Research Article

Polyetherimide Nanofibres as Sorbents for Organochlorinated Pesticides Determination

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Electrospun polyetherimide (PEI) nanofibres were fixed on a steel wire solid phase microextraction (SPME) assembly. The basic properties of the prepared nanofibres were determined by thermogravimetry, differential scanning calorimetry, adsorption, and SEM. The analytical performance of prepared PEI SPME fibres was compared with three commercially available SPME fibres, 7 μm PDMS, 100 μm PDMS, and DVB/Carboxene/PDMS. As model water pollutants, persistent organochlorinated pesticides hexachlorocyclohexanes (HCH) and chlorobenzene (ClB) were chosen as model water pollutants. The fibres were compared in the headspace- (HS-) SPME mode of GC-MS/MS instrumentation. The comparison omitted other method parameters and focused exclusively on the extraction time variability. Lab-made PEI SPME fibres showed significantly better response for the target compounds than the other tested fibres from industrial production. Based on the results, the extraction time could be shortened from 50 to 10 min, if PEI SPME fibres were used as a modification of existing analytical protocol.

1. Introduction

Headspace solid phase microextraction (HS-SPME) is a modern analytical technique for sample introduction into gas chromatographic systems [1]. The HS-SPME technique combines extractive sorption (enrichment) of targets to be quantified with ongoing thermal desorption and injection to the GC system. All of the above-mentioned steps can be performed by an ordinary autosampler [2]. This fact makes the technique attractive, as it meets the current laboratory demands on high sample throughput, precision, and green analytical approach as solventless operation [3]. With the progress in automation of sample preparation steps, HS-SPME is often involved in wider protocols of coupled techniques such as on-fibre derivatization [4, 5].

SPME fibres are commercially available in various geometries: as polymeric coatings on a stainless steel or on a glass core, as polymeric cylinders with a surface membrane, as needle trap devices, and so forth [6, 7]. The most often routinely employed polymers are polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA), or polyethylene glycol (PEG) [8]. Polypyrrole [9], cyclodextrin [10], polymeric ionic

liquids [11], or graphene-based [12] materials were proposed to become the next generation of SPME sorbents.

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 . It should be noted at this point that there is a vast amount of literature and running research on SPME fibres prepared by sol-gel based techniques (see, e.g., the review by Kumar et al. [13]), which are commercially available, for example, from Supelco or CTC Analytics, AG. Our study contributes to the fresh technique of making SPME assemblies from nanofibres. First analytically successful preparations of electrospun SPME assemblies were announced few years earlier: in 2012 for polyamide [14]; in 2014 for polyacrylate-polyethylene glycol copolymer (PA-PEG) [15] and for polyetherimide (PEI) [16]. The latter polymer is also the topic of this research.

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. Various solutions are proposed to avoid the long enrichment times: First of all, the salting out effect is utilized for water samples whereby NaCl addition of up to 10% solution is used [17]. 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 [18]; 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 play an important role [19].

Polyetherimide (PEI) nanofibres were chosen as the polymeric surface of the lab-made steel core SPME assemblies to be evaluated in our study. During the production of PEI nanofibres by needle electrospinning, a lab-made SPME plunger was rotated inside a stream of freshly spewed PEI nanofibres in order to obtain a surface covering. 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 (HCH) and chlorobenzene (ClB) was used. These compounds were selected: (a) as they belong to the group of persistent organochlorinated pesticides listed as POPs under the Stockholm Convention on persistent organic pollutants and have therefore priority attention, (b) as there is a need to perform detailed monitoring of the environmental contamination of HCH and ClB due to their former industrial production in the Czech Republic [20], and (c) as organochlorinated pesticides belong to widely studied groups of target analytes with SPME utilization [21–25]. HCH are always accompanied by ClB in groundwater, as ClB are products of HCH natural transformations [20]. Aside from characterization of PEI SPME analytical performance by GC-MS/MS system response, the prepared assemblies were characterized by thermogravimetry (TGA), differential scanning calorimetry, adsorption (BET isotherm), and scanning electron microscopy (SEM).

2. Materials and Methods

2.1. Materials and Reagents. Lab-made SPME fibres were assembled from a stainless steel capillary and 304H wire supplied by Teseco and RDG810 3D-printer polymer supplied by VeroClear (Figure 2). PEI was obtained from Sigma-Aldrich (CAS: 61128-46-9, melt index 18 g/10 min, 337°C/6.6 kg) and was dissolved overnight in a mixture of dimethylformamide/tetrahydrofuran (Sigma-Aldrich) 80 : 20 into 15% w/w solution (labelled S1) for electrospinning, following the procedure of Bagheri et al. [16].

Chromatographic standards of hexachlorocyclohexanes (HCH), Mix 5 (100 µg·mL⁻¹ in acetone), and chlorobenzene (ClB), Mix 12 (1000 µg·mL⁻¹ in acetone), were purchased from Neochema; isotopically labelled γ-HCH D6

(100 µg·mL⁻¹ in cyclohexane) was obtained from Dr. Ehrenstorfer GmbH (Table 1). SPME commercial fibres were obtained from Supelco (100 µm PDMS and 50/30 µm DVB/Carboxene/PDMS) and CTC Analytics AG (7 µm PDMS).

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. Argon and nitrogen gases of 4.8 purity (Linde Gas) were used for surface area determination. Low purity nitrogen was used for the thermogravimetric and calorimetric measurements.

2.2. Apparatus and Equipment. Mass loss temperature dependence of 100 µm PDMS and PEI fibres was compared by measurements using TGA Q500 (Thermo). Fibres were tested under nitrogen flow (60 mL per min), which resembles GC injector inert conditions rather than air composition. The temperature program was started at 25°C, graduating by 10°C per minute to 750°C, with a hold for 60 min at 250°C.

The appearance of manufactured PEI and Supelco PDMS fibres was documented using SEM microscope Tescan Vega 3 (Figure 2). The specific surface of electrospun PEI fibres was determined by the absorption method nitrogen/krypton upon liquid nitrogen temperature and was evaluated with a BET adsorption isotherm. Measurement was performed on an Autosorb IQ-MP instrument (Quantachrome Instruments).

The temperature of glass transition was determined by differential scanning calorimetry (Mettler Toledo DSC1). The temperature was program started at 0°C, graduating by 10°C per minute to the final temperature of 250°C. The flow of carrier gas (nitrogen) was adjusted to 50 mL per minute. This program was repeated twice, firstly to remove sample thermal history and secondly to determine the real physical properties of the PEI nanofibres.

Analytical performance of all SPME fibres was tested on a gas chromatograph (Thermo Trace 1310) equipped with a mass spectrometer triple quadrupole detector (Thermo TSQ™ 8000), autosampler (CTC Analytics AG, PAL LHX-xt), and a programmed temperature vapourizing injector (PTV). For the 4.5 min long fibre conditioning step, the PTV was set at 255°C in the case of the commercial fibres and at 205°C for lab-made PEI fibres. The split flow was set at 50 mL per min for the conditioning phase. For the 1 min long desorption and injection step, the PTV was set at 200°C in splitless operation.

A VF-5MS chromatographic column (30 m long, 0.25 mm thick with a stationary phase thickness of 0.25 µm, Agilent) was installed in the gas chromatograph. The temperature program of the chromatographic oven started at 60°C, graduating firstly by 10°C per min to 250°C, followed by a temperature gradient of 35°C per min to 300°C and held on this temperature for 3 min. The carrier gas flow was adjusted to 1 mL per min. All of the SPME fibres were tested for graduating extraction (enrichment) time in the headspace of the measured vials: for 1, 2, 3, 4, 5, 10, 30, and 50 minutes at the same incubation temperature of 70°C and an agitator speed of 250 rpm. For each tested fibre, twenty-four tap water samples spiked with the same concentration of HCH and ClB standard (2.5 µg·L⁻¹ of each HCH isomer, 0.3 µg·L⁻¹

TABLE 1: Retention times and SRM transitions of the studied HCH and ClB.

Compound	GC retention time min	Precursor ion <i>m/z</i>	Product ion <i>m/z</i>	Collision energy eV
1,3-Dichlorobenzene	5.88	146	75	20
1,4-Dichlorobenzene	6.01	146	75	20
1,2-Dichlorobenzene	6.30	146	75	20
1,3,5-Trichlorobenzene	7.75	180	109	20
1,2,4-Trichlorobenzene	8.43	180	109	20
1,2,3-Trichlorobenzene	8.93	180	109	20
1,2,4,5 + 1,2,3,5-Trichlorobenzene	10.54	214	108	30
1,2,3,4-Trichlorobenzene	11.24	214	108	30
Pentachlorobenzene	13.04	250	215	18
α -HCH	15.20	181	145	22
Hexachlorobenzene	15.29	284	214	30
β -HCH	15.75	181	145	15
γ -HCH	15.93	181	145	22
γ -HCH D6	15.93	224	150	20
δ -HCH	16.52	181	145	24
ϵ -HCH	16.73	217	181	8

FIGURE 1: The scheme of the needle electrospinning apparatus.

of deuterated γ -HCH, and $0.6 \mu\text{g}\cdot\text{L}^{-1}$ of each ClB) were prepared. Lower concentrations of γ -HCH D6 were used as they are established on this level as a GC-MS/MS internal standard for routine HCH determination via HS-SPME in our laboratory.

The retention times of all of the HCH and ClB isomers were determined previously in the full scan mode of MS detector and, subsequently, selected reaction monitoring (SRM) transitions were specified in order to enhance detector selectivity and sensitivity for HCH and ClB (Table 1).

2.3. Methods

2.3.1. Preparation of PEI Nanofibres. Solution S1 was pumped into the electrospinner needle with a flow of $5 \mu\text{L}$ per min, whereby the needle was connected at 16 kV. The grounded SPME plunger collected the freshly produced nanofibres at a speed of 50 rpm at 25°C and relative humidity of 38% (Figure 1).

FIGURE 2: From left: plastic components, steel capillary and wire for lab-made fibre, 2 pieces of assembled lab-made fibres, and a commercial SPME fibre.

All of the commercial SPME fibres were conditioned according to the manufacturer's instruction before the measurements. Lab-made PEI fibres were conditioned at 200°C for 90 minutes in PTV injector with the flow of carrier gas set to 20 mL per min.

The analytical performance of the HS-SPME fibre was tested in 20 mL vials capped with PTFE/silicon septa and a magnetic cap, with 10 mL of the water sample. These method parameters together with chromatographic and MS settings were used as they had been previously validated on a GC-MS/MS instrument for HCH and ClB determination in water with the legally required sensitivity (LOQ $0.01 \mu\text{g}\cdot\text{mL}^{-1}$ of γ -HCH and $0.02 \mu\text{g}\cdot\text{mL}^{-1}$ of the sum of HCH isomers).

3. Results and Discussion

For the purpose of this study, several pieces of SPME assemblies with plunger tips covered by electrospun PEI were prepared (Figures 2 and 3). Thermogravimetric characterization of both PDMS and PEI SPME fibres shows an insignificant difference in the temperature dependent mass

FIGURE 3: A spent 100 μm PDMS fibre from Supelco (a) and a lab-made PEI fibre (b).

FIGURE 4: HCH response for 3 commercial and PEI fibres (the scale is interrupted at the response value of 1.0×10^6 on all of the graphs, error bars at 1σ , $n = 3$).

FIGURE 5: CIB response for 3 commercial and PEI fibres (the scale is interrupted at the response values of 5.0×10^6 and 8.5×10^7 on all of the graphs, error bars at 1σ , $n = 3$).

loss. This was a prerequisite for fibre analytical utilization because polymer degradation products are not welcome in a GC-MS/MS system.

Calorimetric testing determined the glass transition temperature of PEI to approximately 210°C . This explains the decrease in the sorption capacity of the PEI fibres, when an injector temperature of 250°C was used (data not shown). The data presented (Figures 4 and 5) were collected at an injector temperature of 200°C .

The surface area was the last measured nonanalytical parameter of the prepared nanofibres. A high value of $58.1 \text{ m}^2 \cdot \text{g}^{-1}$ seemed promising in the effort to make the extractive (enrichment) phase the shortest one as possible.

The dependencies of GC-MS/MS peak areas on the extraction time for 6 HCH isomers (including one isotopic labelled isomer) and for four groups of CIB are shown in Figures 4 and 5, respectively. For clarity, CIB data were grouped according to the degree of chlorination (sum of trichlorinated

benzene, sum of tetrachlorinated benzene, pentachlorobenzene, and hexachlorobenzene). The DVB/Carboxene/PDMS fibre appeared to have the absolutely highest response values from commercial fibres. This fibre also did not approach the sorption equilibrium during 50 min of extraction time. Conversely, pure PDMS fibres either reached the sorption equilibrium after 50 min ($7 \mu\text{m}$ fibre) or were close to it ($100 \mu\text{m}$ fibre). The responses at distinct extraction times were noticeably lower for PDMS fibres. In the case of $7 \mu\text{m}$ PDMS fibre the response was only a few % compared to all other fibres.

The PEI fibre performed similarly to the DVB/Carboxene/PDMS fibre in the meaning of high response. However, there are some differences between the PEI and DVB/Carboxene/PDMS fibres. The response of the PEI fibre only reaches about 95% of the DVB/Carboxene/PDMS fibre response of tri-CIB, 150% of the response of tetra-CIB, about 325% of the response of penta-CIB, and about 1100% of

the response of hexa-ClB (see Figure 5). As for HCH isomers, the PEI fibre performed with noticeably higher responses than DVB/Carboxene/PDMS fibre. For some of the HCH isomers, the difference was several times higher (see Figure 5).

There is a validated procedure in our laboratory for HCH and ClB determination in water based on 100 μm PDMS fibre. This procedure fulfils the required LOQ and LOD and employs a 50 min long extraction time. The PEI fibre reaches the corresponding response of a 100 μm PDMS fibre (1×10^7 of arbitrary units) already within a 10 min extraction time.

These results are very promising in terms of the applicability of PEI fibres in the analysis of organochlorinated pesticides. However, long-term performance tests of PEI fibres are still missing. This could be a weak point in the involvement of nanoscaled sorbents in SPME, as the fibres can quickly lose the flexibility during GC temperature cycles. On the other hand, there was no visible damage to the PEI fibre after the 24 injections conducted in this study.

The other parameter, which remains unclear for the laboratory preparation of SPME PEI fibres for routine analytical purposes, is the fibre-to-fibre reproducibility of sorption properties. This aspect could be solved by using fibre quality control samples at the beginning of the work with a new fibre.

4. Conclusions

The feasibility of lab-scale preparation of several pieces of SPME PEI fibres by electrospinning has been proven. The prepared electrospun PEI nanofibres had better performance than three commercial SPME fibres in terms of the GC-MS/MS system response for representatives of organochlorinated pesticides (HCH, ClB). Therefore, the extraction time could be shortened from 50 to 10 min by switching the PEI fibre for the 100 μm PDMS fibre while maintaining the required sensitivity. This practically means considerable reduction of one-sample analysis time to the GC runtime (slightly over 20 min). Fibre conditioning and another sample extraction can be done by GC-MS/MS autosampler in parallel during the GC runtime of the previous sample. As a result, 50 samples could be measured daily with PEI fibre instead of 20 samples with 100 μm PDMS fibre.

Fast sorption and cheap, fast, and easy production of PEI nanofibres are the most beneficial properties in their application as sorbents in the SPME fibres. Based on obtained data, polyetherimide nanofibres as sorbent used in analytical chemistry deserve more detailed future research. Currently, only very few laboratories care about producing their own lab-made SPME fibres. However, with the global availability of all of the necessary components, the concept of lab-made SPME fibres is becoming a more valid option.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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