ELECTROSPUN NANOFIBRES FOR SOLID-PHASE MICROEXTRACTION

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Abstract

Solid phase microextraction has been established as modern analytic method, which provides several benefits such as sensitivity, rapid and solvent free technique for sample preparation in organic analytical chemistry. Nowadays there is a scientific effort dedicated to improve analytical methods based on new and nanostructured materials. Our study follows this trend and contributes to analytical chemistry approach. Explicitly, the investigation of using nanofibrous sorbents for solid phase microextraction.

Nanofibres of polyethersulfone (PES), polyetherimide (PEI) and polysulfone (PSU) were successfully prepared by needle electrospinning and fixed on a thin stainless steel wire SPME assmebly. The geometry of sorbents plays a crucial role in the extraction kinetics of the mass transfer in SPME. The intention of using electrospun fibres geometry is to enhance the sorbent sensitivity and capacity.

The basic properties of the prepared nanofibers were determined by thermogravimetry (TGA) and scanning electron microscope (SEM). The scanning electron microscopy images of prepared nanofibers showed a diameter range from 700 to 1400 nm for polyethersulfone, 300 to 600 nm for polyetherimide and 800 to 1400 nm for polysulfone. TGA analysis proved the thermal stability of all prepared nanofibers up to 250 °C. The extraction efficiency of new lab-made SPME fibres and selected common commercial SPME fibres (PDMS and PDMS/DVB) was investigated by the headspace SPME (HS-SPME) mode of gas chromatograph coupled with tandem mass spectrometer (GC/MSMS).

Hexachlorocyclohexanes isomers (HCH) were selected as model analytes in water matrix. With these pollutants, a set of experiments was conducted to proof the effect of key SPME method conditions extraction time on MSMS response.

Keywords: Solid phase microextraction, nanofibres, polyethersulfone, polysulfone, polyetherimide

1. INTRODUCTION

Solid phase microextraction can be defined as an extraction method (or sample preparation method), when the extraction agent (liquid or solid) had much smaller volume comparison to volume of sample. In equilibrium, the extract fraction of the analyte is often negligible [1]. SPME fibre is composed from carrier material (fused-silica core and stainless steel core), coating [2] and protective layer (if it´s needed, especially during the analysis of complex matrixes in direct mode of SPME [3]). A commercial available coating for GC application includes PDMS, PDMS/DVB, Carboxen/PDMS, DVB/Car/PDMS, polyacrylate amd Carbowax polyethylene glycol coatings. Geometry plays a crucial role in the extraction kinetics of the mass transfer in SPME [4]. The geometry of the fiber, thin film and a round particles was directly compared [5]. A syringe-like SPME fibre geometry appears to be most viable: polymeric coatings, sandwiches and mixtures are placed at the tip of the plunger, which is either hidden in a needle (during the transport phase) or exposed off the needle (during the extraction and thermal desorption phases of the analysis). The usual length of the plunger tip is 10 mm and its diameter is 0.1 mm. Polymeric layer thickness ranges from 7 to 100 μm. Amongst other parameters, the duration of the extractive sorption part of the sample introduction step (enrichment) seems to highly influence the overall time of analysis. This is especially the case if less volatile organic compounds are the target analytes [6]. Temperature is another parameter driving the analyte transfer velocity from the water phase

towards the sorption fibre. However, water vapour competes with organic analytes vapours for sorption places at higher temperatures [7] therefore; temperatures exceeding 80 °C are rarely used even for organic compounds with a low Henry constant. Last but not least, sorption fibre polymeric material affinity for specific analytes and its surface preconditioning plays an important role [8].

Completed SPME assemblies were compared with commercial PDMS and DVB/Carboxene/PDMS fibres with an emphasis on the possible shortening of the duration of the enrichment step. As a matrix for enrichment time tests, water contaminated by hexachlorocyclohexanes was used. These compounds were selected for a few reasons. They belong to the group of persistent organochlorinated pesticides listed as POPs under the Stockholm Convention on persistent organic pollutants. Also HCH was former industrial production in the Czech Republic [9]. And, last but not least, these pesticides belong to widely studied groups of target analytes with SPME utilization [10,11,12].

2. MATERIALS AND METHODS

Lab-made SPME fibers were assembled from a stainless steel capillary and 304H wire supplied by Teseco and a RDG810 3D-printer polymer supplied by VeroClear (**Figures 1 and 2**). Polyetherimide, polyethersulfone and polysulfone pellets (supplied by Sigma-Aldrich) was dissolved overnight in a dimethylformamide into 22 % (PEI), 24 % (PSU) and 28 % (PES) w/w solution. These prepared solutions were pumped into the electrospinner needle with the flow of 3 ml per hour. The lab-made assembly used as a collector electrode was subjected to 20-25 kV voltage. The relative humidity 45 - 55 % and temperature 25 °C was kept during electrospinning of all fibers. SPME commercial fibre 100 µm PDMS for comparison was obtained from Restek. Helium of 5.0 purity and argon of 4.8 purity (Linde Gas) were used as a carrier gas and collision gas for GC-MS/MS measurements, respectively. Chromatographic standard of hexachlorocyclohexanes (HCH) - Mix 5 (100 µg·ml^{-1} in acetone) war purchased from Neochema.

Figure 1 Schema of SPME fibre

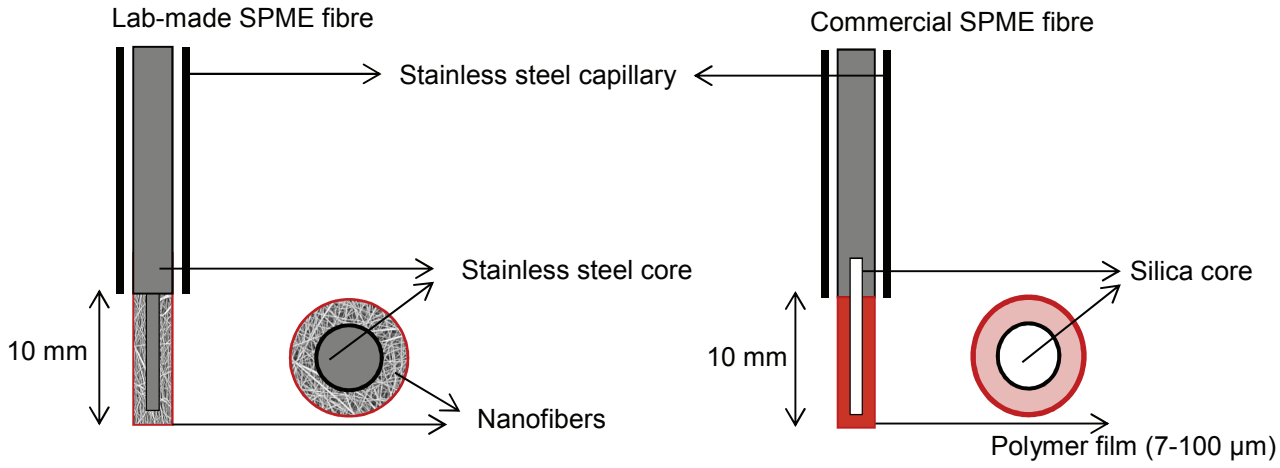


Figure 2 Schema of commercial and lab-made SPME fibre

3. APPARATUS AND EQUIPMENTS

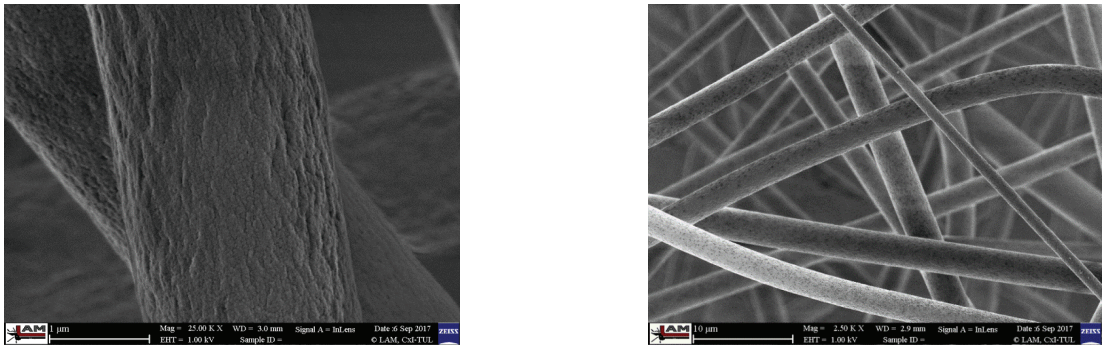
Appearance of produced PEI, PES and PSU nanofibres on lab-made SPME fibers was documented by SEM microscope (UHR FE-SEM Carl Zeiss ULTRA Plus). Analytical performance of all SPME fibers (manufactured and commercial) was tested with gas chromatograph (Thermo Trace 1310) equipped with a mass spectrometer triple quadrupole detector (Thermo TSQTM 8000 EVO) and a programmed temperature vaporizing injector (PTV). For automatic handling of prepared samples was GC/MSMS equipped by an autosampler (CTC Analytics AG, PAL RTC), which was set to headspace operation mode (samples were agitated during enrichment time).

A gas chromatography column DB-5MS (30 m long, 0.25 µm thick and with 0.25 µm film thickness of stationary phase) was installed into GC oven. For the purpose of rapid testing, a very fast method was developed whereby the duration of one GC cycle was reduced to 10 minutes. Temperature program of the chromatographic oven started at 80 °C, graduating by 20 °C per min. to 260 °C. The carrier gas (helium 5.0) flow was adjusted to 1.5 ml per min.

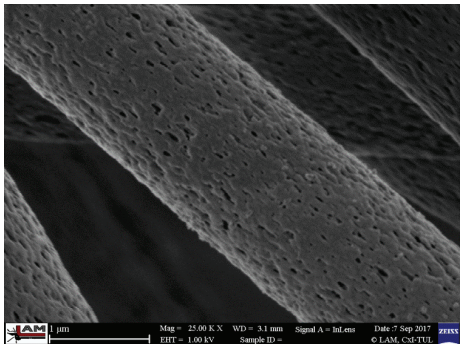
For proper cleaning step of SPME fibres was set desorption step after injection to system. PTV injector was set to hold at 220 °C in splitless mode for 1 minute and for cleaning phase the temperature was set to 240 °C with the flow of carrier gas to 30 ml per min. All of the SPME fibers were tested for different extraction (enrichment) time in the headspace of the measured samples. Enrichment times for all tested fibers were set to: 2, 5, 10, 20, 30, 40 and 50 minutes. Temperatures during the agitations were set to 70 °C with constant speed 250 rpm. For each tested fiber 21 tap water samples spiked with chromatographic standard of hexachlorocyclohexanes (HCH) were prepared in 20 ml vials capped with PTFE/silicon septa and magnetic cap. Samples were spiked to reach the concentration of HCH 5 $\mu g \cdot l^{-1}$.

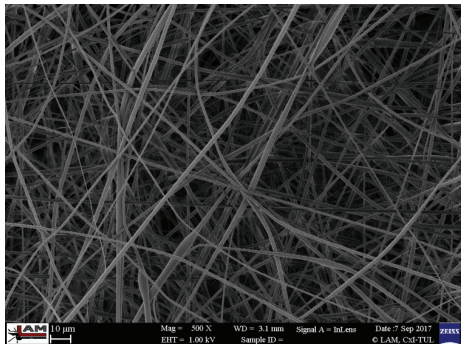
4. RESULTS AND DISCUSSION

Nanostructure surface of produced polyetherimide, polyethersulfone and polysulfone nanofibers were documented by SEM microscope (**Figures 3 - 8**). The scanning electron microscopy images of prepared nanofibers showed a very high number of pores presence at fibres surface. This effect was primarily observed at PES and PSU nanofibers. The diameter of the prepared nanofibers was in range from 700 to 1300 nm for polyethersulfone, 300 to 600 nm for polyetherimide and 800 to 1200 nm for polysulfone. All lab-made fibers with PEI, PES and PSU nanofibers were compared with commercially available SPME fibre - 100 µm PDMS. Enrichment time 2, 5, 10, 20, 30, 40 and 50 minutes was the parameter chosen for the comparison. The dependencies of GC-MS/MS peak areas on the enrichment time are shown on **Figures 9 - 13**. Obtained data indicate that the worst performance of all tested SPME fibers have polyetherimide fibers. PES fiber showed very similar responses as the commercial PDMS fiber. The highest response in all tested enrichment times of all tested fibers had showed PSU fiber. During the longest agitation time, the response of PSU fiber was 50 % bigger than the commercial PDMS fiber.

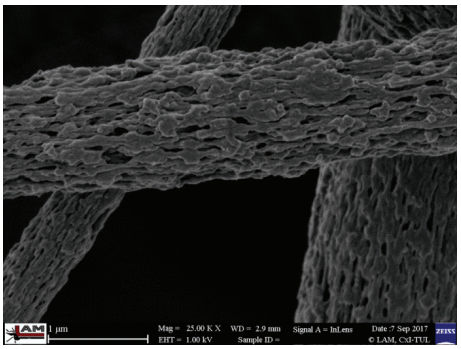


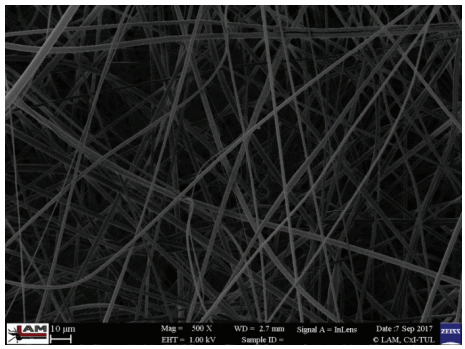
Figures 3 - 4 Electrospun polyetherimide (PEI) nanofibers



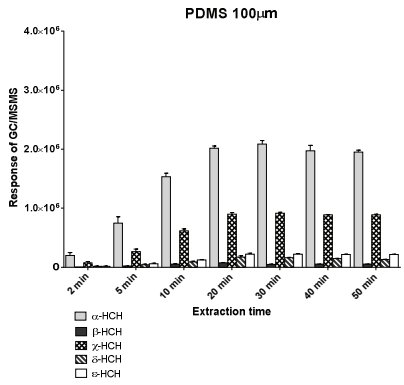


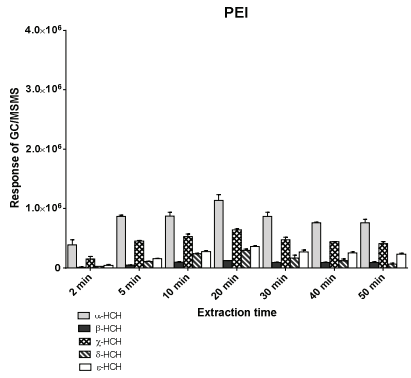
Figures 5 - 6 Electrospun polyethersulfone (PES) nanofibers



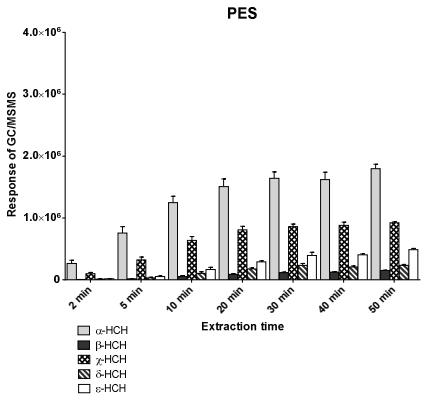


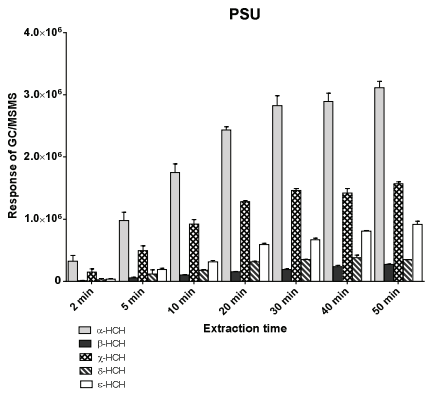
Figures 7 - 8 Electrospun polyethersulfone (PSU) nanofibers





Figures 9 - 10 Comparison of PDMS 100 μm and PEI fibers, GC/MS response after SPME injection (error bars at 1 σ, n = 2)





Figures 11 - 12 Comparison of PES and PSU fibers, GC/MS response after SPME injection (error bars at 1 σ, n = 2)

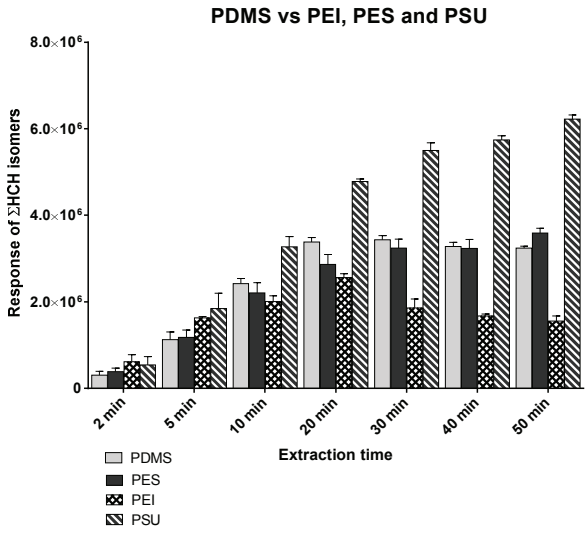


Figure 13 Comparison of commercial PDMS 100 µm fibre vs PEI, PES and PSU fibers, GC/MS response after SPME injection (error bars at 1 σ, n = 2)

5. CONCLUSION

Polyethersulfone, polyetherimide and polysulfone nanofibres were succesfully prepared from polymer solution by needle electrospinning. The scanning electron microscopy images of prepared nanofibers showed a diameter range from 700 to 1300 nm for polyethersulfone, 300 to 600 nm for polyetherimide and 800 to 1200 nm for polysulfone. Even though the achieved diameters for nanofibers wasn´t so small, the images of prepared nanofibres showed a very high number of pores presence at fibres surface, especially on PES and PSU nanofibres. TGA analysis proved the thermal stability of all prepared nanofibres (PEI, PES and PSU) up to 250 °C. BET analysis determined that specific surface was 57 $m^2 \cdot g^{-1}$ for PEI, 32 $m^2 \cdot g^{-1}$ for PES and 10 $m^2 \cdot g^{-1}$ for PSU of prepared nanofibres.

The parameter of the enrichment time had significantly positive influence on the response of MS detector. Obtained data indicate that the worst performance of all tested SPME fibers have polyetherimide fibers. PES fiber showed very similar responses as the commercial PDMS fiber. Saturation was achieved in case of PDMS, PES and PEI fibres. Just in case of polysulfone fibre the saturation wasn´t reached during extraction times 2 - 50 minutes. The highest response in all tested enrichment times of all tested fibers had showed PSU fiber. During the longest agitation time, the response of PSU fiber was 50 % bigger than the commercial PDMS fiber.

Handicap of using nanofibres as sorbent in analytical chemistry could be the homogeneity of producing nanofibres and their possible shorter lifetime during the longer usage. Obtained data indicated that used geometry in form of nanofibres can be successfully used as sorbent in analytical chemistry, especially in case of HS-SPME technique.

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