



Keggin-type polyoxometalate embedded polyvinylidene fluoride for thin film microextraction of organophosphorus pesticides

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ABSTRACT

The present research is the first report on the application of Keggin-type phosphotungstic acid/polyvinylidene fluoride membrane. This compound as a simple, cost-effective and novel sorbent was used for the extraction and pre-concentration of two organophosphorus pesticides in real samples in the thin film solid-phase microextraction (TFME) method. TFME as one of the sub-branches of solid phase microextraction resolves the problems of SPME methods, including their limited absorption capacity. These extraction methods have a high surface-to-volume ratio, which improves their sensitivity compared to other geometries. Under optimal conditions, the limit of detections (LODs), the limit of quantifications (LOQs), and relative standard deviation (RSD) of this method varied in the ranges of 0.29–0.31 $\mu\text{g L}^{-1}$, 0.96–1.0 $\mu\text{g L}^{-1}$, and 3.9%–6.2%, respectively. This method showed a linear dynamic range (LDR) of 1.0–500 $\mu\text{g L}^{-1}$ with a coefficient of determination (r^2) above 0.9978. This promising method was used to analyze malathion and diazinon.

Introduction

Solid-phase extraction (SPE) and liquid–liquid extraction (LLE) are two generally available sample pre-preparation methods (Wang et al., 2019). The use of these methods in pre-concentration processes due to their inherent disadvantages, such as time-consuming procedure and requiring high volume of organic solvent has recently become obsolete (Jafari et al., 2014). In 1990, Pawliszyn et al. developed solid-phase microextraction method as an efficient sample preparation technique (Pawliszyn, 1997). The presented method offers many advantages, including lower solvent consumption, green procedure, short extraction time, and simple instrumentation (Darvishnejad et al., 2020). In this method, the pre-concentration process and extraction of selected analytes are performed in one step (Fu & Zhu, 2012). Thin-film microextraction (TFME) was reported in 2003 by Pawliszyn et al. to resolve the problems of SPME methods, including their limited absorption capacity (Bruheim et al., 2003). These extraction methods have a high surface-to-volume ratio, which can improve their sensitivity compared to other geometries (Mirnaghi et al., 2013). Various sorbents have been developed to increase the efficiency of the TFME method among which, electrospun polystyrene/graphene nanofiber (Huang et al., 2015), LDH/GO/PVDF (Ghani et al., 2018), halloysite-chitosan (Saraji et al., 2019),

urea-linked covalent organic framework (Cao et al., 2022), DUT-52 (Gutiérrez-Serpa et al., 2022), Fe_3O_4 decorated polyaniline – SWCNH (Bera et al., 2017), and MIL-53 / PVDF (Ma et al., 2019) can be mentioned. Although, the developed sorbents increased the extraction efficiency in TFME methods, it should be noted that, their long and difficult synthesis methods often require a large volume of organic solvents. In this regard, novel sorbents based on environmentally friendly substrates with simple preparation procedures are highly welcome.

Polyoxometalates (POMs) are inorganic compounds which are formed in an acidic environment through the condensation of reactions between simple oxo anions such as tungstate, molybdates, and vanadate. POMs can be found in various structures (Dolbecq et al., 2010), such as Keggin. Phosphotungstic acid (PWA) has been used for diverse applications including catalysis or proton conductivity (Mialane et al., 2021) and separation processes. Therefore, PWA-polymer thin films can offer, improved applications due to their higher surface-to-volume ratio (Fontananova et al., 2006).

Organophosphorus pesticides (OPPs) can be found in various compounds, including fruits, vegetables, and agricultural soil. These compounds possess high solubility, toxicity, biological accumulation, and sustainability (L. Wang et al., 2014). Organophosphorus pesticides affect the nervous system by impairing the process of the acetylcholinesterase

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enzyme (Fu et al., 2009). These substances may also result in oncogenic problems and disturb endocrine glands in adults (Farajzadeh et al., 2018). Regarding the harmful effects of organophosphorus pesticides on human and environment, efficient analytical methods should be developed to measure the residual organophosphorus pesticides in dietary and environmental samples (Bagheri et al., 2018). According to research and reports from the European Union, the maximum permissible level of this pesticide in water samples should be about $0.5 \mu\text{g L}^{-1}$, while their maximum allowable value in fruits is 0.01 mg kg^{-1} (Guideline, 1998). Regarding the deficient concentration of these pesticides in nutritional and environmental samples and the complexity of matrices, no direct methods are available to determine the content of these compounds. Hence, sample preparation and pre-concentration processes are essential in determining these types of compounds (Seebunrueng et al., 2012). A suitable sample preparation reduces the amount of interaction in the matrix sample and increases the concentration of selected analytes (Foster et al., 2020). Accordingly, for example gas chromatography-mass spectrometry (GC-MS) (Pelajić et al., 2016; Singh et al., 2018) and high-performance liquid chromatography (HPLC) with ultraviolet (UV) (Sharafi et al., 2015) and HPLC- fluorescence (FLD)) have been presented to measure these pesticides (Asensio-Ramos et al., 2012).

This research is thus aimed to develop a new Kegg-type phosphotungstic acid/ polyvinylidene fluoride sorbent for the extraction of two organophosphorus pesticides, such as malathion and diazinon (as model analytes), from environmental and food samples by using the TFME method. The selected analytes were extracted from the real samples for analysis and then injection into a high-performance liquid chromatography-ultraviolet (HPLC-UV) detection, by using the sorbent followed by elution with desorption solvent. Using the screening process by Plackett-Burman design (PBD), the stirring rate, extraction time, desorption time, pH of the solution, desorption volume, and ionic strength were examined as effective parameters of the extraction process. Afterward, the Box- Behnken -Design (BBD) and response surface methodology (RSM) were utilized to optimize the effective parameters of the extraction method. Finally, the prepared film was used to extract and determine the desired target analytes from several real samples such as agricultural water, carrots, strawberries and apples.

Material and method

Chemical material

Malathion and Diazinon were obtained from Sigma (Sigma-Aldrich, St. Louis, USA). PVDF and phosphotungstic acid (PWA) were obtained from Merck (Darmstadt, Germany). HPLC grade 2-propanol, ethanol methanol, acetonitrile, and dimethyl formamide (DMF) were purchased from Merck (Darmstadt, Germany).

Instrumentation

Different techniques, including Fourier Transform Infra-Red (FT-IR (model: TENSOR 27 spectrophotometer (Bruker, Germany)), X-ray diffraction (XRD) (XRD PHILIPS PW1730) in $\text{Cu K}\alpha$ ($\lambda = 1.540598 \text{ \AA}$) data were achieved, Energy Dispersive X-ray spectroscopy (EDX) and Field emission scanning electron microscope (FE-SEM) (model: ZEISS Sigma 300, operating at 30 kV) were used to characterize the surface morphology.

In order to quantification of the extracted selected analytes, Waters high performance liquid chromatography instrument equipped (C_{18} column ($30 \text{ mm} \times 4.6 \text{ mm I.D.}$, $5 \mu\text{m}$ particle size)), with a dual UV-Vis detector model 2487 (Waters Assoc, Milford, MA, USA), were used. The mobile phase consisted of Methanol and water (80:20). The UV detector was set at 230 nm Malathion and Diazinon were eluted at 6 and 10 min, respectively.

Real sample preparation

The performance of the proposed method was evaluated in real samples including, natural carrot juice, apple juice and strawberry juice purchased from the local market and agricultural land water (Amini et al., 2021). The carrot sample was washed and mixed with a blender to prepare a homogeneous mixture. Homogenized sample (2 g) was weighed and transferred to a falcon containing methanol (50 mL). The final composition was centrifuged at 4000 rpm for 10 min. Then, the solution was diluted with deionized water (1:1) for further analyses (Amini et al., 2021). The apple and strawberry samples were also mixed by a blender. The resulting mixture was inputted in a falcon and centrifuged at 4500 rpm for 10 min. Then, the solution was diluted with deionized water (1:2) and used for more analysis (Farajzadeh et al., 2021). After preparing the real samples, particular concentrations (5, 10, and 20 ppb) of the analytes (malathion and diazinon) were added to the real samples, followed by the extraction process. In this research, agricultural water was used as a real sample without any preparation process.

Preparation of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ / polyvinylidene fluoride membrane

To prepare the film as the extracting phase in the TFME method, 50 mg of polyvinylidene fluoride (PVDF) and 50 mg of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PWA) were mixed with 1 mL of dimethylformamide and dispersed by 10 min of sonication. The obtained homogeneous mixture was then cast onto a glass Petri Dish (50 mm diameter). The solvent present in the prepared film was removed by heating at $60 \text{ }^\circ\text{C}$ for 60 min. The attached film was then separated from the glass Petri Dish surface by immersion in a suitable solvent (methanol). Finally, the obtained film was washed with methanol and completely dried at room temperature. In this study, PVDF film was prepared by the same procedure but without using the PWA compound. At last, the prepared films were cut into particular forms and used to extract the selected analytes.

Extraction procedure

In this research, PWA/PVDF/TFME was used for pre-concentration and extraction of malathion and diazinon (as organophosphorus pesticides). The prepared film was attached to a stainless steel clip and placed in 10 mL of a working solution containing the selected analytes with a concentration of 100 ppb at $\text{pH} = 4$. The working solution was stirred by a magnetic stirrer for 30 min at 1170 rpm. To perform the desorption process, the film was removed from the working solution by using tweezers and placed in a vial containing 200 μL of selected desorption solvent (methanol) for 2 min in an ultrasonic bath. Finally, 25 μL of rich eluent of selected analytes, was injected into the HPLC-UV device.

Optimization strategy

At this step, the effective variables of the extraction process were optimized to achieve maximum extraction efficiency for the selected analytes. Optimal conditions can be achieved through two general methods: the one variable at a time (OVAT) and the design of the experimental (DOE) methods. The parameters of sorbent content, eluent solvent type, stirring rate, extraction time, salt effect ($w/v\%$), pH of the solution, desorption volume, and desorption time were investigated.

In this research, 6 effective factors of the extraction process, including pH of sample solution, stirring rate, extraction time, desorption time, salt effect, and desorption volume were explored based on literature review and preliminary experiments. The Plackett-Burman design was employed to screen the effective factors during the extraction process of the selected analytes. Then, the Box-Behnken design (BBD) was utilized to optimized the screened factors by using Minitab 16 software. The relevant information of the experimental design methods (including PBD and BBD) can be found in the [supporting data](#).

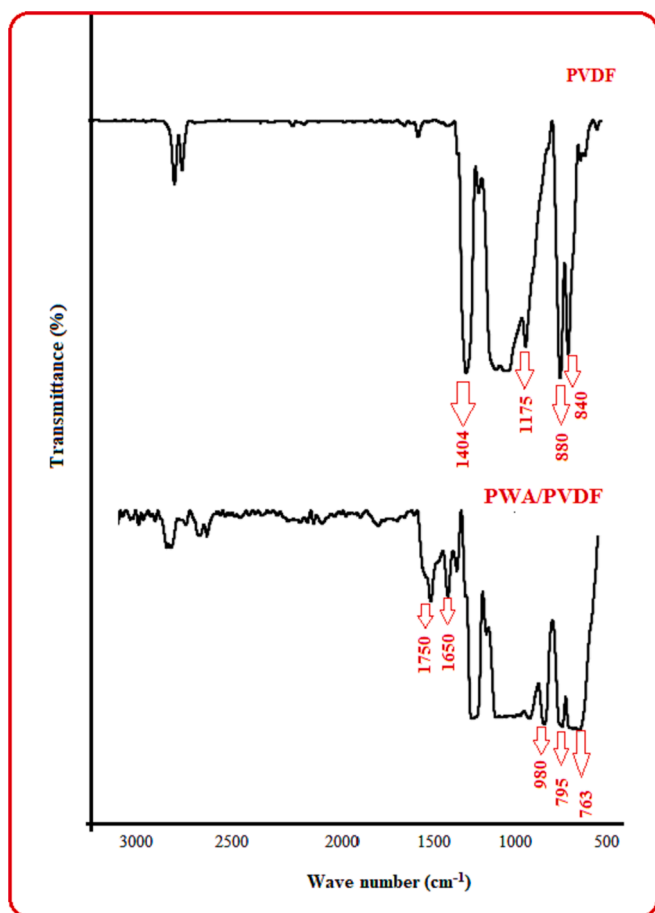


Fig. 1. FT-IR spectrum related to PWA/PVDF and PVDF film.

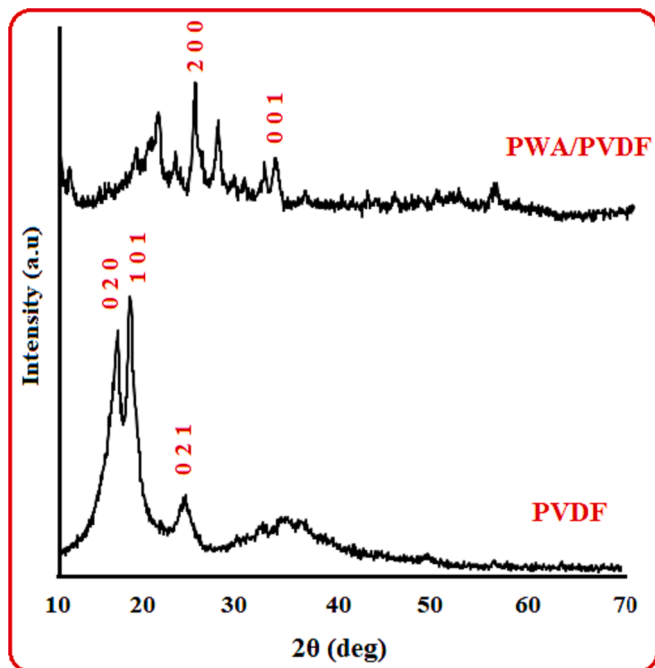


Fig. 2. X-ray diffraction spectrum pattern of PVDF and PWA/PVDF sorbent.

Results and discussion

Characteristics of the prepared membrane

FT-IR spectrum was employed to analyze the PVDF and PWA/PVDF membranes. FT-IR is a chemical technique to identify functional groups of the samples. Accordingly, the absorption peaks at 1404, 1175, 880, and 840 cm^{-1} are characteristic vibrations of CF and CH groups in PVDF. The broad bands between 1650 and 1750 cm^{-1} can be also assigned to the vibration of water molecules attached to PWA (Srisuda & Virote, 2008). The sharp peak at 980 cm^{-1} is attributable to the vibration of W-O bond in PWA (Inoue et al., 2008) (Fig. 1).

Crystal structure of PVDF and PWA/PVDF were determined by powder X-ray diffraction (XRD) (Fig. 2.). The peaks at $2\theta = 18.4, 19.9,$ and 26.3° in pure PVDF correspond to the (020), (110), and (021) planes, respectively. The peaks at $2\theta = 18.4$ and 19.9° have somewhat disappeared after the formation of PWA/PVDF while new peaks emerged at $2\theta = 20.6$ and 36° , which correspond to the planes of (200) and (001), respectively (Chen et al., 2010).

The elemental composition of the samples was investigated by using EDS along with the elemental mapping technique. The results in Fig. S1 (a and b) confirmed the presence of W, P, and O elements. In addition to the EDS investigations, uniform distribution of W, P, and O on the surface, was explored by mapping analysis, which verified the presence of the PWA on the surface of the PVDF substrate.

FE-SEM was used to examine the surface characteristics of PWA/PVDF prepared membrane for the TFME method, as shown in Fig. 3(A-D). As observed, the addition of PWA (Fig. 3-B) to PVDF (Fig. 3-A) altered the overall structure of the PVDF coating. Fig. 3-C and D indicate the presence of spherical PWA nanoparticles on the surface of the PWA/PVDF nanocomposite. The Keggin-type phosphotungstic acid (PWA) formed a soccer ball shape-structure, which makes this group of compounds as a suitable option for combining with polymer materials.

Optimization amount of the PWA dispersed in PVDF membrane

One of the influential parameters in the extraction of selected analytes by the TFME method is the amount of sorbent that was used for dispersion in PVDF. This parameter is optimized based on the OVAT method. The experiments indicated that the pure PVDF membrane did not interact with the selected analytes, thus, extraction did not occur at such conditions. Therefore, different contents of PWA (0.03, 0.05, and 0.07 g) were dispersed in PVDF to be used in the extraction method. Each PWA content was tested in triplicates, under the same conditions (stirring rate: 1000 rpm, extraction time: 20 min, salt effect: 0 (w/v%) NaCl, pH: 6.0, desorption time: 3 min, and desorption volume: 150 μL). Based on Fig. S2, the extraction efficiency for the selected analytes increased with enhancing the amount of sorbent up to 0.05 g. However, further increment of the sorbent dose up to 0.07 led to a decline in the extraction efficiency compared to the presence of 0.05 g sorbent. Enhancement of the sorbent content led to the formation of a more heterogeneous, non-uniform, and compact membrane, which reduced the extraction efficiency. Therefore, the membrane with 0.05 g PWA was selected as the optimal one for further analysis.

Eluent solvent type

At the end of the extraction process, the eluting process was carried out by using a suitable desorption solvent to elute the adsorbed analytes from the PWA/PVDF membrane. The type of suitable desorption solvent is another effective parameter that should be investigated and optimized. In this context, acetonitrile, methanol, ethyl acetate, ethanol, and isopropanol (2 propanol) were investigated as desorption solvents under the same conditions (extraction time: 20 min, stirring rate: 1000 rpm, salt effect: 0 (w/v%) NaCl, pH: 6.0, desorption time: 3 min, desorption volume: 150 μL) (Fig. S3). All experiments were conducted in triplicates.

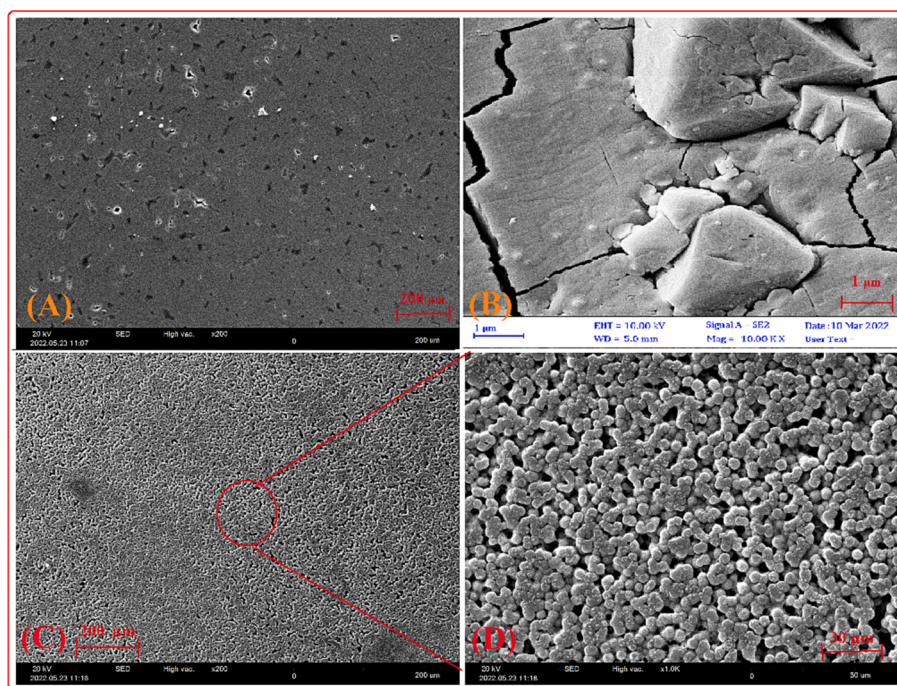


Fig. 3. A-E, FE -SEM image related to PWA/PVDF in different magnification. Corresponding to the PVDF film empty (A), PWA. (B), PWA/PVDF film in different magnifications (C and D).

Methanol was selected as the suitable desorption solvent due to its protic characteristic compared to the other selected eluents.

Analytical features

The figures of merit of the presented method, including the limit of detection (LOD), the limit of quantification (LOQ), linear dynamic range (LDR), enrichment factor (EF), and relative standard deviation (RSD) of the method, were calculated for selected organophosphorus pesticides under optimum experimental conditions (extraction time = 30 min, desorption time = 2 min, pH = 4, desorption volume = 200 μL , salt effect = 0 (% w/v), and stirring rate = 1170 rpm). Based on the results, the linear dynamic range of the method for selected analytes was in the range of 1–500 $\mu\text{g L}^{-1}$ (1–200 and 1–500 $\mu\text{g L}^{-1}$ for malathion and diazinon, respectively). Based on the appropriate linear dynamic range for the selected analytes, the coefficient of determination (r^2) was calculated for malathion and diazinon as 0.9978 and 0.9985, respectively. Here, the signal-to-noise method was used to calculate the LOD

and LOQ of the method. Accordingly, the LOD of the method varied in the range of ($S/N = 3$) 0.29–0.31 $\mu\text{g L}^{-1}$, while its LOQ ($S/N = 10$) was in the range of 0.96 – 1.0 $\mu\text{g L}^{-1}$. To obtain the relative standard deviation of the intraday method, three different concentration levels were investigated (2, 20, and 200 $\mu\text{g L}^{-1}$). The intraday RSDs ($n = 3$) were in the range of 3.9–5.4% for malathion and 4.3–6.2% for diazinon. To determine the interday relative standard deviation of the method, three concentration levels (1, 10, and 100 $\mu\text{g L}^{-1}$) were investigated. The interday RSDs ($n = 3$) were in the range of 4.2–5.6% for malathion and 5.1–6.1% for diazinon. The EF was evaluated as the ratio of the peak areas for the concentrations of analytes in the eluent solvent (C_e) to the primary concentration of the analytes in the aqueous sample (C_0) (Ghani et al., 2021). The results have been reported in the Supplementary information (Table S10). The following equation was used to obtain EF values (Eq. (1)):

$$EF = \frac{C_e}{C_0} \quad (1)$$

This method was compared with other reported methods for the

Table 1

Comparison of the method with other microextraction methods and applied for the extraction and determination of organophosphorus pesticides.

Method	Instrument	Analytes	RSD (%)	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	LDR ($\mu\text{g L}^{-1}$)	Sample type	Ref
DSPME ¹	UHPLC-MS ²	Malathion		4.0	10.0	–	water, fruits and vegetables	(Habiba et al., 2020)
HF-SPME ³	HPLC-UV	diazinon and chlorpyrifos		0.21–0.27	0.72–0.91	–500	tomato, cucumber and agricultural water	(Darvishnejad et al., 2020)
SPME	GC-MS ⁴	Malathion + eleven pesticides		0.01–0.03	–	–75.0	tomato and cucumber samples	(Liang et al., 2017)
DSPME	GC-IMS ⁵	Fenthion, malathion, and chlorpyrifos		0.46–1	2	–1000	well water, river water, farm wastewater, carrot and cauliflower	(Kermani et al., 2019)
TFME	HPLC-UV	Malathion and Diazinon	3.9%–6.2%	0.29–0.31	0.96–1.0	1–500	Agricultural water, Carrot, Strawberry and Apple	This method

¹ Dispersive Solid Phase Microextraction.

² Ultra-performance liquid chromatography-tandem mass spectrometry.

³ Hollow fiber solid-phase microextraction.

⁴ Gas chromatography-mass spectrometric.

⁵ Gas chromatography-ion mobility spectrometry.

Table 2

Summary of results from analysis of organophosphorus pesticides in different real samples with relative and spiking recovery.

		Malathion	Diazinon
Agricultural water	measured	2.3	4.4
	Added	5.0, 10.0, 20.0	5.0, 10.0, 20.0
	found	7.4, 12.2, 21.6	9.5, 14.7, 23.9
	SR (%)	102.0, 99.0, 96.5	102.0, 105.0, 97.5
	RR (%)	100.0, 97.5, 97.0	101.0, 99.0, 98.5
	RSD%	5.4	6.2
	n = 3		
Carrot	measured	1.2	1.6
	Added	5.0, 10.0, 20.0	5.0, 10.0, 20.0
	found	6.4, 11.5, 19.7	6.8, 11.7, 21.1
	SR (%)	104.0, 103.0, 93.0	104.0, 101.0, 97.5
	RR (%)	100.0, 97.0, 95.0	101.0, 99.0, 98.0
	RSD%	5.5	6
	n = 3		
Strawberry	measured	1.1	ND
	Added	5.0, 10.0, 20.0	5.0, 10.0, 20.0
	found	6.3, 11.6, 21.5	5.1, 9.8, 19.2
	SR (%)	104.0, 105.0, 102.0	102.0, 98.0, 96.0
	RR (%)	105.0, 101.0, 102.0	103.0, 97.0, 96.0
	RSD%	3.8	5.2
	n = 3		
Apple	measured	2.5	1.1
	Added	5.0, 10.0, 20.0	5.0, 10.0, 20.0
	found	7.7, 12.1, 22.4	6.2, 10.9, 21.3
	SR (%)	104.0, 96.0, 99.5	103.0, 98.0, 101.0
	RR (%)	98.0, 99.0, 99.0	101.0, 100.0, 101.0
	RSD%	5.6	4.4
	n = 3		

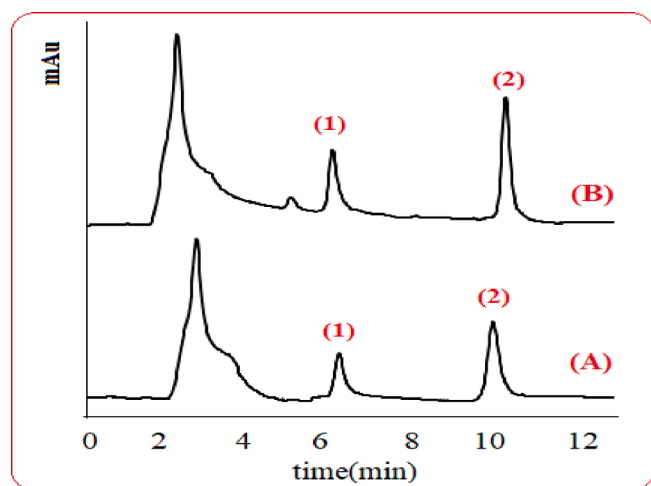


Fig. 4. The chromatogram obtained after TFME of agricultural water sample using proposed sorbent before (A) and after spiking of $20 \mu\text{g L}^{-1}$ of mix standard solution (B). The mobile phase consisted of Methanol and water (80:20 (v/v)). The UV detector was set at 230 nm. Malathion and Diazinon were eluted at 6 and 10 min, respectively.

extraction of diazinon and malathion, reported in Table 1. Based on the results, the figures of merit (LOD, LOQ, RSD, and LDR) of the proposed method are comparable and, in some cases, better than other methods for the target analytes.

Real sample analysis

The effectiveness of PWA/PVDF-TFME was analyzed in detecting the selected organophosphorus pesticides in real samples. Relative recovery and spiking recoveries were calculated for the presented method (Darvishnejad et al., 2020). Selected real samples (e.g. agricultural water, carrot, strawberry, and apple) were spiked at three concentration levels

(5, 10, and $20 \mu\text{g L}^{-1}$). The obtained results are presented in Table 2. The results show relative recovery and spiking recoveries of 96–105% and 93–105% for malathion and diazinon, respectively, this results can suggesting the ability of the method to analyze the selected analytes in real samples. At this step, the extraction process was repeated three times under optimal conditions to achieve the RSD of the method. Accordingly, the RSD was calculated in the range of 4.4–6.2% for diazinon and 3.8–5.6% for malathion, respectively. Fig. 4 shows the chromatograms of the real samples before and after spiking of the standard solution under optimal conditions.

Conclusion

In the present study, polyvinylidene fluoride (PVDF) and phosphotungstic acid (PWA) were combined to prepare a novel membrane for the first time. The prepared sorbent was used as a fast, simple, novel and cost-effective sorbent in thin film solid-phase microextraction method. PWA/PVDF was characterized by X-ray diffraction, energy dispersive X-ray analysis, scanning electron microscopy, and FT-IR spectroscopy. The results showed the high performance of the prepared thin film in the extraction and pre-concentration of organophosphorus pesticides (malathion and diazinon). Regarding the solubility of phosphotungstic acid in oxygenated organic solvents, it cannot be used without modification in extractive processes. Therefore, in addition to using polyvinylidene fluoride as TFME support, the combination of polymer with PWA, prevents the dissolution of this compound in oxygenated solvents, thus improving its ability in the proposed method. Moreover, the prepared film has acceptable analytical features (LOD, LOQ, and LDR). Analysis of different real samples such as agricultural water, carrot, strawberry, and apple revealed acceptable recovery results for the simultaneous analysis of organophosphorus pesticides in complex matrices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fochx.2023.100857>.

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