Figure 3: Rate of benzene recycling from PDMS/CAR fibre at different times.****Table 2: Comparison of BTEX concentration in the samples**

BTEX concentration ($\mu\text{g}/\text{m}^3$)	Number	Mean	SD	Minimum	Maximum
Benzene	35	1932	807	310	3520
Toluene	35	667	405	298	1618
Ethyl benzene	35	148	89	70	543
Xylene	35	340	216	124	856

Discussion and Conclusion

Regarding the fact that the measurement of the concentration of volatile organic substances (benzene, toluene, xylene and ethyl benzene) has not been studied in gas stations in Iran, this study was designed and carried out to fulfill this purpose. Also, as the solid phase microextraction method (SPME) using the Tedlar gas sampling bag was not used to measure BTEX in the air in previous studies; hence, the comparison of the optimized parameters in this method are somehow different from other studies. Nonetheless, a group of studies have recommended the fibre PDMS/CAR for BTEX extraction from gaseous samples (Larroque et al., 2006a; Larroque et al., 2006b; Saba et al., 2001). The findings of the present study revealed that the values of mean concentration for benzene followed by toluene are higher than the other two compounds. Additionally, the mean concentration of air benzene is slightly higher than the permissible limit recommended by the National Technical Committee of Occupational Health (0.5 PPM) showing a value greater than that obtained by Lagorio et al. (1998) who used sampling with active coal. Furthermore, in the study by Ghittori et al. (1993), that used extraction method with active coal and measurement with gas chromatography, the rate of benzene exposure was $736 \mu\text{g}/\text{m}^3$ which was lower than the mean value of exposure ($1920 \mu\text{g}/\text{m}^3$) obtained in our study. The difference in values may be attributed to the high capacity of the selected fibre SPME for the extraction of these compounds. Our value of benzene exposure is almost consistent with the findings of Egeghy et al. (2000) (2.9 ± 5.8). The benzene concentration obtained in this study is consistent with some other studies given in Table 3 (Egeghy et al., 2000; Vainiotalo et al., 1999; Backer et al., 1997).

Most studies have focused on measuring benzene concentration in work environment air, specially at gas stations (Tumbiolo et al., 2004; Almeida et al., 2004;

Saba et al., 2001; Namiesnik et al., 2000; Hippelein, 2006). These studies measured the concentration of toluene, xylene and ethyl benzene in the air under limited conditions. The study by Lagorio et al. (1998) was conducted to measure concentration of toluene and benzene which were 169 and $424 \mu\text{g}/\text{m}^3$, respectively. These values are smaller than those obtained in our study. The concentration of BTEX in the blood was measured by Backer et al. (1997) to assess exposure in gas station. That study did not report the exact amounts of these substances in the air. Also, there was not any statistically significant correlation between increasing temperature and BTEX concentration ($P < 0.05$) which was due to sampling at times when there was no significant fluctuation in air temperature.

Since the range of changes in BTEX concentrations are very wide in this study, there is the need for a great number of air samples so that the exact rate of individuals' exposure to BTEX could be determined. Moreover, noting that the sampling of gas stations was not plausible in a specific hour of a specific day, and due to the fact that provision of this amount of Tedlar gas sampling bags was not possible due to high costs, the samples were collected at different hours of different days with varying air temperatures and under varying windy air condition. Hence, the high fluctuation in the range of BTEX concentrations may be attributed to this issue. On the basis of what was deciphered above, it is recommended that a future study be designed to assess the biomarkers resulting from benzene exposure in the personnel exposed to high levels of benzene.

Acknowledgements

The authors would like to thank the manager of National Iranian Oil Refining & Distribution Company for their cooperation.

References

- Almeida, C.M. and L.V. Boas (2004). Analysis of BTEX and other substituted benzenes in water using headspace SPME-GC-FID: Method validation. *J Environ Monit*, **6(1)**: 80-88.
- Arthur, C.L. and J. Pawliszyn (1990). Solid phase microextraction with thermal desorption using fused silica optical fibers. *Anal Chem*, **62(19)**: 2145-2148.
- Backer, L.C., Egeland, G.M., Ashley, D.L. et al. (1997). Exposure to regular gasoline and ethanol oxyfuel during

Table 3: Comparison of extracted benzene concentration in the previous studies

Year	Country	Mean (mg/m^3)	Maximum (mg/m^3)
1993	United States	1.3	8.4
1997	United States	1.3	2.7
1999	Finland	0.9	NR*
2000	United States	2.9	36

NR*: Not Reported

- refueling in Alaska. *Environ Health Perspect*, **105**(8): 850-855.
- Bahrami, A., Mahjoob, H. and M.J. Asary (2002). Investigation of Urinary Phenol and Benzene Concentration in Breathing Zone of Gasoline Station Attendant. *Urmia Med J*, **4**(2): 180-186.
- Boogaard, P.J. and N.J. van Sittert (1995). Biological monitoring of exposure to benzene: A comparison between S-phenylmercapturic acid, trans, trans-muconic acid, and phenol. *Occup Environ Med*, **52**(9): 611-620.
- Boyd-Boland, A.A. and J.B. Pawliszyn (1996). Solid-phase microextraction coupled with high-performance liquid chromatography for the determination of alkylphenol ethoxylate surfactants in water. *Anal Chem*, **68**(9): 1521-1529.
- Chen, J. and J.B. Pawliszyn (1995). Solid phase microextraction coupled to high-performance liquid chromatography. *Anal Chem*, **67**(15): 2530-2533.
- Egghy, P.P., Tornero-Velez, R. and S.M. Rappaport (2000). Environmental and biological monitoring of benzene during self-service automobile refueling. *Environ Health Perspect*, **108**(12): 1195-1202.
- Ghittori, S., Fiorentino, M.L., Maestri, L. et al. (1993). Urinary excretion of unmetabolized benzene as an indicator of benzene exposure. *J Toxicol Environ Health*, **38**(3): 233-243.
- Harbison, R.D. (editor) (1998). Hamilton & Hardys Industrial Toxicology. 5th ed. Mosby, USA.
- Hippelein, M. (2006). Analysing selected VVOCs in indoor air with solid phase microextraction (SPME): A case study. *Chemosphere*, **65**(2): 271-277.
- Iran Occupational Health Committee (2003). Occupational Exposure Limit. Center of Environmental & Occupational Health, Tehran.
- Keshavarzi Shirazi, H., Halek, F.S. and M. Mir Mohamadi (2004). Investigation and evaluation of VOCs in indoor air and public places. *J Environ Stud (JES)*, **32**(2): 41-46.
- Kozziel, J., Jia, M. and J. Pawliszyn (2000). Air sampling with porous solid-phase microextraction fibers. *Anal Chem*, **72**(21): 5178-5186.
- Lagorio, S., Crebelli, R., Ricciarello, R. et al. (1998). Methodological issues in biomonitoring of low level exposure to benzene. *Occup Med (Lond)*, **48**(8): 497-504.
- Larroque, V., Desauziers, V. and P. Mocho (2006a). Development of a solid phase microextraction (SPME) method for the sampling of VOC traces in indoor air. *J Environ Monit*, **8**(1): 106-111.
- Larroque, V., Desauziers, V. and P. Mocho (2006b). Comparison of two solid-phase microextraction methods for the quantitative analysis of VOCs in indoor air. *Anal Bioanal Chem*, **386**(5): 1457-1464.
- Lynge, E., Andersen, A., Nilsson, R. et al. (1997). Risk of cancer and exposure to gasoline vapors. *Am J Epidemiol*, **145**(5): 449-458.
- Mosaddegh, M.H., Richardson, T., Stoddart, R.W. et al. (2001). Application of solid-phase micro-extraction technology to drug screening and identification. *Ann Clin Biochem*, **38**(5): 541-547.
- Namiesnik, J., Zygmunt, B. and A. Jastrzebska (2000). Application of solid-phase microextraction for determination of organic vapours in gaseous matrices. *J Chromatogr A*, **885**(1): 405-418.
- NIOSH Manual of Analytical Methods. Centers for Disease Control and Prevention. (Accessed in Sep 28, 2012, at <http://www.cdc.gov/niosh/docs/2003-154/>).
- Ouyang, G. and J. Pawliszyn (2006). SPME in environmental analysis. *Anal Bioanal Chem*, **386**(4): 1059-1073.
- Saba, A., Cuzzola, A., Raffaelli, A. et al. (2001). Determination of benzene at trace levels in air by a novel method based on solid phase microextraction gas chromatography/mass spectrometry. *Rapid Commun Mass Spectrom*, **15**(24): 2404-2408.
- Tang, W., Hemm, I. and G. Eisenbrand (2000). Estimation of human exposure to styrene and ethylbenzene. *Toxicology*, **144**(1): 39-50.
- Tumbiolo, S., Gal, J.F., Maria, P.C. et al. (2004). Determination of benzene, toluene, ethylbenzene and xylenes in air by solid phase micro-extraction/gas chromatography/mass spectrometry. *Anal Bioanal Chem*, **380**(5-6): 824-830.
- Vainiotalo, S., Peltonen, Y., Ruonakangas, A. et al. (1999). Customer exposure to MTBE, TAME, C6 alkyl methyl ethers, and benzene during gasoline refueling. *Environ Health Perspect*, **107**(2): 133-140.
- Wexler, P. (1998). Encyclopedia of toxicology, Three-Volume Set: Chemicals and Concepts. 1st ed. Academic Press, Waltham, Massachusetts.