NANOSIZED POLYMERIC FIBRES FOR SOLID-PHASE MICROEXTRACTION SORBENTS

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Abstract

Solid phase microextraction (SPME) has been established as a modern, simple, sensitive, rapid and solvent free technique for sample preparation in organic analytical chemistry. Since SPME was first introduced by Pawliszyn in the early 1990s, several modifications of sorbent geometry were developed. The main goal of using electrospun fibres geometry is to enhance the sorbent sensitivity and capacity. In the present work, electrospun polyetherimide (PEI) nanofibres were prepared from 12.5 % solution (80/20 - DMF/THF) fixed on a steel wire solid phase microextraction (SPME) assembly. Analytical performance of prepared fibres was compared with common commercial available SPME fibres (100 µm polydimethylsiloxane (PDMS), 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) and 85 µm polyacrylate (PA)) in the headspace SPME (HS-SPME) mode of gas chromatograph coupled with mass spectrometer (GC/MS/MS). The chlorophenols were chosen as model water pollutants. To solve instability, tailing peaks, detectability and adsorption problems, chlorophenols were acetylated before GC step of the analysis. Lab-made PEI nanofibres assemblies appeared to have sensitivity comparable to commercial SPME fibres.

Keywords: Solid phase microextraction, electrospun, nanofibres, polyetherimide, chlorophenoles

INTRODUCTION

SPME is a modern analytical technique which is a fast, solvent-free alternative to conventional sample extraction methods [1]. It combines extractive sorption (preconcentration) of the targets analytes to be quantified with ongoing heat desorption and sample injection to the gas chromatographic systems. In the headspace solid phase extraction mode, the analytes establish equilibrium among the sample matrix, the headspace above the sample and a polymer-coated fused fibre (the most common type of the commercial available fibres). Very low detection limits are achieved, because the target compounds are concentrated of the fibre and rapidly delivered to the chromatographic column. All the above mentioned steps could be automatically done by an autosampler [2]. With the progress in automation of the sample preparation, HS-SPME is frequently coupled with techniques such as on-fibre derivatization [3, 4].

The polymeric coatings on stainless steel or on a glass core, polymeric cylinders with surface membrane and needle trap devices are commercially available [5, 6]. The most often used materials and their combination are polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacryle (PA) and polyethyleneglycol (PEG) [7]. The commercial available SPME fibres are still relatively expensive; therefore lab-made fibre coated with nanofibres could be a way for research institutions. In our study, the polyetherimide (PEI) has been selected as a suitable material for steel core SPME fibres produced by needle electrospinning, whereby a lab-made SPME plunger was rotated inside the stream of freshly produced PEI nanofibres.

Chlorophenols were chosen as model pollutant for analytical comparison of commercial and lab-made fibres. There are 19 possible congeners, the 2-chlorphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol ale listed in the Priority Pollutant List of the US Enviromental Protection Agency (U.S. EPA). The most hazardous from all congeners of the chlorophenoles is pentachlorophenol, which is proposed for listing under the Stockholm Convention as a persistent organic pollutant (POP).

1. MATERIALS AND METHODS

Lab-made SPME fibres were assembled from a stainless steel capillary and 304H wire supplied by Teseco and a RDG810 3D-printer polymer supplied by VeroClear (**Figure 1**). Polyetherimide was obtained from Sigma-Aldrich (CAS: 61128-46-9) and it was dissolved overnight in a mixture of dimethylformamide/tetrahydrofuran (Sigma-Aldrich) 80:20 into 12.5 % w/w solution. Prepared solution was pumped into the electrospinner needle with the flow of 5 ml per hour (**Figure 2**). The collector electrode was subjected to 22 kV voltage. The relative humidity 45 - 55 % and temperature 25 °C was kept during electrospinning. Potassium carbonate was obtained from Penta and acetic anhydride was purchased from Sigma-Aldrich. Chromatographic standards: 2,3-dichlorphenol and pentachlorophenol were purchased from Dr. Ehrenstorfer GmbH and 2-chlorophenol, 4-chlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and isotopic labelled pentachlorophenol $^{13}C_6$ were supplied by Sigma-Aldrich. SPME commercial fibres were obtained from Supelco (100 µm PDMS, 65 µm PDMS/DVB and 85 µm PA).

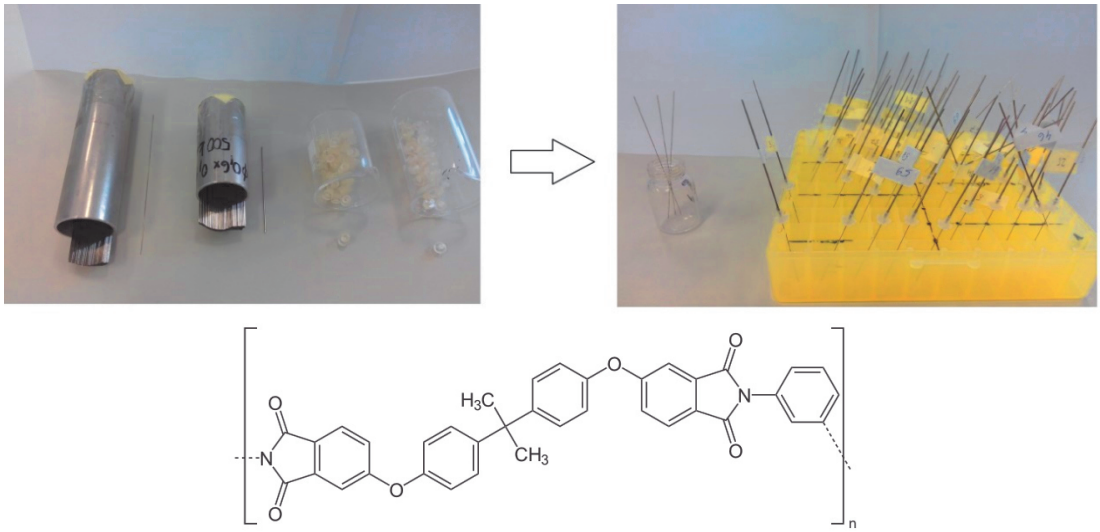

Figure 1 Left up: stainless capillary and wire, plastic parts; right up: final assembly of lab-made SPME fibre. Down: Chemical structure of PEI

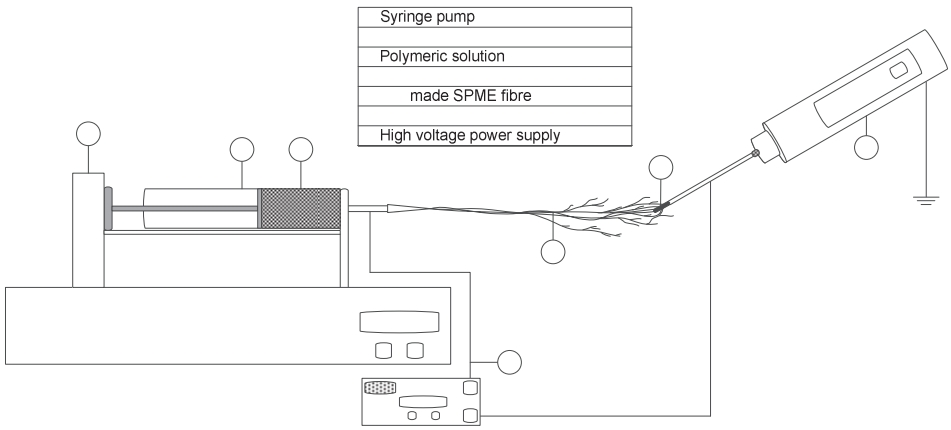

Figure 2 Schema of electrospinning PEI

2. APPARATUS AND EQUIPMENTS

Appearance of produced PEI fibres on lab-made SPME fibres was documented by SEM microscope (Tescan Vega 3) (**Figure 3**). Analytical performance of SPME fibres was tested with gas chromatograph (Thermo Trace

1310) equipped with a mass spectrometer triple quadrupole detector (Thermo TSQ™ 8000 EVO) and a programmed temperature vaporizing injector (PTV). Automatic handling of prepared samples was done by an autosampler (CTC Analytics AG, PAL RTC), which was set to headspace operation mode (samples were agitated during fibre exposure).

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. Temperature program of the chromatographic oven started at 70 °C, graduating by 10 °C per min. to 240 °C, held for 2 minutes. The carrier gas (helium) flow was adjusted to 1 ml per min. During desorption step, PTV injector was hold at 250 °C in splitless mode for 1 minute, for cleaning phase the temperature was set to 265 °C and the flow of carrier gas to 30 ml per min. Only for the lab-made PEI fibre, the temperature was adjusted to 200 °C for desorption and 210 °C for cleaning phase. All of the SPME fibres were tested for different extraction (enrichment) time in the headspace of the measured samples. Enrichment times for all tested fibres were set to: 1, 2, 3, 4, 5, 10, 15, 20 and 30 minutes at the same agitator temperature (70 °C) and speed 250 rpm. For each tested fibre twenty-seven tap water samples spiked with chlorophenols were prepared in 20 ml vials capped with PTFE/silicon septa and magnetic cap. Samples were prepared from 9 ml of water, 10 µl mixture of chlorophenoles and for derivatization 1 ml of 1 molar solution of potassium carbonate and 1 ml of acetic anhydride were added.

The retention times of all analytes were determined previously in the fullscan mode of MS detector. Based on this measurement, selected reaction monitoring (SRM) transitions were adjusted to improve detector sensitivity and selectivity for chosen analytes (**Table 1**).

Table 1 Retention times and SRM transitions of the studied chlorophenoles

Compound (concentration [µg·l^{-1}])	GC retention time [min]	Precursor Ion [m/z]	Product Ion [m/z]	Collision energy [eV]
2-chlorophenol acetate [0.3]	7.07	128	100	5
4-chlorophenol acetate [0.3]	7.56	128	100	5
2,3-dichlorophenol acetate [0.04]	9.47	162	98	15
2,4,6-trichlorophenol acetate [0.03]	10.29	196	132	15
2,3,4,6-tetrachlorophenol acetate [0.02]	12.52	232	131	60
Pentachlorophenol acetate [0.01]	14.53	266	167	20
Pentachlorophenol acetate - 13C^{6} [0.01]	14.53	272	172	20

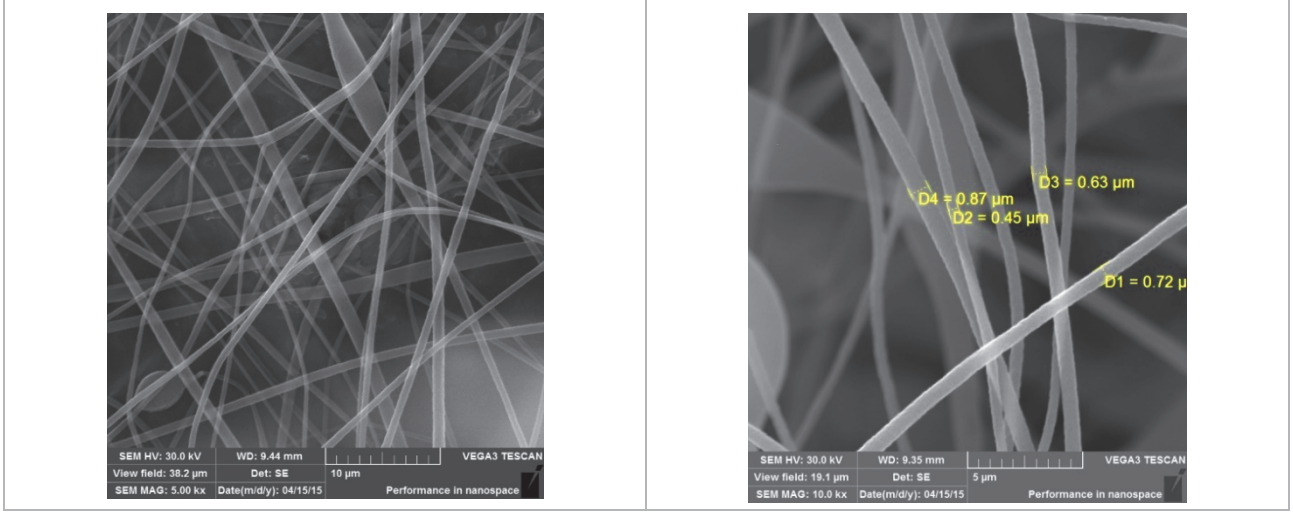

Figure 3 Pictures by SEM microscope (Tescan Vega 3) of electrospun PEI fibres

3. RESULTS AND DISCUSSION

A lab-made fibre with PEI nanofibres were successfully prepared (**Figure 3**) and compared with three different commercially available SPME fibres (100 µm PDMS, 65 µm PDMS/DVB and 85 µm PA). Enrichment time (1 to 30 min) was the main parameter chosen for the comparison. The dependencies of GC-MS/MS peak areas on the enrichment time for seven chlorophenoles acetates (one of them isotopically labelled) are shown on **Figures 4 - 7**. Obtained data indicate that the 100 µm PDMS fibre had the best response for highly chlorinated congeners of chlorophenoles (tetrachlorophenol acetate and pentachlorophenol acetate). The 65 µm PDMS/DVB have highest response for the monochlorphenoles acetate and the 2,3-dichlorphenol acetate. The 65 µm PDMS/DVB fibre appeared to have absolutely highest response values (slightly better than 100 µm PDMS fibre) from all tested commercial fibres. Lab-made PEI SPME fibre performed worst of all tested fibres. The PEI fibre performed similarly as 85 µm PA fibre in case of low chlorinated phenols, however with growing number of chlorine the response was decreasing rapidly.

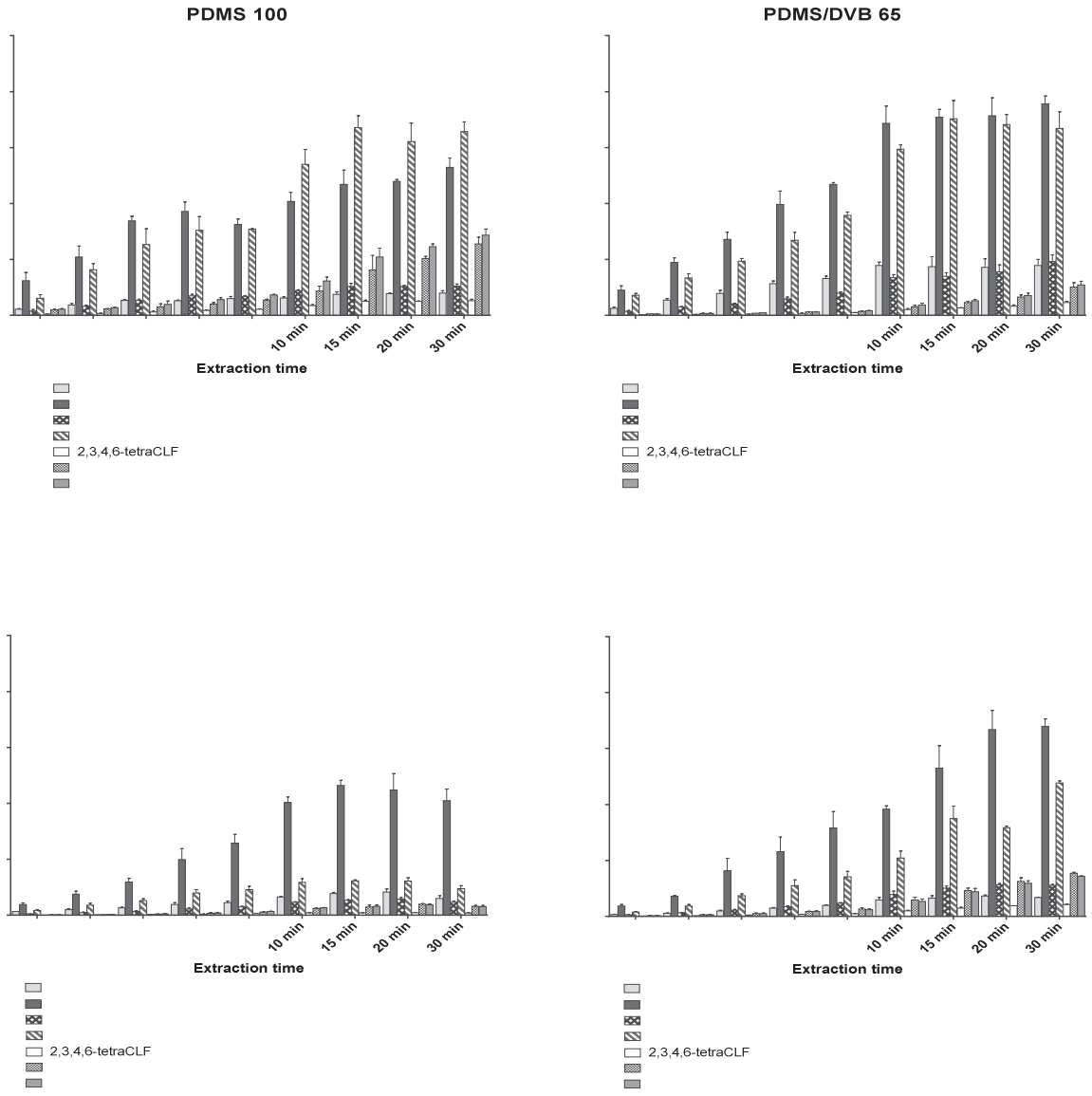

Figure 4 - 7 Comparison of lab-made fibre and commercial SPME fibres, GC/MS response after SPME injection (error bars at 1 σ, n = 3)

4. CONCLUSION

The concept of lab-made SPME with nanofibres used as sorbent for analytical properties has been proved as viable. Preparation of large quantities of lab-made fibres should not be a problem for many research facilities, which could help the expansion of using SPME as modern analytical method. In this study, the prepared electrospun PEI nanofibres didn't reach the performance of three compared commercial SPME fibres in terms of the GC/MS/MS system response for chlorophenoles acetates used as model pollutants. However, with the sensitivity of tandem mass spectrometric detection there is no need to have the sensitivity of commercial fibres. In our case, with using the GC/MSMS, the response of tested lab-made fibre is sufficient.

Speed, easiness and low-end electrospinning equipment needed are the most beneficial properties in PEI nanofibres application as sorbents in the SPME fibres. Based on obtained data, the lab-made SPME with polyetherimide nanofibres deserve more future research.

In ongoing research, we will focus on electrospinning of fibres with smaller diameter and on other thermally stable polymers suitable for electrospinning (polyamide and melamine-formaldehyde resin for example). Also we want to experimentally verify the lifetime of prepared lab-made SPME with nanofibres versus commercial available SPME fibres.

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