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A sol–gel based solid phase microextraction fiber for analysis of aromatic hydrocarbons

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Abstract

A sol–gel based solid phase microextraction fiber for headspace sampling (HP-SPME) and GC determination of benzene, toluene, ethylbenzene and xylenes (BTEX) is introduced. The influences of fiber composition, microextraction conditions such as temperature and time on the fiber performance and desorption temperature and time were investigated. Under optimal conditions, the use of proposed fiber was thermally stable up to 250 °C and demonstrated high sensitive and fast sampling of BTEX from gaseous phase. Depending on the analysed substance, the linear range for a selected fiber and the applied GC-FID technique was from 4 to 80 ng mL^{-1} with limit of detection (LOD) 0.2–0.7 ng mL^{-1} and 100–1000 ng mL^{-1} with LOD 8–20 ng mL^{-1} for gaseous and soil samples, respectively. HP-SPME–GC analysis was highly reproducible—relative standard deviations (R.S.D.) were between 5.0 and 7.9%. The proposed fiber was successfully used for BTEX sampling from indoor air and headspace of soil samples.

Keywords: Sol–gel fiber; Solid phase microextraction; BTEX; Soil analysis

1. Introduction

Aromatic hydrocarbons, in particular benzene, toluene, ethylbenzene and xylenes (BTEX) have acquired great relevance as ubiquitous pollutants of the outdoor and indoor human environment. Due to the toxicological properties of BTEX compounds, they were analyzed in blood and exhaled breath, urine and contaminated water as environmental pollution indicator [1,2]. Therefore, several analytical methods for determination of BTEX have been reported in literature [1,3–9].

Solid phase microextraction (SPME) is highly promising environmentally friendly sample preparation technique of target analytical potential. An important factor contributing to the rapid growth and popularity of SPME is its ability to perform sample extraction and preconcentration without requiring the use of hazardous organic solvents. In SPME, a sorptive stationary phase coating, either on the outer surface of a fused silica fiber and/or on the inner surface of a capillary, plays a vital role in analyte extraction. Due to importance of stationary phase coating, future developments and further SPME applications will greatly depend on new break through in the areas of coating technology. SPME coatings were devolved and evaluated based on polydimethylsiloxane (PDMS) [10], polyacrylate (PA) [11,12], carbowax:template resin [13], carbowax:divinilybenzene, nafion per fluorinated resin [14], and polyvinyl chloride (PVC) [15,16]. Sol–gel coatings have been used for preparation of SPME fibers with high thermal stability in development of methodology for volatile and semi-volatile organic compounds analysis [17–22].

We have recently introduced a PVC based SPME fiber for analysis of ethanol and methanol in human body fluids [16]. In this work, the preparation of a new SPME fiber based on sol–gel is described and it was successfully used for development of headspace solid phase microextraction and gas chromatographic determination of BTEX in indoor air and soil samples.

2. Experimental

2.1. Apparatus

A Chrompack Gas Chromatograph equipped with a FID detector, data processor (mosaic), and split/splitless injector

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was used for this study. A CP-WAX 52CB capillary column (50 m × 0.32 mm i.d., film thickness 1.2 μm) was utilized. A laboratory made SPME device was used in all experiments.

2.2. Reagents

Benzene, toluene, ethylbenzene, xylene isomers, Tetra-*n*-buthylorthototitanat (TBOT), pure graphite and other chemicals were all from E. Merck (Darmstadt, Germany). Helium and hydrogen 99.999% purity was from Roham Gas Co. (Midde East Dubai, United Arab Emirates).

2.3. Preparation of SPME fiber

The sol–gel coating material was prepared by 75:25 (%w/w) mixtures of TBOT and graphite. After a few seconds from mixing the mentioned materials, a viscose suspension was formed. A 1 cm length of silica rod (total length 2 cm) which was placed in a laboratory-made SPME device introduced into the above-mentioned suspension for several times and sol–gel/graphite coating (thickness 30 μm) was formed on a silica rod. The proposed SPME fiber was then conditioned in 240 °C for 8 h to remove any fiber contaminations.

2.4. GC operating conditions

The initial column temperature was maintained at 60 °C for 5 min and then raised at 5 °C min^{-1} to 120 °C and held for 5 min. Helium was used as carrier and makeup gas, which their flow rates are 1.0 and 20 mL min^{-1}, respectively. The injector and detector temperature were held at 240 and 250 °C, respectively. Injections of analytes were made in splitless mode.

2.5. Analytical procedure

2.5.1. Headspace sampling of BTEX from soil samples

An accurately weighed 2.0 g of soil sample was placed in a 25 mL vial then the vial sealed with a silicone septum and solid phase microextraction from headspace of the sample was carried out at 80 °C. After 10 min, the SPME fiber was removed from the vial and was immediately inserted into the hot injection port of GC in splitless mode and stayed for 10 s. The analytes were thermally desorbed and moved through the capillary column by helium as carrier gas and finally detected by FID.

2.5.2. Sampling of BTEX from indoor air

Volatile solvents and chemicals are measured in indoor air for health and environmental purposes or to monitor workplace exposure. It is well established that headspace SPME is ideal technique for sampling of analytes from gaseous phase. The proposed SPME fiber was placed at chemicals store in Petrochemical Co. (Bandar Emam, Iran), for 24 h at 25 ± 2 °C and then it was introduced in injection port of gas chromatograph.

3. Results and discussion

3.1. Effect of fiber composition

In SPME, sample analytes are extracted and concentrated by fiber coating. The efficiency of the coating for an analyte is the most important factor in the successful use of SPME. Selection of the coating is based on the polarity and volatility of the analytes. Therefore, it is important to use the appropriate coating for a given applications [23,24].

For the selection of suitable composition, fibers with various compositions (weight percent) were prepared, and extraction of BTEX from gas phase was performed. The obtained results are shown in Fig. 1. As can be seen among three prepared compositions, fiber no. 3 has maximum extraction efficiency in comparison to the other compositions. However, due to formation of a homogenous coating layer on fiber no. 2 (75% TBOT and 25% graphite) which provides excellent reproducibility for microextraction of BTEX, it was selected as optimum fiber in all experiments.

3.2. Effect of the microextraction temperature

Generally in such studies, high temperature is suitable for increasing volatility of analytes until they are achievable to the fiber. On the other hand, high temperatures are favorable for establishing the analytes distribution equilibrium between the fiber and gaseous phase but adsorption of the analytes on the fiber is undesirable at high temperatures [25]. Therefore, the effect of extraction temperature was investigated. For this purpose, extraction of BTEX was performed from 2.0 g soil samples containing 3000 ng g^{-1} of each compound at various temperatures. The obtained peak areas were plotted *versus* temperature, and are presented in Fig. 2. As can be seen the adsorption of BTEX was increased up to 80 °C and then leveled off. Therefore, 80 °C was selected as a suitable experimental temperature for further studies.

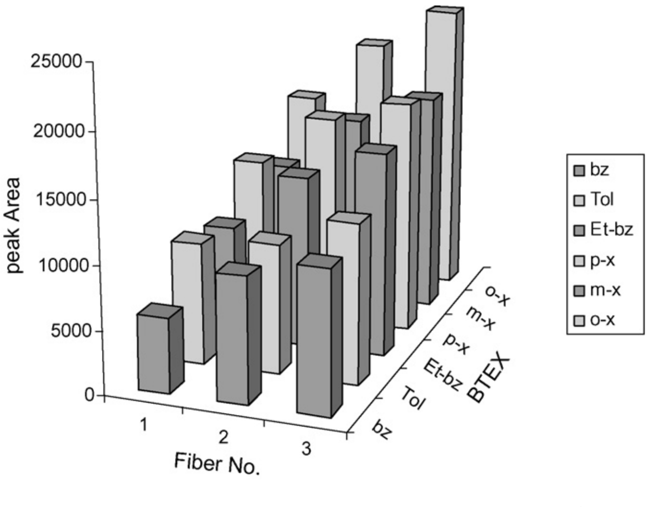

Fig. 1. Effect of fiber composition on BTEX extraction (fiber 1 = 15% (w/w) graphite:85% (w/w) sol–gel; fiber 2 = 25% (w/w) graphite:75% (w/w) sol–gel; fiber 3 = 30% (w/w) graphite:70% (w/w) sol–gel).