

## NANOSIZED POLYMERIC FIBRES FOR SOLID-PHASE MICROEXTRACTION SORBENTS

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### Abstract

Solid phase microextraction (SPME) has been established as a convenient method of sample preparation in organic analytical chemistry since its introduction by Pawliszyn in 1989. Recently, first attempts are reported on the preparation of SPME sorbents by electrospun nanofibres, in contrast to routinely applied sol-gel techniques. The intention of using electrospun fibres geometry is to enhance the sorbent sensitivity and capacity. In this work, polyetherimide (PEI) electrospun nanofibres were prepared from PEI 15 % solution in DMF/THF 80:20 using a needle electrospinner and SPME steel core as electrode under 10 kV, following the work of Bagheri et al., 2013. Adhesion between steel core and polymeric coating was optimized to obtain thermally stable PEI/PDMS SPME fibre assembly. Final laboratory-made SPME fibres were characterized by SEM and TGA and their analytical performance (in determination of hexachlorocyclohexanes - HCH by headspace-SPME GC/MS) was compared with commercially available SPME fibres.

**Keywords:** Solid phase microextraction, nanofibres, electrospinning, polyetherimide, hexachlorocyclohexanes

### Introduction

SPME is a modern analytical technique for sample introduction into chromatographic systems. It combines extractive sorption (preconcentration) of targets to be quantified with ongoing heat desorption and sample injection to the chromatographic system. All the above mentioned steps could be conducted automatically by an autosampler. Thus, laborious sample preparation steps, which are inevitable during traditional liquid-liquid extraction (LLE), are omitted during SPME. Thin fibers of various polymers, which are compatible with autosampler operation, are available from Supelco. Polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA) or polyethyleneglycol (PEG) are used polymers, with the film thickness ranging from 7 to 100 µm. This polymeric coating is a part of plunger tip, which is hidden in a syringe and could be exposed during sorption/desorption. Usual length of a plunger tip is 10 mm and its diameter is 0.1 mm. SPME fibre is either exposed in the liquid sample phase ("direct immersion" SPME) or, as in the case of volatile or semivolatile analytes, could be exposed in the headspace above the liquid or solid sample ("headspace" SPME).

Commercially available SPME fibres are rather inaccessible in higher quantities. Therefore, with the era of 3D-printers, the lab-made and lab-coated SPME fibres come into a question. In the field of nanofibres, analytically successful preparation of electrospun assemblies was announced for polyamide (Bagheri and Aghakhani 2012), polyacrylate-polyethylene glycol copolymer (PA-PEG) (Bagheri et al. 2014) and polyetherimide (PEI) (Bagheri et al. 2014).

In our study, the latter (PEI) polymer has been selected as a potentially suitable material for steel core SPME fibres produced by needle electrospinning, whereby a lab-made SPME plunger was rotated inside the stream of fresh produced PEI nanofibres. Prepared electrospun SPME PEI fibres has been characterised by thermogravimetry (TGA) and scanning electron microscopy (SEM). In the last step, the optimized electrospun PEI fibres were compared under differing gas chromatograph (GC) injection temperature for the hexachlorocyclohexanes (HCH) determination via headspace SPME.

## 1. MATERIALS AND METHODS

Lab-made SPME fibre assemblies were produced from stainless steel capillary and wire 304H supplied from Teseco and VeroClear RDG810 3D-printer polymer (Fig. 1). PEI was obtained from Sigma-Aldrich (melt index 18g/10 min (337 °C/6.6kg)) and it was dissolved overnight in DMF/THF 85:15 into 15 % w/w solution. This solution was pumped into the electrospinner needle with the flow of 0.5 ml per min. The collector electrode was subjected to 15 kV voltage and it was placed to the distance of 15 cm from the needle. SPME plunger has collected the fresh produced nanofibres with the speed of rotation being 50 rpm under 25 °C and a relative humidity of 38 %.

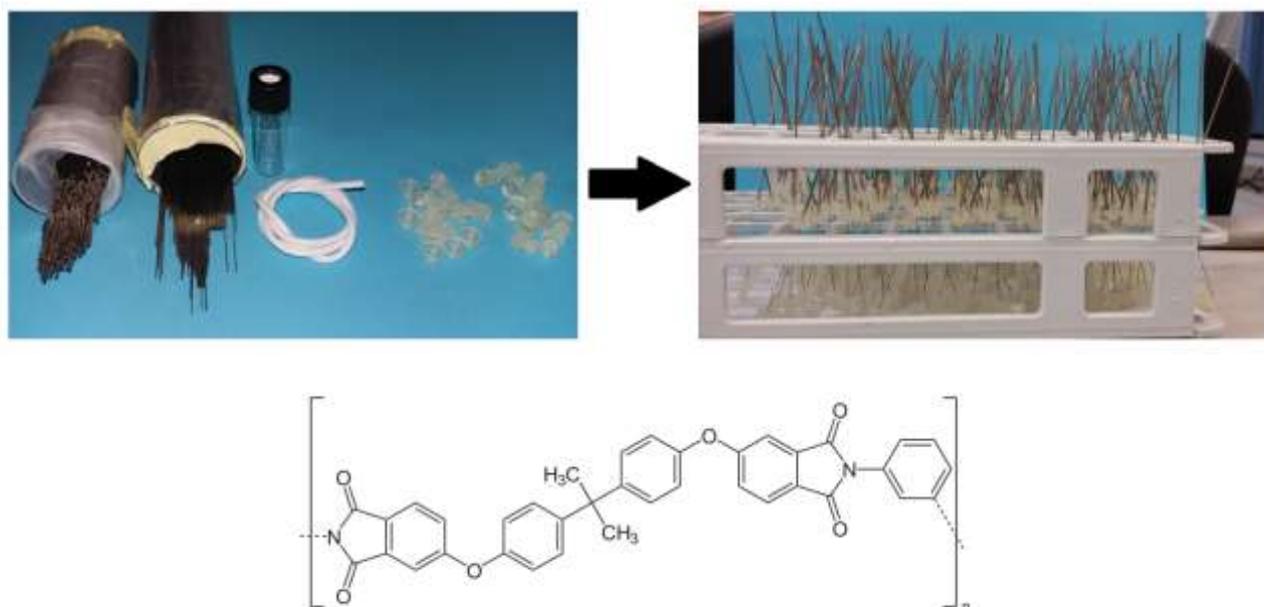


Figure 1: Left up: stainless capillary and wire, plastic parts; right up: final assembly of lab-made SPME fibre.  
Down: Chemical structure of PEI.

## 2. APPARATUS AND EQUIPMENTS

Appearance of PEI fibres was documented with SEM microscope (Tescan Vega 3) (Fig. 2). Mass loss of produced SPME PEI fibres was tested with TGA Q500 (Thermo) (Fig. 3). Performance of lab-made SPME PEI fibres was tested with gas chromatograph and mass spectrometer (Thermo Trace 1310, TSQ 8000 Triple quadrupole MS). Automatic handling of prepared water samples was provided by autosampler (PAL LHX-xt), which worked in headspace operation mode (samples heated and shaken before fibre exposure). The gas chromatograph was equipped with a capillary column VF-5MS (length 30m, thickness 0.25 mm and film thickness 0.25 µm). Temperature program of the chromatographic oven started at 120 °C, then increased by 12 °C·min<sup>-1</sup> to 250 °C, finally increased by 35 °C·min<sup>-1</sup> to final temperature 300 °C and was held for 1 min. Fiber exposure was done for 50 min under 70 °C. For the desorption of HCH, a PTV injector was used under 200 and 250 °C for 1 min. For each tested fibre, ten water samples spiked with same concentration of HCH standard (2.5 µg·l<sup>-1</sup> of each HCH isomers) were prepared. The first manufactured SPME fibre was tested with same extraction temperature (250 °C) as commercial fibre. The other manufactured fibre was tested with lower extraction temperature 200 °C. Conditioning of the SPME fiber was also done in PTV injector immediately after the transfer of HCH on the column. Flow rate of the helium carrier gas was adjusted to 1 ml·min<sup>-1</sup>.

### 3. RESULTS AND DISCUSSION

A nanostructured PEI SPME fibres were successfully prepared in the lab-scale (Fig. 2). Diameters of produced fibres were between 300 and 600 nm. Polymer adhesion to the SPME plunger was sufficient, with no polymer loss during test operations. Thermal stability of PEI was comparable to PDMS fibres (up to 400 °C, Fig. 3 and Fig. 4). On the other hand, PEI fibre has lower sorption capacity towards HCH (Fig. 5), about 60.5 % of PDMS fibre. This parameter would lead to higher limit of quantification, if this fibre would be utilized for complete validation of method for HCH determination with SPME. Fig. 5 also shows, that 2 selected PEI fibres differed significantly in capacity and that fibre subjected to lower injection temperature kept its capacity, whereas the one subjected to high injection temperature lost its capacity quickly.

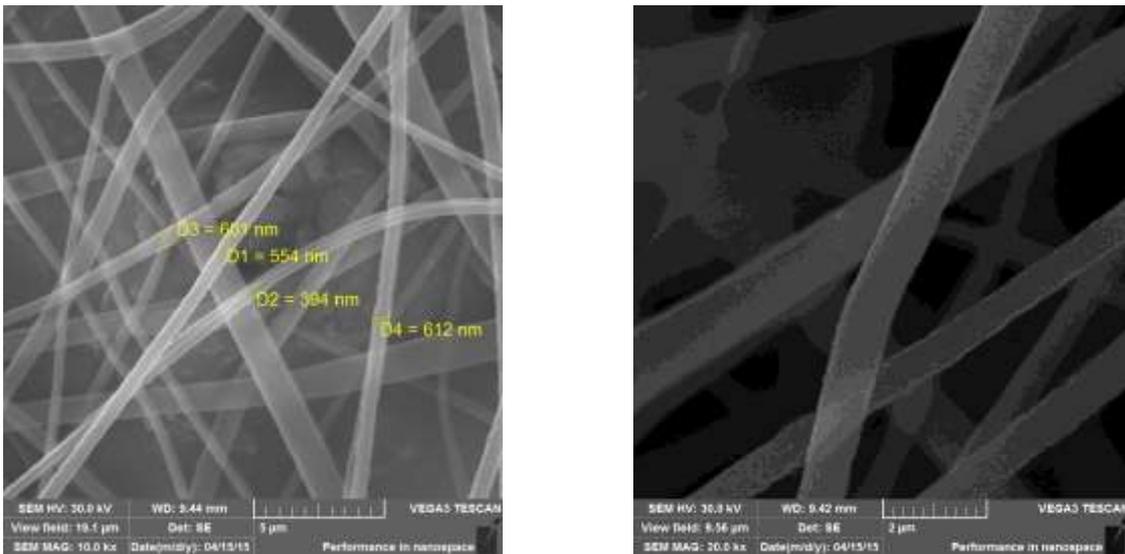


Figure 2: Pictures by SEM microscope (Tescan Vega 3) of electrospun PEI fibres

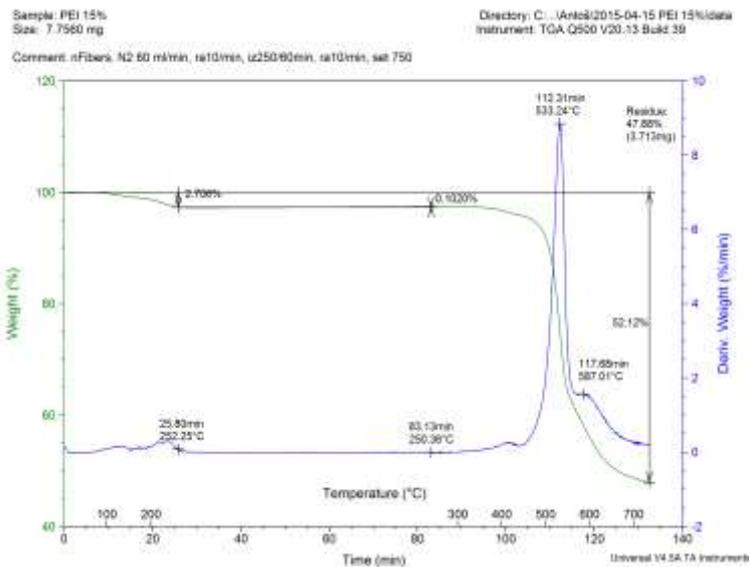


Figure 3: Testing manufactured PEI fibres mass loss on TGA Q500

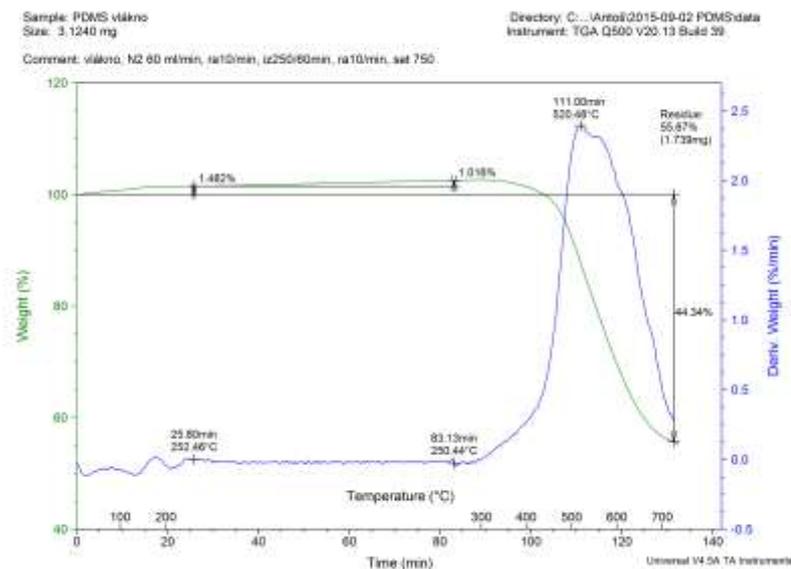


Figure 4: Testing commercial SPME 60 µm PDMS/DVB fibre on TGA Q500

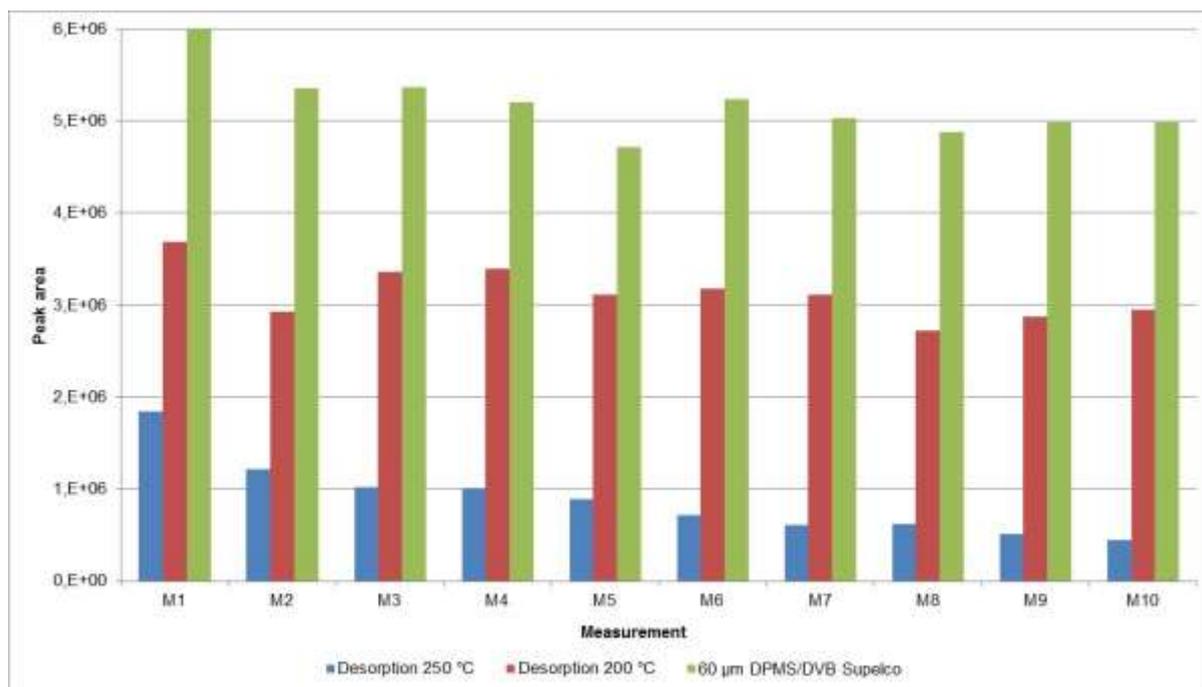


Figure 3: Comparison of lab-made and commercial SPME fibres on measuring HCH

#### 4. CONCLUSION

We report our first results on performance of lab-made SPME assemblies prepared from electrospun PEI. Limited data were gathered concerning analytical performance of prepared fibres. Supelco PDMS/DVB fibres have higher sorption capacity for HCH in comparison with our lab-made SPME fibres. However, due to structural similarity, aromatic target analytes would probably have better sorption properties than tested HCH. We see lab-making of SPME fibre as a viable approach for the supply of sufficient quantity of SPME fibre assemblies for large environmental studies. In ongoing research, we will focus on more detailed

characterization of prepared fibres, kinetics of sorption on fibres, on electrospinning of fibres with smaller diameter and on other thermally stable polymers suitable for electrospinning (polyamide as an example).

## ACKNOWLEDGEMENTS

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