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

Leila Tajik1, Abdulrahman Bahrami1, Alireza Ghiasvand2, Farshid Ghorbani Shahna1

1Hamadan University of Medical Sciences, Center of Excellence for Occupational Health, School of Public Health, Hamadan, Iran
2Lorestan University, Department of Chemistry, Faculty of Science, Khoramabad, Iran
*Corresponding author: e-mail: bahrami@umsha.ac.ir

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 air2, 3. Exposure to the BTEX can cause adverse health effects such as cancer, neurological disorders and damage to respiratory system, liver and kidneys4, 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 procedures7, 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 assessments10, 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 capability12, 13. Since its development, is 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 soil14-16. 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 efficiency17, 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 al22. Since then several authors such as Ghiasvand et al21, 23, Haddadi et al24, 25 and Carasek et al26 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 samples24, 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 (>99.9%), toluene (>99.9%), ethylbenzene (>99.5%), xylene (>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 ultrawater system (TKA, Niederelbert, Germany).

Two stock mixtures of BTEX were prepared in methanol and carbon disulfide with a concentration of 1000 μg 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 N₂ 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°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 μm) 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 1–200 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 compounds11,28. 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