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An on-line coupling of nanofibrous extraction with column-switching high performance liquid chromatography – A case study on the determination of bisphenol A in environmental water samples

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ABSTRACT

Polyamide 6 nanofiber polymers were used as modern sorbents for on-line solid phase extraction (SPE) coupled with liquid chromatography. The on-line SPE system was tested for the determination of bisphenol A in river water samples. Polyamide nanofibers were prepared using needleless electrospinning, inserted into a mini-column cartridge (5 × 4.6 mm) and coupled with HPLC. The effect of column packing and the amount of polyamide 6 on extraction efficiency was tested and the packing process was optimized. The proposed method was performed using a 50-µL sample injection followed by an on-line nanofibrous extraction procedure. The influence of the washing mobile phase on the retention of bisphenol A during the extraction procedure was evaluated. Ascentis® Express C18 (10 cm × 4.6 mm) core-shell column was used as an analytical column. Fluorescence detection wavelengths (λ_{ex} = 225 nm and λ_{em} = 320 nm) were used for identification and quantification of Bisphenol A in river waters. The linearity was tested in the range from 2 to 500 µg L^{-1} (using nine calibration points). The limits of detection and quantification were 0.6 and 2 µg L^{-1}, respectively. The developed method was successfully used for the determination of bisphenol A in various samples of river waters in the Czech Republic (The Ohře, Labe, Nisa, Úpa, and Opava Rivers).

1. Introduction

Finding a reliable sample preparation procedure is still considered to be the bottleneck of the whole analytical method. Current advances in sample preparation have been focused on automation, improving sensitivity and accuracy, low sample and organic solvent consumption, and especially miniaturization. The development of miniaturized sample preparation techniques coupled e.g. with liquid chromatography has shown to be a promising way to achieve these aims. The latest trends in micro-extraction sample clean-up techniques have reduced the volume of organic solvents needed for liquid extraction methods, and have reduced the amount of sorbents in solid phase extraction based methods. Moreover, the development of new extraction materials with improved properties is challenging task in the field of micro-extraction techniques.

Nanofiber polymers, which have demonstrated an excellent potential for extraction purposes, have proven to be new and promising candidates due to their stability, versatility, large surface area due to the small diameter of their fibres (less than 1000 nm), and thus enhanced extraction kinetics and capacity. The most common way to create nanofibers is through electrospinning using an electrostatic field for forming the nanofibers from a solution or melt of polymer [1,2]. The use of nanofibers and nanomaterials in the micro-extraction context has been recently described [3,4]. Solid Phase Micro-Extraction (SPME), Micro-Extraction by Packed Sorbent (MEPS), nanofiber disk SPE, and pipette-tip micro-extractions are the most often used off-line nanofibrous extraction approaches before determination by High Performance Liquid Chromatography (HPLC), Gas Chromatography (GC), or other separation techniques with a suitable detection [3,4]. Nevertheless, the on-line coupling of nanofiber polymers directly with analytical tools has only very rarely been described [3,4]. Therefore, this almost undescribed area shows good potential to simplify the clean-up step and to speed up the analytical run, most notably in liquid chromatography systems.

The typical on-line SPE-HPLC procedure employs a double position column switching valve to perform the extraction and separation steps

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directly in the system. The sample is injected directly onto the extraction pre-column in the first step. The target analytes are retained on the pre-column while the rest of the sample with residual interferences is eluted to the waste. Purification of the sample occurs during the washing mobile phase, which flows through the extraction pre-column. In the second step, the analytes are eluted with a mobile phase to the chromatography column, where separation is carried out [2,5].

An environmental contaminant, bisphenol A (BPA), was chosen as the target analyte for this study. BPA is widely used in the manufacture of plastics and resins. Because of the widespread use of plastics, the presence of residual BPA concentrations in food and environmental samples is widely studied [6–12]. Some works have used various extraction techniques, for example coacervative extraction [6], liquid-liquid extraction [12], dispersive liquid phase microextraction [7,12], and solid phase extraction (SPE) [13–16]. Two works describing the on-line connection of SPE with HPLC for the determination of BPA in samples have been found. In these studies, a C18 cartridge or a methacrylic acid 3-sulfopropyl potassium salt (MASK) modified pre-treatment column were used for the sample extraction [17,18]. Bisphenol A belongs within the group of endocrine disrupting chemicals. Several studies on BPA have focused on its increased estrogenic activity [10,11]. The maximal daily intake of BPA was set at 4 $\mu g\ kg^{-1}$ (body weight) per day (EFSA, January 2015). Despite all these facts, no limits of BPA in environmental water have been established in the Czech Republic.

As far as we know, no work describing on-line nanofibrous extraction for the determination of BPA in river samples has been published yet. Therefore, this work was focused on the testing of a nanofibrous extraction with using polyamide 6 nanofibers, which were connected on-line with a UHPLC system to perform an analysis of BPA in rivers. The polyamide nanofibers used in this work were prepared by needleless electrospinning using a nanospider laboratory machine. In addition to their behaviour, changes in their structure, stability in a high back-pressure on-line SPE system, influence of column packing on extraction efficiency, and repeatability of the extraction steps were individual objectives of the presented study.

2. Materials and methods

2.1. Chemicals

Standard bisphenol A (4,4′-(propane-2,2-diyl)diphenol) (purity ≥ 99%) was provided by Sigma-Aldrich (Prague, Czech Republic) as well as Chromasolv methanol and Chromasolv acetonitrile. The ultra-pure water was purified through a Milli-Q (Millipore, Bedford, MA, USA). Nylon 6 (Ultramid B27) was purchased from BASF (Prague, Czech Republic).

2.2. Instrumentation and software

Analyses were performed using a Nexera X2 UHPLC system (Shimadzu Corporation, Kyoto, Japan). The UHPLC system was equipped with LC-30AD solvent delivery systems, with a DGU-20 A5R degassing unit, an SIL-30AS autosampler, a CBM-20A communication module that was serial connected to an SPD-M30A DAD and an RF-10AXL detector, and a CTO-20AC column oven with an FCV-12AH high-pressure six-port switching valve. The system control and data acquisition and evaluation were performed by the Shimadzu LC LabSolutions software version 5.57 (Shimadzu Corporation, Kyoto, Japan). The nanofibers were prepared using a Nanospider NS1WS500U (Elmarco, Czech Republic) laboratory machine and patented technology.

2.3. Preparation of standard solutions and the sample

A standard stock solution was prepared by dissolving bisphenol A in acetonitrile (a concentration of 1000 mg L^{-1}) and it was stored in the dark at 4 °C. Working standard solutions were prepared daily by dissolving the stock solution in water until the final concentration was reached. The optimal solution for the extraction dimension was at a concentration of 500 $\mu g\ L^{-1}$. Linearity was tested in the range from 2 to 500 $\mu g\ L^{-1}$ using nine calibration points. The repeatability of the on-line SPE-UHPLC system was tested at four different concentration levels (2, 5, 50, 500 $\mu g\ L^{-1}$). The real water samples were stored in glass bottles at a constant temperature of 4 °C. On the day of measurement, the samples were filtered by 0.45 μm PTFE syringe filters and were injected directly into the on-line SPE-UHPLC system.

2.4. Preparation of electrospun nanofibers

Polyamide 6 (PA6) was dissolved in a solution of formic acid and acetic acid (1:2 v/v) at a 12 wt% concentration of PA6. A nanospider was used for the electrospinning. The applied voltage was −24.5 kV (the collecting electrode) and + 55.5 kV (the active electrode). The distance between the electrodes was 198 mm. The humidity level during electrospinning was 32% and the temperature was 22.1 °C. Nanofibers were collected on an antistatic spunbond nonwoven, which moved along the collecting electrode at a constant speed of 90 mm min^{-1}. The surface weight of the obtained nanofibers was 0.75 g m^{-2}.

2.5. Preparation of nanofibrous extraction pre-columns

A nanofibrous extraction pre-column was prepared manually by packing about 40 mg of PA6 nanofibers into a column cartridge (5 × 4.6 mm), which was then placed into a guard pre-column holder. The extraction pre-column was connected with the system using UHPLC fittings. The sorbent was activated with 100% acetonitrile for 15 min with an increasing flow rate from 0.1 mL min^{-1} to 1 mL min^{-1} followed by washing with water for 5 min at a flow rate of 1 mL min^{-1}.

2.6. UHPLC column-switching analysis

The on-line SPE-UHPLC method was used for the simultaneous extraction and determination of BPA in water samples. On-line extraction was carried out by the extraction pre-column filled with nanofibers. Separation was performed on a Supelco Ascentis® Express C18 (10 cm × 4.6 mm) analytical column with a particle size of 5 μm. The washing mobile phase consisted of water and methanol 95:05 (v/v) and the gradient elution mobile phase consisted of water (solvent A) and acetonitrile (solvent B).

A portion of the 50 μL sample solution was injected into the extraction pre-column. The washing mobile phase was used for sample clean-up directly on the extraction pre-column. The pre-column was washed for one minute at a flow rate of 1 mL min^{-1}. BPA was pre-concentrated on the pre-column and the analytical column was equilibrated to the initial conditions of the gradient during this step. The valve was switched at a 1.0-min interval. Thereafter, BPA was eluted from the pre-column onto the analytical column. The gradient program started at the beginning of the analysis at 50% B. The concentration was changed within 2 min to 60% B and after that within 0.5 min to 100% B. Equilibration of the analytical column back to the initial conditions started in the 3.0rd min. The column oven temperature was set at 35 °C for both columns (analytical and extraction). The detection of BPA was carried out using a fluorescence detector set at an excitation wavelength of 225 nm and an emission wavelength of 320 nm. The total run time including the extraction step was 4.30 min.

3. Results and discussion

The on-line coupling of nanofibrous extraction directly with chromatographic separation in one analytical tool was a crucial part of this

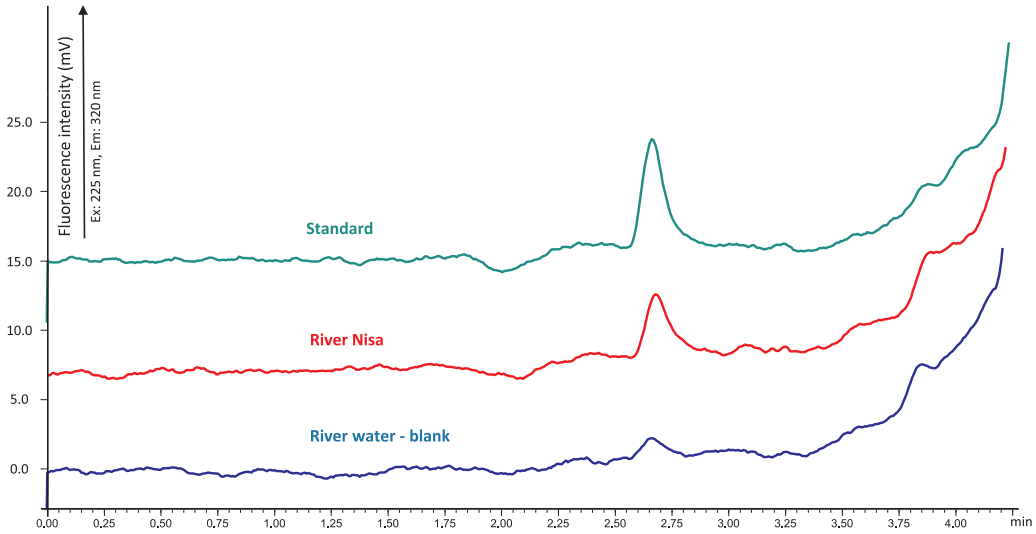

Fig. 1. The chromatograms after on-line extraction on polyamide 6 nanofibers: a standard solution of bisphenol A (5 μg L^{-1}) (the upper line); a chromatogram of contaminated Nisa River water (the middle line); a chromatogram of the blank solution of river water (the bottom line).

work. Therefore, both dimensions had to be adapted to the highest possible compatibility. The nanofibers' behaviour, column packing influence on extraction efficiency, stability in high back-pressure, and washing/elution solvents were the tested objectives in our study.

3.1. Optimization of the on-line SPE-UHPLC nanofibrous extraction procedure

The tested parameters of the extraction were the composition and the flow rate of the washing mobile phase and the duration of the extraction step. The concentration of the standard solution of BPA was 0.5 mg L^{-1}. An injection volume of 50 μL was chosen as the maximum possible volume of the injection loop. The back-flush extraction mode was used to avoid undesirable peak tailing during BPA elution.

The composition of the washing mobile phase was the first tested parameter. The mixtures of the organic solvent and water were tested at concentrations ranging from 0% to 50% of organic solvent. Methanol and acetonitrile were chosen as the organic solvents. These solvents are commonly used for solid phase extraction procedures and the stability of nanofibers in these solvents was confirmed in our previous study. The change in BPA peak area was monitored, and as we expected, the peak area decreased with the increasing proportion of the organic phase. The washing mobile phase containing 5% methanol in water was determined as optimal to avoid the loss of BPA during the extraction process. Using that washing mobile phase, the decrease of the peak area of BPA was minimal (less than 7%). The washing mobile phase with 5% methanol caused the majority of the impurities in the real samples to be washed out during the washing step. The flow rate was tested in the range from 0.5 mL min^{-1} to the 2 mL min^{-1}. It was possible to use the higher flow rates in the UHPLC system because the nanofiber column showed very low flow resistance. The duration of the extraction step depended on the valve switching interval and therefore, this parameter was tested in the range from 1 to 10 min. Extending the duration of the washing step did not offer a more efficient elution of matrix interferences. Thus, to shorten the analysis time as much as possible, the washing period was set at 1 min. The final optimal conditions of the nanofiber extraction procedure included using 5% methanol in water as the washing mobile phase and a flow rate of 1 mL min^{-1} for one minute.

In the next step, the UHPLC conditions of separation were optimized. Three different analytical columns with different chemistries were tested: Supelco Ascentis® Express C18 (10 cm × 4.6 mm, 5 μm), Phenomenex Kinetex Phenyl-hexyl (10 cm × 4.6 mm, 5 μm), and Phenomenex Kinetex Biphenyl (10 cm × 4.6 mm, 5 μm). For all of the columns, the same gradient mobile phase consisting of water (solvent A) and acetonitrile (solvent B) was used. The retention time of BPA and the peak shape were evaluated and compared. The Supelco Ascentis® Express C18 (10 cm × 4.6 mm) column with a particle size of 5 μm enabled a faster analysis and was chosen for the final conditions. Analytical separation was carried out using a gradient mobile phase elution. The final composition and program of the gradient elution is depicted in the subsection entitled "*UHPLC column-switching analysis*". A chromatogram of the standard solution (a concentration of 5 μg L^{-1}) after the on-line SPE-UHPLC process is shown in Fig. 1 (the upper line).

3.2. Stability of the nanofibers

The stability of the polyamide nanofibers during the on-line experiments was tested as well. The cartridge with the nanofibrous sorbent was weighed before and after the experiments. Neither dissolution nor a loss of the polyamide nanofibers was observed after all analyses. About 700 analyses were performed on the nanofiber cartridge. The problem with the reproducibility of packing the nanofibers was eliminated by reusing the nanofibrous precolumn multiple times. A scanning electron microscope (SEM) was used for observing the shape shifts of the tested nanofibers and for evaluating changes in the diameter and structure of the nanofibers. The nanofibers were slightly mechanically deformed, but no significant changes to their diameter were observed. The nanostructure remained the same (Fig. 2).

3.3. Reproducibility/influence of column packing on extraction recovery and repeatability

As stated above, the extraction precolumn was stable and it was possible to use it repeatedly. Despite this fact, the influence of various packing and different weights of nanofibers on extraction efficiency was tested. Five types of extraction pre-columns filled with different amounts of nanofibers (12, 18, 24, 36 and 40 mg) were prepared according the procedure that was described in the subsection entitled *"Preparation of nanofibrous extraction pre-columns"*. A standard solution of BPA with a concentration of 500 μg L^{-1} was used. The extraction efficiencies (evaluated as peak areas) of five pre-columns for the analysis of BPA were compared. The peak area of BPA after on-line extraction on the precolumn filled with the greatest weight of nanofibers (40 mg) was deemed 100%. Interdependence between the weight of nanofibers and the peak area of BPA was proven. Peak areas increased as the amount of nanofibers used in the extraction precolumn increased up to the weight of 23 mg and then it remained about 100%. The influence of the weight of the nanofiber mat on relative extraction efficiency is depicted in Fig. 3. The repeatability of the extraction step on

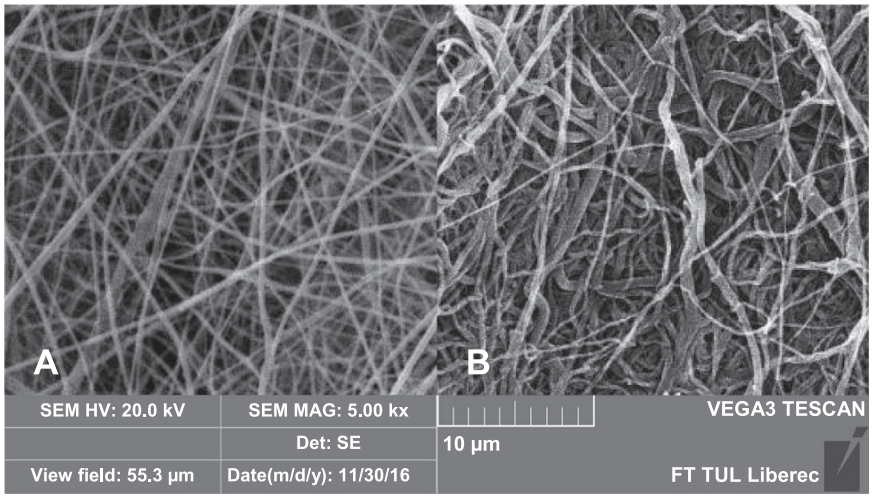

Fig. 2. The structure of nanofibers observed by a scanning electron microscope before (A) and after (B) all of the extractions and analyses.

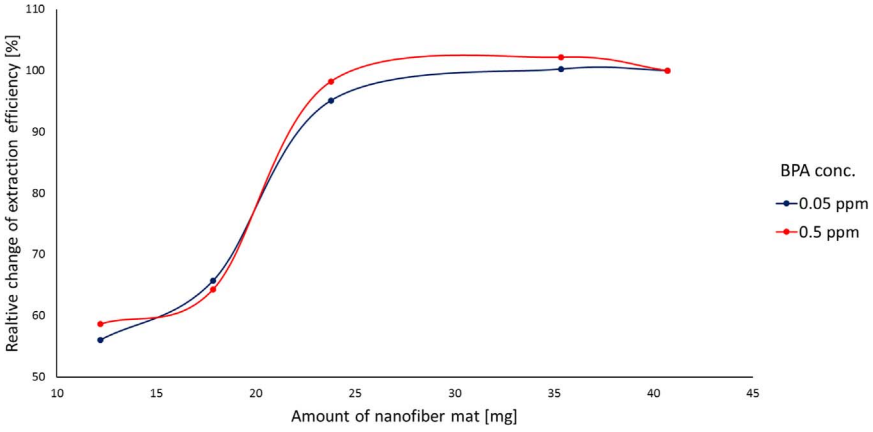

Fig. 3. The effect of the amount of nanofibrous sorbent in the extraction column on relative extraction efficiency; tested at two concentration levels (0.5 ppm and 0.05 ppm).

each nanofibrous precolumn was tested at two different concentration levels of BPA (50 and 500 µg L^{-1}). Repeatability was also affected by the amount of nanofibers. RSD values lower than 1.0% were observed with 36 and 40 mg of PA6 in the extraction precolumn (Table 1). The peak shapes were also different with each weight of nanofibers. Peak symmetry was better and the peak of BPA was narrower with a higher amount of nanofibers (a fully filled cartridge) than with non-fully filled cartridges. The values of the repeatability and the tailing factors are summarized in Table 1. All these effects could be explained by the limitation of dead volumes and by the ability to change the contact area when a higher weight of nanofibers was pressed into the column. With a higher weight of nanofibers, the extraction precolumn was fully filled and there was a limited space for void volume. The verification of the linear response was tested on extraction pre-columns packed with 12 mg and 40 mg of PA6. Good linearity (coefficients of correlation r2 = 0.9999 for PA6 12 mg and r2 = 0.9998 for PA6 40 mg) was achieved in the concentration range from 2 to 500 µg L^{-1} for both tested PA6 amounts. Linear regression parameters were described by the following equation: $A = (8.10^7 \pm 42671)c - (13044 \pm 8118)$ for PA6 40 mg and $A = (1.10^6 \pm 29298)c - (10871 \pm 5574)$ for PA6 12 mg, where A is the peak area of BPA and c is the concentration of BPA. All samples were measured in triplicate.

Table 1
The repeatability values of the on-line extraction procedure for different amount of nanofibers in extraction column, and tailing factor of BPA peak on the on-line SPE chromatogram.

Amount of nanofiber mat [mg]	RSD (%) n = 6		Tailing factor
	50 µg L^{-1}	500 µg L^{-1}	
12.20	1.2	1.0	2.3
17.85	0.7	0.7	1.6
23.78	0.8	1.6	1.7
35.36	0.8	0.3	1.4
40.70	0.4	0.3	1.3

3.4. Validation of the on-line nanofibrous extraction and chromatography method

Method validation was performed to demonstrate the suitability of the method for its intended use. The system suitability test (SST) covering the extraction step and following separation, and the method validation parameters of linearity, intra-and inter-day precision and trueness were evaluated.

The standard solution of BPA was injected eight times to calculate the SST parameters. Repeatability was tested at four different concentration levels (2, 5, 50, 500 µg L^{-1}) and it was expressed as relative standard deviation (% RSD) of the peak areas of BPA. RSD values were less than 5% and 2% for the 2 µg L^{-1} and 5 µg L^{-1} concentrations, respectively. Repeatability less than 1% was determined for the 50 and 500 µg L^{-1} concentrations. The next parameters, such as tailing factor and peak capacity, were tested at a concentration of 5 µg L^{-1}. The tailing factor of the peak of bisphenol A was 1.3 and peak capacity was 3.38. These results show that no undesirable diffusion on the extraction column was observed.

Method linearity was tested in the range from 2 to 500 µg L^{-1} using nine calibration points. Two series of samples for the determination of

Table 2
Intra- and inter-day precision values of the nanofibrous extraction procedure.

Spiked (μg L^{-1})	Intra-day precision RSD (%) n = 8	Inter-day precision RSD (%) n = 3
2	3.2	6.5
5	2.4	1.4
50	0.7	2.2
500	0.9	1.4

Table 3
Recovery values for BPA from river water samples at different concentration levels.

Spiked (μg L^{-1})	Found (μg L^{-1})	Recovery (%) n = 8
0	< LOD	
2	2.00	99.92 ± 3.20
5	5.01	100.25 ± 2.41
50	51.24	102.49 ± 0.72
500	511.45	102.29 ± 0.92

standard calibration and matrix calibration were prepared. A blank river water sample filtered through a PTFE filter (0.45 μm) was used for the dilution of the standard stock solution of BPA in the required concentrations of the matrix calibration. With that approach, the influence of the matrix (river water) was tested.

The limit of detection (LOD) was evaluated by comparing the signal to noise ratio (0.6 μg L^{-1}), and the limit of quantification (LOQ) was the lowest point of the calibration (2 μg L^{-1}). The intra-day precision of the method was assessed at four different concentration levels (2, 5, 50, 500 μg L^{-1}). Four sets of samples were prepared by diluting a standard stock solution of BPA with filtered river water. Each set (one concentration level) was prepared eight times and injected twice. The procedure was repeated for three days to determine inter-day reproducibility. The precision values (% RSD) are summarized in Table 2.

The accuracy parameter was evaluated by the determination of the recovery using a standard addition procedure with river samples spiked with a BPA solution at four different concentration levels (2, 5, 50, 500 μg L^{-1}), each in triplicate. At first, a blank river sample was analysed to ensure that it did not contain any BPA or that the concentration of BPA was below the limit of detection (depicted in Fig. 1 (the bottom line)). Thereafter, intentionally enriched samples and BPA solutions were measured and compared to calculate the recovery. The obtained recovery values are shown in Table 3.

3.5. Comparison with other methods

The main aim of the presented work was to demonstrate the possibility to use nanofibers as a sorbent in an on-line SPE-UHPLC system. BPA was chosen as the model analyte in the pilot study. The developed method is a fully automated procedure using polyamide 6 nanofibrous for extraction. As was reviewed by Abdel-Rehim et al. [4], there is a lack of works dealing with on-line analytical procedures using the nanofibers for extraction. We demonstrated that it is possible to use nanofibers in an on-line SPE-HPLC system and to reuse the nanofibers without any substantial changes occurring in the properties of nanofiber structure or function (Fig. 2). The lone work utilizing Nylon 6 nanofibers for the off-line membrane-based SPE followed by HPLC with UV detection for the determination of PBA in water was published in 2010 [19]. The authors described the possibility of reuse the nanofibrous membrane six times, and the method reached an LOD of BPA 0.15 μg L^{-1}[19]. Modern trends in the analysis of BPA in waters was recently reviewed by Salgueiro-González [20]. The authors concluded that the dominant sample pre-treatment technique is SPE. However, only a small percentage of the methods used on-line automated SPE systems [21–23]. Moreover, the LOQs of these methods were comparable with our results considering the analysed amount of sample (Table S1 Supporting information).

Table 4
The levels of bisphenol A found in the tested river water samples.

River sample	Concentration (μg L^{-1})
Elbe	< LOD
Nisa	2.28
Opava	< LOD
Orlice	< LOD
Úpa	< LOD

3.6. Analysis of real samples

The newly developed method was applied to determine bisphenol A in river water samples collected from the Nisa, Ohře, Úpa, Opava and Labe Rivers. Samples were collected in glass sampling bottles. The concentration of Bisphenol A was determined by interpolation in the matrix calibration curve. The amounts of BPA found in the randomly tested samples were lower than the limit of detection (LOD), except for the sample from the Nisa River. The chromatogram of the Nisa River sample is depicted in Fig. 1 (the middle line). Table 4 shows the concentrations of BPA found in all river water samples.

4. Conclusion

A new on-line SPE-UHPLC method using polyamide 6 nanofibers as the solid phase extraction sorbent was developed and successfully applied for the determination of bisphenol A in river water samples with high recovery, good precision, and a low limit of detection. The effect of nanofiber packing on extraction efficiency was tested as well. The results of this work showed that nanofibrous extraction depends not only on the amount of nanofiber polymer, but also on the packing process. The changes in the nanofibers' structure were tested and insignificant mechanical deformation was observed after 700 extractions. However, no significant changes in the nanofibers' diameter were found and the nanostructure remained intact.

In conclusion, the presented method showed a new approach that can be used in a column switching technique which allowed for a fast sample preparation step and reduced time of analysis. Other significant advantages included the use of a wholly automated workflow with a minimal influence of external conditions, minimal demands on the operator and the possibility to reuse the nanofibrous sorbent in a high-pressure chromatography system.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2017.08.098.

References

[1] N. Sasithorn, L. Martinova, Fabrication of silk nanofibres with needle and roller electrospinning methods, J. Nanomater. (2014).

[2] P. Sadilek, D. Satinsky, P. Solich, Using restricted-access materials and column switching in high-performance liquid chromatography for direct analysis of biologically-active compounds in complex matrices, Trac-Trends Anal. Chem. 26 (5) (2007) 375–384.
[3] E.M. Reyes-Gallardo, R. Lucena, S. Cardenas, Electrospun nanofibers as sorptive phases in microextraction, Trac-Trends Anal. Chem. 84 (2016) 3–11.
[4] M. Ahmadi, H. Elmongy, T. Madrakian, M. Abdel-Rehim, Nanomaterials as sorbents for sample preparation in bioanalysis: a review, Anal. Chim. Acta 958 (2017) 1–21.
[5] C. Fernandez-Ramos, D. Satinsky, B. Smidova, P. Solich, Analysis of trace organic compounds in environmental, food and biological matrices using large-volume sample injection in column-switching liquid chromatography, Trac-Trends Anal. Chem. 62 (2014) 69–85.
[6] X. Wu, Y. Li, X. Zhu, C. He, Q. Wang, S. Liu, Dummy molecularly imprinted magnetic nanoparticles for dispersive solid-phase extraction and determination of bisphenol A in water samples and orange juice, Talanta 162 (2017) 57–64.
[7] M. Sadeghi, Z. Nematifar, N. Fattahi, et al., Determination of bisphenol A in food and environmental samples using combined solid-phase extraction-dispersive liquid-liquid microextraction with solidification of floating organic drop followed by HPLC, Food Anal. Meth. 9 (6) (2016) 1814–1824.
[8] B. Chanbash, H.K. Lee, Alkylphenols and bisphenol-A in the coastal environment of Singapore and their rapid extraction from seawater and biological materials, Abstr. Pap. Am. Chem. S 222 (2001) (U443-U443).
[9] E. Radu, R. Stoica, C. Calin, et al., Validation of a RP-HPLC-UV method for the determination of bisphenol A at low levels in natural mineral water, Rev. Chim. 67 (2) (2016) 236–240.
[10] H.S. Lee, E.J. Park, J.H. Oh, et al., Bisphenol A exerts estrogenic effects by modulating CDK1/2 and p38 MAP kinase activity, Biosci. Biotechnol. Biochem. 78 (8) (2014) 1371–1375.
[11] P. Alonso-Magdalena, A.B. Ropero, S. Soriano, et al., Bisphenol-A acts as a potent estrogen via non-classical estrogen triggered pathways, Mol. Cell. Endocrinol. 355 (2) (2012) 201–207.
[12] Q.X. Zhou, G.Q. Wang, G.H. Xie, Preconcentration and determination of bisphenol A, naphthol and dinitrophenol from environmental water samples by dispersive liquid-phase microextraction and HPLC, Anal. Methods 6 (1) (2014) 187–193.
[13] X.L. Sun, J.C. Wang, Y. Li, et al., Highly selective dummy molecularly imprinted polymer as a solid-phase extraction sorbent for five bisphenols in tap and river water, J. Chromatogr. A. 1343 (2014) 33–41.
[14] J. Sajiki, Determination of bisphenol A in blood using high-performance liquid chromatography-electrochemical detection with solid-phase extraction, J. Chromatogr. B. 755(1-2) (2001) 9–15.
[15] J. Yin, Z.H. Meng, Y.S. Zhu, et al., Dummy molecularly imprinted polymer for selective screening of trace bisphenols in river water, Anal. Methods 3 (1) (2011) 173–180.
[16] S.J. Zhang, J.M. You, C.H. Song, et al., Purification and determination of bisphenol A and alkylphenol in river sediments by high performance liquid chromatography with fluorescence detection, Anal. Methods 4 (12) (2012) 4030–4036.
[17] T. Tanigawa, Y. Watabe, T. Kubo, K. Hosoya, Determination of bisphenol A with effective pretreatment medium using automated column-switching HPLC with fluorescence detection, J. Sep. Sci. 34 (20) (2011) 2840–2846.
[18] M. Careri, L. Elviri, A. Mangia, Development and validation of a method using on-line solid-phase extraction and liquid chromatography with ultraviolet detection for the determination of bisphenol A, octylphenol, and nonylphenol in groundwater, J. AOAC Int. 84 (5) (2001) 1383–1392.
[19] W. Shu-Yan, X. Qian, C. Tian-Shu, et al., Determination of bisphenol A in plastic bottled drinking water by high performance liquid chromatography with solid-membrane extraction based on electrospun nylon 6 nanofibrous membrane, Chin. J. Anal. Chem. 38 (2010) 503–507.
[20] N. Salgueiro-González, S. Muniategui-Lorenzo, P. López-Mahía, D. Prada-Rodríguez, Trends in analytical methodologies for the determination of alkylphenols and bisphenol A in water samples, Anal. Chim. Acta 962 (2017) 1–14.
[21] H. Gallart-Ayala, E. Moyano, M.T. Galceran, On-line solid phase extraction fast liquid chromatography–tandem mass spectrometry for the analysis of bisphenol A and its chlorinated derivatives in water samples, J. Chromatogr. A. 1217 (2010) 3511–3518.
[22] H. Gallart-Ayala, E. Moyano, M.T. Galceran, Analysis of bisphenols in soft drinks by on-line solid phase extraction fast liquid chromatography–tandem mass spectrometry, Anal. Chim. Acta 683 (2011) 227–233.
[23] L. Brossa, E. Pocurull, F. Borrull, R.M. Marce, A rapid method for determining phenolic endocrine disrupters in water samples, Chromatographia 56 (2002) 573–576.