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New nanostructure of polydimethylsiloxane coating as a solid-phase microextraction fiber: Application to analysis of BTEX in aquatic environmental samples

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ABSTRACT

Electrospinning technique was used to convert polydimethyl siloxane (PDMS) sol-gel solution to a new nanostructure on a stainless steel wire. The surface morphology of the fiber was observed by scanning electron microscopy (SEM). It showed a diameter range of 30–60 nm for PDMS nanoparticles with a homogeneous and porous surface structure. The applicability of this coating was assessed for the headspace SPME (HS-SPME) of benzene, toluene, ethylbenzene and xylenes (BTEX) from water samples followed by gas chromatography–mass spectrometry. The important parameters affecting extraction efficiency such as extraction time and temperature, desorption conditions, agitation rate and ionic strength were investigated and optimized.

Under the optimized conditions, LODs and LOQs of 0.3–5 $\mu g L^{-1}$ and 1–10 $\mu g L^{-1}$ were obtained, respectively. The method showed linearity in the broad range of 1–5000 $\mu g L^{-1}$ with correlation coefficient of >0.99. Inter-day and intra-day precisions of the developed method ranged from 2.43% to 6.54% and from 5.24% to 13.73%, respectively. The thermal stability of the fiber was investigated on stainless steel wire. It was found to be durable at 260 °C for more than 360 min. Furthermore, the proposed method was successfully applied for quantification of BTEX in real water samples.

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1. Introduction

Solid phase microextraction (SPME) is one of the most suitable pretreatment techniques for analysis of volatile compounds in aqueous media [1]. It combines sampling, extraction, preconcentration and sample introduction in one step. This technique was introduced into analytical practice in the early 1990s by Pawliszyn and co-workers [2]. Because of the rapidity and simplicity of use, short sample processing time, eliminating the use of organic solvents and desorption of the extracted analytes directly in the injector of the chromatographic system, SPME has been widely validated for various applications such as: analysis of food [3,4], environmental [5,6], medicinal [7,8], biological and pharmaceutical samples [9].

The extraction efficiency of SPME is predominantly determined by interactions between the analyte species and the extracting phases [10]. Fused silica fiber has been successfully used as supporting substrate for extracting coatings since the first introduction of SPME technology [2], but it is fragile and must be handled with great care, and it has limited lifetime. Flexible metal wires have attracted the attention as supporting substrates for SPME fibers. Metal wires have strong physical strength, and can be handled with great convenience [11]. Stainless steel, like other metallic substrates, has enough strength, rigidity and thermal stability that almost in all electrospinning studies for preparing sorbents on SPME fibers, stainless steel has been employed as a substrate for fiber coatings [14–17].

The extracting coatings of SPME fibers have the most impact on the extraction efficiency [12]. Nowadays different techniques are considered for SPME fiber preparation [12,13]. Electrospinning is a method for preparing nano-dimensional sorbents on SPME fibers [14–17], in which a high electric field is applied between a viscous

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Abbreviations: HS-SPME, head-space solid-phase microextractio; GC–MS, gas chromatography-mass spectrometry; SIM, selected ion monitoring; LOD, limit of detection; LOQ, limit of quantification; RSD, relative standard deviation; PDMS, polydimethyl siloxane; BTEX, benzene toluene ethylbenzene xylenes; MRLs, maximum residue limits.

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polymeric solution and a conductive collector (e.g., a metal wire). When the electric field is so strong that the electrostatic repulsive forces overcome the surface tension of the droplet, a Taylor cone is formed. Following the creation of the Taylor cone, polymeric nanofibers are ejected toward the conductive collector [14]. High surface area to volume ratio in this kind of coating increases the interactions between the desired analytes and the sorbent.

Due to applying high temperatures in SPME technique for desorbing analyte from fiber, using of polymers with low melting point is prohibited. Polydimethylsiloxane (PDMS) is one of the most popular coating fibers in SPME because of its high thermal stability and enhanced solute diffusion capabilities. PDMS has a very low glass transition temperature and as a result, this material cannot be electrospun under normal conditions [18]. The electrospinning of block copolymers [19] and graft copolymers of PDMS [18–20] have been investigated.

In this work, sol-gel solution was used for electrospinning and preparation of PDMS nanoparticles. Using the sol–gel technology seems to be a feasible option to enhance the operational stability of electrospinning SPME fibers. The thickness of polymeric layer can be controlled by varying the electrospraying time. The fibers resulted in this way have a suitable morphology and porous surface. Higher surface area to volume ratio of this coating should also provide enhanced extraction efficiency in SPME. The applicability of this coating was assessed for SPME of BTEX from aqueous samples using a homemade SPME unit.

In this regard it is mentioning that BTEX compounds (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene) are presented in environment by way of emissions from motor vehicles, aircraft exhaust, and losses during petrol marketing, spills and cigarette smoke. BTEX can be introduced into water by industrial effluents and atmospheric pollution, but releases of BTEX to water are mainly related to spills of petrol and petroleum products or proximity to natural deposits of petroleum and natural gas (IPCS 1985, 1993, 1996, 1997). The World Health Organization (WHO) drinking water guidelines have established the permissible levels for BTEX in drinking water [21]. Drinking water guidelines are set according to an acceptable daily intake based on a 70 kg person drinking 2 liters of water every day for 70 years.

2. Experimental

2.1. Chemicals and reagents

Poly (methylhydrosiloxane) (PMHS), tetramethyl orthosilicate, trifluoroacetic acid (TFA), BTEX (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene mixture) standard and sodium hydroxide were purchased from Merck (Darmstadt, Germany). PDMS was from Fluka (Buchs, Switzerland)

2.2. Apparatus

SPME fiber holder was purchased from Supelco (Bellefnote, PA). The SPME fiber assembly was prepared in the laboratory [22]. Ultra pure water was prepared by an Ultra Clear TWF EI-Ion (SG Germany).

A HV50P OV high voltage power supply was purchased from Fanavaran Nano-Meghyas (Tehran, Iran). The surface morphology of the fabricated nanofibers was investigated by a KY KY Technology development Ltd EM3200 (Beijing, China). A KDS100 syringe pump (Kd Scientific Co., USA) was used for the polymer solution delivery in the electrospinning process.

An Agilent 6890N series gas chromatograph equipped with a split/splitless injector and a 5975C mass spectrometer (GC–MS) and Combi PAL auto sampler (Switzerland) was used for both the liquid and head space SPME fiber injections. Helium (99.999%) was employed as the carrier gas (flow rate was adjusted to 1 ml/min). The separation was performed on a 30 m × 250 μm i.d. fused-silica capillary column coated with a 0.25 μm bonded film of HP-5 MS. The thermal desorption step was carried out in the splitless mode. On completion of the thermal desorption step, the split vent was opened and kept in that position for the rest of the chromatographic run. The electron impact (EI) ion source, quadrupole mass analyzer, and the interface temperature were maintained at 230, 150, and 280 °C, respectively. The MS was operated in the selected ion monitoring (SIM) mode considering two or three characteristic ions for each compound (Supplementary File, Table S1), with dwell time of 100 ms for each ion.

The column temperature was programmed at 50 °C for 9 min, and then was increased at a rate of 50 °C/min to 280 °C.

2.3. Preparation of SPME fiber

Sol-gel solution of PDMS was prepared as previously reported [23]. 0.5 ml of the clear liquid (sol) from the bottom was loaded into a 1.0 ml syringe which was eventually located in a syringe pump. The diameter of steel needle of syringe was 0.3 mm whose tip was filed flat.

A homemade SPME fiber assembly was mounted into the machined Teflon block which assembled on an armature. A 2 cm stainless steel wire was mounted into the SPME fiber assembly in a way that 1 cm of its end be coated by electrospun nanofibers. The rotating SPME fiber assembly (collector) was placed in perpendicular position with respect to the syringe and the rotation rate of the collecting SPME fiber assembly was 45 rpm. The schematic diagram of the apparatus used in the electrospinning process is shown in Fig. 1. A high voltage (20 kV) was applied between collector and the syringe needle while they were kept in 10 cm distance. The flow rate of polymer solution was set at 0.1 ml h^{-1} and electrospining was performed for 20 min. All the electrospinning processes were performed under ventilation. Finally, the prepared SPME fiber was conditioned in Combi PAL fiber conditioning station at 260 °C for 2 h.

2.4. Preparation of standards

The stock solution of BTEX compounds were prepared in methanol at concentration of 100 mg L^{-1} and stored at −4 °C. Other standard solutions were prepared daily by diluting the stock solutions in ultra-pure water.

2.5. Headspace SPME procedure

BTEX solution (3 ml, 0.5 mg L^{-1}) was introduced into a vial (8 ml). The vial was sealed with a silicon septum and open-top aluminum cap. Sample vial was heated and was agitated in the agitator heater. The SPME fiber was exposed to the headspace of this vial. After performing the extraction, the fiber was withdrawn and then it was immediately inserted into the GC injector port for thermal desorption of the analytes.

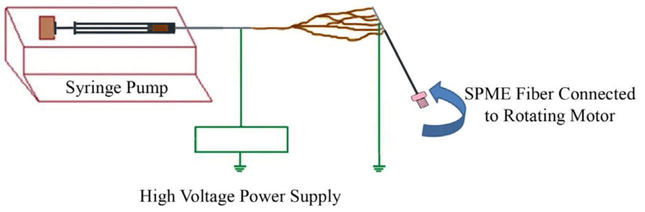

Fig. 1. Scheme of the electrospinning set up.

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