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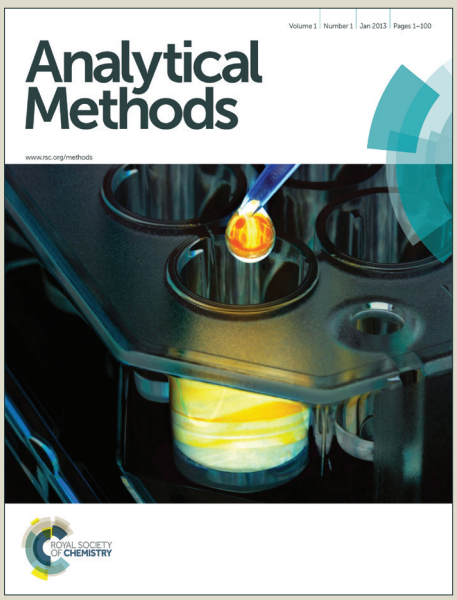

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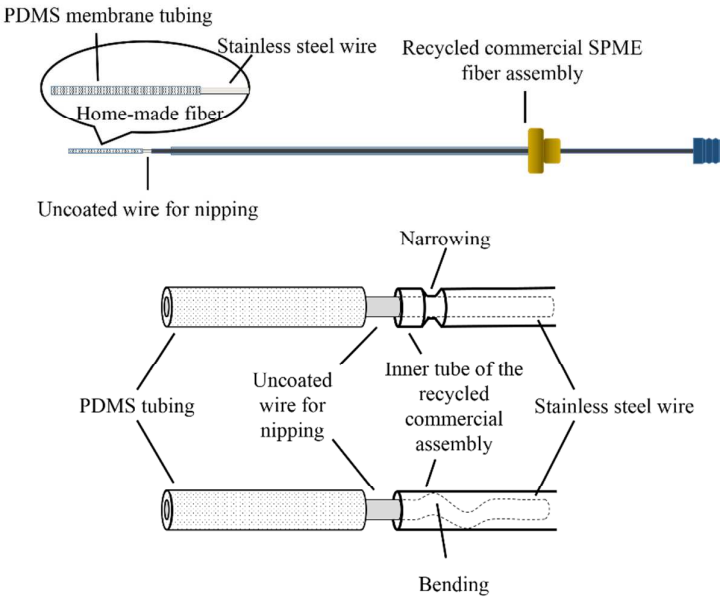

An extremely low-cost SPME fiber was prepared by mounting commercially available polydimethylsiloxane tubing on stainless steel wire with epoxy glue.

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Disposable solid-phase microextraction fiber coupled with gas chromatography-mass spectrometry for complex matrix analysis

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Abstract

Recent development of solid-phase microextration (SPME) in biological and environmental analysis calls for robust and low-cost fibers that are prone to batch preparation with good reproducibility. However, the expensive commercial fibers and low reproducible home-made fibers cannot fully cater these requirements. In the present study, an extremely low-cost (less than one dollar) SPME fiber with good intra-fiber (RSDs% ≤ 1.6%, n=6) and inter-fiber reproducibility (RSDs% ≤ 6.2%, n=6) was prepared by mounting a piece of commercially available polydimethylsiloxane (PDMS) tubing on a stainless steel wire with epoxy glue. This configuration was stable for more than 100 extraction/thermal desorption cycles. In addition, compared with previously used thicker PDMS fiber, the capability of direct thermal desorption in gas chromatograph of the present fiber not only simplified the sample preparation process but also enhanced the analysis sensitivity. Excellent inter-fiber reproducibility and low cost even made the fiber disposable when used in complex matrices.

Keywords: solid phase microextraction, disposable fiber, batch preparation, complex matrix

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1. Introduction

Solid-phase microextraction (SPME) is currently convinced to be very suitable for biological and environmental analysis among scientific communities.[1-8] Along with the latest exploration of SPME in these two areas, new requirements upon the SPME fibers were urged. First, since the biological and environmental samples are characterized as complex matrices, in which severe fouling effects may be imparted on SPME fibers during sampling,[4-8] fouling effects are required to be well handled to ensure the data accuracy, by utilizing fouling-resistant coatings or replacing the fouled fibers with new ones.[5] Second, as *in situ* analysis of sediments,[9,10] *in vivo* analysis of in vein blood [6,11] and semi-solid tissues [12,13] are emerging in SPME applications, new fibers should be robust enough to penetrate into compact matrices and be not fractured when embedded in tissues of living animals. Moreover, *in situ* environmental analysis may also need a large quantity of SPME fibers for sampling in multiple sites.[14,15] Therefore, SPME fibers that are accessible in quantity, robust and able to handle fouling effects are in demand for the current applications in biological and environmental analysis.

Nowadays, several commercial SPME fibers (or prototypes) can probably fulfill the aforementioned requirements for the current applications in biological and environmental analysis.[7,8,12,16] However, the relative high costs may still limited the extensive uses in these areas. Therefore, home-made fibers were frequently the attractive alternatives.[11,13,15]

The previously reported home-made SPME fibers introduced new coating materials,

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novel preparation methods [17-21] and robust supporting cores [22-24], which can address the requirements above. These home-made fibers have been utilized for many specific tasks, and were reported to be superior to the commercial ones on many aspects.[25] However, the inconsistent coating thicknesses resulted from the preparation methodologies spoiled the inter-fiber reproducibility, and made them difficult to be utilized for extensive applications, especially in the occasions large quantities of fibers were required. For example, one of the most used coating methods, sol-gel method, is sensitive to the initial conditions that significantly influence the coating thickness of the final products.[3] Another example is the preparation of molecularly imprinted polymer (MIP) coatings whose thickness is difficult to be controlled unless new techniques were introduced.[26,27] Therefore, developing preparation methodologies with reliable reproducibility is a vital consideration for extending SPME in environmental and biological analysis. Meanwhile, expense should be cut down with the newly developed preparation methodologies. For analysis of complex matrices, the low cost of the fiber makes it more flexible to replace the fouled fiber, which deviously copes with the fouling effects.

In the present study, a novel SPME fiber was proposed to meet the aforementioned requirements for complex matrix analysis. The fiber preparation methodology was fully evaluated in terms of reproducibility, lifespan and extraction efficiency. The fiber was also applied to the sampling of organophosphorus pesticides (OPPs) in fish muscle to evaluate its feasibility and sensitivity for analysis of complex matrix.

2. Materials and methods

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2.1. Chemicals and materials

The volatile compounds including benzene, toluene, ethylbenzene and *p*-xylene (BTEX) were purchased from Aladdin Co., Ltd. (Shanghai, China) and dissolved in methanol (HPLC grade, Anpel Co., Ltd., Shanghai, China) to prepare a stock solution with a concentration of 1000 $\mu g \cdot mL^{-1}$ for each compound. The standard solution of sixteen polycyclic aromatic hydrocarbons (PAHs) (1000 $\mu g \cdot mL^{-1}$) including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene and benzo[ghi]perylene were purchased from Sigma-Aldrich (St. Louis, MO, USA). Six oragnophosphorus pesticides (OPPs), propetamphos, parathion methyl, malathion, fenthion, quinalphos and triazophos (Dr. Ehrenstorfor Gmbh, Augsburg, Germany) were dissolved in methanol of HPLC grade to prepare a stock solution of 100 $\mu g \cdot mL^{-1}$ for each compound. The PDMS tubing (i.d. 212 μm, o.d. 300 μm) was purchased from Helixmark (Carpinteria, CA, USA) and the stainless steel wire (diameter of 127 μm) was purchased from Small Parts (Miami Lakes, FL, USA). Epoxy glue was purchased from Henkel Inc. (Mississauga, ON, Canada). SPME holder and fiber assembly (dimension of the out needle, 24 gague) for manual sample introduction were purchased from Supelco (Bellefonte, PA, USA).

2.2. Fiber preparation

Stainless steel wire was cut into pieces of 3 cm length and sonicated in acetone and deionized water for 15 min respectively, to remove the impurity. After drying at room

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temperature, one end of the pretreated stainless steel wire was coated with a thin layer of epoxy glue for about 1 cm. Then, a piece of well-cut PDMS tubing (1.0 cm) was wore on the end of the stainless steel wire covered with a very thin layer epoxy glue, and redundant glue was wiped away with a piece of tissue. The home-made fiber was dried in the air at room temperature for 24 h till the glue was solidified completely. A recycled commercial fiber assembly was used to fix the home-made fiber after removing the original coating core from the inner tube (Fig. 1a). Two methods were proposed to immobilize the home-made fiber to the inner tube. The first method was to narrow the inner tube on an appropriate place (about 0.2-0.5 cm away from the end of the inner tube) by using a clamp (Fig. 1b). About 0.2 cm of the uncoated core was left outside the inner tube for replacing the fiber after use. The other method was to little bend the uncoated end of stainless steel wire to a certain angle (about 10º) with tweezers to ensure the fiber being locked in the inner tube (Fig. 1c). Similarly to the first method, a short piece of uncoated stainless steel wire was left outside the inner tube. Another kind of PDMS tubing mounted fiber with the coating thickness of 165 μm was prepared and conditioned according to Ref. 13 without any further modification.

2.3. Headspace and direct immersion SPME of water

The home-made fibers were conditioned in the nitrogen flow at 250 ºC for 30 min in the GC injection port prior to use. BTEX solutions and PAHs solutions were prepared by spiking the stock solutions in deionized water. Twenty milliliter aqueous solution in 40 mL glass vial was prepared for headspace (HS) extraction, while 38 mL aqueous

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solution for direct immersion (DI) extraction. Magnetic stirring with a speed of 1500 rpm was utilized for both HS and DI extraction. During sampling, the SPME fiber assembly was pierced through the septum of the vial, and the PDMS tubing was exposed in the headspace or inside the solution to extract BTEX and PAHs, respectively. After a certain extraction duration, the fiber was retracted to the outer needle and transferred to the GC injection port for thermal desorption. The desorption time were 1 min and 10 min for BTEX and PAHs at 250 ºC, respectively. HS extraction of BTEX was also carried out with an autosampler for 100 circles sampling to evaluate the lifespan of a single fiber, with glass vials of 20 mL filled with 10 mL of solution.

2.4. SPME of spiked fish dorsal-epaxial muscle

Tilapias (*Oreochromis mossambicus*) about 700 ± 200 g were purchased from a local market. The dorsal-epaxial muscle was removed from the fish body and homogenized sufficiently with a blender. Two grams of the homogenized muscle was accurately weighted and spiked with OPPs stock solution. Both presently reported home-made fiber and the previously reported thicker PDMS fiber [13] were used to extract the OPPs. After being embedded into the spiked fish muscle for 20 min, the fibers were removed and rinsed with deionized water and wiped with Kimwipe. Then, the home-made fiber reported in the present study was directly introduced into the GC injection port for thermal desorption of 7 min (the optimized result of desorption time was presented in Fig. S1). While the previously reported thicker fiber was desorbed in 50 μL of nitrile for 60 min, and then 2 μL of the desorption solvent was injected into the GC for

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analysis (the optimized result of solvent desorption was presented in Fig. S2). Animal experiment was performed according to the Laboratory Biosafety Administration Protocols of Sun Yat-Sen University approved by the Laboratory Biosafety Committee of Sun Yat-Sen University.

2.5. Instrumental analysis

Instrumental analysis was performed on an Agilent 6890N gas chromatograph coupled to a 5975 mass spectrometer with an electron ionization (EI) source (Agilent Technologies, CA, USA). A HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm, Agilent Technologies, CA, USA) was used for separation. Ultra-pure helium was employed as the carrier gas. The temperature programs for BTEX and PAHs were presented in detail in the supporting information.

3. Results and discussion

3.1. Evaluation of the preparation methodology

PDMS was documented to be biocompatible and fouling-resistant,[4,5] and was a widely used fiber coating for a large range of analytes in various sample matrices.[12-15,28,29] Fibers would be more robust when stainless steel wires were used to replace the fragile fused silica supporting cores.[22-24] In the present study, both the PDMS tubing and stainless steel wires were commercially available, reproductive batch preparation of the home-made fiber was easily achieved with the simple fiber preparation methodology. It was also much notable that the cost for each fiber was less than one US dollar in total. Mayer et al. developed a commercial optic fiber as one of the

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cheapest SPME fibers, while the fiber might be fragile for environmental and biological analysis because of its glass core.[30]

As described in the experimental section, there were two approaches to fix the home-made fiber into the inner tube of SPME fiber assembly by narrowing the inner tube or little bending the uncoated end of the stainless steel wire inside the inner tube. By both methods, the fiber was firmly locked inside the inner tube and not scraped by the outer tube after repeated the procedure of pulling in/pushing out the inner tube for more than 100 times. However, we preferred the bending approach because the inner tube of the recycled SPME fiber assembly remained undamaged. The bending approach was also much simpler than the gluing approach, which was formerly proposed by Zewe and colleagues.[31]

Experimental results showed that the epoxy glue did not affect the extraction efficiency of the coating (Fig. S3), while it did make the coating firmly bind to the stainless steel wire mechanically. Lifespan experiments also proved that the home-made fiber could resist high temperature. One hundred times desorption in GC injection port at 250 ºC did not damage the extraction efficiency of the fiber (view section 3.2). And no negative effect was observed on the extraction efficiency after heat treatment under 280 ºC in nitrogen flow (data not shown).

3.2. Lifespan and extraction efficiency

A Gerstel MPS2 autosampler was used to evaluate the lifespan of the home-made fiber by continuous sampling from the headspace of BTEX solutions for 100 times. The sampling lasted for 5 min at 35 ºC after 2 min of incubation. During the 100

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sampling, there was no extraction efficiency decline observed with satisfactory RSDs ranging from 7.6% to 10.6% (Fig. 2).

Moreover, the extraction efficiency of the home-made fiber was also compared with a commercial PDMS fiber (thickness of 30 μm) for HS extraction of BTEX. Result showed that the obtained peak areas of the home-made fiber were 2.11 to 2.28 times those of the commercial fiber (Fig. S4), which was consistent with the ratio of two coating volumes. It might be concluded the approximately equivalent extraction efficiencies between the home-made fiber and commercial fiber taking the coating volumes into consideration.

3.3. Reproducibility

The intra-fiber and inter-fiber reproducibility of the home-made fiber was evaluated by both HS sampling of volatile compounds (BTEX) and DI sampling of less volatile compounds (PAHs) from the aqueous solutions.

For HS sampling of BTEX, aqueous solution was spiked to a concentration of 1 $\mu g \cdot mL^{-1}$ for each compound. The intra-fiber RSDs for six replicate extractions were less than 2%, and the inter-fiber RSDs ranged from 4.8% to 6.2% with six randomly selected fibers (Table 1). For DI sampling of less volatile compounds (16 PAHs), sampling was conducted at room temperature for 60 min with concentration of 1 $ng \cdot mL^{-1}$ for each PAH. The intra-fiber RSDs for 16 compounds were less than 10.0%, while the RSDs of six randomly selected fibers ranged from 5.5% to 11.8%. The relatively high RSDs for the less volatile compounds may result from the relatively short extraction time used in this experiment. For DI sampling of PAHs from the

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aqueous solution, the equilibrium times were much longer than 60 min, especially for the heavier molecules.

3.4. Extraction of OPPs from homogenized fish muscle

Under the pre-set extraction conditions and optimized desorption conditions (Figs. S1 and S2), the extraction efficiencies of OPPs from the spiked homogenized fish dorsal-epaxial muscle with the present home-made fiber and the previously reported thicker home-made fiber [13,28,29] were compared. The presently reported home-made fiber was directly introduced to the GC injection port for thermal desorption after extraction. As the desorption time was optimized, almost all the extracted analytes were introduced to the GC system for analysis, and high sensitivity could be realized. By contrary, solvent desorption was necessary for the thicker fiber due to the larger size. And only a small portion (2 μL out of 50 μL of the desorption solution) of the extracted analytes was injected into the GC/MS for analysis. Fig. 3 presented the higher sensitivity of the presently reported thinner fiber than the previously reported one after parallel sampling. Moreover, the utilization of direct thermal desorption also simplified the sample introduction procedure, eliminated errors introduced by the volatilization of desorption solvent, and avoided swelling of the fibers by solvents. However, on the occasion of LC analysis, where solvent desorption is inevitable, the thicker fibers would achieve higher sensitivity than our thinner fibers.[13] Therefore, it could be concluded that the presently reported home-made fiber would be more helpful to extract less polar analytes followed by GC analysis.

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The inter-fiber RSDs of six parallel extractions from the homogenized fish muscle were in the range of 8.4-17.9% for the present fiber, and 10.8-17.4% for the previous thicker fiber (Fig. 3). Good linearity was obtained in the range of 10-1000 $ng \cdot g^{-1}$, and the limits of detection (LODs) were also quite satisfactory for the analysis of complex samples (Table 2). The relatively high LOD for parathion methyl might originate from the matrix effects.

Fiber fouling is the most cumbersome issue for SPME applications in complex matrices. Matrix fouling changes the coating extraction properties and leads to data bias for parallel extractions. Although PDMS coating was reported to be fouling-resistant,[4,5] possible fouling cannot be fully excluded in severe fouling matrices, and the coating is still risky to be aged or scraped in sample matrices after several uses. Then, a new fiber should be used to replace the spoiled one. Whereas the inter-fiber reproducibility was guaranteed, no significant inter-fiber deviations would be introduced to the final results after replacing the spoiled fibers with new ones. In addition, the low cost of the presently reported fiber can even make it a disposable device, when the fouling effect is severe.

Furthermore, compared to the previous thicker fiber,[13,28,29] the presently reported thinner fiber would be less invasive to living animals when embedded in the tissues, and would be more suitable for *in vivo* sampling in future studies..

4. Conclusions

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In the present study, a simple preparation methodology was developed by mounting PDMS tubing on stainless steel wire with epoxy glue to prepare the home-made fiber. The fiber possessed appealing low cost, mechanically stable configuration and high thermal stability, as well as satisfactory intra- and inter-fiber reproducibility. In addition, higher sensitivity and simpler sample preparation procedure over a previously reported thicker PDMS fiber were obtained by directly introducing the fiber into GC injection port for thermal desorption after DI-SPME of complex matrix. These features met the requests raised for biological and environmental analysis, and declared the feasibility of this home-made fiber to be applied in these two fields.

Moreover, the present fiber was also applicable for conventional use in cleaner matrices. The capability of assembling this home-made fiber to an autosampler can improve analysis efficiency in laboratories.

It is notable that the methodology we used in the present study can be transferred to any other polymer tubings at the similar dimensions as that we employed, especially if the polymer tubing is commercially available.

Acknowledgments

This research was supported by National Science Fund for Distinguished Young Scholars (21225731), Research Fund for the Doctoral Program of Higher Education of China (20120171110003) and the Fundamental Research Funds for the Central Universities (131gjc11).

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Figure Captions:

Figure 1. (a) The schematic diagram of a recycled commercial SPME fiber assembly fixed with a home-made fiber. (b) Fix of a home-made fiber by narrowing the inner tube of the fiber assembly. (c) Fix of a home-made fiber by bending the uncoated end of the stainless steel wire.

Figure 2. Evaluation of the lifespan of a single home-made fiber.

Figure 3. Efficiencies of the previously reported thicker fiber [13,28,29] and the presently reported fiber for analysis of OPPs in homogenized fish dorsal-epaxial muscle. Extraction duration for both fibers were 20 min, spiked concentrations were 2.5 $\mu g \cdot g^{-1}$. Error bars are SDs of six parallel extractions with six fibers.

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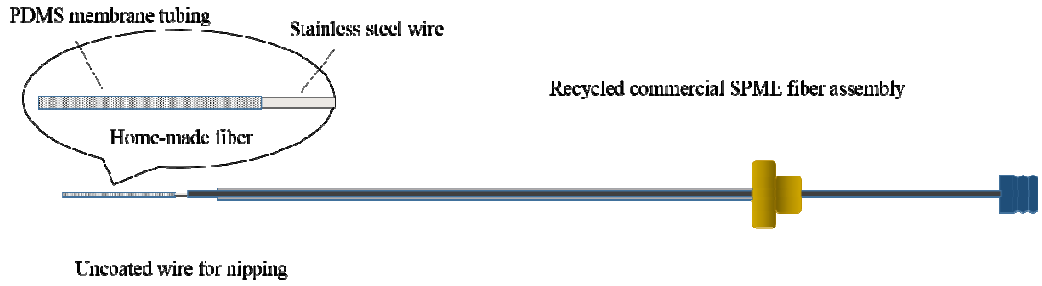
Figure 1.

(a)



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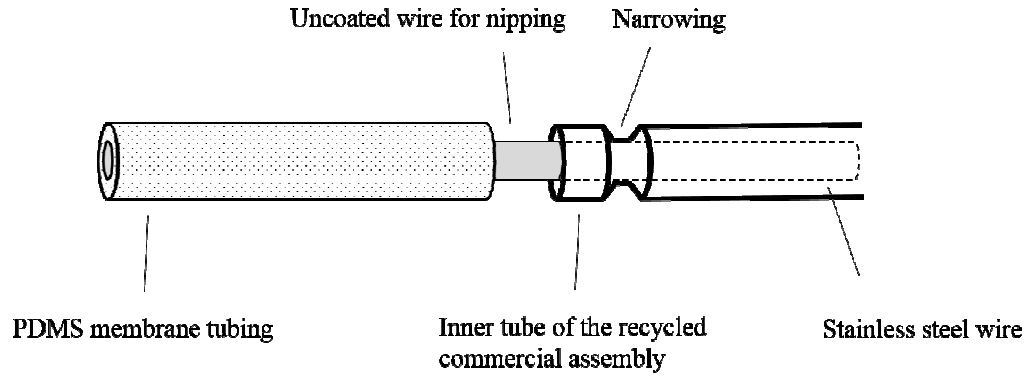

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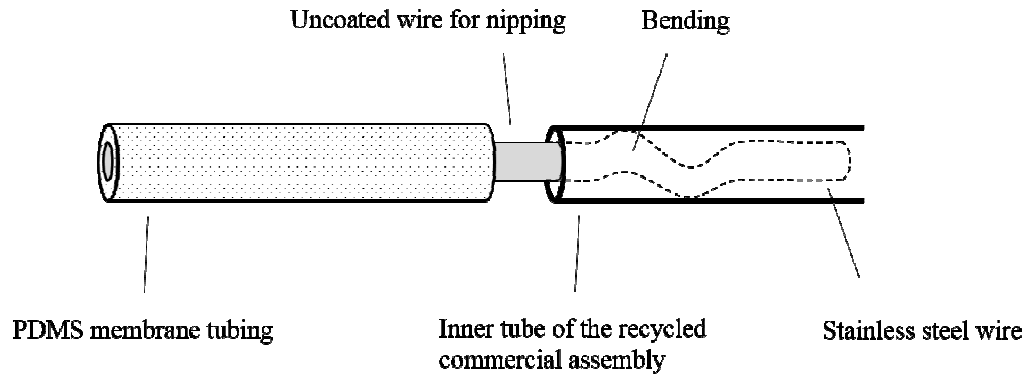

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Figure 2.

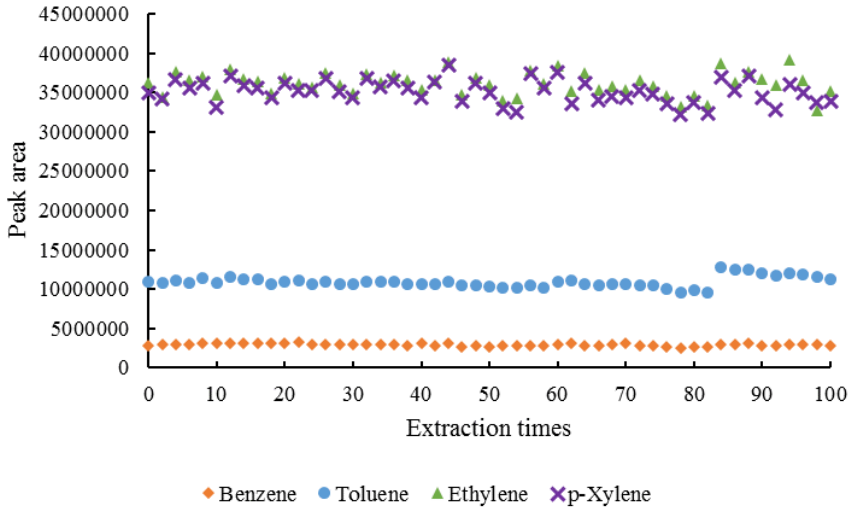

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Figure 3.

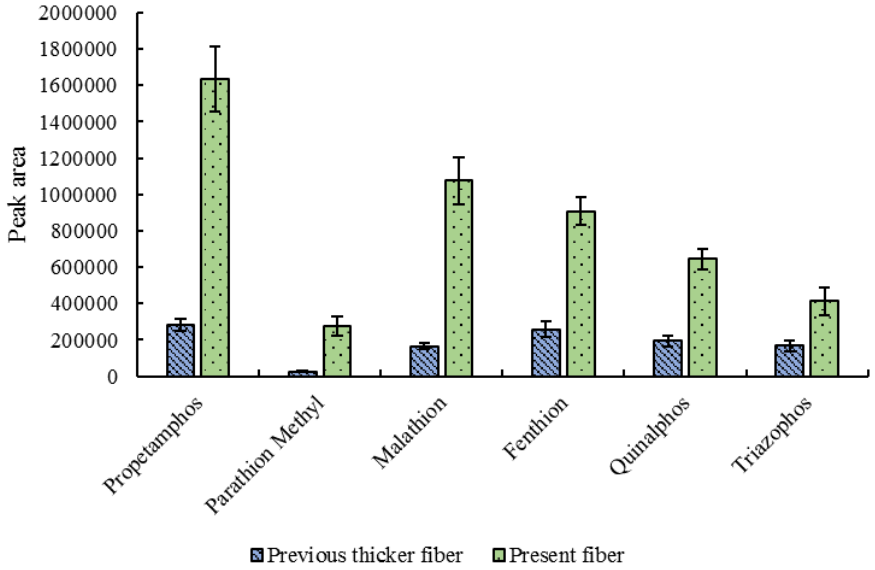

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Table 1. Intra-fiber reproducibility and inter-fiber reproducibility for extraction BTEX in aqueous solution.

Compounds	RSD (%)	
	intra-fiber (n=6)	inter-fiber (n=6)
Benzene	1.2	6.2
Toluene	1.7	5.3
Ethylbenzene	1.5	4.8
p-Xylene	1.6	4.9

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Table 2. Linearity (R^2) at the working range and LODs when the home-made fibers were used for the extraction of OPPs from homogenized fish muscle.

Compounds	R^2 (Working range)	LODs ($\mu g \cdot kg^{-1}$)
Propetamphos	0.9989 (10-1000 $ng \cdot g^{-1}$)	0.9
Parathion methyl	0.9930 (10-1000 $ng \cdot g^{-1}$)	7.5
Malathion	0.9531 (10-1000 $ng \cdot g^{-1}$)	3.1
Fenthion	0.9671 (10-1000 $ng \cdot g^{-1}$)	2.5
Quinalphos	0.9867 (10-1000 $ng \cdot g^{-1}$)	2.5
Triazophos	0.9882 (10-1000 $ng \cdot g^{-1}$)	0.3

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