

Research Article

Ali Esrafil, Mahnaz Ghambarian*, Mahmood Yousefi, and Sharieh Hosseini

Application of MXene as a new generation of highly conductive coating materials for electromembrane-surrounded solid-phase microextraction

<https://doi.org/10.1515/ntrev-2022-0147>

received March 17, 2022; accepted June 9, 2022

Abstract: For the first time, highly conductive thickly layered two-dimensional titanium carbide (MXene) was applied as a new coating agent for electromembrane-surrounded solid-phase microextraction (SPME) of triadimenol and iprodione as two model analytes. Preparation of the desired coated electrode was carried out using electrophoretic deposition of MXene on the surface of platinum electrode. Characterization of the prepared coated electrode was conducted using scanning electron microscopy and energy-dispersive X-ray spectroscopy. The coated electrode was located inside a hollow fiber membrane impregnated by 2-nitrophenyl octyl ether as the supported liquid membrane (SLM), while an aqueous solution was injected inside the hollow fiber lumen. Separation and quantification of the analytes were carried out using a gas chromatography instrument equipped with mass spectrometric detection. The effective parameters of the microextraction procedure comprising pHs of sample solution and the acceptor phase, composition of the SLM, extraction time, and the applied voltage were optimized using one-variable at-a-time method. Under the optimal conditions, the calibration curves of the analytes were linear

($R^2 > 0.9973$) in the range of 0.3–250.0 and 0.5–250.0 ng mL⁻¹ for triadimenol and iprodione, respectively. The limit of detections was determined to be 0.10 and 0.15 ng mL⁻¹ for triadimenol and iprodione, respectively. Repeatability and reproducibility of the method were evaluated by the calculation of intra-day and inter-day relative standard deviations (%). The applicability of the method was evaluated by quantitative analysis of the model analytes in environmental water samples. Relative recoveries in the range of 87.31–102.7% confirmed that the prepared coated electrode can be considered a reliable option in electromembrane-surrounded SPME techniques.

Keywords: two-dimensional titanium carbide, MXene, electromembrane extraction, solid phase microextraction, gas chromatography-mass spectrometry, environmental water samples

1 Introduction

Highly conductive materials have been enormously considered in materials science for the fabrication of different surfaces for various purposes [1]. During the past decades, different types of conductive materials comprising graphene and graphene oxide [2], carbon nanotubes [3], conductive polymers (CPs) [4], and metal–organic frameworks [5] have been introduced as new conductive materials. Recently, another conductive material has been added to this family composed of different layers of metal-carbide building blocks. These conductive materials contain two-dimensional structures of early transition metal carbides and nitrides that are known simply as MXene [6]. The name refers to the composition of $M_{n+1}AX_n$ where M is the early transition metal, A is an element from groups 13 and 14, and X is carbon or nitrogen, which is abbreviated to MAX phase. Due to the similarities between such structures and graphene, these materials are simply called MXene [7].

* **Corresponding author: Mahnaz Ghambarian**, Iranian Research and Development Center for Chemical Industries, ACECR, Tehran, Iran, e-mail: ghambarian.m@gmail.com

Ali Esrafil: Research Center for Environmental Health Technology, Iran University of Medical Sciences, Tehran, Iran; Department of Environmental Health Engineering, School of Public Health, Iran University of Medical Sciences, Tehran, Iran

Mahmood Yousefi: Department of Environmental Health Engineering, School of Public Health, Iran University of Medical Sciences, Tehran, Iran

Sharieh Hosseini: Department of Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran

Thanks to the possibility of changing M, A, and X elements in MXene structures, different types of MXene materials can be achieved. Moreover, the X element can be simply replaced by different functional groups acquiring different types of MXene with various properties [8]. Along with the diverse types of MXene structures that can be obtained, the synthesis of these materials is quite straightforward as different synthetic methods such as spin coating, electrospray, spray drying, and electrophoretic deposition have been reported during the past years. To name a few, $-F$, $-OH$, and $-O$ functionalizations have been the most common derivatives of MXene structures [9].

Sorbent-base extraction and microextraction methods are fundamentally material-based procedures in which different types of materials can be applied for extraction, purification, and cleaning up of analytes with various physicochemical properties from different sample matrices [10]. During the past years, different extraction and microextraction methods have been reported in the literature, which have been basically relied on materials. Conventional solid-phase extraction (SPE) based on disks or cartridges [11–13], dispersive SPE [14], magnetic SPE [15], stir bar sorptive dispersive microextraction [16], solid-phase microextraction (SPME) [17–21], thin-film SPME [22], and pipette-tip micro-SPME [23] are the most well-known sample preparation methods that are based on the materials used in the extraction or microextraction procedures.

SPME is a sample preparation method that was conventionally carried out by direct immersion of the SPME fiber into the sample solution. Along with the efficiency of the method, this procedure lacks high sample cleanup values and selectivity due to the direct contact between the solid phase as the acceptor phase and the complicated sample solution as the donor phase. To resolve this problem, different strategies have been reported during the past decades. Headspace SPME has been the reliable alternative to direct immersion SPME [24]. However, this method is suitable for volatile or semi-volatile compounds. In 2013, Rezazadeh *et al.* reported an interesting strategy based on the combination of SPME and electromembrane extraction called electromembrane-surrounded solid phase microextraction (EM-SPME). They simply utilized a pencil lead fiber as the SPME fiber inside a hollow fiber lumen [25]. Since then, different types of materials have been used instead of pencil lead fiber to enhance the efficiency of the procedure [26–28]. The key point in all reported studies is that the applied material must be conductive to effectively pass the electricity from the SPME fiber through the sample solution.

In the present study, a platinum electrode was successfully coated with titanium carbide nanolayers as the

MXene structure and used as the SPME fiber in an EM-SPME procedure. The MXene layers were coated on the electrode through a simple electrophoretic deposition procedure. This EM-SPME setup was applied for preconcentration and extraction of two model analytes, triadimenol and iprodione, from environmental water samples. Separation and determination of the analytes were carried out using a gas chromatography-mass spectrometry (GC-MS) instrument.

2 Materials and methods

2.1 Chemicals and reagents

Synthetic grade Ti_2AlC as the majority phase with approximately 30 wt% Ti_3AlC_2 (MAXTHAL) was purchased from Forsman Scientific Co. Ltd (Beijing, China). Titanium carbide (TiC) with a purity of 99% was bought from Sigma-Aldrich (Milwaukee, WI, USA). Analytical grades sodium chloride (NaCl), hydrochloric acid (HCl), 2-nitrophenyl octyl ether (NPOE), di-(2-ethylhexyl)phosphate (DEHP), and tris(2-ethylhexyl)phosphate (TEHP) were obtained from Merck (Darmstadt, Germany). The applied platinum electrodes were from Pars Platin Co. (Tehran, Iran). The Q3/2 Accurel polypropylene hollow fiber was purchased from Membrana (Wuppertal, Germany). The inner diameter of the hollow fiber was 600 μm , the thickness of its wall was 200 μm , and the pore size was 0.2 μm . The water was purified on an AquaMax ultra-pure water purification system from Younglin (Seoul, South Korea).

2.2 Instrumentation

The electrophoretic deposition of MXene nanolayers was carried out using a potentiostat/galvanostat obtained from Novin Ebtakar (Tehran, Iran). The size and morphological properties of the synthesized sorbent were evaluated using a Philips CM30T electron microscope (200 kV), equipped with an energy-dispersive X-ray analyzer (EDX) to obtain the chemical composition of the SPME fiber. A Thermo Scientific Nicolet IR100 (Madison, WI, USA) Fourier transform infrared (FT-IR) spectrometer was used to obtain specific functional groups of the coating material. X-ray diffraction (XRD) patterns of MXene and MAX were recorded on a Rigaku diffractometer using $Cu-K\alpha$ radiation in the range of 3–90°. The thermal behavior of the coating was evaluated using thermogravimetric analyzer (TGA) (Perkin

Elmer model TG/DTA 6300, USA). The required voltage for the microextraction procedure was obtained from a power supply instrument purchased from Paya Pajooesh Pars (Tehran, Iran). Separation and determination of the CPs were performed using an Agilent 7890A (Wilmington, USA) GC system equipped with an Agilent MSD 5975 C quadrupole mass spectrometer. A $30\text{ m} \times 0.25\text{ mm}$ i.d., $0.25\text{ }\mu\text{m}$ film thickness, DB-5MS (5% phenyl-methylsiloxane) fused-silica column was used. Helium (99.999%) was the carrier gas, at a flow rate of 1.0 mL min^{-1} . The gas chromatograph operated at the splitless mode and the temperature of the injection port was 250°C . To assess the successful separation of the target analytes, the following temperature program was employed. The oven temperature was set at 60°C and remained for 1 min, increased to 250°C at a rate of $10^\circ\text{C min}^{-1}$, and kept at this temperature for 20 min [29]. The injection volume was $1\text{ }\mu\text{L}$. Data acquisition was performed in the full scan mode (m/z in the range of 45–700) to confirm the retention times of analytes and in the selected ion monitoring mode for the quantitative determination of the pesticides.

2.3 Electrophoretic deposition of MXene nanolayers

Preparation of the desired MXene-coated electrode was conducted according to the previous studies in the literature. Basically, the synthesis of MXene contains three separate steps comprising preparation of the MAX phase, preparation of MXene colloidal MXene suspension, and electrophoretic deposition of MXene colloids on the electrode.

To prepare the MAX phase powder containing Ti_3AlC_2 , MAXTHAL powder was mixed with TiC in the ratio of 1:1 based on the Ti_2AlC_2 as the main component of the MAXTHAL powder. These reactants were mixed in a thick polyethylene container with zirconia balls for 24 h. Then, the mixture was packed into an alumina combustion boat under the continuous Ar flow. This mixture was placed inside a furnace to be heated at the rate of 5°C h^{-1} up to a temperature of $1,350^\circ\text{C}$. The mixture remained at this temperature for about 2 h. The obtained brick was sieved to achieve Ti_3AlC_2 uniform powders.

In order to synthesize MXene, two grams of Ti_3AlC_2 was slightly added into 20 mL of a solution containing 11.7 M HCl and 1.32 g LiF to obtain the molar ratio of 5:1 of salts to MAX. This mixture was stirred for 72 h at the temperature of 35°C obtained by an oil bath. Afterward, the black sediments were washed with water and centrifuged several times. Next, the resulted MXene sediments

were separated from the excess water as much as practicable by a vacuum pump.

To obtain a colloidal phase for the electrodeposition step, 2.5 g of the still-damp MXene powders was dispersed into the ultrapure water; 0.7 mL of this suspension was poured into a glass container. Two platinum electrodes were connected to the power supply, while they were inserted into the MXene colloidal suspension. Constant direct current (DC) voltage of 1–25 V was applied to the electrochemical cell for around 10 min. The MXene-electrodeposited electrode was washed several times with ultrapure water to get rid of impurities and unreacted materials.

2.4 EM-SPME setup

The equipment utilized for the EM-SPME procedure was a 30 mL glass vial as a sample container. Two platinum electrodes as cathode and anode with a diameter of 0.25 mm. The cathode electrode was the MXene-coated platinum as the SPME fiber. The electric power was obtained by a power supply connected to the two electrodes, where practical voltages were in the range of 0–200 V and the current output of 0–500 mA. The electromembrane extraction unit consisted of a piece of 2 cm of hollow fiber membrane mechanically sealed. The pores of the hollow fiber membrane were filled with NPOE as the supported liquid membrane (SLM), while the hollow fiber lumen was filled with water as the acceptor phase. The extraction procedure was carried out using a magnetic stirrer with a stirring rate of 0–1,250 rpm via a 1.5×0.5 magnetic bar.

2.5 EM-SPME procedure

Twenty-three milliliters of the sample containing the model analytes was poured into a capped vial; 2.8 cm of hollow fibers was cut and dipped into the NPOE to impregnate the pores. Then, the excess amount of organic solvent was removed with the aid of a piece of Kleenex. Pure water was used as the acceptor phase which was introduced into the lumen of impregnated hollow fiber using a Hamilton micro-syringe. The lower end of the hollow fiber was mechanically sealed, and the coated SPME fiber was inserted into the hollow fiber from the upper side. The whole structure was directed into the vial containing the sample solution and magnet. A platinum wire acting as the anode was placed into the sample solution as well.

The extraction unit was placed on a Heidolph stirrer with a stirring rate of 1,250 rpm. The electrodes were connected to a power supply set in a DC voltage of 120 V. Once the extraction was completed, the SPME fiber acting as the cathode was removed and inserted into an SPME syringe. Afterward, the fiber was directed into the GC injection port for thermal desorption of the analytes at the temperature of 250°C for 2 min.

Table 1: Elemental analysis of the MXene-coated platinum electrode using EDX spectroscopy

Element	Measure (%)
Pt	58.37
Ti	25.91
C	9.37
O	4.70
F	1.65

3 Results and discussions

3.1 Characterization of the prepared SPME fiber

To make sure of the successful electrodeposition of MXene on the electrode, scanning electron microscopy (SEM), FT-IR spectroscopy, TGA, and XRD followed by EDX elemental analysis were carried out. Figure 1a illustrates the SEM

image of the MXene-electrodeposited platinum electrode. According to this figure, the layered structure of the synthesized material confirms the successful deposition of MXene nanosheets on the surface of the electrode with a thickness of about 30 μm . Along with the morphological properties of the coating material, elemental compositions of the prepared MXene-coated electrode were evaluated using EDX analysis. Table 1 represents the elemental composition of the prepared SPME fiber. As can be seen in this table, relative amounts of the elements confirm

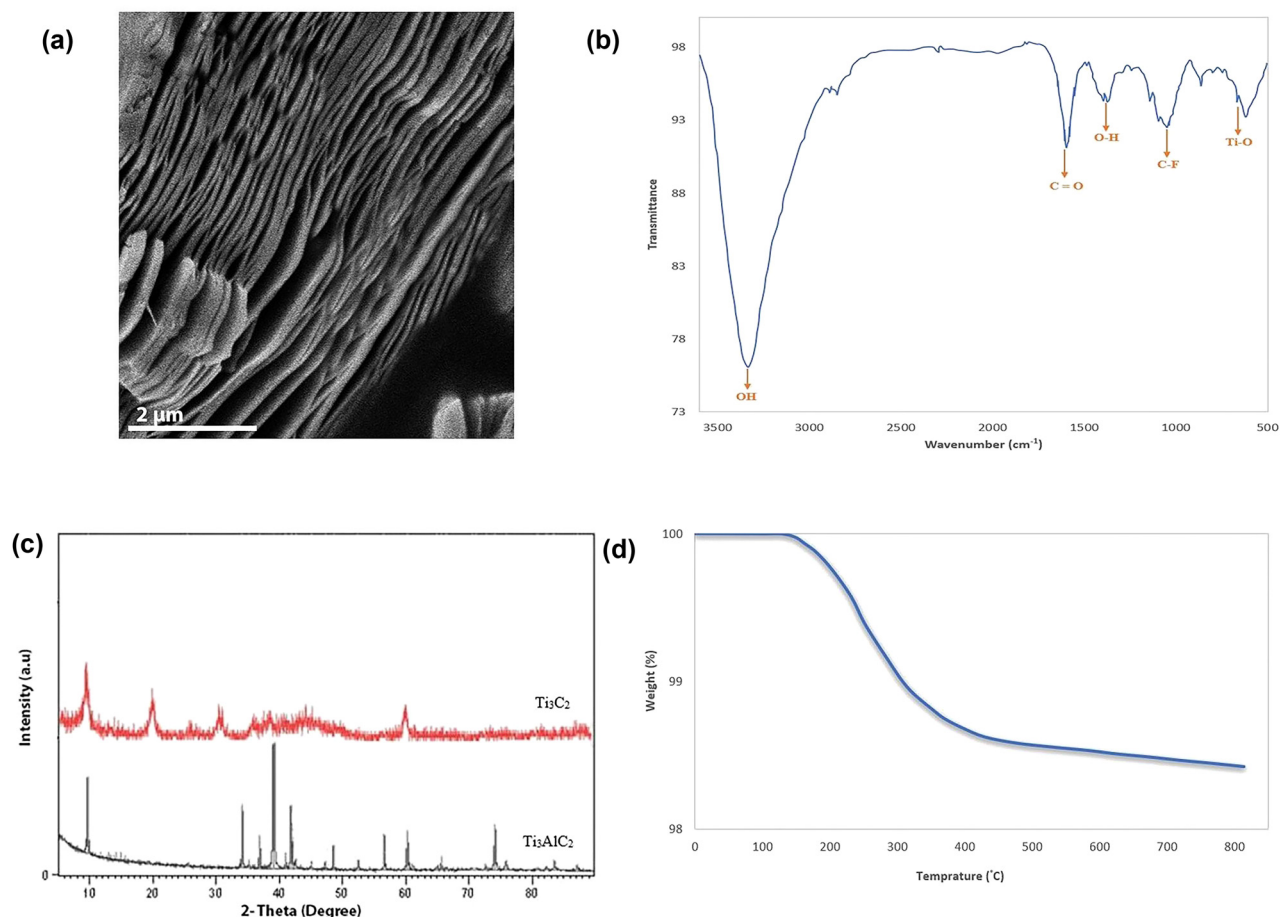


Figure 1: (a) SEM image of the MXene coated platinum electrode, (b) FT-IR spectrum of MXene, (c) XRD spectra of Ti_3C_2 and Ti_3AlC_2 , and (d) TGA curve of Ti_3AlC_2 .

that the electrodeposition procedure was successfully accomplished. The function groups on the surface of the coating were examined using FT-IR Spectroscopy. As shown in Figure 1b, peaks at 3,430, 1,630, 1,390, 1,100, and 662 cm^{-1} can be attributed to the stretching vibrations of -OH , C=O , O-H , C-F , and Ti-O bonds.

Figure 1c shows the XRD patterns of coating material. After the Ti_3AlC_2 was treated by HF, the peak of Ti_3AlC_2 at 9.65° shifted toward a lower angle at about 8.7° . Meanwhile, the strong peak representing $2\theta = 38.8^\circ$ of the Al layer in Ti_3AlC_2 was disappeared. According to these results, etching away of Al layers and forming of the $\text{Ti}_3\text{C}_2\text{T}_x$ phase were confirmed. TGA was conducted to determine the thermostability of coating materials in the temperature range of 30–800 $^\circ\text{C}$ under a nitrogen atmosphere. As shown in Figure 1d, when the temperature was raised from 30 to 200 $^\circ\text{C}$, the weight loss of coating materials can be ascribed to the removal of moisture and HF residue from the coating surface. At above 200 $^\circ\text{C}$, the weight loss was caused by the dehydroxylation of terminated OH groups and the elimination of physisorbed water embedded between the layers. At temperatures $> 300^\circ\text{C}$, no significant weight loss was observed in the TGA curve, which demonstrated that most volatile species were eliminated at temperatures below this threshold. The excellent thermal stability of coating material was revealed that MXene nanosheets are suitable to be used as SPME fibers in a GC inlet.

3.2 Optimization of the microextraction procedure

TGA was conducted to determine the thermostability of coating materials in the temperature range of 30–800 $^\circ\text{C}$ under a nitrogen atmosphere. As shown in Figure 1d, when the temperature was raised from 30 to 200 $^\circ\text{C}$, the weight loss of coating materials can be ascribed to the removal of moisture and HF residue from the coating surface. At above 200 $^\circ\text{C}$, the weight loss was caused by the dehydroxylation of terminated OH groups and the elimination of physisorbed water embedded between the layers. At temperatures $> 300^\circ\text{C}$, no significant weight loss was observed in the TGA curve, which demonstrated that most volatile species were eliminated at temperatures below this threshold. The excellent thermal stability of coating material revealed that MXene nanosheets are suitable to be used as SPME fibers in a GC inlet.

In order to achieve the best method performance, the effective parameters of the microextraction procedure were

identified and optimized. These parameters were type and composition of the SLM, the applied voltage, and the extraction time. All the effective parameters were optimized through the one-variable at-a-time method.

3.2.1 Optimization of SLM composition

The first parameter effective parameter was the type and composition of the SLM. SLM composition is one of the most influential parameters of the efficiency of electromembrane extraction (EME). The exploited solvent to impregnate the hollow fiber should have certain characteristics like immiscibility with water, compatibility with polypropylene structure, certain viscosity, and conductivity. Based on these required features, NPOE and 1-octanol have widely been used as SLM in EME. While 1-octanol has proved to be the best solvent for extraction of acidic species, NOPE is the most well-suited solvent for basic analytes. The latter issue is mainly due to the H-donor/acceptor groups that existed in each solvent. Considering the basic nature of analytes of interest, NPOE was chosen as the main SLM solvent in our study. Then, the composition of NPOE was modified with different ratios of DEHP or TEHP in the range of 0–10%. According to the results, none of the mentioned carries had a positive effect on the extraction efficiencies of the analytes of interest. Therefore, NPOE was selected as the SLM in the rest of experiments.

3.2.2 Optimization of applied voltage

In EME, analytes migrate under the influence of an electrical field applied across the SLM. Considering the fixed position of the electrodes, magnitude of the electrical field is dependent on the value of applied voltage. In other words, the mobility of ionized analytes is dependent on the applied voltage and the applied voltage is responsible for mass transfer of analytes. Although it is expected that the increase in applied voltage will result in enhanced efficiency, in higher voltage value the electrolysis reactions, bubble formation, partial loss of SLM, and even SLM punctuation due to the Joule heating can occur. Therefore, the value of applied voltage should be optimized to guarantee efficient and stable extractions. To this end, the effect of the applied voltage was investigated within the range of 70–160 V. According to the obtained results shown in Figure 2, the best results were obtained in the voltage value of 110 V, which was set in all subsequent studies.

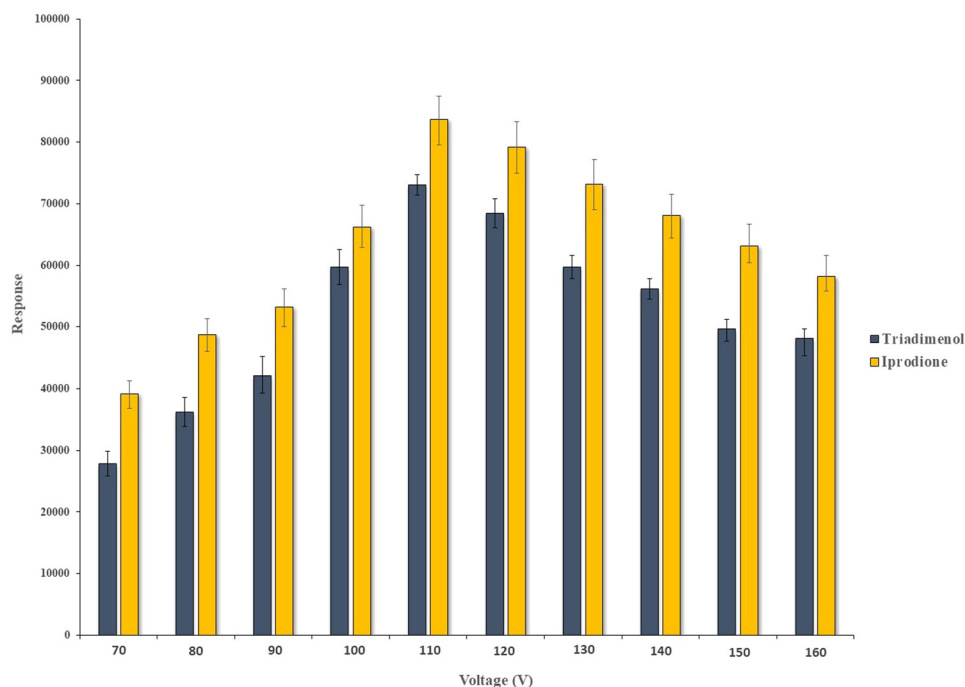


Figure 2: Effect of the applied voltage on the extraction efficiencies of the target analytes.

3.2.3 Optimization of extraction time

Extraction time is another important factor that needs to be optimized in all non-exhaustive extraction methods like EME. In EME, the extraction recoveries are limited

by the time in which the system reaches the equilibrium. After the equilibrium, the higher extraction time would not result in higher recovery. More importantly, in EME, higher extraction times can deteriorate the stability of the extraction system due to the partial loss of SLM and joule

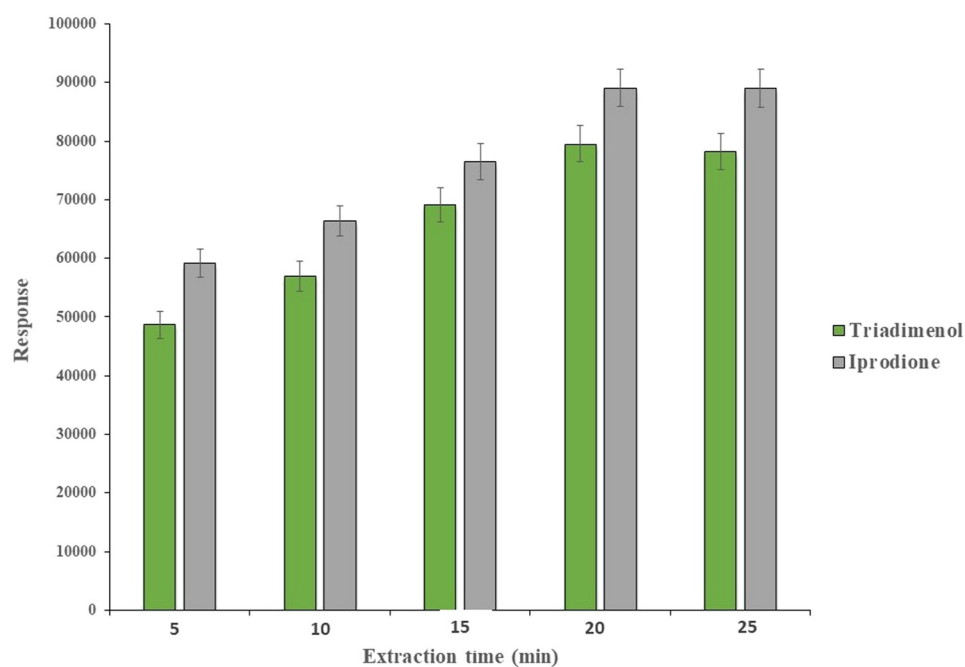


Figure 3: Effect of the extraction time on the extraction efficiencies of triadimenol and iprodione.

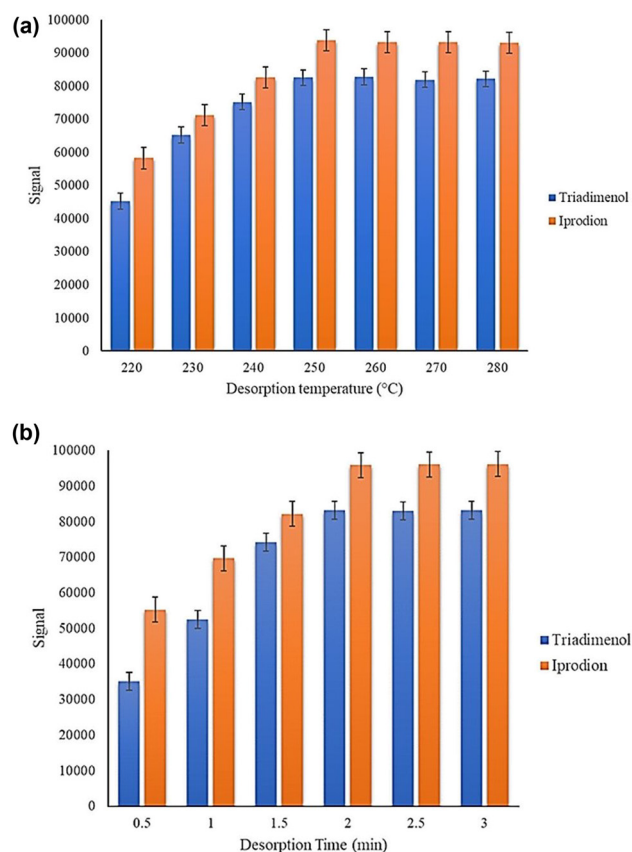


Figure 4: Influence of (a) desorption temperature and (b) desorption time, on extraction efficiencies of triadimenol and iprodione.

heating as a result of the extensive migration of ions. Therefore, the effect of this parameter was evaluated within the range of 5–25 min. The obtained are shown in Figure 3, according to which, the highest extraction efficiencies were obtained after 20 min that was selected for the rest of the studies.

3.3 Desorption conditions

In subsequent experiments, the temperature and time of desorption were investigated to ensure the complete desorption of the analytes from the coating fiber. Therefore, the desorption temperature was evaluated in the range of 220–280°C by adjusting the temperature of the injection port. The peak areas of analytes were enhanced with increasing temperature from 220 to 250°C. Above 250°C, almost no change was observed (Figure 4a). Consequently, the desorption time was investigated from 0.5 to 3 min. The results demonstrated that the highest peak areas were achieved at 2 min (Figure 4b). These experiments revealed that the optimum desorption condition was at 250°C for 2 min.

4 Method validation

To evaluate the analytical performance of the method, figures of merit of the microextraction procedure were calculated for each analyte under the optimal conditions. For this purpose, the calibration curves were plotted for extracted analytes in aqueous sample solutions. Limits of detections (LODs) of the analytes were calculated by the extraction of the target analytes from aqueous samples at low concentration levels until distinguishable signals from the noise were obtained. Furthermore, extraction recovery (EE%) for each analyte was calculated according to the following equations:

$$EE\% = \frac{n_{i,a}}{n_{i,d}} \times 100 = \frac{C_{i,a}V_a}{C_{i,d}V_d} \times 100, \quad (1)$$

where $n_{i,a}$ and $n_{i,d}$ are the number of moles of the analyte in acceptor and donor phases, $C_{i,a}$ and $C_{i,d}$ are the concentrations of the analyte in acceptor and donor phases, and V_a and V_d are the volumes of the donor and acceptor phases, respectively. It should be mentioned that $C_{i,a}$ can be obtained according to the peak area of the extracted analyte in the GC-MS system and the calibration curve obtained from direct injection of the analytes into the GC-MS instrument. Table 2 represents the obtained figures of merit for both analytes. According to this table, the calibration plots were linear in the range of 0.3–250.0 and 0.5–250.0 ng mL⁻¹ ($R^2 > 0.9973$) for triadimenol and iprodione, respectively. The overall ER% of the analytes was 12.71 and 14.87% for triadimenol and iprodione, respectively. The relatively low values of the ER% for the analytes are due to the two cumulative extraction procedures, where the ER% of the EME procedure multiplied by the ER% of the SPME method. The precisions of the method were also calculated in terms of inter-assay and intra-assay relative standard deviations (%). According to the results, RSD% values lower than 9.71% show the proposed method brought about favorable repeatability and reproducibility.

To compare the analytical performance of the method with other extraction and microextraction methods, the results are listed in Table 3. As can be seen in this table, the obtained results are quite comparable with the previous works published in the literature. Along with the low values of LODs, the linear dynamic ranges are better in comparison with some of the previous studies. Therefore, MXene can be considered a novel coating material for SPME approaches.

4.1 Real sample analysis

To investigate the applicability of the method in real samples analysis, three different environmental samples

Table 2: Figures of merit of EM-SPME-GC-MS for triadimenol and iprodione in water samples

Analyte	LOD ^a (ng mL ⁻¹)	LOQ ^b (ng mL ⁻¹)	Linearity (ng mL ⁻¹)	R ²	ER% ^c	RSD% ^d (n = 5)	
						Inter-assay	Intra-assay
Triadimenol	0.100	0.300	0.300–250.0	0.9973	12.71	5.38	7.54
Iprodione	0.150	0.500	0.500–250.0	0.9984	14.87	9.71	6.11

^aLimit of detection.^bLimit of quantification.^cExtraction recovery.^dRelative standard deviation.**Table 3:** Comparison of the analytical performance of EM-SPME-GC-MS method in determination of triadimenol and iprodione with other published studies (ng mL⁻¹)

Method	Matrix	Analyte	Analytical instrument	LOD	Linearity	RSD%	Ref.
LLE-GPC ^a	Fruits	Triadimenol iprodione	GC-ECD ^b	5.0	—	12.4	[30]
SPME ^c	Water	Triadimenol iprodione	GC-ECD	0.479	1–50	24.9	[31]
SPE ^d	Vegetables	Triadimenol iprodione	GC-MS	2.0	—	6.0	[32]
DSLLME ^e	Water	Triadimenol iprodione	HPLC-DAD ^f	0.08	0.5–200	5.7	[33]
EM-SPME	Environmental waters	Triadimenol iprodione	GC-MS	0.100	0.30–250	7.54	This work
				0.150	0.15–250	9.71	

^aLiquid–liquid extraction (LLE) followed by gel-permeation chromatography (GPC).^bGC with electron capture detector (ECD).^cSolid-phase microextraction (SPME).^dSolid-phase extraction (SPE).^eDispersion-solidification liquid–liquid microextraction (DSLLME).^fHigh-performance liquid chromatography (HPLC) with a diode array detector (DAD).

comprising lake water, river water, and irrigating water were analyzed. Table 3 shows the obtained results of the quantitative analysis of the target analytes in such samples. The accuracy of the method in quantitative analysis of the desired analytes was tested by calculating the

relative recoveries (RR%) for each analyte according to the following equation:

$$RR\% = \frac{C_{\text{found}} - C_{\text{real}}}{C_{\text{added}}} \times 100,$$

Table 4: Quantitative analysis of triadimenol and iprodione in environmental water samples by EM-SPME-GC-MS technique

Sample	Analyte	C _{real} (ng mL ⁻¹)	C _{added} (ng mL ⁻¹)	C _{found} (ng mL ⁻¹)	RR% ^a	RSD% (n = 3)
Lake water	Triadimenol	n.d. ^b	10.00	9.31	93.06	7.84
			25.00	21.83	87.31	5.61
	Iprodione	n.d.	10.00	9.74	97.44	8.12
			25.00	23.55	94.21	6.51
River water	Triadimenol	<LOQ	10.00	9.98	99.78	6.39
			25.00	24.63	98.51	7.08
	Iprodione	n.d.	10.00	8.99	89.94	7.19
			25.00	23.30	93.19	7.63
Irrigating water	Triadimenol	11.31	10.00	21.58	102.7	6.77
			25.00	36.38	100.3	5.19
	Iprodione	n.d.	10.00	9.92	99.18	6.71
			25.00	24.51	98.03	7.79

^aRelative recovery.^bNot detected.

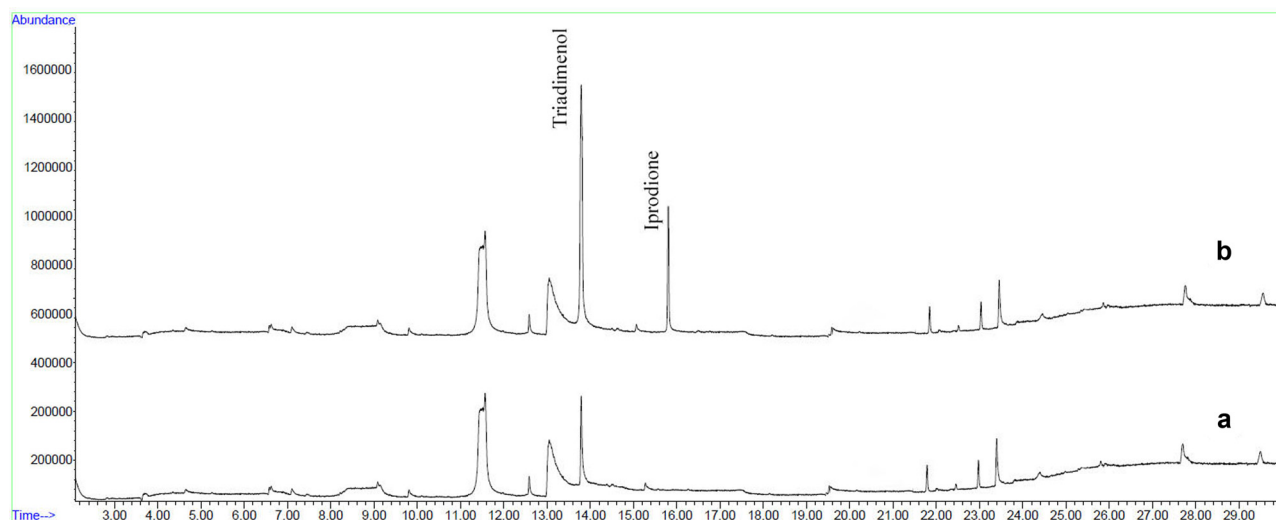


Figure 5: Chromatograms obtained from EM-SPME analysis of an irrigating water sample (a) before and (b) after spiking 20.0 ng mL^{-1} of triadimenol and iprodione.

in which C_{found} is the obtained concentration of the analyte with the addition of an exact amount of its standard solution in the real sample, C_{real} is the initial concentration of the analyte in the sample solution, and C_{added} is the amount of the analyte spiked into the real sample solution. According to the results shown in Table 4, the method had desirable accuracy as the RR% values were in the range of 87.31–102.7%. Figure 5 illustrates a chromatogram (a) before and (b) after spiking 20.0 ng mL^{-1} of both analytes into an irrigating water sample. According to what was mentioned, the method is applicable in quantitative analysis of the analytes in real samples containing a variety of contaminants. To evaluate the reusability of the coated fiber, the peak areas were investigated at different cycle times. After 80 times of use, no significant change was observed in the peak areas of target analytes, demonstrating the excellent reusability of the prepared coating fiber.

5 Conclusions

In this research, to the best of our knowledge, the newly arrived conductive nanolayers called MXene were utilized as a coating material for EM-SPME. The main aim of using electromembrane extraction prior to SPME was to achieve higher cleanup values since direct-immersion SPME usually lacks favorable cleanup in quantitative analysis of analytes in complex matrices. Thanks to the acceptable adhesion of MXene to the electrode as the substrate, the SPME fiber was directly injected into the GC-MS

instrument for separation and quantification of the target analytes. These phenomena were proved according to the clean chromatograms obtained after each GC-MS analysis of real samples. Acceptable enrichment factors as well as favorable related standard deviations showed MXene material was quite capable to be used as a new conductive coating material in sorbent-based extraction techniques.

Funding information: The author gratefully acknowledges the financial support of the Research Center for Environmental Health Technology, Iran University of Medical Sciences, Tehran, Iran (Grant Number: 99-3-61-19482; Ethics Code: IR.IUMS.REC.1399.1335).

Author contributions: All authors have accepted responsibility for the entire content of this manuscript and approved its submission.

Conflict of interest: The authors state no conflict of interest.

References

- [1] Scida K, Stege PW, Haby G, Messina GA, García CD. Recent applications of carbon-based nanomaterials in analytical chemistry: critical review. *Anal Chim Acta*. 2011;691:6–17.
- [2] Liu Q, Shi J, Jiang G. Application of graphene in analytical sample preparation. *TrAC Trends Anal Chem*. 2012;37:1–11.
- [3] Trojanowicz M. Analytical applications of carbon nanotubes: a review. *TrAC Trends Anal Chem*. 2006;25:480–9. doi: 10.1016/j.trac.2005.11.008.

- [4] Bagheri H, Ayazi Z, Naderi M. Conductive polymer-based microextraction methods: a review. *Anal Chim Acta*. 2013;767:1–13.
- [5] Wang Y, Rui M, Lu G. Recent applications of metal–organic frameworks in sample pretreatment. *J Sep Sci*. 2018;41:180–94.
- [6] Lei J-C, Zhang X, Zhou Z. Recent advances in MXene: Preparation, properties, and applications. *Front Phys*. 2015;10:276–86.
- [7] Sinha A, Zhao H, Huang Y, Lu X, Chen J, Jain R. MXene: An emerging material for sensing and biosensing. *TrAC Trends Anal Chem*. 2018;105:424–35.
- [8] Xue Q, Zhang H, Zhu M, Pei Z, Li H, Wang Z, et al. Photoluminescent Ti3C2 MXene quantum dots for multicolor cellular imaging. *Adv Mater*. 2017;29:1604847.
- [9] Collini P, Kota S, Dillon AD, Barsoum MW, Fafarman AT. Electrophoretic deposition of two-dimensional titanium carbide (MXene) thick films. *J Electrochem Soc*. 2017;164:D573–80.
- [10] Seidi S, Yamini Y, Rezazadeh M. Electrochemically assisted solid based extraction techniques: a review. *Talanta*. 2015;132:339–53.
- [11] Romero-González R, Martínez Vidal JL, Aguilera-Luiz MM, Garrido A. Frenich, Application of conventional solid-phase extraction for multimycotoxin analysis in beers by ultrahigh-performance liquid chromatography–tandem mass spectrometry. *J Agric Food Chem*. 2009;57:9385–92.
- [12] Liu W, Wang J, Song S, Hao L, Liu J, An Y, et al. Facile synthesis of uniform spherical covalent organic frameworks for determination of neonicotinoid insecticides. *Food Chem*. 2022;367:130653.
- [13] Wu Q, Song Y, Wang Q, Liu W, Hao L, Wang Z, et al. Combination of magnetic solid-phase extraction and HPLC-UV for simultaneous determination of four phthalate esters in plastic bottled juice. *Food Chem*. 2021;339:127855.
- [14] Han L, Liu X, Zhang X, Li M, Qin P, Tian S, et al. Preparation of multivariate zirconia metal–organic frameworks for highly efficient adsorption of endocrine disrupting compounds. *J Hazard Mater*. 2022;424:127559.
- [15] Li W, Zhang J, Zhu W, Qin P, Zhou Q, Lu M, et al. Facile preparation of reduced graphene oxide/ZnFe₂O₄ nanocomposite as magnetic sorbents for enrichment of estrogens. *Talanta*. 2020;208:120440–8.
- [16] Qin P, Han L, Zhang X, Li M, Li D, Lu M, et al. MIL-101(Fe)-derived magnetic porous carbon as sorbent for stir bar sorptive-dispersive microextraction of sulfonamides. *Microchim Acta*. 2021;188:340.
- [17] Zhu W, Qin P, Han L, Zhang X, Li D, Li M, et al. Gas-cycle-assisted headspace solid-phase microextraction coupled with gas chromatography for rapid analysis of organic pollutants. *Chem Commun*. 2021;57:8810–3.
- [18] Li J, Zhao B, Guo L, Wang Z, Wang C, Wang Z, et al. Synthesis of hypercrosslinked polymers for efficient solid-phase microextraction of polycyclic aromatic hydrocarbons and their derivatives followed by gas chromatography-mass spectrometry determination. *J Chromatogr A*. 2021;1653:462428–36.
- [19] Li J, Xiao Z, Wang W, Zhang S, Wu Q, Wang C, et al. Rational integration of porous organic polymer and multiwall carbon nanotube for the microextraction of polycyclic aromatic hydrocarbons. *Microchim Acta*. 2020;187:284–91.
- [20] Zang X, Pang Y, Li H, Chang Q, Zhang S, Wang C, et al. Solid phase microextraction of polycyclic aromatic hydrocarbons from water samples by a fiber coated with covalent organic framework modified graphitic carbon nitride. *J Chromatogr A*. 2020;1628:461428.
- [21] Xu M, Wang J, Zhang L, Wang Q, Liu W, An Y, et al. Construction of hydrophilic hypercrosslinked polymer based on natural kaempferol for highly effective extraction of 5-nitroimidazoles in environmental water, honey and fish samples. *J Hazard Mater*. 2022;429:128288.
- [22] Bruheim I, Liu X, Pawliszyn J. Thin-film microextraction. *Anal Chem*. 2003;75:1002–10.
- [23] Seidi S, Tajik M, Baharfar M, Rezazadeh M. Micro solid-phase extraction (pipette tip and spin column) and thin film solid-phase microextraction: Miniaturized concepts for chromatographic analysis. *TrAC Trends Anal Chem*. 2019;118:810–27.
- [24] Zhang Z, Pawliszyn J. Headspace solid-phase microextraction. *Anal Chem*. 1993;65:1843–52.
- [25] Rezazadeh M, Yamini Y, Seidi S, Ebrahimpour B. Electro-membrane surrounded solid phase microextraction: a novel approach for efficient extraction from complicated matrices. *J Chromatogr A*. 2013;1280:16–22.
- [26] Abedi H, Ebrahimzadeh H. Electromembrane-surrounded solid-phase microextraction coupled to ion mobility spectrometry for the determination of nonsteroidal anti-inflammatory drugs: a rapid screening method in complicated matrices. *J Sep Sci*. 2015;38:1358–64.
- [27] Shamsayei M, Yamini Y, Rezazadeh M, Asiabi H, Seidi S. Self-assembled benzyl mercaptan monolayer as a coating in electromembrane surrounded solid-phase microextraction of antihistamines in urine and plasma samples. *N J Chem*. 2016;40:5268–76.
- [28] Mohammadkhani E, Yamini Y, Rezazadeh M, Seidi S. Electromembrane surrounded solid phase microextraction using electrochemically synthesized nanostructured polypyrrole fiber. *J Chromatogr A*. 2016;1443:75–82.
- [29] Matisová E, Kakalíková L, Leško J, de Zeeuw J. Application of porous carbon for solid-phase extraction of dicarboximide fungicide residues from wines in combination with high-resolution capillary gas chromatography and gas chromatography-mass spectrometry. *J Chromatogr A*. 1996;754:445–54.
- [30] Sannino A, Bandini M, Bolzoni L. Multiresidue determination of 19 fungicides in processed fruits and vegetables by capillary gas chromatography after gel permeation chromatography. *J AOAC Int*. 1999;82:1229–38.
- [31] Sampedro MC, Martín O, De Armentia CL, Goicolea MA, Rodríguez E, De Balugera ZG, et al. Solid-phase microextraction for the determination of systemic and non-volatile pesticides in river water using gas chromatography with nitrogen-phosphorous and electron-capture detection. *J Chromatogr A*. 2000;893:347–58.
- [32] González-Rodríguez RM, Rial-Otero R, Cancho-Grande B, Simal-Gándara J. Determination of 23 pesticide residues in leafy vegetables using gas chromatography–ion trap mass spectrometry and analyte protectants. *J Chromatogr A*. 2008;1196:100–9.
- [33] Wang C, Wu Q, Wu C, Wang Z. Application of dispersion–solidification liquid–liquid microextraction for the determination of triazole fungicides in environmental water samples by high-performance liquid chromatography. *J Hazard Mater*. 2011;185:71–6.