



# Thermally stable ionic liquid-based sol–gel coating for ultrasonic extraction–solid-phase microextraction–gas chromatography determination of phthalate esters in agricultural plastic films

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## ABSTRACT

A novel sol–gel-coated ionic liquid-based ([AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO) fiber was successfully applied for the determination of phthalate esters (PAEs) in agricultural plastic films by ultrasonic extraction (UE) combined with solid phase microextraction–gas chromatography (SPME–GC) due to its high thermal stability, specific selectivity and extraction efficiency. The extractant for UE and the adsorption time for SPME were optimized to achieve higher extraction efficiency. The desorption temperature and time were also optimized to avoid the carryover effect of previous extraction, and ultimately improve the precision and accuracy of the method. The [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber showed comparable, or even higher response to most of the investigated PAEs than the commercial PDMS, PDMS–DVB and PA fibers. The carryover problem, often encountered when using commercial fibers, had been eliminated when desorption was performed at 360 °C for 8 min. The proposed SPME–GC method showed good linearity over three to four orders of magnitude, and low limits of detection ranged from 0.003 to 0.063 μg L<sup>-1</sup>. The relative standard deviation values obtained were below 10%, and the recoveries were in the ranges of 90.2–111.4%. Some of the PAEs studied were detected at very high concentration in these agricultural plastic film samples, resulting in a potential risk of crop damage, environmental contamination and human health exposure.

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## 1. Introduction

Plastic films were widely used in agriculture and particularly in protected horticulture to conserve water and fertilizer, to

provide a better microenvironment for the plants, and to protect against adverse climatic conditions over the last decades [1]. They have played an important and irreplaceable role in improving the agricultural productivity and developing the agricultural economy. Unfortunately, the extensive and expanding use of plastics in agriculture will result in increased accumulation of plastic wastes in farming circumstance, which will lead to soil compaction, and thus retarded crop growth [2]. Furthermore, phthalate esters (PAEs)—the commonly used plasticizers in plastic films, will be easily and continuously leached from the plastic wastes into the environment [3]. This ubiquitous presence of PAEs in agricultural soils will bring about potential contamination of crops, vegetables and food chains, and thus result in direct or indirect human exposure [4]. Nowadays, the US Environmental Protection Agency (EPA) and its counterparts in several other countries have classified PAEs as priority pollutants and endocrine disrupting compounds [5].

Analysis of PAEs in agricultural plastic films and their polluted soils is a difficult task, because of the high complexities of

**Abbreviations:** [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>], 1-Allyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide; OH-TSO, Hydroxy-terminated silicone oil; KH-570, γ-Methacryloxypropyltrimethoxysilane; PMHS, Poly(methylhydrosiloxane); TEOS, Tetraethoxysilane; TFA, Trifluoroacetic acid; PAEs, Phthalate esters; UE, Ultrasonic extraction; SPME, Solid phase microextraction; EPA, Environmental Protection Agency; DMP, Dimethyl phthalate; DEP, Diethyl phthalate; DBP, Dibutyl phthalate; DAP, Diamyl phthalate; DiOP, Diisooctyl phthalate; DnOP, Di-n-octyl phthalate; DNP, Dinonyl phthalate; DDP, Didecyl phthalate; PP, Polypropylene; PE, Polyethylene.

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the sample matrixes and the low concentrations at which these compounds are usually present. It is usually necessary to carry out extensive sample pretreatment prior to instrumental analysis in order to obtain reproducible, accurate and sensitive quantitative results. Until now, various pretreatment techniques have been proposed for the extraction and concentration of PAEs from plastic, sediment, sludge, leachate and soil samples, such as ultrasonic extraction (UE) [6], microwave assisted extraction [7,8], supercritical fluid extraction [9,10], accelerated solvent extraction [11,12], soxhlet extraction/solid phase extraction [13,14], microwave assisted extraction/dispersive solid phase extraction [15], solid phase microextraction (SPME) [16] and UE/SPME [17]. However, most of these methods require large volumes of toxic organic solvents which are environmentally unfriendly, and the extraction processes are complicated, tedious and time-consuming.

SPME has broken a new path for sample pretreatment over the last two decades due to its solvent-free and miniaturization characteristics [18]. In the past few years, there have been several papers that deal with the SPME analysis of PAEs using different fibers such as calix[4]arene [17], carbowax-divinylbenzene [19], polyacrylate [20], polyaniline [21] and calix[6]arene [22]. However, some of these fibers are not so stable that they cannot tolerate too high desorption temperature [23]. For example, the recommended maximum operation temperature for PDMS (100  $\mu\text{m}$ ) fiber was 280 °C. This temperature is not high enough for complete desorption of PAEs from this fiber since PAEs have very high molecular masses and boiling points. Therefore, the precision was poor for some of these fibers [5,19].

Ionic liquids, as a class of non-molecular ionic solvents, have many favorable properties [24]. These unique properties have made ionic liquids desirable extraction media and selective stationary phases in SPME [25–35]. In our previous work, a chemically bonded ionic liquid-based organic–inorganic hybrid SPME fiber, 1-allyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide–hydroxy-terminated silicone oil ([AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO), was prepared by sol–gel method and free radical cross-linking technology [36]. This fiber was found to be highly selective and sensitive to phenolic environmental estrogens and aromatic amines compared with commercial PDMS, PDMS–DVB and PA fibers. It also has high thermal stability with a transition temperature of 402 °C, good solvent resistance, satisfactory coating preparation repeatability and long lifetime. All these advantages make it very suitable for the analysis of PAEs in plastic films used in agriculture.

In this study, the sol–gel-coated [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber was developed and employed for the determination of PAEs in several agricultural plastic films by UE combined with SPME–GC. The solvent types used for UE and the adsorption time used for SPME were optimized. To avoid carryover effect of previous extraction, the temperature and time needed for complete desorption of PAEs from this fiber was also determined.

## 2. Experimental

### 2.1. Apparatus

A SP-6890 capillary GC system (Shandong Lunan Ruihong Chemical Instrument Corporation, Shandong, China) equipped with a capillary split/splitless injector and a flame ionization detector was employed for the UE–SPME–GC analysis of PAEs. On-line data collection and processing was accomplished with N2000 Chromastation Software (Zhejiang University Zhida Information Engineering Co., Ltd, Hangzhou, China). The chromatography

separations were performed using a SE-54 fused silica capillary column (30 m  $\times$  0.25 mm I.D., 0.25  $\mu\text{m}$  film thickness) (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China). The column temperature program was: 150 °C for 2 min, and then programmed at 15 °C min<sup>-1</sup> to 300 °C, held for another 20 min. The injection port temperature was maintained at 360 °C and the detector temperature was at 380 °C. Nitrogen gas was used as the carrier gas at a linear velocity of 12–15 cm s<sup>-1</sup> in the 1:20 split mode for all the analytes. An ultrasonicator model SB-3200 (Branson Ultrasonics Co., Ltd, Shanghai, China) was used for the extraction of PAEs from the agricultural plastic film samples. A magnetic stirrer DF-101B (Zhengzhou Greatwall Scientific Industrial and Trading Co., Ltd, Zhengzhou, China) was used for stirring the sample solution during extraction. The homemade SPME syringes with sol–gel-derived [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fibers were applied to the extraction of PAEs from the methanolic extracts of the agricultural plastic film samples. The commercial PDMS (100  $\mu\text{m}$ ), PDMS–DVB (65  $\mu\text{m}$ ) and PA-coated fibers (85  $\mu\text{m}$ ) for comparison were purchased from Supelco (Bellefonte, PA, USA).

### 2.2. Reagents and materials

The fused-silica fiber (125  $\mu\text{m}$ , O.D.) with protective polyimide coating was purchased from Fibrehome Telecommunication Technologies Co., Ltd. (Wuhan, China). [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] was obtained from Chengjie Chemical Co., Ltd. (Shanghai, China). OH-TSO and poly(methylhydrosiloxane) (PMHS) were purchased from Xinli Chemical Industry Co., Ltd. (Zigong, China). Tetraethoxysilane (TEOS) and  $\gamma$ -methacryloxypropyltrimethoxysilane (KH-570) were obtained from the Chemical Plant of Wuhan University (Wuhan, China). Trifluoroacetic acid (TFA) and benzophenone were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), diamyl phthalate (DAP), diisooctyl phthalate (DiOP), di-n-octyl phthalate (DnOP), dinonyl phthalate (DNP), didecyl phthalate (DDP), NaCl, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>OH, and acetone were analytical-reagent grade and supplied by Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. A stock standard solution was prepared by dissolving 10 mg of each PAEs compound in 10 mL methanol in a volumetric flask to reach a concentration of 1 mg mL<sup>-1</sup>. Six kinds of polypropylene (PP) and polyethylene (PE) plastic films used in agriculture were purchased from the market of agricultural machinery in Wuhan. The PP films have no specific thicknesses which can only be divided into three different categories: thin, medium and thick, and the most thickness of which is less than 0.06 mm. The thicknesses of the PE films are 0.06 mm, 0.08 mm and 0.10 mm, respectively.

### 2.3. Fiber preparation

The sol–gel coated [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber was prepared as follows: A 50 mg of [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] was dissolved in 300  $\mu\text{L}$  of CH<sub>2</sub>Cl<sub>2</sub>. Then 90 mg of OH-TSO, 100  $\mu\text{L}$  of TEOS, 50  $\mu\text{L}$  of KH-570, 10  $\mu\text{L}$  of PMHS and 8 mg of benzophenone were added and mixed thoroughly by ultrasonic agitation. A 60- $\mu\text{L}$  portion of 95% TFA in water was subsequently added dropwise to the resulting solution under vigorous ultrasonic agitation. The mixture was then centrifuged at 12,000  $\times g$  for 8 min to remove the precipitate. The clear supernatant was transferred to another clean plastic tube for further use in the coating process. The treated fused-silica fiber was dipped in the sol solution for 2–3 h to facilitate the formation of IL-based organic–inorganic copolymer and its chemical bonding to the fiber substrate. After that, the fiber was drawn out from the sol solution to volatilize the solvents, and inserted vertically into the sol solution once more. A sol–gel

coating with an appropriate thickness was formed on the outer surface of the treated fiber end after several repetitions of the inserting and drawing out processes. Finally, the fiber was irradiated under ultraviolet light for 30 min, then placed in a desiccator for 24 h at room temperature and conditioned in the GC injection port for 2 h at 360 °C under nitrogen atmosphere. The sol-gel-derived OH-TSO fiber was also coated with the same procedure for comparison except that IL was not added into the sol solution.

#### 2.4. SPME procedures for the analysis of PAEs in standard solutions

For PAEs analysis, a 10- $\mu\text{L}$  portion of this stock solution was diluted with 8 mL deionized water saturated with 3 g NaCl. Before the first usage, the [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber was conditioned in the GC injection port at 360 °C for 2 h. The extraction of PAEs was carried out by direct immersion of the fiber in the sample solution for 40 min at 30 °C. The aqueous sample was continuously stirred at a speed of 750 rpm with a magnetic stir bar during extraction. In order to protect the coating from being destroyed by the NaCl particles formed and deposited on the fiber surface during thermal desorption, the fiber was rinsed with distilled water before being introduced to the GC injector. To prevent the samples from being adsorbed on the glass wall, the amber vials were acid washed and silanized prior to the SPME experiments.

#### 2.5. Validation of the method

A series of standard solutions at 0.0001, 0.001, 0.01, 0.1, 0.5 and 1 mg mL<sup>-1</sup> were prepared by dilution of the stock solution at a concentration of each 1 mg mL<sup>-1</sup>. 10  $\mu\text{L}$  of these standard solutions were spiked to 8 mL deionized water saturated with 3 g NaCl to yield concentrations ranging from 0.125 to 1250  $\mu\text{g L}^{-1}$ . Each concentration level was analyzed in triplicate to obtain the linear ranges, the calibration curves and the limits of detection (LODs). The LODs were estimated by calculating the concentrations of PAEs that produce signals three times the background noise (signal/noise=3). The precision, expressed as relative standard deviation (RSD), was determined by performing five consecutive extractions of the spiked aqueous samples containing 1250  $\mu\text{g L}^{-1}$  of each PAEs.

#### 2.6. UE combined with SPME for the analysis of PAEs in plastic films used in agriculture

The plastic films used in agriculture were cut to pieces of approximately 0.5  $\times$  0.5 cm<sup>2</sup> in size. A 0.200 g of these fragments were taken and mixed with 10 mL of methanol, and then shaken for 30 min by ultrasonic agitation at room temperature. For SPME analysis, a 100  $\mu\text{L}$  of methanolic extracts of the agricultural plastic film samples was injected into 8 mL saturated NaCl solution in a 12-mL amber vial, and then sealed with butyl rubber stopper and aluminum cap by capping machine. The extraction and desorption procedures were identical with that described in Section 2.4. PAEs in these agricultural plastic film samples were identified by comparison of retention time with known standards, and their concentrations were calculated from the calibration curves obtained in Section 2.5.

To evaluate the accuracy of the proposed method, a 10- $\mu\text{L}$  portion of the PAEs stock solution was spiked to 8 mL saturated NaCl solution containing 100  $\mu\text{L}$  of methanolic extracts of the PE agricultural film (0.06 mm). Both spiked and unspiked samples were analyzed in triplicate and the average values were reported.

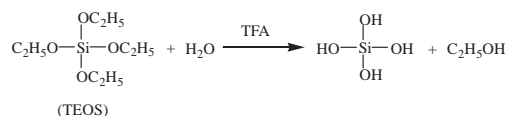
Percentage recovery was calculated as [(final amount found in the spiked sample – initial amount found in the unspiked sample)/the amount added]  $\times$  100.

### 3. Results and discussion

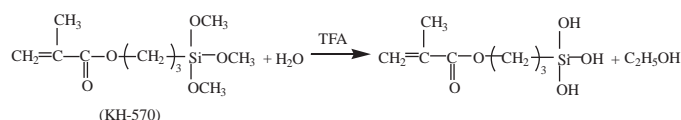
#### 3.1. Preparation of sol-gel coated [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber

In this work, a chemically bonded [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO hybrid coating was prepared with the aid of KH-570 as a bridge using the sol-gel method employing a cross-linking technique. The key sol-gel reactions involved in the coating procedure are:

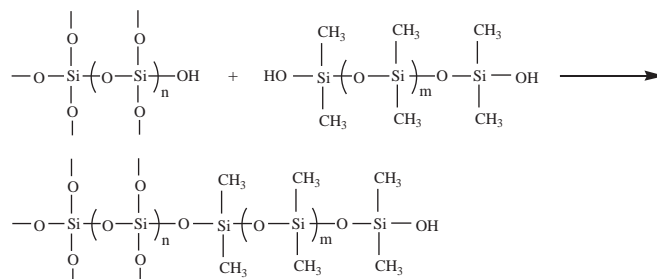
##### (1) catalysis hydrolysis of the alkoxysilane precursor TEOS



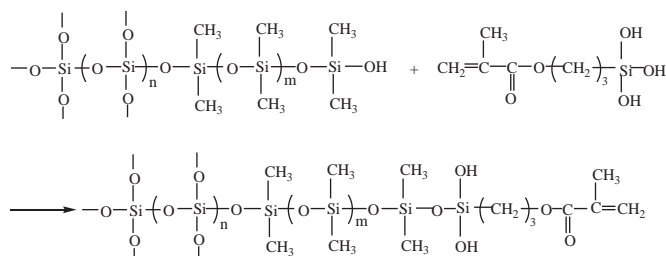
##### (2) catalysis hydrolysis of the coprecursor KH-570



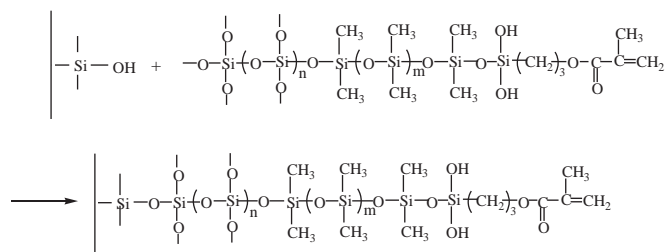
##### (3) polycondensation of the hydrolyzed TEOS with OH-TSO to form a three-dimensional silica network



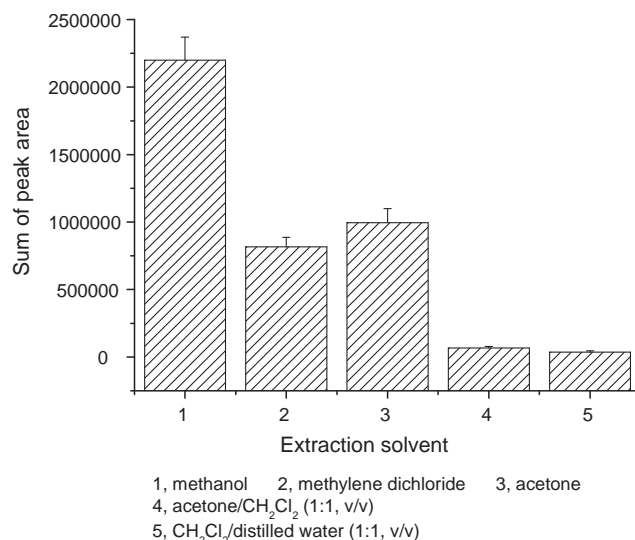
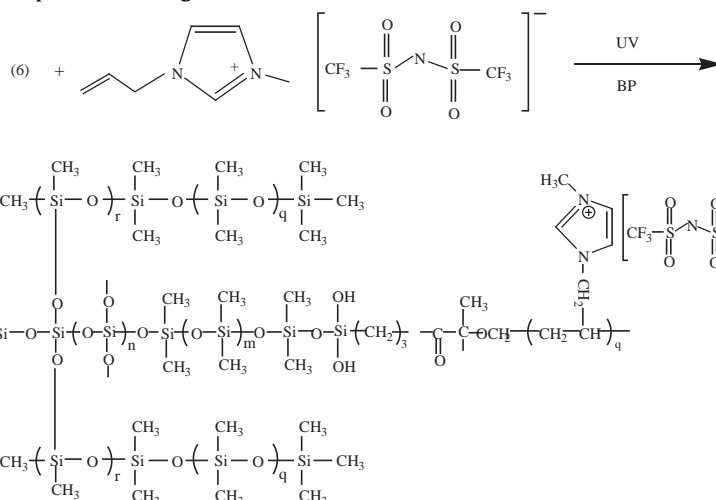
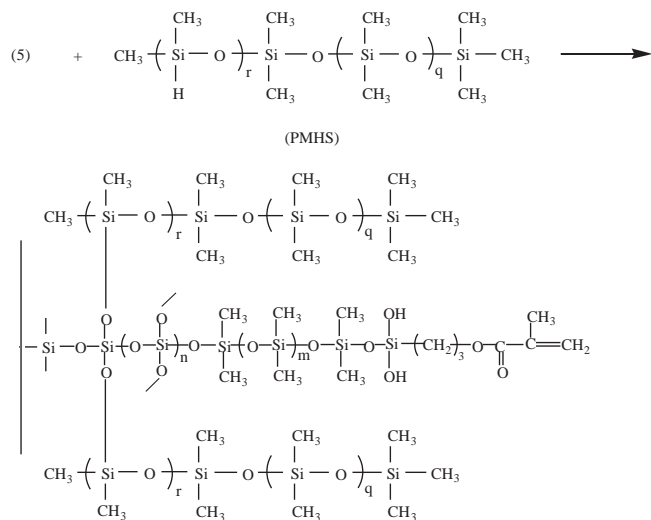
##### (4) chemical bonding of the hydrolyzed KH-570 to the evolving sol-gel network



##### (5) chemical bonding of the formed sol-gel silica substrate to the outer surface of the fused-silica fiber to create a surface-bonded polymeric coating



(6) deactivation of the surface silanol groups of the formed sol-gel silica substrate with PMHS



**Fig. 1.** Comparison of the amounts of PAEs extracted from agricultural plastic film samples by UE using different solvents. SPME-GC conditions: injection port temperature, 300 °C; detector temperature, 300 °C; oven temperature, 150 °C for 2 min, programmed at 15 °C min<sup>-1</sup> to 300 °C, held for another 20 min; splitless injection. Extraction temperature, 30 °C; extraction time, 40 min; desorption time, 5 min; NaCl, 40% (m/m); stirring rate, 750 rpm.

### 3.2. Optimization of UE conditions

The effect of solvent type on UE of PAEs from agricultural plastic film samples was studied and optimized, as shown in Fig. 1. These solvents include CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>OH, acetone, acetone/CH<sub>2</sub>Cl<sub>2</sub> (1:1, v/v) and CH<sub>2</sub>Cl<sub>2</sub>/distilled water (1:1, v/v). Three replicated analyses were performed by UE for each considered solvent. The solvent extracts of these agricultural plastic film samples were analyzed by SPME combined with GC, as described in Section 2.6. The y-axis values represented the total peak areas of all these PAEs extracted. The results showed that the amount of PAEs extracted was largest when methanol was selected as the extractant.

### 3.3. Optimization of SPME operating conditions

To obtain maximum extraction efficiency, several critical variables were studied and optimized for SPME of PAEs, including extraction time, desorption temperature and desorption time.

#### 3.3.1. Extraction time

The effect of extraction time on the extraction efficiency was studied by monitoring the peak area as a function of time. Three replicated analyses were performed for each time. In order to reduce the diffusion layer and quicken the mass transfer, magnetic stirring at a constant rate was applied throughout the extraction process. The extraction time profiles are shown in Fig. 2. The results showed that the amount of PAEs extracted did not reach equilibrium even at 70 min. It is not necessary to attain extraction equilibrium if the experimental conditions are tightly controlled during the extraction [37]. An extraction time of 40 min was, therefore, selected for subsequent analysis in order to assure adequate sensitivity, while not to increase time-consuming.

#### 3.3.2. Desorption temperature and time

Carryover effect is a common problem encountered in the analysis of PAEs by SPME-GC method. To avoid cross contamination between samples, the temperature and time needed for complete desorption of PAEs from the [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber

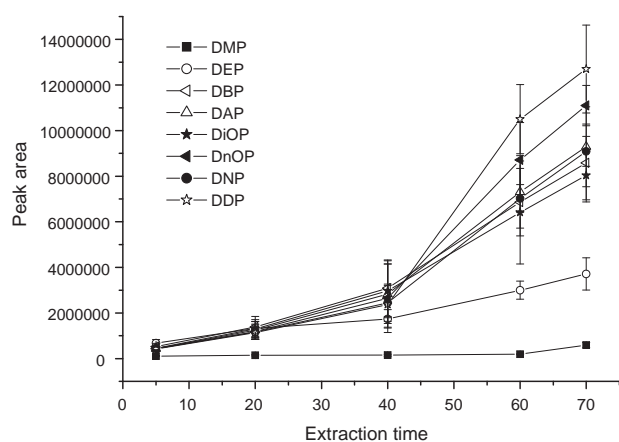
**Table 1**  
Effect of desorption conditions on the carryover of PAEs in the sol-gel-coated [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber.

Desorption conditions	Carryover percentage (%)							
	DMP	DEP	DBP	DAP	DiOP	DnOP	DNP	DDP
280 °C, 5 min	0.1 ± 0.1	1.1 ± 0.1	13.5 ± 4.9	19.3 ± 3.4	28.6 ± 5.2	28.0 ± 4.3	34.3 ± 8.6	20.3 ± 9.5
300 °C, 5 min	– <sup>a</sup>	0.5 ± 0.4	8.5 ± 2.1	16.0 ± 5.7	21.1 ± 1.9	21.6 ± 5.6	28.7 ± 9.9	19.8 ± 8.7
320 °C, 5 min	–	0.4 ± 0.2	7.3 ± 3.5	15.6 ± 5.9	20.6 ± 0.3	20.6 ± 2.3	23.3 ± 1.0	18.0 ± 7.9
340 °C, 5 min	–	–	4.7 ± 2.4	14.1 ± 3.6	15.2 ± 2.8	–	14.3 ± 4.5	–
360 °C, 5 min	–	–	–	2.3 ± 1.8	3.3 ± 2.5	–	–	–
280 °C, 8 min	–	0.3 ± 0.2	7.4 ± 3.6	13.0 ± 4.2	24.3 ± 7.4	24.1 ± 3.6	30.0 ± 8.5	19.7 ± 8.6
300 °C, 8 min	–	0.3 ± 0.2	5.2 ± 3.8	8.9 ± 2.5	18.9 ± 6.8	13.9 ± 5.7	24.0 ± 9.7	18.0 ± 9.0
320 °C, 8 min	–	0.2 ± 0.1	4.1 ± 1.6	6.2 ± 1.3	15.3 ± 3.8	11.0 ± 0.3	22.0 ± 3.1	15.3 ± 7.1
340 °C, 8 min	–	–	2.7 ± 1.6	5.7 ± 1.8	12.8 ± 3.4	–	9.4 ± 4.6	–
360 °C, 8 min	–	–	–	1.5 ± 1.2	2.2 ± 2.0	–	–	–

SPME-GC conditions: oven temperature, 150 °C for 2 min, programmed at 15 °C min<sup>-1</sup> to 300 °C, held for another 20 min; detector temperature, 380 °C; splitless injection. Extraction temperature, 30 °C; extraction time, 40 min; NaCl, 40% (*m/m*); stirring rate, 750 rpm.

<sup>a</sup> No carryover.

were determined, as shown in Table 1. The experiment process was as follows: When an extraction was finished, the fiber was pulled back and inserted into the GC injection port (280, 300, 320, 340 or 360 °C) for several minutes (5 or 8 min) of thermal desorption. This desorption process was repeated several times after the GC analysis was completed, until no chromatographic peak was determined. Two replicated experiments were undertaken for each desorption condition. The carryover percentage of an analyte was calculated as [(sum of peak area of each desorption – peak area of the first desorption)/sum of peak area of each desorption]. High percentage of carryover was found for most of the PAEs studied when analyte desorption was carried out at 280 °C for 5 min. This desorption condition is commonly recommended for some of the commercially available fibers. The carryover of PAEs in the developed fiber can be reduced by an appropriate increase of desorption temperature and time. However, the lifetime of the fiber will become short if desorption time is too long, or if too high temperature is required for the desorption process. Moreover, the chromatogram peak will become wide and tailed if desorption time is too long. Therefore, the desorption time investigated was not increased beyond 8 min. As revealed from the table, the carryover effect of previous extraction can be eliminated when desorption was performed at 360 °C for 8 min, owing to the high thermal stability of the sol-gel-coated [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber. Moreover, it was still stable and reusable after undergoing 122 times of thermal desorption

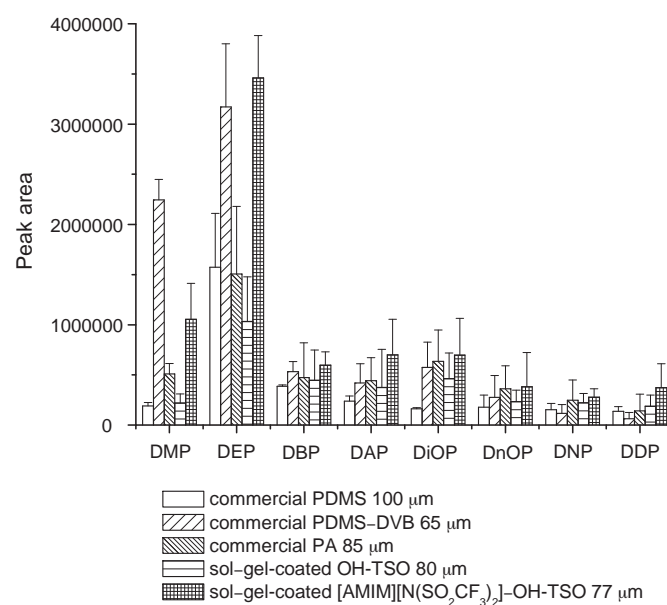


**Fig. 2.** The extraction time profile of PAEs on the sol-gel-coated [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber. SPME-GC conditions: injection port temperature, 300 °C; detector temperature, 300 °C; oven temperature, 150 °C for 2 min, programmed at 15 °C min<sup>-1</sup> to 300 °C, held for another 20 min; splitless injection. Extraction temperature, 30 °C; desorption time, 5 min; NaCl, 40% (*m/m*); stirring rate, 750 rpm.

processes during the carryover experiment. This result indicated that the developed fiber can ensure a long lifetime even under such high desorption temperature. Therefore, in this paper, the fiber was desorbed at 360 °C for 8 min for subsequent analysis.

### 3.4. Selectivity and extraction efficiency

Fig. 3 compares the amounts of PAEs extracted by sol-gel derived OH-TSO, [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO and commercial PDMS, PDMS-DVB and PA fibers. To make a standard comparison, desorption temperature was maintained at 260 °C for all these fibers, considering that the maximum temperature for commercial PDMS, PDMS-DVB and PA fibers was 280, 270 and 320 °C, respectively. The extraction was undertaken in quadruplicate for each fiber. As revealed from this figure, the sol-gel [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO-coated fiber provides a much higher response to PAEs than does the sol-gel OH-TSO-coated fiber, owing to the introduction of ionic liquid in the hybrid organic-inorganic coating. Undoubtedly, ionic liquid, as a selective adsorbent, plays an



**Fig. 3.** Comparison of the amounts of PAEs extracted by the sol-gel-coated OH-TSO, [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO and commercial PDMS, PDMS-DVB and PA fibers. SPME-GC conditions: injection port temperature, 260 °C; detector temperature, 300 °C; oven temperature, 150 °C for 2 min, programmed at 15 °C min<sup>-1</sup> to 300 °C, held for another 20 min; splitless injection. Extraction temperature, 30 °C; extraction time, 40 min; desorption time, 8 min; NaCl, 40% (*m/m*); stirring rate, 750 rpm.



**Table 2**  
Linear ranges, LODs, precisions and accuracies for SPME–GC analysis of PAEs in agricultural plastic films with the sol–gel-derived [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber.

PAEs	Linear range ( $\mu\text{g L}^{-1}$ )	Regression equations	LOD <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	Precision ( $n = 5^b$ , RSD%)	Relative recoveries <sup>c</sup> (%)
DMP	0.125–1250	$y = 24655 + 82x$	0.003	8.0	90.2
DEP	0.125–625	$y = 1377 + 417x$	0.038	9.3	97.3
DBP	0.125–1250	$y = 8635 + 407x$	0.005	6.6	103.7
DAP	0.125–1250	$y = 5815 + 235x$	0.003	8.7	108.8
DiOP	0.125–625	$y = 11810 + 307x$	0.003	0.7	111.4
DnOP	0.125–1250	$y = 3447 + 240x$	0.010	8.3	109.4
DNP	0.125–1250	$y = 7599 + 151x$	0.013	5.8	99.5
DDP	0.125–625	$y = 2128 + 92x$	0.063	7.8	103.5

SPME–GC conditions: injection port temperature, 360 °C; detector temperature, 380 °C; oven temperature, 150 °C for 2 min, programmed at 15 °C min<sup>-1</sup> to 300 °C, held for another 20 min; splitless injection. Extraction temperature, 30 °C; extraction time, 40 min; desorption time, 8 min; NaCl, 40% (*m/m*); stirring rate, 750 rpm.

<sup>a</sup> LODs were estimated on the basis of 3:1 signal-to-noise ratios.

<sup>b</sup> Precisions were evaluated by the RSD values of five consecutive extractions of PAEs from the standard solutions under the same analytical conditions.

<sup>c</sup> XXX Relative recovery (%) =  $\frac{\text{final amount found in the spiked sample} - \text{initial amount found in the unspiked sample}}{\text{the amount added}} \times 100$ .

**Table 3**  
The contents and precisions of PAEs determined in agricultural plastic film samples with the developed UE–SPME–GC method.

Agricultural plastic film samples	Sample 1 PP (thin)	Sample 2 PP (middle)	Sample 3 PP (thick)	Sample 4 PE (0.06 mm)	Sample 5 PE (0.08 mm)	Sample 6 PE (0.10 mm)	
DMP	Content <sup>a</sup> ( $\mu\text{g g}^{-1}$ ) Precision <sup>c</sup> (%)	610.5 ± 30.5 5.0	nd <sup>b</sup> –	644.1 ± 64.4 10.0	1170 ± 63.2 5.4	392.3 ± 37.7 9.6	1240 ± 111.6 9.0
DEP	Content ( $\mu\text{g g}^{-1}$ ) Precision (%)	80.4 ± 3.3 4.1	nd –	44.9 ± 4.5 10.1	78.8 ± 7.5 9.5	nd –	nd –
DBP	Content ( $\mu\text{g g}^{-1}$ ) Precision (%)	202.2 ± 14.4 7.1	nd –	344.7 ± 36.2 10.5	nd –	nd –	nd –
DAP	Content ( $\mu\text{g g}^{-1}$ ) Precision (%)	512.5 ± 40.0 7.8	nd –	491.9 ± 52.1 10.6	54.1 ± 2.4 4.4	60 ± 2.8 4.7	nd –
DiOP	Content ( $\mu\text{g g}^{-1}$ ) Precision (%)	146.8 ± 2.3 1.6	nd –	1300 ± 93.6 7.2	39.5 ± 2.1 5.2	433.6 ± 33.8 7.8	89.8 ± 7.4 8.2
DnOP	Content ( $\mu\text{g g}^{-1}$ ) Precision (%)	17.9 ± 1.4 7.7	nd –	868.5 ± 25.2 2.9	110.4 ± 6.2 5.6	992.1 ± 102.2 10.3	270 ± 29.4 10.9
DNP	Content ( $\mu\text{g g}^{-1}$ ) Precision (%)	51.7 ± 2.3 4.5	246.3 ± 23.9 9.7	2754 ± 250.6 9.1	25.3 ± 2.2 8.5	362.3 ± 27.2 7.5	190 ± 12.7 6.7
DDP	Content ( $\mu\text{g g}^{-1}$ ) Precision (%)	2440 ± 247.7 10.2	nd –	2732 ± 248.6 9.1	54.9 ± 4.6 8.3	1583 ± 87.1 5.5	nd –

SPME–GC conditions are the same as in Table 2.

<sup>a</sup> The quantification was carried out by the external standard method. Each analysis was performed in triplicate.

<sup>b</sup> Not detected.

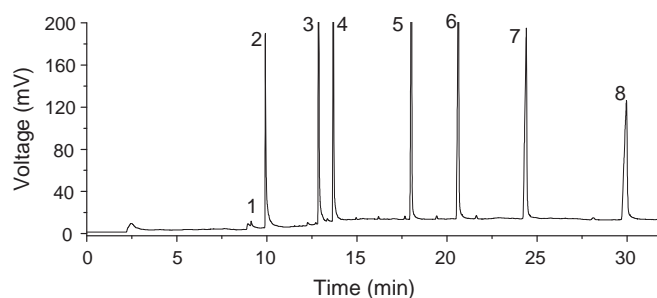
<sup>c</sup> Precisions were evaluated by the RSD values of three consecutive extractions of PAEs from the agricultural plastic film samples under the same analytical conditions.

important role in the extraction. The extraction ability of the ionic liquid-based sol–gel coating was superior to that of PDMS. It was also comparable to that of PDMS–DVB and PA fibers for most of the PAEs studied. The amount of the more polar DMP extracted by the ionic liquid-based fiber was, however, lower than that extracted by the PDMS–DVB fiber. This is maybe because the former has a weaker polarity than the latter. However, if the desorption temperature is enhanced to 360 °C, the developed ionic liquid fiber maybe has higher response to most of the PAEs due to its higher thermal stability and lower carryover effect in comparison with these commercial fibers. The high selectivity and extraction efficiency of the sol–gel [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO-coated fiber is mainly attributed to these two facts: (1) the strong electrostatic and  $\pi$ – $\pi$  interactions between [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] and PAEs; (2) the higher surface area and sample capacity of sol–gel coating in comparison with commercial coatings prepared by physical deposition. In addition, the error bars are very large for all these fibers when desorption temperature is maintained at 260 °C, indicating that high desorption temperature is necessary for the improvement of the precision and accuracy of the SPME–GC analysis of PAEs.

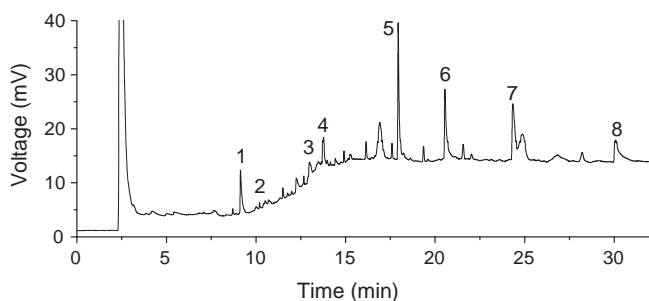
### 3.5. Validation of the method

Table 2 lists the linear ranges, limits of detection (LODs), precisions and accuracies for SPME–GC analysis of PAEs in agricultural plastic films with the sol–gel-derived [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber. The linearity was very good in the range of

0.125–1250  $\mu\text{g L}^{-1}$  for most analytes. The relative standard deviation (RSD) values were below 10% in all cases, ranging from 0.7% to 9.3%, which were much lower than those obtained with commercial fibers [19]. This is because the carryover effect of previous extraction is not obvious under such high desorption temperature (about 360 °C). The low carryover helps to obtain a satisfactory precision for the proposed method. Low LODs, varying from 0.003 to 0.063  $\mu\text{g L}^{-1}$ , were achieved for most of the PAEs studied owing to the high selectivity and sensitivity of this ionic liquid-based sol–gel coating. Although validation experiments were carried out using



**Fig. 4.** Typical SPME–GC chromatogram of an aqueous solution spiked with 1250  $\mu\text{g L}^{-1}$  of PAEs using the sol–gel-coated [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber. SPME–GC conditions are the same as in Table 2. Peaks: (1) DMP, (2) DEP, (3) DBP, (4) DAP, (5) DiOP, (6) DnOP, (7) DNP, and (8) DDP.



**Fig. 5.** Typical SPME–GC chromatogram of methanolic extracts of the agricultural plastic film sample by UE using the sol–gel-coated [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO fiber. SPME–GC conditions are the same as in Table 2. Peaks: (1) DMP, (2) DEP, (3) DBP, (4) DAP, (5) DiOP, (6) DnOP, (7) DNP, and (8) DDP.

standard solutions, no significant matrix effects were observed for these samples from the recovery experiments. This is because only 100  $\mu\text{L}$  of methanolic extracts of the agricultural plastic film sample was injected into 8 mL saturated NaCl solution for subsequent SPME analysis, that is to say, the sample matrix is diluted to 1/80 of its original concentration. The relative recoveries obtained for PAEs ranged from 90.2% to 111.4%, demonstrating that the accuracy of the developed UE–SPME–GC method was satisfactory for the analysis of PAEs in plastic films used in agriculture. Fig. 4 shows a typical SPME–GC chromatogram of an aqueous solution spiked with 1250  $\mu\text{g L}^{-1}$  of PAEs.

### 3.6. Analysis of PAEs in plastic films used in agriculture

The proposed UE–SPME–GC method was used for the determination of PAEs in six kinds of PP and PE agricultural plastic films with different thicknesses. The contents and precisions of PAEs determined in these agricultural plastic film samples are shown in Table 3. It showed that most of the investigated agricultural plastic film samples were found to have very high content of PAEs, especially the commonly occurring DMP, DEP, DBP and DOP, which were identified as priority pollutants by the US EPA. Moreover, the variety and content of plasticizers determined were different from each other depending on the thicknesses and the materials used for the manufacture of the agricultural plastic films. For example, the content of DMP in most of these samples ranged from 392.3  $\mu\text{g g}^{-1}$  to 1240  $\mu\text{g g}^{-1}$ . The content of DEP and DBP in Sample 1 reached to 80.4  $\mu\text{g g}^{-1}$  and 202.2  $\mu\text{g g}^{-1}$ , and that of DiOP and DnOP in Sample 3 reached to 1300  $\mu\text{g g}^{-1}$  and 868.5  $\mu\text{g g}^{-1}$ , respectively. The content of DDP was also very high in some of these agricultural plastic film samples, attaining 2240  $\mu\text{g g}^{-1}$  for Sample 1, 2732  $\mu\text{g g}^{-1}$  for Sample 3 and 1583  $\mu\text{g g}^{-1}$  for Sample 5. These results demonstrated that PAEs were still used as plasticizers during the manufacturing of the agricultural plastic films. This will lead to a potential risk of harm to the crops, the environment, and ultimately the human health due to the continuous release of these compounds to the environment. Fig. 5 represents a typical SPME–GC chromatogram of the methanolic extracts of the agricultural plastic film sample by UE.

## 4. Conclusions

In this paper, a novel UE–SPME–GC method was developed for the determination of PAEs in agricultural plastic films using methanol as extractant and sol–gel-derived [AMIM][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]-OH-TSO coating as SPME fiber. This ionic liquid-based SPME fiber exhibited higher or comparable selectivity and extraction efficiency for most of the PAEs studied compared to commercial PDMS, PDMS–DVB and PA fibers. Carryover effects,

commonly occurred during the SPME analysis of PAEs, had been eliminated by enhancing the GC injector temperature (360 °C) and desorption time (8 min), resulting in an improved precision and accuracy. The proposed UE–SPME–GC method was successfully applied to the determination of PAEs in six kinds of PP and PE agricultural plastic films. The results showed that most of the PAEs were detected in these investigated agricultural plastic film samples, indicating a potential risk of crop damage, soil and water pollution.

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