

Determination of benzene, toluene, ethylbenzene and xylene in field and laboratory by means of cold fiber SPME equipped with thermoelectric cooler and GC/FID method

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A simple and effective cooling device based on a thermoelectric cooler was applied to cool the SPME fiber. The device was used for quantitative extraction of aromatic hydrocarbons in the air. Several factors such as coating temperature, extraction temperature and relative humidity in the laboratory setting were optimized. Comparison of the results between the cold fiber SPME (CF-SPME) and NIOSH 1501 method on standard test atmosphere indicated a satisfactory agreement. The CF-SPME and SPME method were also compared. The results revealed that CF-SPME has the most appropriate outcome for the extraction of aromatic hydrocarbons from the ambient air. The cold fiber SPME technique showed good results for several validation parameters. Under the optimized conditions, the limits of detection (LOD) and the limits of quantification (LOQ) ranged from 0.00019 to 0.00033 and 0.0006 to 0.001 ng mL⁻¹, respectively. The intra-day relative standard deviation (RSD) showed ranging from 4.8 to 10.5%.

Keywords: aromatic hydrocarbons, air sampling, cold fiber, solid-phase microextraction.

INTRODUCTION

BTEX (benzene, toluene, ethylbenzene, and xylene) are common hazardous volatile organic compounds (VOCs) and toxic air pollutants emitted into the atmosphere from natural and artificial sources¹. These compounds are widely used in industries, such as paint, printing, synthetic rubber and resin, detergent, ink and pesticides. Vehicle fuel combustion and industrial processes are the major sources of emission of these pollutants in the outdoor air^{2,3}. Exposure to the BTEX can cause adverse health effects such as cancer, neurological disorders and damage to respiratory system, liver and kidneys^{4,5}.

Due to the potential health problems and environmental impacts that VOCs may cause, several sampling and analysis methods have been developed for air monitoring of these pollutants, of which the passive or active sampling by sorbent tubes, gravimetric filters, impingers and canisters followed by solvent or thermal desorption using gas chromatography for detection purposes are the most predominant ones⁶. Despite their fair reliability, many of these methods have several serious drawbacks, such as the need for considerable sampling expertise, complex, laborious, multistep and lengthy sample collection and preparation along with sophisticated equipment and complicated and costly extraction procedures^{7,8}. In many cases, conventional air-sampling methods are not applicable to indoor and outdoor air sampling, particularly in cases where very low LOD are required⁹. Recently, extensive efforts towards modernization of analytical instruments and elimination of multistep sample-preparation techniques have led to the widespread application of solvent-free approaches in environmental and occupational exposure assessments^{10,11}.

Solid phase microextraction (SPME) is an innovative technique with several major advantages, including simplicity of use, faster implementation, low solvent consumption, higher time and cost-efficiency and automation

capability^{12,13}. Since its development, it has been shown to be convenient for field and laboratory analysis and has been successfully applied to the sampling and analysis of various contaminants in the air, water, and soil^{14–16}. Nonetheless, due to several limitations particularly in terms of selectivity, sensitivity and extraction capability of SPME, researchers proposed new configurations for this technique in order to minimize its exothermic effect and improve the extraction efficiency^{17,18}.

The cold fiber SPME (CF-SPME) was introduced in 1995 to significantly overcome some of these drawbacks¹⁹. The cold fiber method involves simultaneous increase in sample temperature and decrease in fiber temperature²⁰. Heating the sample to the elevated temperatures usually provides the necessary energy for the target analytes to overcome the barriers that bind them to the sample matrix, and therefore improves the mass transfer process and maximizes the vapor pressure of the analyte. On the other hand, due to the exothermic nature of the adsorption, application of high temperature can adversely affect the partition coefficient of the analytes and reduce the extraction capabilities. In order to tackle this problem, the coating temperature is therefore lowered, which in turn, significantly improves the extraction process²¹.

The first cold fiber SPME device was introduced in 1995 by Zhang and Pawliszyn for the extraction of BTEX compounds from clay soil and sand samples¹⁹. Such device was then miniaturized and automated by Chen et al.²². Since then several authors such as Ghiasvand et al.^{21,23}, Haddadi et al.^{24,25} and Carasek et al.²⁶ have applied the automated device in the quantitative extraction of several volatile and semi-volatile compounds.

A review of the previous studies reveals that CO₂ and N₂ gases have been widely used as coolant agents for sampling and determination of several volatile compounds in solid and aqueous samples^{21,27}. As the use of such techniques usually entails high voltage and

heavy equipment, the portability and cost-effectiveness characteristics of them along with the instability in controlling the fiber temperature are the most considerable problems associated with the utilization of these gas cooling techniques.

Referring to the previous studies conducted in this field it is almost evident that CF-SPME has been mostly used for sampling and determination of VOCs compounds in solid and aqueous samples. Air sampling with CF-SPME, however, is the novel application of this technique that has been less investigated than the other techniques in this field. The purpose of the current study is to investigate the applicability of CF-SPME as a monitoring tool in air sampling particularly in occupational and/or environmental assessment studies. In this research a CF-SPME device was constructed based on thermoelectric cooler (TEC) for cooling the SPME fiber in order to improve extraction efficiency and resolve the remaining problems with ordinary SPME fibers. The cooling device described in this study has proven to be an effective, inexpensive, fast, environmentally safe and reliable technique for the determination of volatile organic compounds in ambient air. However, to the best of our knowledge there is no similar study based on cooling techniques for quantification of these compounds in the air.

EXPERIMENTAL

Reagents and material

Benzene ($\geq 99.9\%$), toluene ($\geq 99.9\%$), ethylbenzene ($\geq 99.5\%$), xylene ($\geq 99.5\%$) (BTEX) were obtained from Merck. Carbon disulfide (99%) and HPLC grade methanol were also supplied from Merck (Darmstadt, Germany). Deionized water was purified by an ultra-water system (TKA, Niederelbert, Germany).

Two stock mixtures of BTEX were prepared in methanol and carbon disulfide with a concentration of $1000 \mu\text{g ml}^{-1}$ for each compound. They were stored in a refrigerator at 4°C . Standard working solutions of the analytes were prepared daily from the stock solution in methanol.

Instruments

Gas chromatographic analyses of the air samples were performed by a Shimadzu GC-2010 system (Kyoto, Japan) equipped with a split/splitless injector and flame ionization detector (FID). Analytes were separated using an Rtx®-5 (30 m*0.25 mm*0.25 μm) fused silica column from Restek (Bellefonte, PA, USA). Ultra pure N_2 at a flow rate of 1.1 and 40 ml min^{-1} was used as a carrier and make-up gas, respectively. The column temperature was initially held at 35°C for 1 min and gradually increased to 100°C at a rate of 4°C min^{-1} and then to 200°C at a rate of $20^\circ\text{C min}^{-1}$. The temperatures associated with the injector and detector were set and kept at 290 and 250°C , respectively.

An Alfa hs-810 model hot plate- stirrer (Tehran, Iran) was used in a humidity generation system for adjusting the relative humidity inside the standard chamber. Temperature controller (Busan, South Korea), the thermoelectric cooler and related heat sink and fan (Busan, South Korea) and other electronic components were

purchased from the electronic stores. The SPME holder and carboxen/polydimethylsiloxane (CAR/PDMS, $75 \mu\text{m}$) fiber were provided by Supelco (Bellefonte, PA, USA). When new, the fiber was conditioned in a GC injector according to manufacturer instructions.

A syringe pump, JMS SP-510 (Hiroshima, Japan), was used for preparing the standard concentration and thereby determined the calculated amount of target analytes injected into the sampling chamber. A high volume sampling pump SKC (PA, USA) was used for drawing air through the chamber. A low volume sampling pump (SKC 222 series, PA, USA), with a sampling flow rate of $1\text{--}200 \text{ mL min}^{-1}$ and 150 mg charcoal sorbent tubes (SKC Inc., PA) were used for the performance evaluation of CF-SPME device and accurate drawing of air through the sorbent bed.

Cold fiber-SPME device

A simple, inexpensive and effective cooling device based on the use of a thermoelectric cooler (TEC) as the cooling source was applied to cool the SPME fiber via SPME needle. The schematic illustration of the cold fiber SPME device is shown in Figure 1. A heat sink, fan and silicon-oil based thermal grease were attached to the hot side of the thermoelectric cooler in order to dissipate the generated heat and make it cool. To achieve more efficient cooling and improve the contact between the SPME needle and the cold side of TEC, A copper plate was mounted on the cold surface of the TEC. A thermocouple was embedded in this copper plate to monitor the temperature of the cold side of the TEC. A temperature controller was also used to adjust and precisely control the fiber temperature.

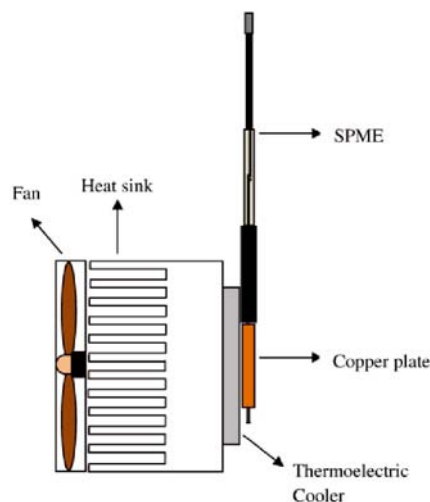


Figure 1. Schematic of the device for CF-SPME

Selection of SPME fiber

Choosing of an appropriate coating is the most important step in the sampling and analysis of the analytes in the air. The selected coating should have a good sensitivity toward the target analytes. CAR/PDMS is the mixed coating which is mainly composed of microporous structure that make it appropriate for the analysis of small molecular and non-polar compounds^{11,28}. In the current study, CAR/PDMS was chosen as a proper coating for simultaneous extraction of BTEX, because it has better sensitivity and higher selectivity for extraction of aromatic

compounds than other types of available fibers and also it is recommended by the Supelco fiber selection guide for gases and low molecular weight compounds^{4, 29, 30}.

Standard gas generating system and Sampling by CF-SPME device

A dynamic gas generation system was applied to prepare certain concentrations of gaseous standards in the range of interest for laboratory testing. Predetermined amount of each analyte was injected using a syringe pump into a flow direction line connected to the sampling chamber in order to provide dynamic standard concentration of BTEX inside a chamber. The sampling temperature was adjusted to 20, 30 and 40°C using a thermostated lighting radiation lamp inside a heat control chamber, located upstream of the standard chamber. This temperature controller system managed to adjust the temperature inside the chamber in a defined range. For adjusting the relative humidity inside the chamber, a humidity generation system consisted of an impinger, heater and control valve for changing air flow rate and temperature of water in the impinger was used, and relative humidity was also successfully set at two levels of 30% and 70%. A hygrometer was applied to monitor relative humidity. A high volume sampling pump was used to draw air through the sampling chamber. A dry test meter (Elster-Handel, Germany) that had been calibrated according to the primary standard device was employed to continuously check the diluent gas flow rate in the system. Figure 2 shows the sampling set used in this study. Sampling and adsorption of the analytes were performed by inserting the SPME needle into the sampling chamber and exposing the fiber to the analytes. After sampling, analysis was performed by thermal desorption of adsorbed analyte in GC injection port (by GC/FID system).

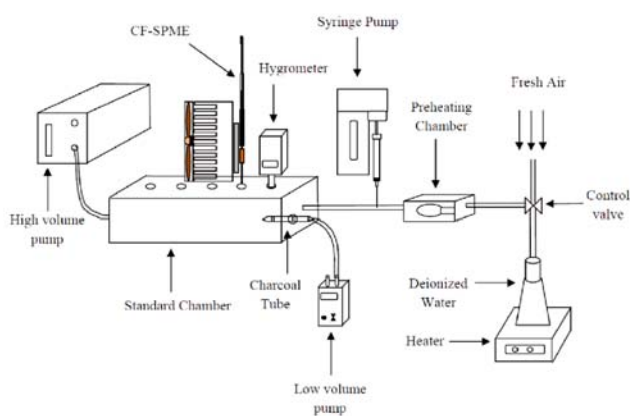


Figure 2. Sampling system used to generate a gaseous standard mixture of VOCs compounds

The effects of temperature, relative humidity and coating temperature on the sampling phase were examined. The type of fiber coating and GC desorption time and temperature parameters were also determined from the other studies. Having optimized the performance parameters of the SPME for use as a passive sampler, the device was applied to the determination of BTEX concentrations in several gas stations and car painting workshops.

Active sampling

Active air sampling was performed according to NIOSH 1501 method. According to this method, a personal pump calibrated at 100 ml/min flow rate, drew a specified volume of air to the charcoal tubes. Samples were extracted with 1 ml of carbon disulphide, agitated with a rotary shaker for 30 minutes and then analyzed by GC-FID³¹.

RESULTS AND DISCUSSION

Parameters related to the laboratory phase of the study

The sampling rate of SPME could be affected by environmental parameters. In order to achieve the best sampling efficiency, several factors such as coating temperature, extraction temperature and relative humidity inside the standard chamber, were investigated and optimized.

Effect of coating temperature on sampling efficiency

To determine the ideal fiber temperature for CF-SPME technique, the effect of this parameter on the sampling rate was investigated in the range 5–20°C. As it is illustrated in Figure 3, the extraction capabilities increased by decreasing the coating temperature to 5°C. Regarding the exothermic nature of the adsorption process of volatile compounds onto SPME fiber, these compounds tend to retain in the fiber at lower temperatures³². Therefore, 5°C was finally chosen as the optimum coating temperature for the subsequent evaluations.

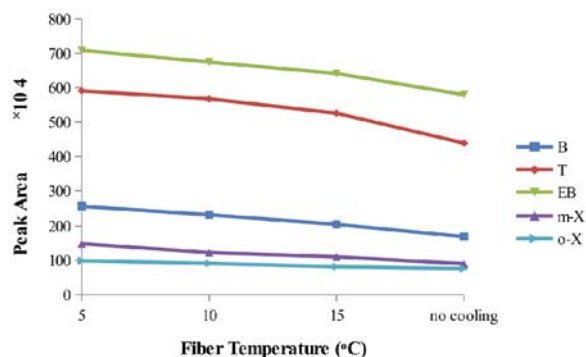


Figure 3. Effect of fiber temperature on the CF-SPME efficiency. (40°C extraction temperature, 15 min sampling time, and 30% relative humidity)

Effect of temperature on sampling efficiency

To use SPME and CF-SPME in the field, the effect of the field related parameters on the sampling efficiency and the performance of the new device was investigated. The air temperature in the sampling chamber was varied from 20 to 40°C, to study its effect on sampling efficiency.

For SPME, an increase in extraction temperature caused a decrease in extraction rate and peak area responses of the GC analysis³³. The reason for such phenomenon is adverse effect of temperature on the distribution coefficient. In other words, the increase in temperature usually enhances headspace extraction and simultaneously reduces the fiber coating/sample distribution constant. Since the adsorption is an exothermic process, reduction in extracted mass at equilibrium is

usually expected in high extraction temperature. Thus, an extraction temperature of 20°C was found to be optimal.

For CF-SPME, the amount of adsorbed analytes increased almost linearly with the increase in air temperature from 20 to 40°C. In CF-SPME extraction mode, adverse effect of the high temperature on the distribution constant and extraction efficiency is resolved by lowering the coating temperature. As a result, sampling in higher temperature is possible. With this regard, 40°C was identified as an optimal extraction temperature (Fig. 4).

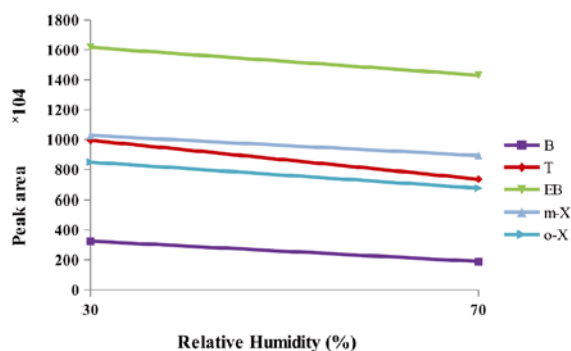


Figure 4. Effect of sampling temperature on the CF-SPME efficiency. (5°C fiber temperature, 15 min sampling time, and 30% relative humidity)

Effect of humidity on sampling efficiency

The effect of 30 and 70% relative humidity on sampling efficiency was investigated. In general, relative humidity had a negative effect on the extracted amount of both techniques; i.e., less mass was adsorbed at high level of RH (Fig. 5). The findings of the current study are consistent with those of Koziel (2000) and Zare Sakhvidi (2012) who found that an increase in the relative humidity caused a decrease in extraction rate^{14, 34}. It seems that, the competition between water molecules and target analytes for occupying active adsorption sites is the reason of such decrease in the amount of adsorbed analytes. In fact, condensation of water molecules at the surface of coating alters the coating properties and fiber selectivity and thereby reduces the sampling rates^{34, 35}.

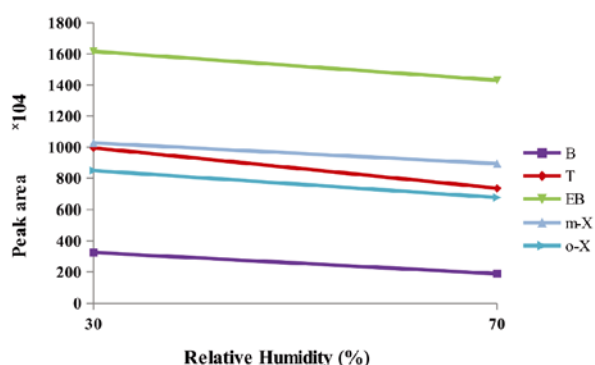


Figure 5. Effect of relative humidity on the CF-SPME efficiency. (5°C fiber temperature, 20°C extraction temperature, and 15 min sampling time)

Validation with NIOSH method

NIOSH 1501 method and the CF-SPME method were compared, in terms of accuracy, under laboratory-controlled conditions (Table 1). Laboratory results indicated that there is a fair agreement between the results ob-

tained with the CF-SPME and NIOSH method under the laboratory conditions. Table 1 also revealed that the reproducibility of the CF-SPME technique was to some extent better than the conventional charcoal tube method for air sampling.

Comparison and validation of the optimized method

In order to demonstrate the effect of cold fiber on the extracted amount, SPME and CF-SPME approach were compared under the optimum sampling conditions. As can be seen from Figure 6, the extraction rate in CF-SPME is more efficient than SPME. This high sampling rate can be attributed to the large distribution coefficient of target analytes at lower coating temperature and high sample temperature. Therefore, to obtain high sensitivity, CF-SPME was applied for further analysis.

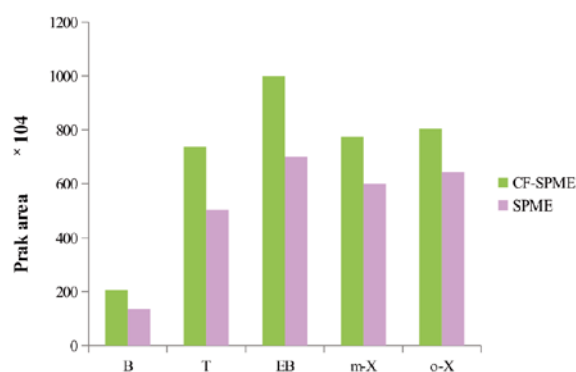


Figure 6. Comparison of extraction efficiencies of the aromatic hydrocarbons in gas generation system with CF-SPME and SPME

In order to verify the CF-SPME method for the analysis of the air samples, analytical characteristics of this technique such as limit of detection (LOD), limit of quantification (LOQ) and repeatability were investigated. The quantification of the BTEX using CF-SPME device was based on the calibration curves obtained under non-equilibrium conditions and 15 min sampling time. Calibration curves were plotted using five concentration levels ranging from 0.03 to 160 ng ml⁻¹, with three extraction replicates for each level. The LOD and LOQ were estimated according to the recommendations of Eurachem Guide³⁶ using ten measurements of the blank.

The LOD and LOQ for all analytes ranged from 0.00019 to 0.00033 and 0.0006 to 0.001 ng ml⁻¹, respectively. Repeatability of the method was examined by calculating the relative standard deviation (RSD) of peak response of five samples at the concentration level of 2 and 50 ng ml⁻¹ on the same day. The RSDs also demonstrated a reasonable repeatability for the proposed method (see Table 2). The calculated relative standard deviation indicated a range of 8.2% to 10.5% at the low level and from 4.8% to 9.4% for the high level.

Field sampling by CF-SPME device

Having optimized all aspects of SPME sampling in the laboratory, the device was applied to determine the concentration of BTEX in several petrol stations and car painting shop to test the method. Four calibrated CAR/PDMS fibers were used for air sampling purpose in each environment. Sampling was performed using

Table 1. Comparison of target VOC concentrations in standard air (in ppm) measured using 75 µm CAR/PDMS and charcoal tubes

	Method	Measured Avg.	RSD [%]	Theoretical ^a
Benzene	CF-SPME	14.5	3.8	14
	NIOSH	15	8.6	
Toluene	CF-SPME	13.5	4.9	14
	NIOSH	13.5	11.3	
Ethylbenzene	CF-SPME	14.3	5.6	14
	NIOSH	13.8	9.1	
m-Xylene	CF-SPME	15.1	8	14
	NIOSH	14.8	11	
o-Xylene	CF-SPME	15	7.5	14
	NIOSH	14.2	13	

Note: The CF-SPME and NIOSH values are based on n = 5 samples. Sampling time for CF-SPME = 15 min; sampling time for the NIOSH-1501 = 1 hr; ^abased on syringe pump injection rate and measured air flow rates.

Table 2. Figure of merits of the proposed method for determination of BTEX

Analyte	LOD [ng m ⁻³]	LOQ [ng m ⁻³]	Correlation coefficient [R ²]	RSD [%](n = 5)	
				2 [ng ml ⁻³]	50 [ng ml ⁻³]
Benzene	0.00019	0.0006	0.998	8.2	6.4
Toluene	0.00027	0.0009	0.995	8.6	4.8
Ethyl benzene	0.0002	0.0007	0.996	9.5	7.1
m-Xylene	0.00033	0.001	0.991	9.7	8.7
o-Xylene	0.0003	0.001	0.991	10.5	9.4

SPME and NIOSH 1501 techniques in the respiration zone (about 1.70 m above the ground level). Immediately after sampling, all fibers were withdrawn into the barrel and capped with a new and clean silicone septum and placed on a dry ice bed. As the analytes were highly volatile, all SPME fibers were analyzed during maximum 2 h after sampling in order to avoid volatilization. The analytical results for determination of these analytes in air samples are given in Table 3. At the petrol station

capability of the method for trace level analysis in different environments.

Table 3. Concentrations (mg/m³) of the analytes in outdoor and indoor air samples by CF-SPME

Analyte	petrol station (N = 4) Mean± SD		Car painting (N = 4) Mean± SD	
	CF-SPME	NIOSH	CF-SPME	NIOSH
Benzene	1±0.04	1.2±0.1	3.1±0.1	2.8±0.2
Toluene	5.6±0.3	5.1±0.6	9.1±0.4	7.9±0.9
Ethyl benzene	0.9±0.05	1.1±0.1	3.5±0.2	3±0.3
m-Xylene	3.9±0.3	3.5±0.4	8.9±0.7	7.8±1
o-Xylene	5.1±0.4	4.8±0.6	10.1±0.8	9.5±1

NIOSH recommended threshold limit value for benzene = 0.32 mg/m³, toluene = 377 mg/m³, ethylbenzene and xylenes = 434 mg/m³

and painting shop the concentrations of toluene, ethyl benzene and xylenes were lower than those recommended by NIOSH recommended exposure limits (RELs) but benzene concentration in both environments was higher than the recommended value (0.32 mg/m³).

CONCLUSION

The current study detailed the development of an alternative approach for the analysis of aromatic compounds in ambient air with cold fiber solid phase microextraction (CF-SPME). It was concluded that the proposed method was relatively precise, fast and sensitive for quantitative extraction of volatile compounds in air samples. The method also demonstrated good sensitivity and precision for the range of environmental interest. Comparison of the CF-SPME and NIOSH method showed that the proposed technique is a powerful alternative for NIOSH-based field sampling. The applicability of the method for outdoor and indoor air samples demonstrated the

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