



# A nanocomposite prepared from a zinc-based metal-organic framework and polyethersulfone as a novel coating for the headspace solid-phase microextraction of organophosphorous pesticides

Hasan Bagheri<sup>1</sup> · Hatam Amanzadeh<sup>2</sup> · Yadollah Yamini<sup>2</sup> · Mohammad Yaser Masoomi<sup>2</sup> · Ali Morsali<sup>2</sup> · Jamileh Salar-Amoli<sup>3</sup> · Jalal Hassan<sup>3</sup>

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## Abstract

The authors describe a zinc-based metal-organic framework/polyethersulfone nanocomposite (TMU-4/PES) coating deposited on a stainless steel wire via a single-phase inversion method. The nanocomposite represents a novel fiber coating for headspace solid-phase microextraction of organophosphorous pesticides (OPPs) from environmental water and soil samples. The synergistic effects of the high surface area and unique porous structure of TMU-4 as well as the rich  $\pi$  electron stacking and mechanical attributes of the PES polymer result in a high affinity of the composite for OPPs. Following thermal desorption, the OPPs were quantified by gas chromatography with a nitrogen-phosphorus detector. The preparation of the coating is simple, and the coated fiber is highly stable and reusable in that it can be used in about 100 consecutive extractions/desorption cycles. A central composite design was used for assessing the effect of the experimental parameters on the extraction process. Under optimized conditions, the limits of detection are in the 5–8 ng mL<sup>-1</sup> range for the OPPs diazinon, fenitrothion, malathion and chlorpyrifos. The average repeatability and fiber-to-fiber reproducibility are 6.5% and 8.7%, respectively. The method was applied to the trace determination of OPPs in (spiked) water and soil samples where it gave good recovery (88–108%) and satisfactory reproducibility (5.9–10.1%).

**Keywords** Sample preparation · Gas chromatography · Nitrogen-phosphorus detector · Water · Soil · Central composite design

## Introduction

Organophosphorous pesticides are a class of pesticides frequently used to control pests and prevent diseases that affect various fruits and vegetables [1]. The

extensive or inappropriate use of OPPs can result in the contamination of the atmosphere, water, soil, and agricultural products [2]. Therefore, it is of great importance to develop a sensitive and reliable analytical method for screening OPPs residues in environmental samples to prevent their detrimental effects on environmental pollution and human health.

Since its introduction by Pawliszyn and co-workers in 1990 [3], solid phase microextraction (SPME) has demonstrated unquestionable advantages as an efficient sample preparation technique for several applications over traditional methods in more than the last two decades. This technique offers numerous benefits such as minimum solvent use, integration of sampling and sample preparation steps, high sensitivity, simple operation, low cost, easy coupling with chromatographic techniques, and the possibility of an on-line analytical procedure [4, 5]. In SPME, the type and properties of the coating material is the most important key to improving its extraction efficiency (i.e., sensitivity, selectivity,

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✉ Yadollah Yamini  
yyamini@modares.ac.ir

<sup>1</sup> Chemical Injuries Research Center, Systems Biology and Poisonings Institute, Baqiyatallah University of Medical Sciences, Tehran Postal code 1435916-471, Iran

<sup>2</sup> Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

<sup>3</sup> Toxicology and Poisoning Research Center, Department of Toxicology, Faculty of Veterinary Medicine, University of Tehran, P.O. Box 14155-6453, Tehran, Iran

repeatability, and reproducibility) [6]. Although during the last years several different commercial SPME fibers have been supplied to the market. Unfortunately, they have some drawbacks such as fragility, significant batch-to-batch variation, and limited sorption capacity. Thus, many researchers have focused on developing various novel home-made SPME fiber coatings with high extraction efficiency, high thermal and chemical stability, and low cost using novel preparation procedures and new sorbent materials. Most of the sorbents developed for SPME include liquid/polymeric ionic liquids [7, 8], metal/metal oxide nanoparticles [9, 10], carbon-based nanomaterials (e.g., carbon nanotubes and graphene) [11, 12], conducting polymers [13], and molecularly imprinted polymers [14]. Also, to obtain a robust and uniform coating with a controllable thickness, different coating techniques, such as physical coating, sol-gel technique, chemical bonding and electrochemical procedures, have been successfully employed for the preparation of SPME fiber coatings [15–19].

Metal-organic frameworks (MOFs), which are composed of metal ions and organic linkers, are an intriguing class of hybrid materials that have received great attention owing to their impressive structural properties. The most remarkable structural features of MOFs are the ultrahigh porosity (up to 90% free volume) and extremely high surface area (up to more than  $5000 \text{ m}^2 \text{ g}^{-1}$ ), which play an important role in functional applications, typically in hydrogen storage, gas separation, sensing, and catalysis [20]. Also, these unusual features have made MOFs an attractive choice for being applied to adsorption, especially in sample pretreatments [21–23]. Despite the remarkable advances in MOFs, the main issue in their application as the sorbent phase in SPME is associated with the coating procedure where the preparation of MOFs on fiber and conditioning of SPME fiber are time-consuming.

Here, a quick phase inversion process was applied to prepare the composite coating involving zinc metal-organic framework (TMU-4) and polyethersulfone on the unbreakable metallic substrate. Typically, this technique provides a useful approach for coating the polyethersulfone polymer/nanoparticles composites as the sorbent material for SPME directly on the SS wire. In addition, the method offers the advantages of a quick way for the preparation of fibers because the coating process is only based on physical phase inversion method and involves no chemical reaction. Furthermore, the composite film surrounding the SS wire is slightly shrunk during the drying process, resulting in a coating that covers the fiber tightly. The prepared SPME coating was applied for the extraction of ultra-trace amounts of organophosphorous pesticides from water and soil samples.

## Experimental

### Reagents and materials

Zinc acetate ( $\text{Zn}(\text{OAc})_2$ ) and 4,4'-oxybis(benzoic acid) ( $\text{H}_2\text{oba}$ ) were obtained from Merck Company (Darmstadt, Germany, [www.merckmillipore.com](http://www.merckmillipore.com)). The ligand 4-bpdb (1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene) was prepared by the reported method [24]. The OPPs standards of diazinon, fenitrothion, malathion, and chlorpyrifos were purchased from Sigma-Aldrich (St. Louis, MO, USA, [www.sigmaaldrich.com](http://www.sigmaaldrich.com)). Polyethersulfone (PES) was purchased from BASF (Ludwigshafen, Germany, [www.basf.com](http://www.basf.com)). All of the organic solvents such as methanol and acetone were of HPLC-grade and obtained from Sigma-Aldrich. The ultra-pure water was prepared by a model Aqua Max-Ultra Youngling ultra-pure water purification system (Dongan-gu, South Korea, [eng.younglin.com](http://eng.younglin.com)). 5 mg of each analyte (OPPs) was dissolved in 5.0 mL HPLC grade methanol to prepare a standard solution of  $1000 \text{ mg L}^{-1}$  and working standard solutions were prepared daily by appropriately diluting the stock solution in methanol. All solutions were stored at  $4 \text{ }^\circ\text{C}$  protected from light.

### Apparatus

Gas chromatographic measurements were performed on Varian CP-3800 gas chromatograph equipped with a nitrogen phosphorus detector and a split/splitless injector. The CP-Sil 8CB Varian wall coated fused silica capillary column ( $30 \text{ m} \times 0.25 \text{ mm i.d.}$ , film thickness  $1.0 \text{ }\mu\text{m}$ ) was used for all chromatographic separations. The injector was operated in the splitless mode and was maintained at  $220 \text{ }^\circ\text{C}$ . The detector temperature was held at  $300 \text{ }^\circ\text{C}$ . High purity nitrogen ( $\geq 99.999\%$ ) was used as the carrier gas at the constant flow rate of  $1.2 \text{ mL min}^{-1}$ . The oven temperature was initially set at  $70 \text{ }^\circ\text{C}$  for 2 min, ramped at  $5 \text{ }^\circ\text{C min}^{-1}$  to  $200 \text{ }^\circ\text{C}$ , and then increased by  $10 \text{ }^\circ\text{C min}^{-1}$  to  $280 \text{ }^\circ\text{C}$ , at which it was held for 10 min. The flow rate of the makeup gas (nitrogen) was  $25 \text{ mL min}^{-1}$  for NPD. A Varian Workstation 5 software was used for data collection and processing. Scanning electron microscope (SEM) model Mira3 LM Tescan (Brno, Czech Republic) was used to evaluate the surface morphology of the nanocomposite fiber coatings. The thermal behavior of the coatings was measured on a TGA-STA 1500, from Rheometric Scientific STA (Los Angeles, CA, USA) at a rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in a static atmosphere of argon.

### Fabrication of TMU-4/PES nanocomposite coated SPME fiber

TMU-4 ( $\{[\text{Zn}_2(\text{oba})_2(4\text{-bpdb})].2\text{DMF}\}_n$ ) was synthesized according to previously reported method [24]. Briefly, it

was prepared by sono-chemical reaction of a mixture of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  and N-donor ligand 4-bpdb for 60 min. Comparison between the simulated and experimental (resulting from the sono-chemical powder) powder X-ray diffraction (PXRD) pattern revealed that TMU-4 was successfully synthesized via sono-chemical reaction (Fig. S1). The TMU-4/PES nanocomposite coating was prepared via the phase inversion method. 0.1 g PES powder was first dissolved in 1.0 mL dimethylformamide (DMF) and stirred for 2 h at room temperature to obtain a solution containing 10 wt% PES. Then, 100 mg of TMU-4 powder was added to the above solution and it was sonicated until the suspension became completely dispersed and homogeneous. The SS wires with a length of 5.0 cm were used to fabricate the SPME fibers. Prior to coating, the SS wire was washed sequentially with acetone, methanol, and then gently with ultrapure water, and dried in the air. The TMU-4/PES suspension was then cast on the SS wire by dipping the tip 1.0 cm segment of the SS wire into the suspension. Afterwards, the coating was precipitated by immersing it into a coagulation bath of distilled water at room temperature for 2 h. The fiber was dried at room temperature. The coating thickness obtained after described coating procedure was around 30  $\mu\text{m}$ . Then, the fiber was installed into the SPME device and was conditioned in the GC injection port under nitrogen flow at 220 °C until a stable GC baseline was obtained.

### Headspace solid phase microextraction procedure

All SPME experiments were performed at the mode of headspace in the aqueous samples. To perform the extraction, 10 mL of a sample solution containing 30% w/v NaCl was placed in the 15-mL glass sample vial. Magnetic stirring with a Teflon-coated stir bar was used to stir the solution at the maximum rate (1200 rpm). The vial was sealed with a Teflon-faced septum and its temperature was adjusted to  $75 \pm 1$  °C. A thermostatic water bath was used to control the extraction temperature. The needle of the SPME holder was passed through the septum and the nanocomposite coated SPME fiber was pushed to be exposed to the headspace above the sample solution. After 40 min extraction, the fiber was removed from the vial and immediately inserted in to the GC inlet for thermal desorption at 220 °C in the splitless mode for 6 min.

### Sample preparation

Water samples including well and farm waters were collected from Tehran farmlands. These samples were analyzed immediately after sampling without any pretreatment process. Soil samples were collected from a farmland. For the extraction of

OPPs from soil samples, the following procedure was performed: after being air-dried at room temperature, 1.0 g of the soil sample was accurately weighed and placed into a centrifuge tube and was extracted with 2.0 mL of methanol for 20 min using a sonicator. Then, the mixture was centrifuged at 3000 rpm for 5 min. The supernatant liquid was filtered by PTFE syringe filter (13 mm, 0.22  $\mu\text{m}$ ) to remove particles and was evaporated to dryness under nitrogen flow. Afterwards, the dry residue was re-dissolved in 100  $\mu\text{L}$  of methanol and diluted with 10 mL of water and, then, the HS-SPME process was followed according to the method used for the water samples.

### Data analysis and statistical methods

Response surface methodology (RSM) is a remarkably effective and efficient design of experimental technique for analyzing more than one factor at a time [25]. Many studies have indicated that it is useful for developing, improving and optimizing processes. Thus, here, the response surface methodology based on CCD was employed to simultaneously optimize the effective variables in extraction efficiency of the HS-SPME method. CCD consists of factorial points, star or axial points ( $\alpha$ ) and center points. Therefore, the total number of design points needed ( $N$ ) is determined by the following equation:

$$N = 2^f + 2f + C_p$$

Where  $f$  is the number of significant factors,  $2^f$ ,  $2f$ , and  $C_p$  are the number of the factorial points, axial points and center points, respectively. Here, a CCD consisting of an eight-factorial design with six star points positioned at  $\pm \alpha$  from the center of the experimental domain was performed. Also, the analysis of variances (ANOVA) was used to assess the influence of the main parameter and the interaction effects between them. To this end, design generation and statistical analyses were performed by means of the Design-Expert software 8.0.6 trial version (Stat-Ease Inc., MN, USA).

## Results and discussion

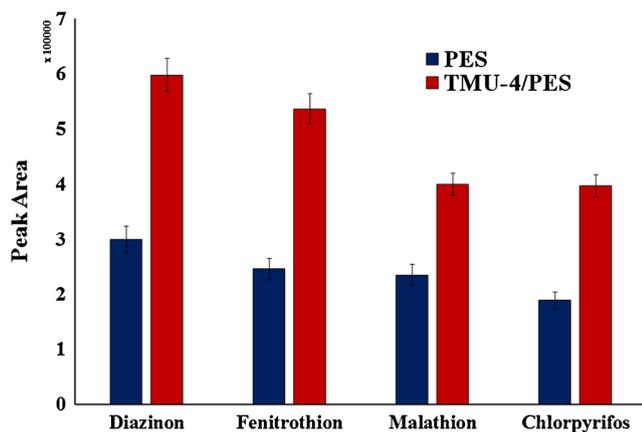
### Choice of materials

To utilize a material as a sorbent in SPME, it should be stable under extraction conditions, capable of interacting with target analytes through different mechanisms, robust, and of high thermal stability for GC applications. Most of the reported MOFs in the literature have not the mentioned features. Zn-based MOF (TMU-4) not only is stable at high temperatures and in most solvents but also it showed outstanding extraction efficiency due to rich

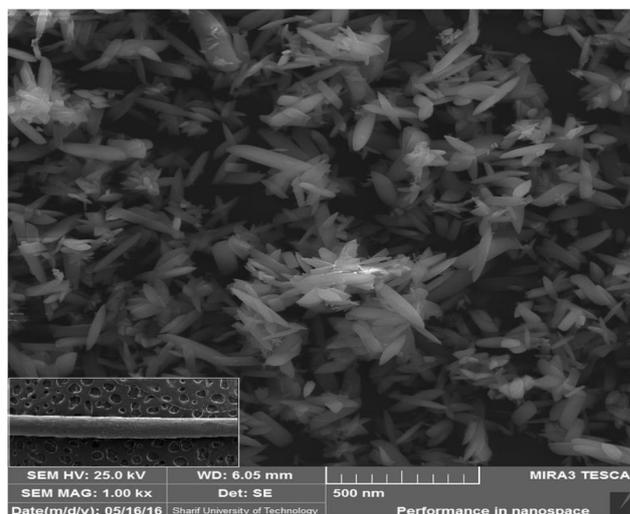
$\pi$ - $\pi$  stacking interactions. In the coating, Zn-based MOF is the main adsorptive material and PES is used for adhesion of the coating on the SS substrate. Besides, PES can contribute to the extraction of the analytes due to  $\pi$ - $\pi$  stacking interactions.

### Optimization of composition and characterization of fiber coating

The extraction ability of the TMU-4/PES composite coating was preliminarily evaluated in comparison with the PES coating under the same operation conditions. The coatings thickness was around 30  $\mu\text{m}$ . As shown in Fig. 1, the extraction efficiency of the composite coating is much higher than that of PES, and it can be attributed to the high surface area and unique porous structure of TMU-4 and the rich  $\pi$  electron stacking of PES. In the next step, the ratio of MOF and PES concentrations during the nanocomposite preparation process was optimized to achieve the maximum extraction efficiency of the SPME fiber towards OPPs. Therefore, various concentrations of the PES solution including 5, 10, 15, and 20 wt% were prepared in 1 mL DMF. Then, 100 mg of the MOF powder was dispersed into these solutions and the coating process was followed according to the procedure described in section 2. 3. As can be seen in Fig. S2, the peak areas of OPPs rose up to 10 wt% PES. Thus, 10 wt% PES have a beneficial effect on the extraction of the analytes. Consequently, the synergistic effect of MOF and PES causes an increase in the response. The thermal gravimetric analysis shows that the coating is stable at temperatures below 310  $^{\circ}\text{C}$  (Fig. S3). The SEM images of the coating are shown in Fig. 2. The fiber surfaces became porous after coating, and the morphologies of the coatings on the fibers were relatively homogeneous.



**Fig. 1** Comparison of the extraction performance for OPPs between PES coated fiber and TMU-4/PES coated fiber. Conditions: Extraction temperature, 70  $^{\circ}\text{C}$ ; extraction time, 20 min; salt, 20% w/v; stirring rate 1200 rpm, desorption temperature, 220  $^{\circ}\text{C}$



**Fig. 2** Scanning electron micrographs of coated SPME fiber

### Optimization of HS-SPME procedure

There are various parameters that potentially affect the extraction performance of the HS-SPME-GC-NPD method. Based on OPPs properties and the literature regarding the improvement of the extraction efficiency of the analytes, variables such as extraction temperature, extraction time, salt addition (extraction parameters), and desorption temperature and time (desorption parameters) were selected as the most critical ones. Respective data and Figures (Fig. S4 and S5) are given in the Electronic Supporting Material. The following experimental conditions were found to give best results: (a) Extraction temperature of  $75 \pm 1$   $^{\circ}\text{C}$ ; (b) Extraction time of 40 min; (c) NaCl addition of 30% w/v; (d) desorption temperature of 220  $^{\circ}\text{C}$ ; (e) desorption time of 6 min.

$$\begin{aligned} \text{Total peak area} = & +1.935 \times 10^7 - 1.272 \times 10^6 A + 3.026 \\ & \times 10^6 B + 1.709 \times 10^6 C + 1.087 \\ & \times 10^6 AB + 22177.42 AC - 6.431 \\ & \times 10^5 BC - 7.433 \times 10^5 A^2 - 1.214 \\ & \times 10^6 B^2 \end{aligned}$$

### Evaluation of method performance

The analytical evaluation parameters for HS-SPME of OPPs using the TMU-4/PES nanocomposite coated fiber including linear range with correlation coefficient ( $R^2$ ), limit of detection (LOD), limit of quantitation (LOQ), single fiber repeatability and fiber-to-fiber reproducibility were examined under the optimized conditions.

**Table 1** Analytical characteristics of the HS-SPME-GC-NPD method for extraction and determination of OPPs

Compound	LOD <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	LOQ <sup>b</sup> ( $\mu\text{g L}^{-1}$ )	LR <sup>c</sup> ( $\mu\text{g L}^{-1}$ )	R <sup>2</sup>	One fiber repeatability (RSD <sup>d</sup> % $n=5$ )	Fiber to fiber reproducibility (RSD % $n=3$ )
Diazinon	0.005	0.015	0.015–50	0.9963	6.0	8.1
Fenitrothion	0.006	0.020	0.02–50	0.9943	7.3	9.1
Malathion	0.008	0.025	0.025–50	0.9960	6.4	8.5
Chlorpyrifos	0.008	0.025	0.025–50	0.9918	6.1	9.0

<sup>a</sup> Limit of detection<sup>b</sup> Limit of quantitation<sup>c</sup> Linear range<sup>d</sup> Relative standard deviation

Calibration curves were plotted using eight spiking levels of the target compounds at concentrations ranging from 0.015–50  $\mu\text{g L}^{-1}$ . As can be seen in Table 1, the HS-SPME-GC-NPD method showed satisfactory linearity for all the tested analytes from the LOQs to 50  $\mu\text{g L}^{-1}$ , with correlation coefficients above 0.9918. LODs and LOQs defined respectively as three and ten times the signal-to-noise-ratio were assayed by extracting an aqueous solution spiked at different levels. The values of LODs and LOQs were varying from 0.005 to 0.008  $\mu\text{g L}^{-1}$  and 0.015 to 0.025  $\mu\text{g L}^{-1}$ , respectively, which are satisfactory for the trace determination of analytes in the real samples. The repeatability of the method using the single nanocomposite coated fiber (run-to-run RSD), investigated by five replicate analyses, varied between 6.0 and 7.1%. The fiber construction reproducibility (fiber-to-fiber RSD) was also evaluated applying three different fibers prepared using the same way, and was found in the range of 8.1–9.1%. These results proved that the repeatability of the HS-SPME-GC method and also reproducibility of the fiber construction are reliable. The lifetime of the coating over time is an important factor in the SPME technique, which can affect the precision and accuracy of the analysis. To evaluate the endurance and reusability of the TMU-4/PES coated fiber, a single fiber was subjected to a series of

consecutive extractions for OPPs from aqueous solutions. The results showed that a single fiber can be used up to 100 headspace extraction/desorption cycles without any significant loss of its extraction performance (Fig. S6). Hence, 100 extraction/desorption cycles were assumed as the admissible lifetime of the fiber, which indicates the coating property is quite stable and robust.

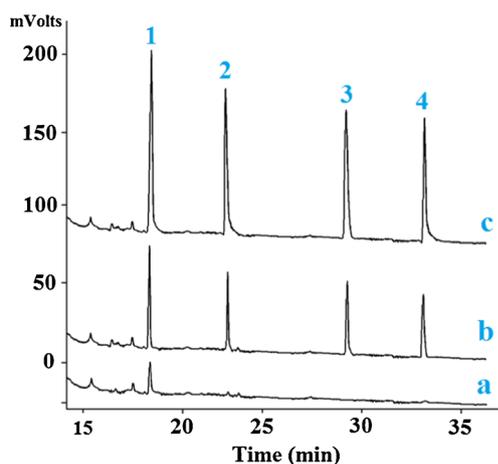
### Real sample analysis

The reliability and versatility of the HS-SPME methodology coupled to the GC-NPD system using the TMU-4/PES nanocomposite coated fiber was evaluated by determining OPPs in water and soil samples collected from various sources. The analytical results and the typical chromatograms are shown in Table 2 and Fig. 3, respectively. As results show, no target OPPs were detected in the well water sample. However, diazinon was found in the farm water sample at a concentration of 0.9  $\mu\text{g L}^{-1}$ . To evaluate the accuracy of the method, the recoveries of the OPPs were investigated by spiking the standard solution of the OPPs into the water samples at the concentrations of 2.0 and 5.0  $\mu\text{g L}^{-1}$ . For each concentration level, five replicate experiments were performed. No target OPPs were detected in the soil sample. In order to

**Table 2** Analytical results for determination of OPPs in real samples

Compound	C initial	Well water				C initial	Farm water				C initial	Soil			
		Added 2 $\mu\text{g L}^{-1}$		Added 5 $\mu\text{g L}^{-1}$			Added 2 $\mu\text{g L}^{-1}$		Added 5 $\mu\text{g L}^{-1}$			Added 5 $\mu\text{g Kg}^{-1}$		Added 10 $\mu\text{g Kg}^{-1}$	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Diazinon	ND <sup>a</sup>	95	6.7	93	8.3	0.9	95	7.7	93	6.6	ND	90	10.1	88	9.9
Fenitrothion	ND	105	6.1	103	7.3	ND	92	5.9	108	7.8	ND	93	8.4	92	9.2
Malathion	ND	94	5.9	95	9.1	ND	93	8.0	95	7.7	ND	92	7.9	90	9.7
Chlorpyrifos	ND	92	8.4	91	6.8	ND	97	9.1	94	9.0	ND	91	8.8	94	8.9

<sup>a</sup> Not detected



**Fig. 3** Typical GC-NPD chromatograms obtained by the method for farm water sample (a) blank sample (b) spiked sample with  $2 \mu\text{g L}^{-1}$  of OPPs and (c) spiked with  $5 \mu\text{g L}^{-1}$  of OPPs. (1) Diazinon; (2) Fenitrothion; (3) Malathion; (4) Chlorpyrifos

evaluate the accuracy of the method and potential matrix effects, 5 mL standard methanol solution of 10 and  $20 \mu\text{g L}^{-1}$  OPPs mixture was added to 10 g of the soils to give a spiked level of 5 and  $10 \mu\text{g kg}^{-1}$  for each of the target compounds. Extractions were performed after 2 h to ensure the solvent had evaporated. The relative recoveries of the method were expressed as the mean ratios between the amounts found and the ones spiked. As shown in Table 2, satisfactory recoveries ranging from 88 to 108% were obtained by the TMU-4/PES coated fiber for all the studied analytes. The results showed the feasibility of the TMU-4/PES fiber for the HS-SPME of trace residues of OPPs in environmental samples.

**Table 3** Comparison of the new method with other extraction and microextraction techniques for determination of OPPs in water samples

Extraction method	LOD ( $\mu\text{g L}^{-1}$ )	Detection method	Relative recovery (%)	RSD%	Extr. time (min)	Ref.
HF-LPME <sup>a</sup>	0.006-0.200	GC-MS	68.2–88.9	4.6–6.8	30	[26]
SPE <sup>b</sup>	0.05-0.13	GC-NPD	93.8–104.5%	2.9–4.3	–	[27]
LPME-SFO <sup>c</sup>	0.01-0.04	GC-FPD	96–104%	3.5–8.9	20	[28]
DLLME <sup>d</sup>	0.003-0.02	GC-FPD	78.9–107	4.6–6.5	3	[29]
HS-SPME <sup>e</sup>	0.02-0.03	GC-MS	97–105	8.0–9.0	45	[30]
DI-SPME <sup>f</sup>	0.016–0.021	GC-NPD	92–98	11.0–12.0	30	[31]
MSPE <sup>g</sup>	0.0010-0.0019	GC-iECD	78–108	6.2–8.3	10	[32]
HS-SPME	0.01–0.09	GC-MS	101–106	4.3–9.2	60	[33]
HS-SPME	0.005–0.008	GC-NPD	88–108	5.9–10.1	40	This study

<sup>a</sup> Hollow fiber liquid-phase microextraction

<sup>b</sup> Solid-phase extraction

<sup>c</sup> Liquid-phase microextraction based on solidification of a floating drop

<sup>d</sup> Dispersive liquid-liquid microextraction

<sup>e</sup> Headspace solid-phase microextraction

<sup>f</sup> Direct immersion solid-phase microextraction

<sup>g</sup> Magnetic solid-phase extraction

## Comparison of the HS-SPME-GC-NPD method with other reported approaches

To evaluate the HS-SPME-GC-NPD method, it was compared with other reported methods in the literature for the extraction and determination of the organophosphorous pesticides. The results of the comparison are shown in Table 3. The data illustrate that the current method has comparable linear ranges, RSDs, relative recoveries, and extraction time with other reported methods and also the sensitivity of the current method is better than or comparable with that of other reported techniques. All of the results indicate that the procedure is a sensitive, reliable, and practical method for monitoring the OPPs in environmental samples.

## Conclusions

In summary, a new SPME coating (TMU-4/PES nanocomposite) was prepared by single-phase inversion on SS wire, and it was used for the extraction and preconcentration of ultra-trace amounts of organophosphorous pesticides from environmental water and soil samples prior to GC-NPD detection. The coated fiber showed high stability and reusability and can be used for more than 100 replicate extractions without measurable performance loss. Low selectivity may be its limitation. The experimental results presented clearly that the TMU-4/PES coating are suitable for the HS-SPME of OPPs. The combination of HS-SPME using nanocomposite coating with GC-NPD can achieve low LODs, and can be applied to determine OPPs and other volatile or semi-volatile compounds in environmental samples.

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**Compliance with ethical standards** The author(s) declare that they have no competing interests.

## References

- Seebunrueng K, Santaladchaiyakit Y, Srijaranai S (2014) Vortex-assisted low density solvent liquid-liquid microextraction and salt-induced demulsification coupled to high performance liquid chromatography for the determination of five organophosphorus pesticide residues in fruits. *Talanta* 132:769–774. <https://doi.org/10.1016/j.talanta.2014.10.020>
- Nan J, Wang J, Piao X, Yang C, Wu X, Quinto M, Li D (2015) Novel and rapid method for determination of organophosphorus pesticide residues in edible fungus using direct gas purge microsyringe extraction coupled on-line with gas chromatography-mass spectrometry. *Talanta* 142:64–71. <https://doi.org/10.1016/j.talanta.2015.04.035>
- Arthur CL, Pawliszyn J (1990) Solid phase microextraction with thermal desorption using fused silica optical fibers. *Anal Chem* 62(19):2145–2148. <https://doi.org/10.1021/ac00218a019>
- Ghaemi F, Amiri A, Yunus R (2014) Methods for coating solid-phase microextraction fibers with carbon nanotubes. *TrAC - Trend Anal Chem* 59:133–143. <https://doi.org/10.1016/j.trac.2014.04.011>
- Ouyang G, Vuckovic D, Pawliszyn J (2011) Nondestructive sampling of living systems using in vivo solid-phase microextraction. *Chem Rev* 111(4):2784–2814. <https://doi.org/10.1021/cr100203t>
- Spietelun A, Kloskowski A, Chrzanowski W, Namieśnik J (2013) Understanding solid-phase microextraction: key factors influencing the extraction process and trends in improving the technique. *Chem Rev* 113(3):1667–1685. <https://doi.org/10.1021/cr300148j>
- Ho TD, Joshi MD, Silver MA, Anderson JL (2012) Selective extraction of genotoxic impurities and structurally alerting compounds using polymeric ionic liquid sorbent coatings in solid-phase microextraction: alkyl halides and aromatics. *J Chromatogr A* 1240:29–44. <https://doi.org/10.1016/j.chroma.2012.03.080>
- Hsieh YN, Huang PC, Sun IW, Whang TJ, Hsu CY, Huang HH, Kuei CH (2006) Nanofiber membrane-supported ionic liquid-solid phase microextraction for analyzing ultra trace PAHs in water samples. *Anal Chim Acta* 557(1–2):321–328. <https://doi.org/10.1016/j.aca.2005.10.019>
- Amanzadeh H, Yamini Y, Moradi M (2015) Zinc oxide/polypyrrole nanocomposite as a novel solid phase microextraction coating for extraction of aliphatic hydrocarbons from water and soil samples. *Anal Chim Acta* 884:52–60. <https://doi.org/10.1016/j.aca.2015.05.018>
- Feng J, Sun M, Liu H, Li J, Liu X, Jiang S (2010) Au nanoparticles as a novel coating for solid-phase microextraction. *J Chromatogr A* 1217(52):8079–8086. <https://doi.org/10.1016/j.chroma.2010.10.089>
- Wu F, Lu W, Chen J, Liu W, Zhang L (2010) Single-walled carbon nanotubes coated fibers for solid-phase microextraction and gas chromatography-mass spectrometric determination of pesticides in tea samples. *Talanta* 82(3):1038–1043. <https://doi.org/10.1016/j.talanta.2010.06.016>
- Zhang S, Du Z, Li G (2011) Layer-by-layer fabrication of chemical-bonded graphene coating for solid-phase microextraction. *Anal Chem* 83(19):7531–7541. <https://doi.org/10.1021/ac201864f>
- Bagheri H, Mir A, Babanezhad E (2005) An electropolymerized aniline-based fiber coating for solid phase microextraction of phenols from water. *Anal Chim Acta* 532(1):89–95. <https://doi.org/10.1016/j.aca.2004.10.040>
- Barahona F, Turiel E, Martín-Esteban A (2011) Supported liquid membrane-protected molecularly imprinted fibre for solid-phase microextraction of thiabendazole. *Anal Chim Acta* 694(1–2):83–89. <https://doi.org/10.1016/j.aca.2011.03.052>
- Aziz-Zanjani MO, Mehdinia A (2014) A review on procedures for the preparation of coatings for solid phase microextraction. *Microchim Acta* 181(11):1169–1190. <https://doi.org/10.1007/s00604-014-1265-y>
- Chen J, Zou J, Zeng J, Song X, Ji J, Wang Y, Ha J, Chen X (2010) Preparation and evaluation of graphene-coated solid-phase microextraction fiber. *Anal Chim Acta* 678(1):44–49. <https://doi.org/10.1016/j.aca.2010.08.008>
- Matin AA, Biparva P, Amanzadeh H, Farhadi K (2013) Zinc/aluminum layered double hydroxide-titanium dioxide composite nanosheet film as novel solid phase microextraction fiber for the gas chromatographic determination of valproic acid. *Talanta* 103:207–213. <https://doi.org/10.1016/j.talanta.2012.10.034>
- Zhang S, Yang Q, Wang W, Wang C, Wang Z (2016) Covalent bonding of metal-organic Framework-5/graphene oxide hybrid composite to stainless steel fiber for solid-phase microextraction of Triazole fungicides from fruit and vegetable samples. *J Agric Food Chem* 64(13):2792–2801. <https://doi.org/10.1021/acs.jafc.5b05831>
- Mohammadkhani E, Yamini Y, Rezazadeh M, Seidi S (2016) Electromembrane surrounded solid phase microextraction using electrochemically synthesized nanostructured polypyrrole fiber. *J Chromatogr A* 1443:75–82. <https://doi.org/10.1016/j.chroma.2016.03.067>
- Zhu Q-L, Xu Q (2014) Metal-organic framework composites. *Chem Soc Rev* 43(16):5468–5512. <https://doi.org/10.1039/C3CS60472A>
- Cui X-Y, Gu Z-Y, Jiang D-Q, Li Y, Wang H-F, Yan X-P (2009) In situ hydrothermal growth of metal-organic framework 199 films on stainless steel fibers for solid-phase microextraction of gaseous benzene homologues. *Anal Chem* 81(23):9771–9777. <https://doi.org/10.1021/ac901663x>
- Y-Y W, Yang C-X, Yan X-P (2014) Fabrication of metal-organic framework MIL-88B films on stainless steel fibers for solid-phase microextraction of polychlorinated biphenyls. *J Chromatogr A* 1334:1–8. <https://doi.org/10.1016/j.chroma.2014.01.079>
- L-Q Y, Yan X-P (2013) Covalent bonding of zeolitic imidazolate framework-90 to functionalized silica fibers for solid-phase microextraction. *Chem Commun* 49(21):2142–2144. <https://doi.org/10.1039/C3CC00123G>
- Masoomi MY, Morsali A, Junk PC (2014) Ultrasound assisted synthesis of a Zn(II) metal-organic framework with nano-plate morphology using non-linear dicarboxylate and linear N-donor ligands. *RSC Adv* 4(88):47894–47898. <https://doi.org/10.1039/C4RA09186H>
- Bezerra MA, Santelli RE, Oliveira EP, Villar LS, Escalera LA (2008) Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta* 76(5):965–977. <https://doi.org/10.1016/j.talanta.2008.05.019>
- Chen P-S, Huang S-D (2006) Determination of ethoprop, diazinon, disulfoton and fenthion using dynamic hollow fiber-protected liquid-phase microextraction coupled with gas chromatography-mass spectrometry. *Talanta* 69(3):669–675. <https://doi.org/10.1016/j.talanta.2005.10.042>
- Ballesteros E, Parrado MJ (2004) Continuous solid-phase extraction and gas chromatographic determination of organophosphorus pesticides in natural and drinking waters. *J Chromatogr A* 1029(1–2):267–273. <https://doi.org/10.1016/j.chroma.2003.12.009>
- Khalili-Zanjani MR, Yamini Y, Yazdanfar N, Shariati S (2008) Extraction and determination of organophosphorus pesticides in water samples by a new liquid phase microextraction-gas

- chromatography-flame photometric detection. *Anal Chim Acta* 606(2):202–208. <https://doi.org/10.1016/j.aca.2007.11.032>
29. Berijani S, Assadi Y, Anbia M, Milani Hosseini MR, Aghae E (2006) Dispersive liquid-liquid microextraction combined with gas chromatography-flame photometric detection. Very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water *J Chromatogr A* 1123(1):1–9. <https://doi.org/10.1016/j.chroma.2006.05.010>
  30. Lambropoulou DA, Albanis TA (2001) Optimization of headspace solid-phase microextraction conditions for the determination of organophosphorus insecticides in natural waters. *J Chromatogr A* 922(1–2):243–255. [https://doi.org/10.1016/S0021-9673\(01\)00953-0](https://doi.org/10.1016/S0021-9673(01)00953-0)
  31. Lambropoulou D, Sakkas V, Albanis T (2002) Validation of an SPME method, using PDMS, PA, PDMS–DVB, and CW–DVB SPME fiber coatings, for analysis of organophosphorus insecticides in natural waters. *Anal Bioanal Chem* 374(5):932–941. <https://doi.org/10.1007/s00216-002-1549-7>
  32. Mehdinia A, Einollahi S, Jabbari A (2016) Magnetite nanoparticles surface-modified with a zinc(II)-carboxylate Schiff base ligand as a sorbent for solid-phase extraction of organochlorine pesticides from seawater. *Microchim Acta* 183(9):2615–2622. <https://doi.org/10.1007/s00604-016-1894-4>
  33. Abolghasemi MM, Hassani S, Bamorowat M (2016) Efficient solid-phase microextraction of triazole pesticides from natural water samples using a Nafion-loaded trimethylsilane-modified mesoporous silica coating of type SBA-15. *Microchim Acta* 183(2):889–895. <https://doi.org/10.1007/s00604-015-1724-0>