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Original Article

Trace Analysis of Xylene in Occupational Exposures Monitoring

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Abstract

Background: Determination of organic pollutants usually requires extraction of the pollutants from samples, using hazardous solvent. Solid phase micro-extraction (SPME) is a solvent-free equilibrium extraction method, in which, proper calibration can allow quantitative measurements of organic pollutants at a very good sensitivity without the use of any organic solvent. Because individual VOCs are generally present in urine only at trace levels, a sensitive and accurate determination technique is essential.

Methods: This study describes the optimization of headspace solid phase micro-extraction (HS-SPME) followed by gas chromatography equipped with flame ionization detector (GC-FID) for xylene in spiked urine. Through this investigation, the parameters affecting the extraction and GC determination of xylene, including extraction time, temperature, desorption temperature, desorption time, salt addition, sample pH, sample volume and sample agitation were studied.

Results: An optimized headspace extraction was carried out at 30°C for 6 min in presence of 0.2 gml^{-1} of NaCl in the sample solution. Desorption of the xylene was carried out for 60 sec. at 250°C. The optimized procedure was also validated with three different pools of spiked urine samples and showed a good reproducibility over six consecutive days as well as six within-day experiments. In this study, the accuracy, linearity, and detection limits were also determined.

Conclusion: The HS-SPME-GC-FID technique provided a relatively simple, convenient, practical procedure, which can be successfully applied for determination of xylene in spiked urine when an occupational exposure monitoring is required.

Keywords: *Headspace, Solid phase microextraction, Gas chromatography, Xylene*

Introduction

Because of increasing concern about toxic substances such as organic solvents in the environment and workplaces, it is becoming more important to monitor such pollutants in order to evaluate risk hazards and potential problems caused by exposure to toxic compounds (1- 2). Xylene is a colorless, flammable liquid that smells like gasoline. It is found in natural products such as coal tar and petroleum as well as in manufactured products such as inks, insecticides, and paints. Xylene is also used as a solvent to make other chemical compounds. People might be exposed to xylene through many ways including breathing air, particularly in areas near factories or highways, drinking contaminated tap water, working in an industry where xylene is used or made, and using products containing it, such as gasoline, carpet glues, varnishes, and paints. Limited information is available on the effects of xylene on people's health. However, because this pollutant has a similar chemical structure to benzene and toluene, it can cause dizziness, throat and eye irritation, tightening of the chest, and a burning sensation in the eyes of people who are exposed to high levels of xylene in air. Although xylene is present at low level in urine of exposed individuals, trying to find some sensitive methodology of direct determination of trace amount of this environmental and industrial pollutant can be a suitable alternative way to overcome the problems may associate with determination of its metabolite (methyl hippuric acid) in urine. Thereby, an exact determination can be performed for monitoring of occupational and environmental exposures to xylene.

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Sample pretreatment for the isolation of organic compounds, such as xylene, from aqueous solution is the most challenging and time-consuming steps in an analytical procedure (3). Liquid-liquid extraction (LLE) (4) solid phase extraction (SPE) (5-10), has been commonly used for the extraction of pollutants from aqueous matrices. Solid phase micro-extraction has been successfully applied to the extraction of VOCs and other organic compounds from water, solid, and air samples (11-13). The principle behind SPME is the partitioning of analytes between the sample matrix and the extraction medium with subsequent sorption onto a liquid polymeric coating which is supported on a fused silica fiber. The adsorption efficiency depends mainly on the retention characteristics of the selected sorbent for the type of organic compounds being sorbed (12). This technique uses a thin polymer film coating to extract analytes from aqueous or gaseous samples. Then, the fiber inserted directly into the injector of a gas chromatography system, and the extracted analytes are thermally desorbed and analyzed. SPME can integrate sampling, extraction, preconcentration, and sample introduction into a single step. Nowadays, among the most recommended techniques, SPME is employed for the extraction and pre-concentration of volatile and semi-volatile pollutants at trace levels in variety of matrices (14). Introduction of new polymeric fibers, development of new experimental configurations, and the improvement of automatic devices will undoubtedly lead to the application of SPME to different fields of chemical pollutants analysis.

The aim of this study was to establish a practical, fast, inexpensive, selective, and reliable method for trace analysis of urinary xylene using SPME for evaluation of occupational ex-posure.

Material and Methods

Reagents and Chemicals

Xylene as a standard was obtained from Aldrich. The stock solution of xylene was prepared at a concentration of 0.1 μgml^{-1} in methanol. The model solution containing the required amount of analyte (0 to 500 $ngml^{-1}$) was prepared daily by diluting standard solution with double distilled water to study extraction performance under different conditions. Stock and working standard solutions were stored at 4 °C. Methanol (GC grade), sodium chloride, and standard buffered solutions at three pH values (4.00± 0.02, 7.00± 0.02, 9.00± 0.02) were obtained from Merck, Germany. To define effects of real matrices on extraction performance, spiked urine prepared by 5 ml urine of unexposed persons with xylene, 5 ml standard me-thanolic solution of xylene at each concentration and 40 ml double distilled water was used.

Apparatus

Fibers with polypyrrole having a film thickness of 16 µm coated on the surface of a platinum (prepared by a research team in Faculty of Chemistry in Tarbiat Modarres University, Tehran, Iran) (14). SPME fiber holder for manual sampling was purchased from Azar Electrode, Ourumieh, Iran. 10 ml volume vials obtained from Supelco Mississauga, Ontario. A digital pH meter from Hanna, Singapore, was used for pH adjustment. The amount of reagents were measured, using a CP 225D Sartorius balance (Sartorius, Germany) for milligram, or lower, quantities. The RH-B-KT/CS2 hot plate stirrer, Germany was used to agitate the aqueous samples. A stir bar 8×3.14 mm used to mix aqueous samples for this study were from Fisher Scientific Nepean, Ontario. The GC apparatus used in this study was for Varian, 3800/USA included the following equipments: The analytical column, CP Sil8, 50m×0.53 mm I.D., 0.25 µm (film thickness); detector, FID, carrier gas, He (99.999%), flow rate 10 $mlmin^{-1}$; make up gas, N_2, flow rate 25 $mlmin^{-1}$. Fiber was introduced into the chromatographic column using splitless injection. The GC split valve was closed for 5 min. The detector gases flow rates were 300 $mlmin^{-1}$ of air and 30 $mlmin^{-1}$ of hydrogen. The separation of xylene on GC-FID was performed by a temperature program as follows: 65 °C for 5 min increased to 280 °C at a rate of 30 °C min^{-1} and held at 280 °C for 10 min.

Headspace extraction procedure

Aaqueous solution spiked with the xylene (5 ml) was extracted with polypyrrole fiber using the HS-SPME mode. The polypyrrole fiber housed in manual SPME holder was used. The fiber was conditioned prior to use by inserting into the GC injection port for three hours at 200, 250, and 300 °C for each hour, respectively. Sample (5 ml) containing the target analyte was placed in a 10 ml glass vial with a PTFE silicon septum. After the addition of sodium chloride and magnetic stirring bar, the vial was tightly sealed with an aluminum cap to prevent sample loss due to evaporation. During the extractions, the sample vials were heated by using a hot plate accommodated in a glass beaker contained some water and a thermometer was placed in it. So, the sample was heated indirectly. The polypyrrole fiber was exposed to the headspace over the stirring liquid sample for 10 min. After completion of sampling step, the fiber was withdrawn into the needle and removed from the sample vial. The fiber was then immediately inserted into the injection port of the GC. For application of SPME to measure spiked urinary xylene, xylene was extracted by a laboratory made fiber with an absorbent from headspace (HS) of samples, and measured by GC. In this study, the extraction conditions, including extraction time, addition of salt, temperature, sample pH, sample concentration, sample volume, and agitation, reproducibility, and linearity of the calibration curve of HS-SPME were optimized.

Results

Optimization of chromatographic analysis

Optimization of desorption temperature

The high thermal stability of polypyrrole fibers enables the desorption temperature to be increased and therefore, the efficiency of thermal desorption can be improved. Therefore, complete desorption of thermally stable compounds such as xylene can be achieved. Desorption in the GC injection port was measured in the temperature range of 200 °C to 300 °C for xylene. A symmetrical peak was achieved for xylene at 250 °C (Fig.1). So, this temperature selected as optimum temperature in this study.

Optimization of desorption time

Cary over means the percentage of analyte may be left on fiber after thermal desorption of the analyte from fiber in the injection port of the GC, causing loss in recovery of analyte in SPME. To avoid this deficiency, after complete thermal desorption of the analyte in about two minutes (100%), the optimum desorption time in the GC injection port was evaluated compare to the complete thermal desorption in the range of 20 to 100 second at optimized desorption temperature (250 °C). Fig. 2 shows the dependence of carry over of xylene on desorption time. From these results, it is apparent that, desorption of xylene from fiber in injection port is completed after 1 minute at 250 °C. Therefore, after each injection, it is necessary to leave fiber in the injection port of the GC for at least 1 minute in order to complete thermal desorption of xylene.

Optimization of solid phase microextraction

Effect of sample pH

Adjusting sample pH value of the solution can change the ionic strength of the solution in aquatic samples and increase analyte extraction efficiencies. So, in this experiment, 5 ml of sample at different sample pH values of 3, 5, 7, 9, and 11 were applied. Fig. 3 shows the influence of sample pH on extraction efficiency. Results showed that, increasing the sample pH up to 7, improved the extraction efficiency; however, recovery of xylene was not improved when the sample pH was increased more than 7. Therefore, the neutral sample pH (pH= 7) was selected as the optimum pH.

Effect of sample volume

Condensed phase, the gaseous phase, and the coating are involved in an HS-SPME process. The effect of the volume of the phases on the kinetics and thermodynamics of HS-SPME procedures is very complex, even in equilibrium conditions. It is strongly dependent on the partition constants. Because the sensitivity of

SPME procedures is proportional to the amount of analyte in the sample, it is expected that, increasing sample volume will augment responses. However, from the SPME theory, if the sample volume becomes significantly larger than fiber and headspace capacities, no enhancement of the responses can be achieved by increasing the volume of sample. In order to evaluate the sample volume effect on the HS-SPME efficiency, a set of experiments were carried out. The total volume of the vial (sample plus headspace) was 10 ml, and the range of sample volume tested was 2 to 6 ml. Samples were extracted at optimized pH for 10 min. (Fig. 4). Results show that, increasing volume up to 5 ml can increase the extraction efficiency, afterward; there is no significant effect on the extraction recovery.

Effect of extraction temperature

Based on vapor pressure, the concentration of the analyte in the sample headspace can be increased and partitioning of the analyte between the sample and headspace can reach equilibrium more quickly. On the other hand, the distribution constant for the analyte between the sample headspace and fiber coating is also temperature-dependent. By increasing the temperature, especially at high temperature, the affinity of the analyte for the fiber coating decreases. For investigation of influence of temperature on extraction efficiency, the effect of five different extraction temperatures (20, 25, 30, 40, and 50 °C) was investigated. As shown in Fig. 5, the high extraction efficiency was obtained at temperature 30 °C, and there was no significant increase afterward. So, this temperature was chosen as an optimized temperature.

Effect of NaCl

A ranging from 0 to 0.4 gml^{-1} was added to the samples and after complete mixing, the extraction process was performed. The obtained results showed that, by adding salt to the solution up to 0.2 gml^{-1}, the extraction efficiency can be improved, however, for amounts of sodium chloride greater than 0.2 gml^{-1}, the extraction efficiency reach a plateau and remains constant (Fig. 6). Therefore, this amount was selected for optimized salt addition.

Effect of sample agitation

Efficiency of the method was investigated from 5 ml model solutions containing 100 ppb of xylene at different stirring speeds at the range of 200 to 1000 rpm (Fig. 7). The obtained results showed that, the extraction efficiency increases with stirring speed, and for speeds more than 600 rpm, the extraction profile is flat. Therefore, for the next experiments the sample solutions were stirred at 600 rpm.

Effect of extraction time

The fiber was exposed to the gaseous sample into headspace area for 2, 4, 6, 8 and 10 min. Then, the fiber retracted into the needle, transferred into injection port of GC and desorbed analyte was determined. As is shown in Fig. 8, after 6 min the extraction equilibrium was established. Therefore, this extraction time was chosen for further experiments.

Effect of sample concentration

A range of concentration of xylene in the solution from 50 to 400 ppb was prepared to define the influence of sample concentration on extraction efficiency. As shown in Fig. 9, by changing the concentration, the peak area is also increased, illustrating linear sensitivity of the method.

Validation of optimized method

For validation of the optimized method, the working samples were made in aquatic solution. Therefore, further experiments were carried out on urine. A preliminary validation of the possible use of the optimized method for determining xylene in urine was performed, using spiked samples and standards. Samples of 50 ml were used for extraction. Linear standard curves (extracted) over the range of 50, 200 and 400 ppb were obtained each day (n= 6) with a correlation coefficient of 0.995 or greater. The day-to-day and within-day relative standard deviation of the method was investigated by spiking urine sample with xylene. Table 1 shows the results obtained from this experiment.

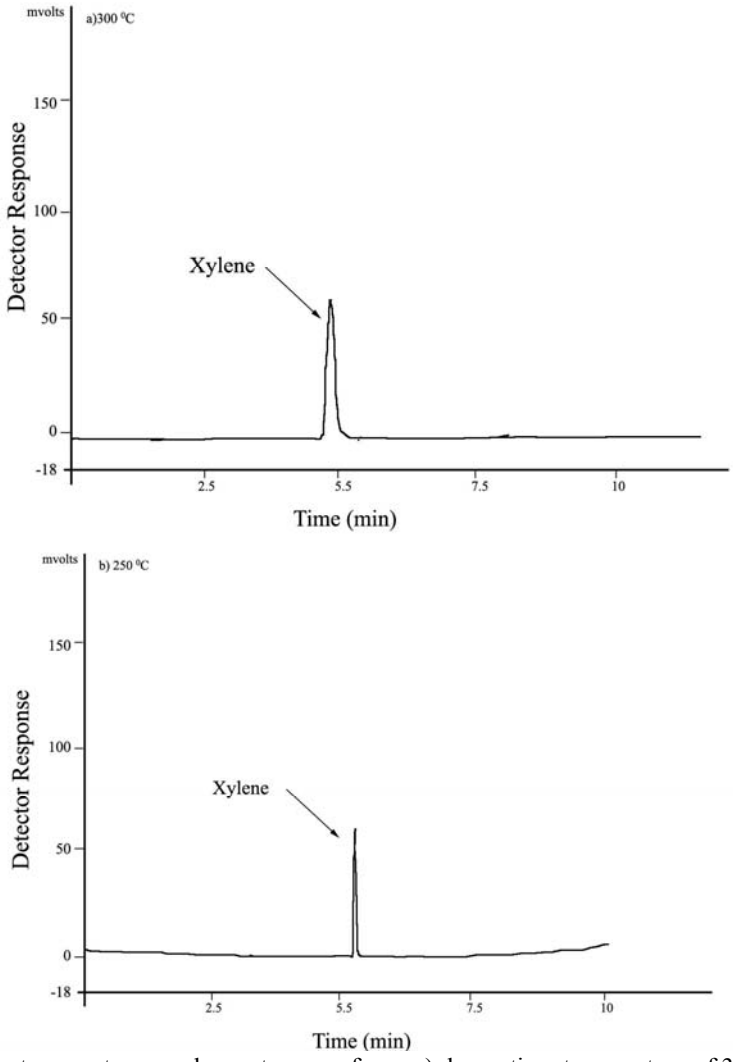

Fig.1: Effect of desorption temperature on chromatograms form, a) desorption temperature of 300 °C, b) desorption temperature of 250 °C

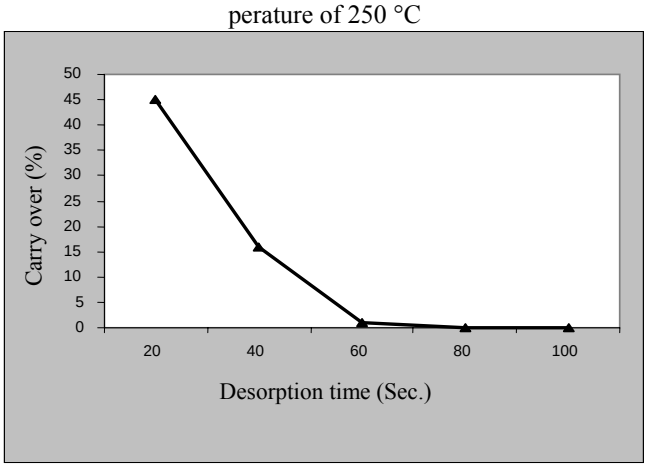

Fig. 2: Effect of desorption time on carry-over of xylene at optimized desorption temperature (250°C)

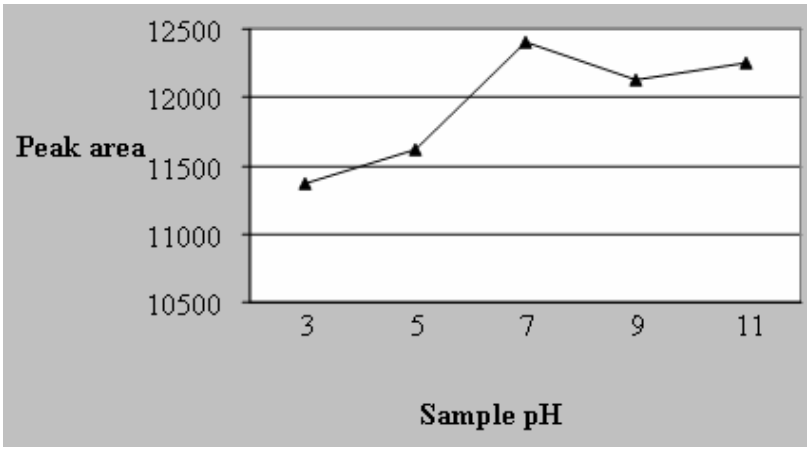

Fig. 3: Effect of sample pH on extraction efficiency

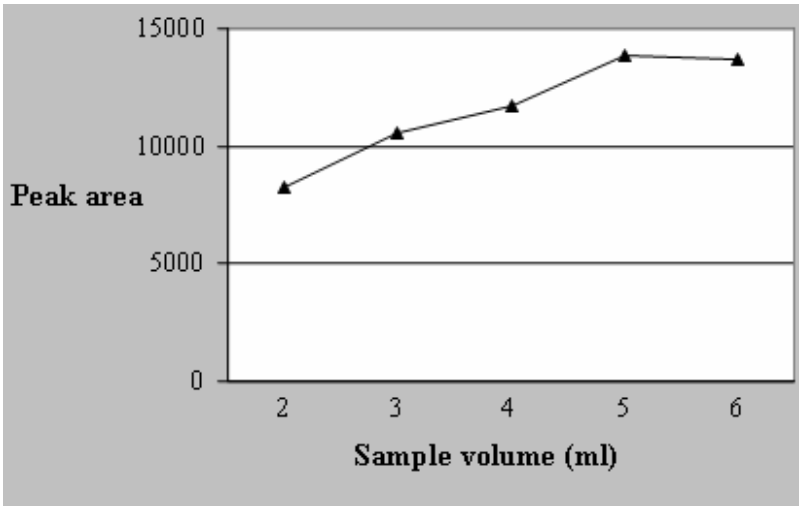

Fig. 4: Effect of sample volume on extraction efficiency

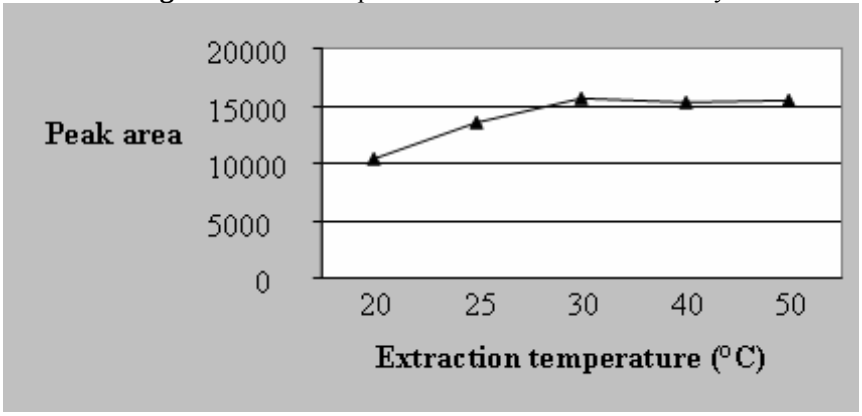

Fig. 5: Effect of different extraction temperature on extraction efficiency

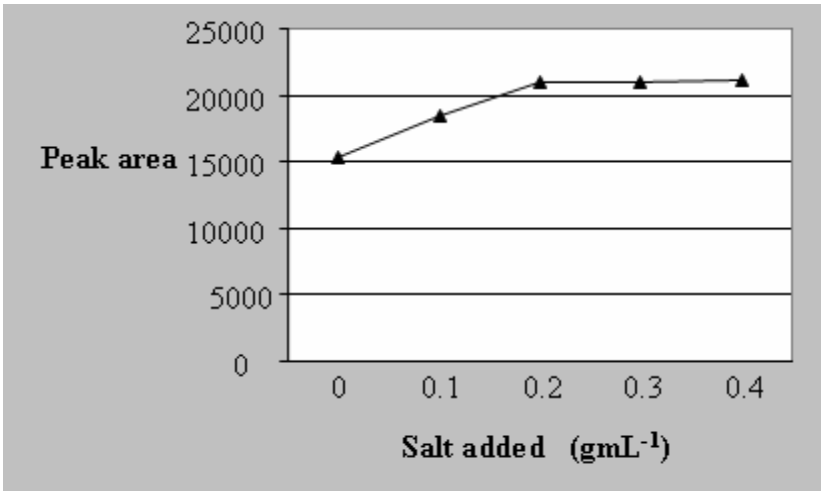

Fig. 6: Effect of different amounts of salt addition on extraction efficiency

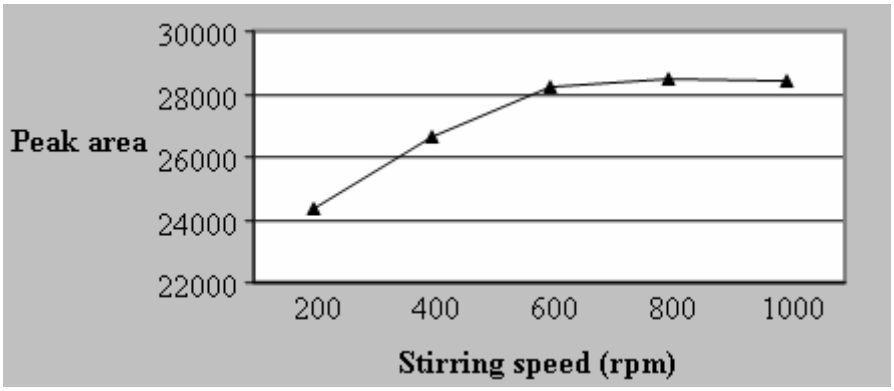

Fig.7: Effect of various stirring speed in the solution on extraction efficiency of xylene

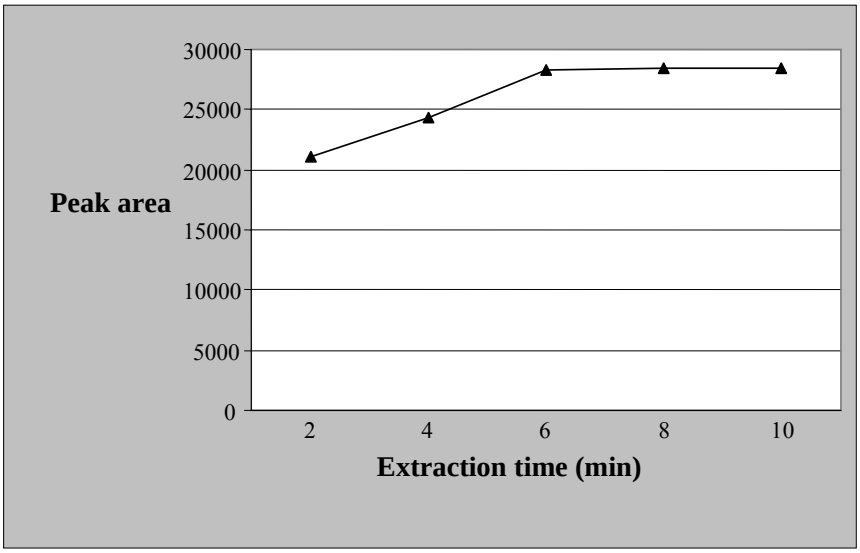

Fig. 8: Effect of time on amount xylene extracted by SPME fiber

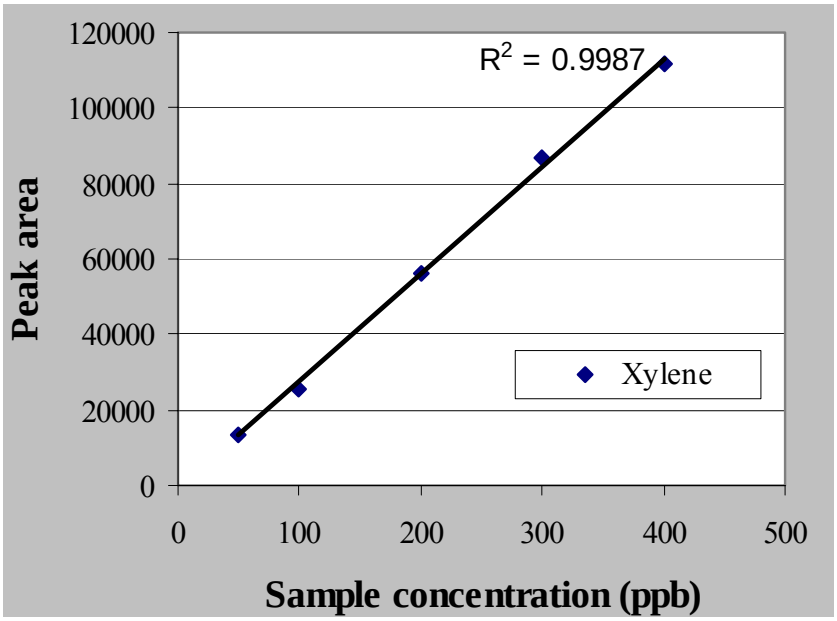

Fig. 9: Effect of various sample concentration on extraction efficiency of xylene

Table 1: Day-to-day (D-day) and within-day (W-day) reproducibility of xylene in urine, sample volume: 50 ml, N=6

	Concentration added ($\mu g ml^{-1}$)					
	50		200		400	
	D-day	W-day	D-day	W-day	D-day	W-day
Mean	47.41	46.16	196.91	197.83	399.01	396.25
SD	2.41	2.48	5.98	1.72	3.65	1.89
CV%	5.08	5.37	3.03	0.87	0.91	0.47

Discussion

To obtain the aim of this study, it was required to optimize parameters affecting the extraction of the analyte by testing the effect of each parameter at different ranges. The sample pH is a main parameter which can theoretically affect on extraction efficiency of xylene. The ionic strength of analytes can be changed by increasing or decreasing the pH. To investigate the role of sample pH on extraction of xylene by HS-SPME, a range of pH from 3 to 11 was tested on standard solutions. For changing the sample pH, standard buffers of NaOH and HCl was used. As can be seen in Fig.3, pH up to 7 increases the extraction of xylene, then, reaches a plateau and remains constant. Theoretically, it seems that, xylene by itself is a pH-independent solution and at low pH of 2-7, ionic environment of matrix can push xylene to be moved out inside of sample headspace and then equilibrium is reached. So, the neutral pH (pH= 7) was chosen as optimized sample pH for further experiments. Since xylene is a volatile organic compound, it can easily be existed in the headspace of sample. On the other hand, there is a direct relationship between the volume of aqueous solution and the gaseous phase. So, it is obvious that, in a constant vial, by increasing the volume of sample in aqueous phase, the volume of sample in the gaseous phase is decreased. Thereby, the amount of analyte increases in the gaseous phase and extraction of xylene per-

forms in a concentrated phase. For optimizing the sample volume, since the size of headspace vials was 10 ml, a range of volume of sample from 2 to 6 ml was tested. As can be seen in Fig. 4, by increasing the volume of sample to 5 ml, the amount of analyte extracted can be increased; however, there was no significant difference ($\alpha < 0.05$) between the extraction efficiency afterward. Therefore, the volume of 5 ml was selected as optimized volume and was used in further experiments. Temperature is another parameter can mainly affect on the extraction of xylene in HS-SPME. In fact, by raising the temperature, the partition constant of xylene is increased in favor of gaseous sample; therefore, partitioning of xylene between the sample and headspace of sample can reach equilibrium more quickly; therefore, xylene can be existed in headspace of sample and extracted by the SPME fiber. Theoretically, by increasing the there will be an increase in the amount of extracted xylene. In this study, a range of temperature from 20 °C to 50 °C was tested to evaluate effect of temperature on extraction efficiency. The obtained results indicated that, temperature up to 30 °C can increase the amount of extracted analyte, then, reached a plateau and remained constant. No significant effect was seen at greater temperature (see Fig. 5). However, at the higher temperatures, some extra peaks on the chromatographic analyses were seen, resulting from fiber materials. Salt is also a parameter that can affect on extraction efficiency. Because, in presence of salt, the partition constant of xylene can be changed and therefore, allow more analyte to be existed in headspace of sample. In fact, the solubility of analyte decreases by adding salt. To study the effect of salt addition on extraction efficiency of xylene, a range of salt (NaCl) from zero to 0.4 gml^{-1} was added to 5 ml of sample solution, and after complete mixing of solution, the extraction and analysis were performed. As shown in Fig. 6, by adding salt up to 0.2 gml^{-1} the amount of extracted analyte is increased, and then, the amount of extraction remains constant. Addition of salt followed by its dissolving to an aquatic solution can facilitate the extraction of organic compound. It is taken place because salt can be dissolved in aquatic solution and therefore, organic phase can be pushed out easier in the sample head space. However, there was no significant difference ($\alpha < 0.05$) between amounts of 0.2, 0.3, and 0.4 gml^{-1}. So, 0.2 gml^{-1} of salt was chosen as the optimum amount of salt addition. Sample agitation is another important affecting parameter that should be optimized. It can increase the extraction efficiency of xylene, exactly similar to the temperature enhancement explained beforehand. Therefore, to optimize sample agitation, a range of speed from 200 to 1000 rpm was tested using a magnetic stirring bar. As shown in Fig. 7, by increasing the sample agitation to 600 rpm, extraction efficiency is also increased, and then, no significant effect ($\alpha < 0.05$) was seen on the amount of extracted analyte. So, 600 rpm was chosen as an optimum sample agitation for further experiment. The effect of extraction time at the range of 2 to 10 min, on extraction efficiency of xylene by the SPME fiber, indicated that, in all experiments, just after 6 min, the equilibrium of xylene between the fiber coating and the headspace of sample was established, and up to 6 min, no significant effect ($\alpha < 0.05$) on extraction efficiency was indicated (see Fig. 8).

For evaluating the effect of sample concentration on extraction efficiency, a range of 50 to 400 ppb of sample concentration was prepared. By applying the other optimized parameters, the extraction and analysis was performed. As shown in Fig. 9, in all experiments, a direct proportion was seen between xylene in the sample and the xylene adsorbed by the SPME fiber. This relationship was linear ($r^2 > 0.99$). It means that, in the SPME, sample concentration cannot affect the extraction efficiency, in other words, it can decrease extraction time through increasing the amount of xylene in the certain volume. Therefore, at the range of concentrations examined, efficient extraction can be observed. However, since SPME is a preferred method for extraction of low concentration, the concentration

of 100 $\mu g ml^{-1}$ was chosen. Finally, to validate the optimized method, a preliminary validation of the possible use of the optimized method for determining xylene in urine was performed, using spiked samples and standards. The day-to-day and within-day relative standard deviation of the method was investigated by spiking urine sample with xylene. Linear standard curves (extracted) over the range of 50 (low), 200 (medium), and 400 ppb (high) were obtained each day (n= 6) with a correlation coefficient of 0.999 or greater. Table 1 shows the results obtained from this experiment. As can be seen in Table 1, at the low concentration (50 ppb), in all days, percentage of coefficient of variation (CV%) was higher than moderate and high concentrations of 200 and 400 ppb, respectively. However, the optimized method is sensitive enough for all rang of applied concentrations including low, moderate, and high. It is worth mentioning that, in this study, the selected concentrations were rather low (at ppb level), as well as excellent linearity (greater than 0.999) was obtained for all applied concentrations. However, at very trace concentration (50 ppb), which is closed to limit of detection (30 ppb), obtained in this study may cause some analyte to be lost from SPME fiber during handling operation of syringe (it is probably due to loss of xylene from fiber through evaporation when transporting SPME device from vial to injector). Of course, by applying an automated system for injection, the amount of xylene loss can be diminished and extraction efficiency can be increased. So, the concentration of 100 ppb was chosen in this study. This concentration was as low as needed and it had an appropriate sensitivity, considering limit of detection obtained in this research (30 ppb), and allow having very sharp and symmetrical peak at all chromatographic analysis. Based on reported methods (15), for optimizing SPME, authors generally have used commercial fibers such as PDMS to evaluate the extraction efficiency of analyte, while, in this study, a laboratory made fiber was used which is more available and inexpensive than commercial fibers. Moreover, to make an advantage from this study compare to other studies (16-17), further experiments of reproducibility of the method were carried out on spiked urine samples to validate the possible use of the optimized SPME for measuring xylene when biological monitoring of worker exposed to such pollutant is required. Based on obtained results, it is concluded that, HS-SPME is an appropriate method as well as simple, fast, selective, and reliable for determining and evaluating of urinary xylene in occupational exposure.

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The authors declare that they have no conflict of interests.

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