

## 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 the nineties of the 20<sup>th</sup> century. 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. 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

### 1. 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. Thin fibers of various polymers, which are compatible with autosampler operation, are available e.g. from Supelco. Polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA) or polyethyleneglycol (PEG) are the most often used polymers, with the film thickness ranging from 7 to 100  $\mu\text{m}$ . This polymeric coating is a part of a 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 sample ("headspace" SPME).

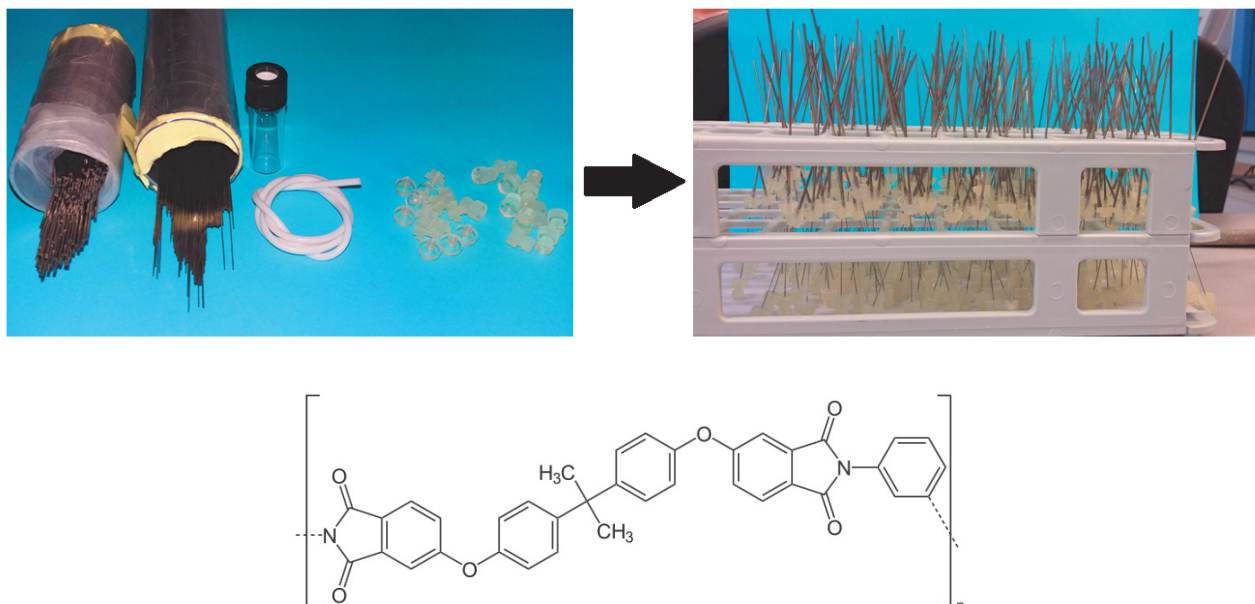
Commercially available SPME fibres are rather inaccessible in higher quantities. Therefore, with the era of 3D-printers, the lab-made and lab-coated SPME fibres come into a question. In the field of nanofibres, analytically successful preparation of electrospun assemblies was announced for polyamide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

### 2. 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 the mixture of 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 freshly produced nanofibres at the speed of rotation of 50 rpm under 25 °C and a relative humidity of 38 %.



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

### 3. 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 performed by an autosampler (PAL LHX-xt), which worked in headspace operation mode (ie. samples were heated and shaken before fibre exposure). The gas chromatograph was equipped with a capillary column VF-5MS (of 30 m length, 0.25 mm thickness and 0.25  $\mu\text{m}$  stationary phase thickness). Temperature program of the chromatographic oven started at 120 °C, graduating firstly by 12 °C·min<sup>-1</sup> to 250 °C, secondly by 35 °C·min<sup>-1</sup> to final temperature of 300 °C, which was held for 1 min. SPME fiber was exposed for 50 min under 70 °C. For the desorption step, a PTV injector was operating under 200 or 250 °C for 1 min. For each tested fibre, ten water samples spiked with the same concentration of HCH standard (2.5  $\mu\text{g}\cdot\text{l}^{-1}$  of each HCH isomer) were prepared. The first manufactured SPME fibre was tested with the same extraction temperature (250 °C) as commercial fibre. The other manufactured fibre was tested with lower extraction temperature of 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>.

### 4. 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 that of PDMS fibres (up to 400 °C, **Fig. 3** and **Fig. 4**). On the other hand, PEI fibre has lower affinity towards HCH (**Fig. 5**), about 60.5 % of that of PDMS fibre. Therefore, higher limit of quantification would be achieved, if this fibre would be utilized for complete validation of method for HCH determination with SPME. **Fig. 5** shows, that 2 selected PEI fibres

differed significantly in affinity towards HCH and that the one subjected to lower injection temperature kept its affinity, whereas the one subjected to higher injection temperature lost its capacity quickly.

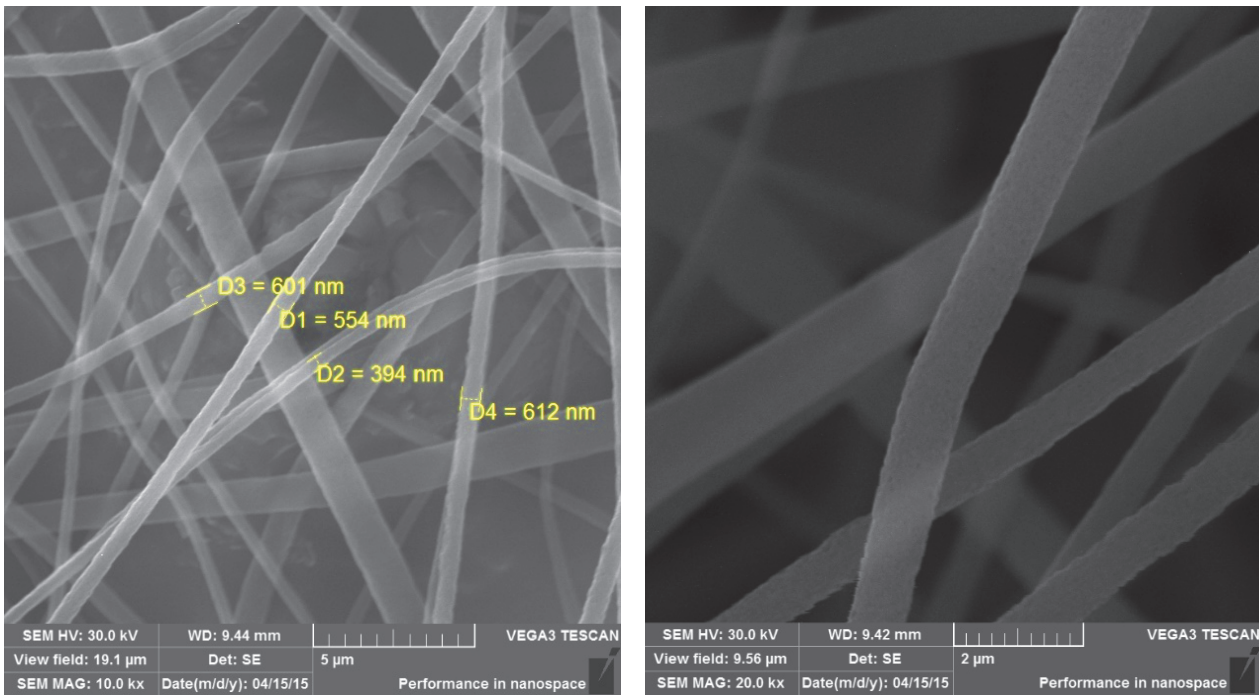


Fig. 2 Pictures by SEM microscope (Tescan Vega 3) of electrospun PEI fibres

Sample: PEI 15%  
Size: 7.7560 mg

Instrument: TGA Q500 V20.13 Build 39

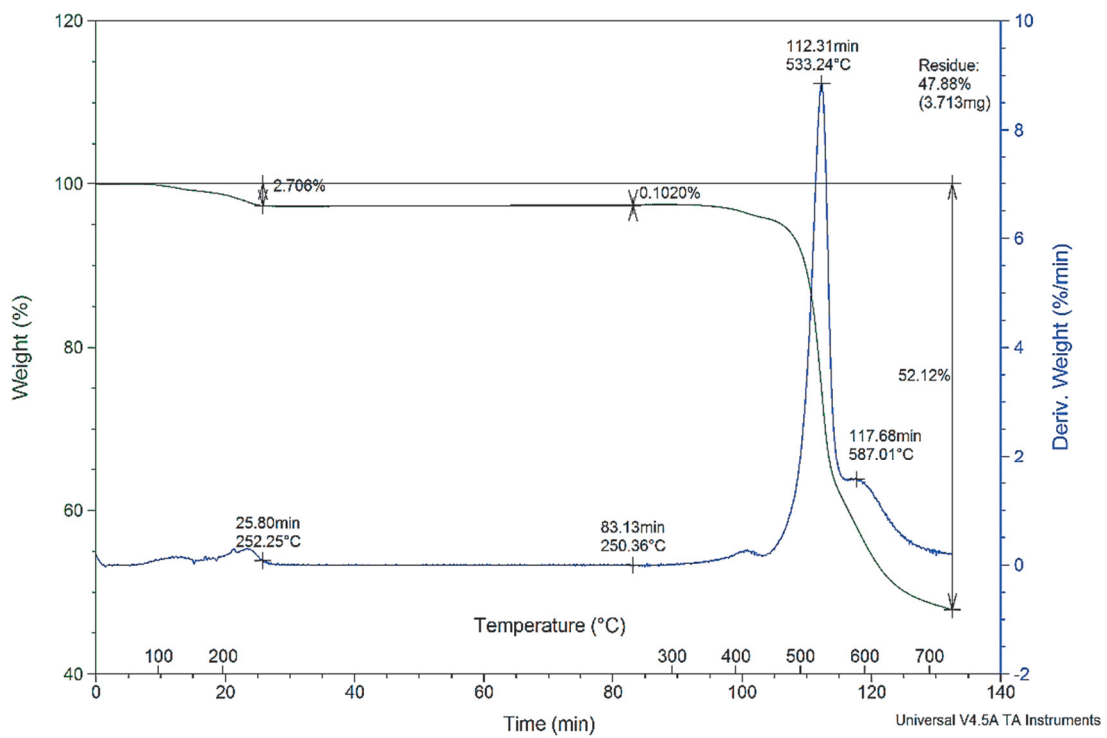


Fig. 3 Mass loss of lab-made PEI SPME fibres

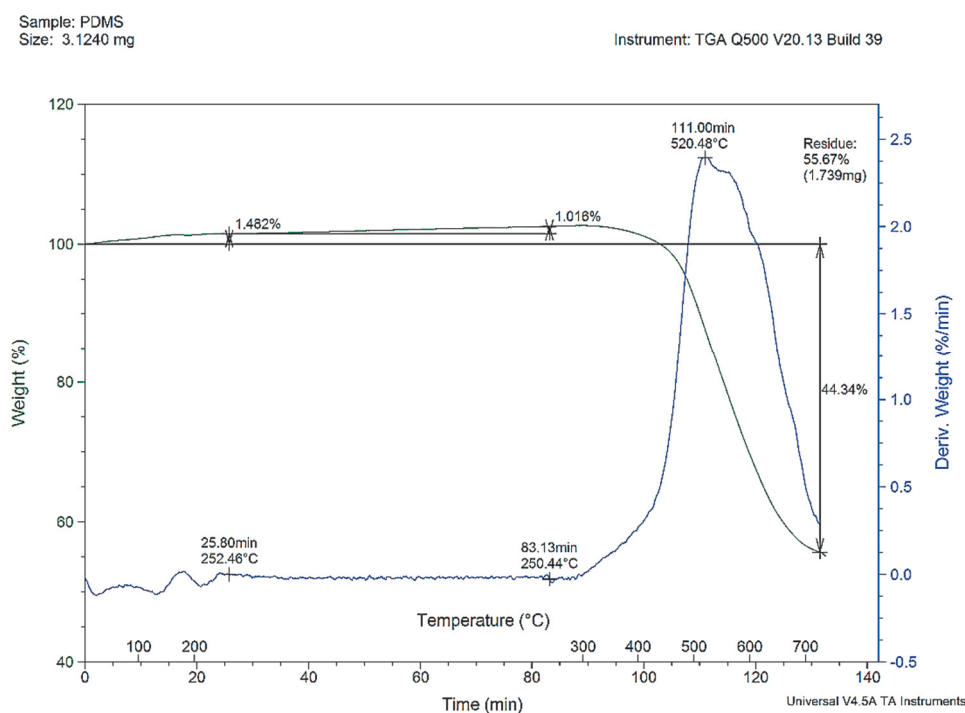


Fig. 4 Mass loss of commercial SPME fibre, 60 µm PDMS/DVB phase

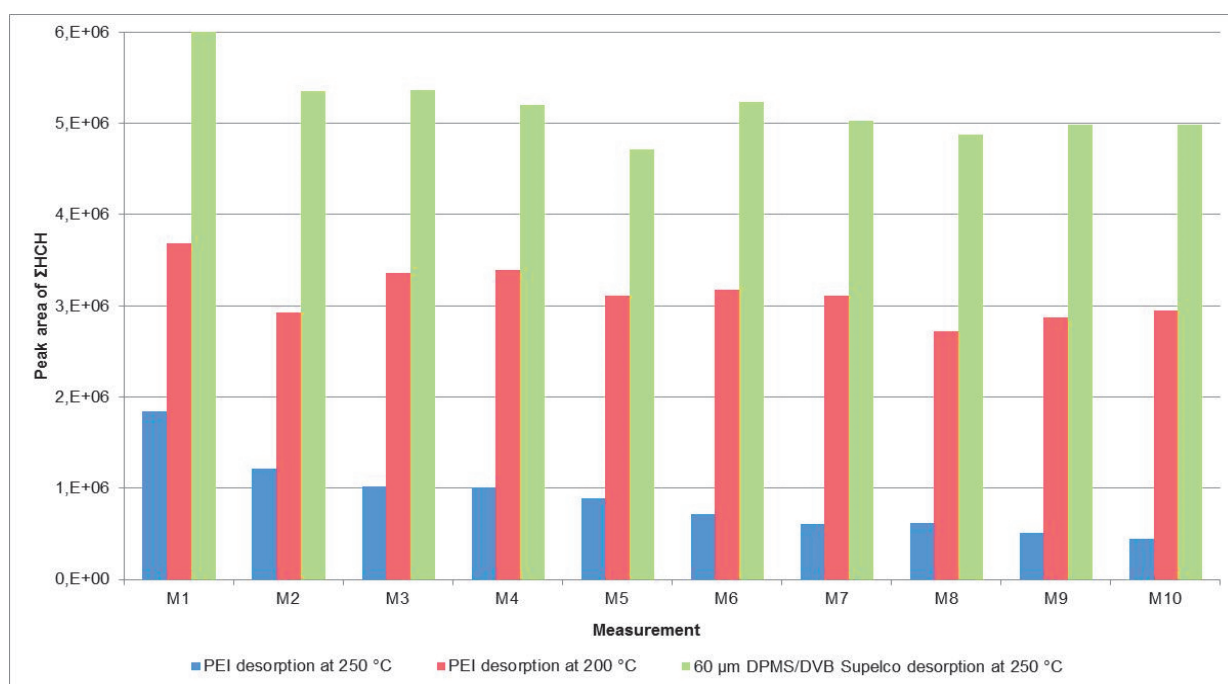


Fig. 5 Comparison of lab-made and commercial SPME fibres, GC/MS signal after SPME injection

## 5. 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 shown higher affinity towards HCH than our lab-made PEI SPME fibres. However, aromatic target analytes would probably have better sorption properties. 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

*The research in this article was supported by the project OPR&DI Institute for Nanomaterials, Advanced Technologies and Innovation (CZ.1.05/2.1.00/01.0005) a National programme for sustainability I (L01201). The work of Vojtěch Antoš was supported by the Ministry of Education of the Czech Republic within the SGS project no. 21066/115 on the Technical University of Liberec.*

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