

## Validation of a New Method for the Monitoring of Environmental Benzene at Low Concentration Using the Needle Trap Device

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### Abstract

Benzene has been emitted from most industrial chemicals and automobile gasoline, environmental and occupational exposure to a wide range of benzene has been observed. The needle trap device is a novel and in-progress exhaustive extraction trap which fluid can pass through it by pump. In this study, NTD consisted of a needle gauge 21 with 10 cm length that's packed with Carboxen-1000 for adsorbing benzene. Samples were analyzed by gas chromatography coupled with flame ionization detector and peak verification was examined by gas chromatography-mass spectrometry. Linear range concentration was 25-2500 ppb and limit of detection; limit of quantitation and bias were 10, 20 ppb and -0.12 respectively. The agreement of atmospheric standards analyzed by the method of this study and OSHA's method was examined by the Bland-Altman plot. According to this method, the agreement of two sets of data was established. 20 samples were taken to check the applicability of the developed method in a refinery unit. Benzene concentrations were measured in the range of 0.15 to 1.2 ppm. The results showed that needle trap device carboxen-1000 is a reliable and effective approach and more sensitive and powerful technique for the sampling and analysis of low concentration of benzene in the atmosphere.

**Keywords:** Validation method; Benzene; Environmental monitoring; Needle trap device; Carboxen-1000

**Abbreviations:** LOD: Limit of Detection; LOQ: Limit of Quantitation; NTD: Needle Trap Device; VOCs: Volatile Organic Compounds; WHO: World Health Organization; OSHA: Occupational Safety and Health Administration; NIOSH: National Institute Occupational Safety and Health; EPA: Environmental Protection Agency; AOP: Auto-Oil Program; IARC: International Agency for Research on Cancer; GC-FID: Gas Chromatography-Flame Ionization Detector; GC-MS: Gas Chromatography-Mass Spectrometry; GC: Gas Chromatography; BTV: Breakthrough Volume; SPME: Solid Phase Micro Extraction; ppm: Part per million; ppb: Part per billion; min: Minute;  $\mu$ m: Micro meter; cm: Centimetre; SD: Standard Deviation; S/N: Signal to Noise; C: Celsius; ml: Millilitre; ml/min: Millilitre per minute;  $\mu$ l: Micro liters; h: hours

### Introduction

Benzene is the aromatic hydrocarbon and a good solvent that is regarded as an important industrial chemical [1,2]. Benzene has been used as a solvent in the industrial chemicals such as adhesives, waxes, paraffin and inks for the printing industry [3,4]. High levels of occupational exposures to benzene have been reported in refineries [5] as well as petrochemical [6], automobile repair, shoe manufacturing [7] and rubber manufacturing [8,9] industries. In the past, benzene was added to gasoline for its ability to induce better engine performance [8]. However, in recent years the concentration of benzene in gasoline has been reduced due to its pronounced toxicity and the carcinogenicity of benzene [10]. In accordance with the Air Quality Report of the first Auto-Oil Program (AOP), a 56% reduction in urban emissions of benzene was targeted for 1990 to 2010 years. Moreover, AOPI reported that vehicular traffic, fuel distribution, the chemical industry and petroleum refineries are the main sources of ambient benzene in Europe, with proportional contributions of 80-85%, 2.6-6%, 1.3-13% and 0.3-1.3% respectively [11].

The cumulative effects of benzene exposure on health, including

a headache, drowsiness, nausea, dizziness, confusion, severe damage to the kidney, the liver and the nervous system, and the irritation of the nose were reported [12-15]. Acute exposure through inhalation can cause illnesses such as headaches, drowsiness, dizziness, and irritation of the skin, whereas chronic exposure may cause more severe ailments, including aplastic anemia and leukemia at the occupational settings [16,17]. Due to its potential health threats, in according to the International Agency for Research on Cancer (IARC) classified, benzene is a group 1 human carcinogen [18].

Occupational exposure to benzene occurs in the chemical and petrochemical industries in developed countries. Refinery workers carry out various tasks involved in controlling the processing of hydrocarbon streams containing benzene in the production of gasoline components and operators tend to experience intermittent benzene exposures in the range of 9.4 ppb to 12.46 ppm during the performance of their job tasks [19]. These levels of exposures are considered to be hazardous to their health and comprise unacceptable risks for refinery workers [20]. Measurement of airborne benzene is typically performed through sampling with a sorbent tube and subsequent gas chromatographic detection in ppm range [21]. The common sorbent for trapping benzene is active charcoal granules as reported in the NIOSH No.1501 [22] and the OSHA No. 12 methods [23]. Sorbent material is subsequently

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**Received** December 21, 2017; **Accepted** February 08, 2018; **Published** February 13, 2018

**Citation:** Bayatian M, Azari M, Ashrafi K, Jafari M, Mehrabi Y (2018) Validation of a New Method for the Monitoring of Environmental Benzene at Low Concentration Using the Needle Trap Device. J Pollut Eff Cont 6: 214. doi: [10.4172/2375-4397.1000214](https://doi.org/10.4172/2375-4397.1000214)

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extracted by hazardous carbon disulfide [24,25] and analyzed by gas chromatograph equipped with flame ionization detector (GC-FID) [22,23,25] or gas chromatography-mass spectrometry (GC-MS) [26]. Also, the American Environmental Protection Agency (EPA) presented an advanced method No.325, which is applied to airborne volatile organic compounds through collecting air samples in canisters and subsequent analysis with double stage thermal desorption application and GC-MS, and this method has received international acceptance for monitoring atmospheric pollution [27].

New methods of sampling volatile organic compounds include Solid Phase Micro Extraction (SPME) [28] and Needle Trap Devices (NTDs) [29]. SPME is used for sampling benzene and other volatile organic compounds and this sampler does not require a solvent for extraction; it is directly injected into the injection port of the GC for analysis. However, linear range concentration and other validation parameters were, not reported [30-33]. NTDs have been developed in recent years. This sampler could be used for passive and active sampling respectively. Also, its sampling capacity can be maximized by increasing the sorbent material [34]. Until now, NTD has been used with some commercial sorbents, such as Carboxen-1000, Carboxen X, and Tenax. Carboxen-1000 has an average pore diameter larger than that of the Carboxen packing (70Å versus 39Å) but it has a large surface area than Carboxen S-II (approximately 1200 m<sup>2</sup>/g versus 1000 m<sup>2</sup>/g) and higher efficiency of Carboxen-1000 for absorbability of volatile organic compounds were reported [35].

Another advantage of the NTD over SPME is the durability of the sampler; this is because the NTD is not as fragile as the SPME fiber [36]. The reliability and sensitivity issues concerning the analysis of low concentration of chemicals in environmental and occupational exposures have been reported for both the NTD and the SPME sampling analysis [37]. Other authors have reported the advantages of NTD over SPME in terms of higher precision and sensitivity [12,38]. Due to diverse quantities of environmental exposures to benzene in petroleum refineries, a more comprehensive method with higher precision and sensitivity for the environmental monitoring of workers exposed to benzene has been requested by researchers [39]. Therefore, the main objective of this study was to validate the NTD-Carboxen-1000 for sampling and analysis of benzene with GC-FID for subsequent use of environmental monitoring of workers in and around the Catalytic Reforming Unit of a petroleum refinery in 2016.

## Materials and Methods

In this study, 10 cm stainless needles (Hamilton Co.) size 21-gauge was packed for 5 cm (2 mg) with Carboxen-1000 (Supelco Co.) with 60-80 µm mesh (Figure 1). This sorbent has a large surface area and is suitable for low volume sampling of very volatile organic compounds with a sufficient breakthrough volume (35). At first, the needle tip was blocked with three-millimetre glass wood, then 2 mg of Carboxen-1000 was packed into the needle from the other end using a metallic fiber and finally, Carboxen-1000 were supported by using three-millimetre glass wood. Eventually, the NTD was thermally conditioned in an oven

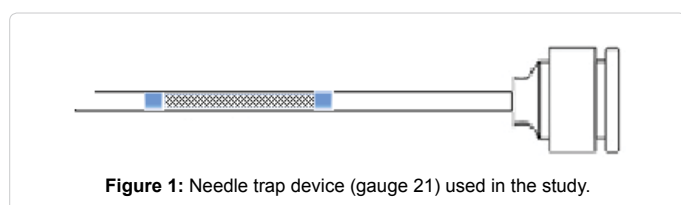


Figure 1: Needle trap device (gauge 21) used in the study.

at 250°C for 2 h and subsequently washed with clean nitrogen gas prior to sampling.

Atmospheric standards were prepared with ultra-pure air purchased from the Iranian Akhavan Company in 10 L Tedlar bags. Benzene and cumene (as an internal standard) were purchased from the Sigma Company. Ten standard atmospheres of benzene were prepared in the range of 0.01-10 ppm, containing cumene compound at 1 ppm as an internal standard. Atmospheric standards were prepared by serial dilution of standards by using a gas-tight syringe (10-100 µl) Hamilton Co. The atmospheric standards were used for sampling by NTD at 12 ml/min flow rate and 298 K air temperature. After sampling, the NTD connected to a glass syringe 500 µl equipped with a Luer-Lock valve (Hamilton Co.), was inserted instantly into the injection port of a GC-FID, and then, kept for 75 seconds at a temperature of 180°C for thermal desorption. Subsequently, thermally desorbed compounds were injected with 200 µl of pure air into the GC. The GC (Shimadzu model No 17A) was equipped with a length of 30 m, an inner diameter of 0.32 mm and a 0.32 µm film thickness capillary column (BP1 purchased from SGE analytical science). The GC oven was initially kept at 40°C for 1 min and it was gradually increased (5°C per minute) to 100°C and kept this temperature for one minute; the total run time was 14 min. The column flow and injection port temperature were set at 2 ml/min and 180°C respectively. In addition, the FID detector was set for the highest detection level.

Validation processes of NTD as a sampler and subsequent GC-FID analysis of benzene were examined according to the Gong Y method [29]. Accuracy and precision of analysis of the atmospheric benzene standards containing cumene as an internal standard were determined. Inter/intra-day variations were obtained over a 5-day period. Linear range concentration for benzene using internal standard cumene was determined. The limit of detection (LOD) and the limit of quantitation (LOQ) was estimated based on signal-to-noise ratios (S/N) of 3 and 10 respectively [40]. In addition, the bias based on the mean of the difference of the test results obtained from the reference samples from the true value given for the reference sample was calculated [41]. For the final phase of validation of the developed method in this study, two sets of identical standards of benzene in the range of 0.01-10 ppm was sampled by using NTD developed in this study with subsequent GC-FID analysis and also Specification of (SKC Co.) with a mesh size (20-40) according to the method by OSHA No.12 [23]. Charcoal tubes were, subsequently, desorbed with 1 ml carbon disulfide (CS<sub>2</sub>) in a closed 2-ml vial, equipped a PTFE septum. Finally, 1 µl of desorbed compounds were injected into the GC-FID for analysis. Peak verification of benzene and cumene was examined by GC-MS (Agilent 5975c) with the same column and chromatography conditions [42].

The agreement of two sets of identical atmospheric standards analyzed NTD-Carboxen-1000 and GC-FID analysis and OSHA's Method No. 12 in this study was examined by the Bland-Altman plot. The agreement could be true when the differences between the two sets of data obtained from the two methods fall within two standard deviations (2SD) from the average of the differences [43]. Finally, for checking the applicability of the proposed method of this study (NTD- Carboxen-1000 and GC-FID analysis), twenty environmental samples were taken from critical locations in and around the Catalytic Reforming Unit of a refinery unit. Environmental sampling and analysis was conducted similar to experimental validation described earlier. However, ambient air temperature was measured as a routine practice and appropriate corrections were considered.

## Results and Discussion

Atmospheric standards of benzene in the range of 0.001-10 ppm with an internal standard of 1 ppm cumene were used for the development of a new NTD sampling and GC-FID analysis. Breakthrough volume (BTV) of the NTD sampler was examined by connecting of the two samplers in series formation. The BTV of the NTD sampler, at a volume of 1800 ml, was measured. The retention times of standard atmosphere benzene and cumene were identified at 2.02 and 6.5 minutes, respectively (Figure 2). Benzene and cumene analysis by GC-FID in this method were verified according to the retention times (benzene: 2.019 min and cumene: 6.578 min) of GC-MS and the mass signatures of these compounds (Figures 3 and 4).

The validation parameters of the developed method in this study and the OSHA No.12 method were reported in Table 1. Linear range concentration was obtained in the range of 25 ppb to 2.5 ppm with the linear regression equation of  $Y=375.51x+227.01$  ( $R^2=0.9961$ ). Validation parameters in terms of LOD, LOQ and bias were measured

in values of 10 ppb, 20 ppb, and -0.12, respectively. Other validation parameters such as precision (inter-day and intra-day variations) and accuracy (inter-day and intra-day recoveries) were calculated for values of 3.25%, 1.61%, 97.3% and 95.6% respectively. These values are different from a similar study by Trefz et al. [28] which might be due to, using needles size 22-gauge with side holes packed for 1 cm with Carboxen-1000 in their study.

To compare the validity of the developed method in this study with the standard method by OSHA, duplicate atmospheric standards in the range of 10 ppb to 10 ppm were analyzed according to OSHA's method No.12 and validation parameters were also calculated (Table 1). Linear range concentration was obtained in that 400 ppb to 10 ppm range with linear regression equation of  $Y=8.2534-11.058x$  ( $R^2=0.9935$ ). The developed method, using an NTD sampler and direct thermal desorption without the use of toxic solvents, demonstrated better sensitivity for the monitoring of benzene in a refinery setting compared

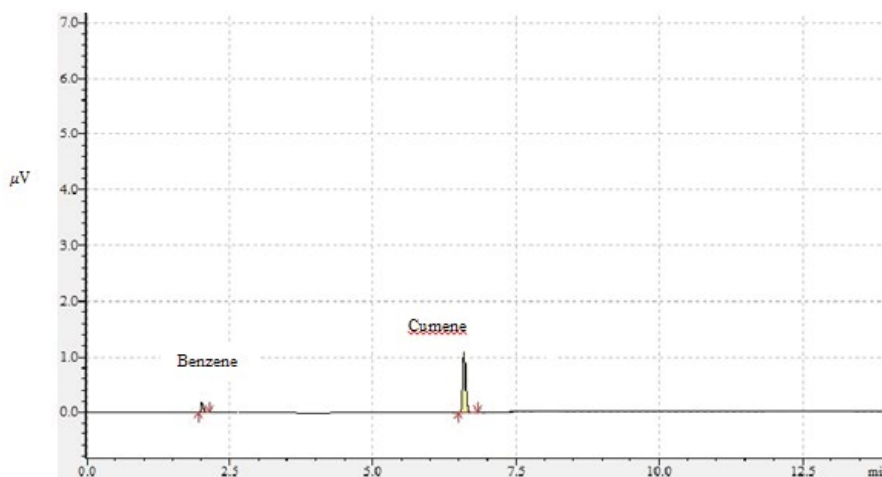


Figure 2: The retention times of benzene and cumene.



Figure 3: Confirmation peak benzene and cumene with GC-MS.

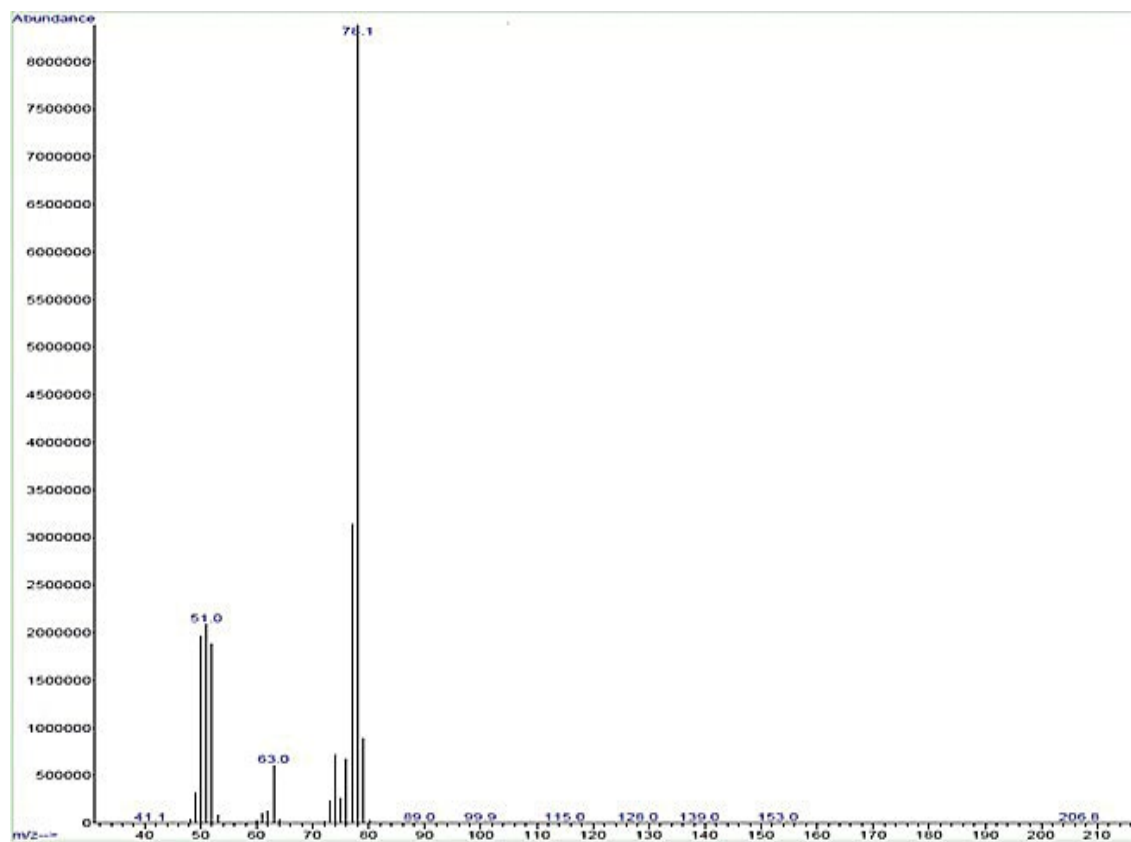


Figure 4: Mass signature of benzene with GC-MS.

Methods	Linear range concentration	LOD (ppb)	LOQ (ppb)	Bias	Intra-day		Inter-day	
					Precision%	Accuracy%	Precision%	Accuracy%
NTD	25-2500 ppb	10	20	-0.12	1.61	95.6	3.25	97.3
OSHA	0.4-10ppm	125	375	0.19	4.28	91.3	5.51	93.8

Table 1: Summary of assay validation data.

Samples	Concentration (ppm)	Samples	Concentration (ppm)
1	0.20	11	0.50
2	0.19	12	0.91
3	0.18	13	1.2
4	0.15	14	1.13
5	0.36	15	0.74
6	0.87	16	0.76
7	0.79	17	1.17
8	0.62	18	0.78
9	0.17	19	0.54
10	0.15	20	0.15

Table 2: Atmospheric concentrations of benzene as ppm according to carboxen NTD sampling and GC-FID analysis.

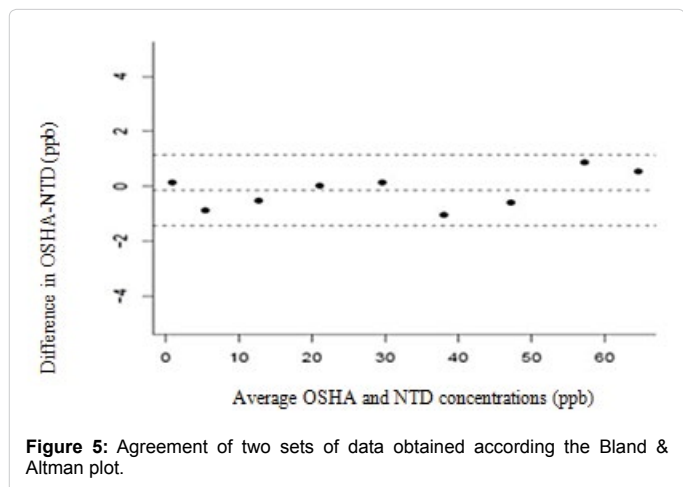


Figure 5: Agreement of two sets of data obtained according the Bland & Altman plot.

to other conventional methods presented by NIOSH No. 1501 [22] and OSHA No.12 [23].

The agreement of two sets of identical atmospheric standards

analyzed by the method of this study and OSHA’s method was examined by the Bland-Altman plot, which is displayed in Figure 5. From the average of the differences, since the differences were within  $\pm 2$  SD, the agreement of the two sets of data was established. Environmental and occupational exposure of workers to benzene at the designated refinery was measured in the range of 0.15 to 1.2 ppm (Table 2).

### Conclusion

This study focused on sampling using NTD and subsequent GC-FID analysis for determining the low concentration of benzene. The NTD used for analysis of environmental and occupational monitoring of benzene was checked for its validity. However, comparable information for the SPME sampler using thermal



desorption was not presented [38,44]. Generally, the monitoring of low range environmental concentrations of benzene in the ppb range concentration has been reported by using the EPA method [45]. However, such a method is not suited for the occupational monitoring of workers. The performance of the developed method using the NTD sampler demonstrated linear concentration range of 25-2500 ppb. The linear concentration range of the developed method in this study is not as good as the EPA's method [21]. However, the EPA method requires very complicated and expensive instrumentations for just monitoring atmospheric, environmental, benzene pollution. The presented method of this study could offer an adequate applicability for the monitoring low environmental and occupational concentrations compared to other methods using chemical desorption and even SPME sampler using thermal desorption. Despite favorable validation results of this study for sampling and analysis of environmental benzene, further collaborative studies for full accreditation of the method with other academic institutions is recommended.

### Acknowledgements

This study was conducted as a partial fulfillment of a Ph.D. thesis at the Shahid Beheshti University of Medical Sciences and authors thank their university officials for the financial support for this research.

### References

- Hosseini SY, Azari MR, Rahimian RT, Tavakkol E (2014) Occupational risk assessment of benzene in rubber tire manufacturing workers. *Int J Occup Hyg* 6: 220-226.
- Smith MT, Jones RM, Smith AH (2007) Benzene exposure and risk of non-Hodgkin lymphoma. *Cancer Epidemiol Biomarkers Prev* 16: 385-391.
- Roma-Torres J, Teixeira JP, Silva S, Laffon B, Cunha LM, et al. (2006) Evaluation of genotoxicity in a group of workers from a petroleum refinery aromatics plant. *Mutat Res Genet Toxicol Environ Mutagen* 604: 19-27.
- WHO (2000) Benzene, air quality guidelines. (2nd edn), WHO regional office for Europe Copenhagen, Denmark.
- Karakitsios S, Papaloukas C, Kassomenos P, Pilidis G (2007) Assessment and prediction of exposure to benzene of filling station employees. *Atmos Environ* 41: 9555-9569.
- USEPA (2009) Benzene, TEACH chemical summary. Toxicity and exposure assessments for children's health.
- Benzene health monitoring guidelines (2012) Workplace Health and Safety Queensland, Australia.
- Weisel CP (2010) Benzene exposure: an overview of monitoring methods and their findings. *Chem Biol Interact* 184: 58-66.
- Eyayo F (2014) Evaluation of occupational health hazards among oil industry workers: A case study of refinery workers. *J Environ Sci Toxicol Food Technol* 8: 22-53.
- Kao SH, Palmer ER, Shipman DR, Tung C (2008) Consider options to lower benzene levels in gasoline. *Hydrocarbon processing* 87.
- Institute inquinamento atmosferico (1998) Council directive on ambient air quality assessment and management working group on benzene.
- Hasan NH, Said MR, Leman AM (2013) Health effect from volatile organic compounds and useful tools for future prevention: A review. *Int J Env Eng Sci Tech Res* 1: 28-36.
- Khalade A, Jaakkola MS, Pukkala E, Jaakkola JK (2010) Exposure to benzene at work and the risk of leukemia: A systematic review and meta-analysis. *Environ Health* 9: 31.
- Smith MT (2010) Advances in understanding benzene health effects and susceptibility. *Annu Rev Public Health* 31: 133-148.
- Li T (2013) Cumulative impact of benzene emission and a potential approach to improve the ontario air quality standard. Master of engineering and public policy, McMaster University.
- Hosseini SY, Azari MR, Zendehelel R, Souri H, Rahimian RT (2015) Feasibility the biological monitoring of workers exposed to benzene and toluene via measuring the parent compounds in the exhaled breath. *Health Scope* 4: 25774.
- Glass DC, Gray CN, Jolley DJ, Gibbons C, Sim MR, et al. (2003) Leukemia risk associated with low-level benzene exposure. *Epidemiol* 14: 569-577.
- WHO (2010) IARC Monographs on the evaluation of carcinogenic risk to human. *Internat agency Res cancer* 93: 1-466.
- Capleton AC, Levy LS (2005) An overview of occupational benzene exposures and occupational exposure limits in Europe and North America. *Chem Biol Interact* 153-154: 43-53.
- Guo H, Lee SC, Chan LY, Li WM (2004) Risk assessment of exposure to volatile organic compounds in different indoor environments. *Environ Res* 94: 57-66.
- USEPA (2011) United States Environmental Protection Agency. Air monitoring and sampling addendum to the sampling and analysis plan.
- NIOSH (2003) TNIfOsaH, analytical method, hydrocarbons, aromatic, NIOSH NO 1501.
- OSHA (2002) OsaHA-analytical method, hydrocarbons, aromatic, OSHA NO 15 2002.
- Newhook C, Meek B, Newhook C (2002) WHO. Concise international chemical assessment document 46, carbon disulfide.
- Chang SJ, Shih TS, Chou TC, Chen C-J, Chang HY, et al. (2003) Hearing loss in workers exposed to carbon disulfide and noise. *Environ Health Perspect* 111: 1620-1624.
- Woolfenden E (1997) Monitoring VOCs in air using sorbent tubes followed by thermal desorption-capillary GC analysis: summary of data and practical guidelines. *J Air Waste Manage Assoc* 47: 20-36.
- ALS (2016) Analysis of VOCs by thermal desorption analysis.
- Trefz P, Kischkel S, Hein D, James ES, Schubert JK, et al. (2012) Needle trap micro-extraction for VOC analysis: Effects of packing materials and desorption parameters. *J Chromatography A* 1219: 29-38.
- Gong Y, Eom IY, Lou DW, Hein D, Pawliszyn J (2008) Development and application of a needle trap device for time-weighted average diffusive sampling. *Anal chem* 80: 7275-7282.
- Alonso M, Cerdan L, Godayol A, Anticó E, Sanchez JM (2011) Headspace needle-trap analysis of priority volatile organic compounds from aqueous samples: application to the analysis of natural and waste waters. *J Chromatogr A* 1218: 8131-8139.
- Go UJ, Eom IY (2014) Development of syringe pump assisted headspace sampler. *J Chromatography A* 1361: 88-94.
- Laaks J, Jochmann MA, Schmidt TC (2012) Solvent-free microextraction techniques in gas chromatography. *Anal Bioanal chem* 402: 565-571.
- Koziel JA, Pawliszyn J (2001) Air sampling and analysis of volatile organic compounds with solid phase microextraction. *J Air & Waste Manage Assoc* 51: 173-184.
- Warren JM, Pawliszyn J (2011) Development and evaluation of needle trap device geometry and packing methods for automated and manual analysis. *J Chromatogr A* 1218: 8982-8988.
- SUPLCO (1994) Efficient analyses of permanent gases, light hydrocarbons, and light polar compounds by GSC. Application Note 10.
- Bigham S, Medlar J, Kabir A, Shende C, Alli A, et al. (2002) Sol-gel capillary microextraction. *Analy Chem* 74: 752-761.
- Panahi D, Azari M, Akbari ME, Zendehelel R, Mirzaei HR, et al. (2016) Development of a new method for sampling and monitoring oncology staff exposed to cyclophosphamide drug. *Environ Monitor Assess* 188: 238.
- Heidari M, Bahrami A, Ghiasvand AR, Shahna FG, Soltanian AR (2012) A novel needle trap device with single wall carbon nanotubes sol-gel sorbent packed for sampling and analysis of volatile organohalogen compounds in air. *Talanta* 101: 314-321.
- IFC (2007) International finance corporation, environmental, health and safety guidelines for petroleum refining.
- Sanagi MM, Ling SL, Nasir Z, Ibrahim WAW, Naim AA, et al. (2009) Comparison of signal-to-noise, blank determination and linear regression methods for the

- 
- estimation of detection and quantification limits for volatile organic compounds by gas chromatography. *J AOAC Intern* 92: 1833-1838.
41. Moses GC (2009) Measurement uncertainty, how to calculate it in the medical laboratory, National director, Gamma-Dynacare medical laboratories.
42. Fereherm F (2014) Quantitation and confirmation of blood ethanol content using a new GC/FID/MS blood alcohol analyser. Agilent Technol.
43. Bland JM, Altman DG (1986) Statistical methods for assessing agreement between two methods of clinical measurement. *Lancet* 8476: 307-310.
44. Heidari M, Bahrami A, Ghiasvand AR, Shahna FG, Soltanian AR (2013) A needle trap device packed with a sol-gel derived, multi-walled carbon nanotubes/silica composite for sampling and analysis of volatile organohalogen compounds in air. *Analytica Chimica Acta* 785:67-74.
45. USEPA (1997) Compendium Method TO-14A. (2nd edn), Determination of volatile organic compounds (VOCs) in ambient air using specially prepared canisters with subsequent analysis by gas chromatography.