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Polymeric ionic liquid sorbent coatings in headspace solid-phase microextraction: A green sample preparation technique for the determination of pesticides in soil

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ABSTRACT

In this work, a green approach utilizing novel polymeric ionic liquid (PIL) coatings for headspace solid-phase microextraction (HS-SPME) of four current-use pesticides from soil samples was studied for the first time. Epoxiconazole, fluroxypyr, metribuzin, and oxyfluorfen were the target pesticides. Three PIL coatings containing 1-vinylbenzyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide (PIL1 and PIL2) and 1-vinyl-3-(10-hydroxydecyl)imidazolium bis[(trifluoromethyl)sulfonyl]imide (PIL3) monomers, and 1,12-di(3-vinylbenzylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imide (PIL1) and 1,12-di(3-vinylbenzimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imide (PIL2 and PIL3) crosslinkers were employed in this study. The performance of these PIL coatings was evaluated and compared with commercial SPME coatings based on polydimethylsiloxane/divinylbenzene (PDMS/DVB) and polydimethylsiloxane (PDMS) at the different extraction temperatures (50–90 °C) and sampling times (15–60 min). HS-SPME at 90 °C for 60 min provided the highest sensitivity and adequate reproducibility for the majority of analytes. Despite having a lower thickness, PIL2 and PIL3 coatings provided similar extraction effectiveness of analytes, and 24–247% higher coating volume-normalized responses compared to the commercial PDMS/DVB coating. The use of the PIL1 sorbent coating resulted in excellent linearity ($R^2 = 0.995$–0.999) and lower detection limits (0.06–0.4 ng g^{-1}) for all analytes. The optimized method provides acceptable recoveries of spiked concentrations with better performance (84–112%) achieved with the PIL1 coating. Compared to other known methods for target pesticides in soil, the proposed method provides the highest compliance with the principles of green analytical chemistry evaluated using Analytical Eco-Scale and Green Analytical Procedure Index tools.

1. Introduction

Pesticides are the largest group of intentionally released environmental toxicants requiring intensive regulatory monitoring in the environment [1,2]. The use of pesticides increases every year in all parts of the world, with Asia, South America, North America, and West Europe being the highest consumers [1,2]. However, with the implementation of state and regional regulations, worldwide pesticide use trends show shifting towards safer formulations, and the list of most common pesticides used in agriculture has changed over the last couple of decades [3]. Similarly, there is a shift towards safer and greener methods for environmental analyses of pesticides.

Pesticides are generally determined by gas chromatography (GC) or high-performance liquid chromatography (HPLC) methods in combination with mass spectrometry (MS) [4,5]. However, due to the complexity of the analyzed samples and the low concentration in which the target analytes are present, sample preparation methods are normally required prior to GC or HPLC analysis. Traditional sample preparation

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Abbreviations: DVB, divinylbenzene; GC, gas chromatography; HPLC, high-performance liquid chromatography; IL, ionic liquid; PIL, polymeric ionic liquid; PDMS, polydimethylsiloxane; SIM, selected ion monitoring; SPME, solid-phase microextraction

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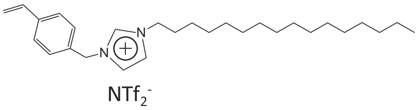
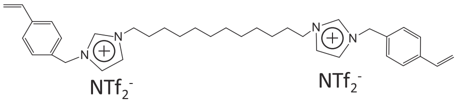
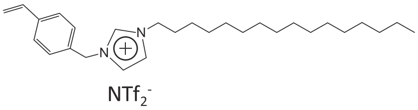
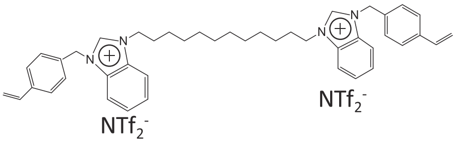
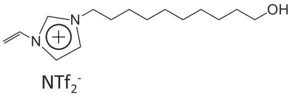
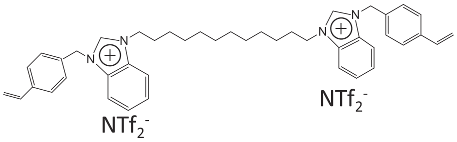
Table 1
Structural composition and approximate film thickness of the PIL-based sorbent coatings examined in this study.

Fiber	IL monomer	IL crosslinker	Approximate film thickness (μm)	Volume (μL)[a]
PIL1			23 ± 3	0.115
PIL2			31 ± 10	0.166
PIL3			50 ± 20	0.306

[a] Calculated using the following expression: $Volume = \pi (R^2 - r^2)l$, being r the inner radio of the solid support, R the total radio (solid support + coating film thickness) and l the coating length).

methods employed for pesticide determination are based on solvent extraction [6,7]. These methods use large amounts (10–50 mL) of organic solvents and require extra clean-up steps of the extracts, which limits automation and decreases sample throughput [8,9]. In addition, they are cost-, time-, labor-consuming, and require special skills and equipment. Implementation of greener, simpler, and automated sample preparation methods are of particular importance for the analysis of pesticides, especially considering the wide range of analytes and potential contamination in multiple matrices of concern.

Headspace solid-phase microextraction (HS-SPME) is a greener alternative method for solvent-free and straightforward extraction and microextraction, which combines sampling, concentration, and clean-up into one automated operation [10]. SPME has been successfully applied for the determination of restricted pesticides with sufficiently high Henry's law constants, such as some of the organochlorine [11–13] and organophosphorus pesticides [14]. However, the application of HS-SPME for the determination of pesticides with low Henry's law constants is limited as it requires elevated extraction temperatures and long sampling times, but also due to the low affinity of analytes to the available fiber coatings. Currently, the methods for the determination of target pesticides based on solvent-free HS-SPME are not available for target pesticides.

To overcome the limitations of commercially available SPME coatings, sorbent coatings based on polymeric ionic liquids (PIL) have been introduced [15–17]. PIL fibers offer a great variety of coating compositions that can be designed to provide specific interactions with a wide variety of analytes [18]. Highly robust PIL-based fiber coatings were used for the determination of analytes with varied volatilities, including organochlorine [19] and organophosphorus [20] pesticides in water and food samples, both in the direct immersion (DI-) and HS-SPME modes. However, PIL-based SPME methods have not been reported for the determination of pesticides in complex matrixes such as soil.

The aim of this work was to study the efficiency of PIL-based SPME coatings in HS-SPME for the determination of the current-use pesticides epoxiconazole, fluroxypyr, metribuzin, and oxyfluorfen in soil samples. The PIL-based fibers were explicitly designed to interact with pesticides at extreme extraction temperatures without sacrificing extraction effectiveness. The extraction performance of the PILs was compared with two commercially available sorbent coatings (polydimethylsiloxane/divinylbenzene, PDMS/DVB, and polydimethylsiloxane, PDMS) at different extraction temperatures (50, 70, and 90 °C) and sampling times (15, 30, 60 min). A study of the analytical performance was conducted for all studied fibers in order to compare the PIL-based and commercial fiber coatings.

2. Materials and methods

2.1. Reagents, materials and samples

The studied pesticides belong to different groups based on their structure and purpose (see Table S1 in Supplementary Material). Epoxiconazole (98.8%), metribuzin (99%), and oxyfluorfen (98.0%) were purchased from AccuStandard (New Haven, CT, USA). HPLC grade acetonitrile (Fisher Scientific, Fair Lawn, NJ, USA) was used for the preparation of standard solutions. Heavy loam soil with humus content 0.90% collected in Central Kazakhstan was used for the preparation of model and calibration samples. HS-SPME was conducted in 20 mL crimp-top headspace vials (HTA, Italy) sealed with PTFE/silicone septa and aluminum caps (Zhejiang Aijiren Technology Co., China).

Three PIL coatings were evaluated in this study in comparison with a commercial coating based on 65 μm PDMS/DVB and a 100 μm PDMS (Supelco, Bellefonte, PA).

2.2. Preparation of polymeric ionic liquid coatings

The IL monomer/crosslinker compositions and approximate film thicknesses of the PIL sorbent coatings are provided in Table 1. The fibers PIL1 and PIL2 were based on 1-vinylbenzyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($[VBzC_{16}IM][NTf_2]$), and PIL3 based on 1-vinyl-3-(10-hydroxydecyl)imidazolium bis[(trifluoromethyl)sulfonyl]imide ($[VC_{10}OHIM][NTf_2]$). Two different crosslinkers were employed, namely 1,12-di(3-vinylbenzylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imide ($[(VBzIM)_2C_{12}]2[NTf_2]$), for PIL1; and 1,12-di(3-vinylbenzyl(benzimidazolium))dodecane bis[(trifluoromethyl)sulfonyl]imide ($[(VBz(BIM))_2C_{12}]2[NTf_2]$), for PIL2 and PIL3.

All IL monomers and crosslinkers used in this study were prepared according the procedures described previously [21–24]. The procedures used for the synthesis of the ILs and crosslinkers are described in the Procedure S1 in Supplementary Material. The PIL of all SPME fibers was supported onto nitinol wires derivatized with vinyltrimethoxysilane, that were glued onto a commercial SPME assembly. The PIL material was not coated on the derivatized wire. In contrast, a mixture of IL monomer, IL crosslinker and radical initiator was coated onto the derivatized nitinol wire according to Feng et al. [25] and on-fiber UV copolymerization was carried out to obtain the PIL.

The maximum allowable desorption temperature of the PIL-based coatings is 250 °C.

The approximate film thickness of the PIL coatings was determined by averaging the results of 30 segment measurements using the optical Micro Zoom system (Scienscope, USA). The optical zoom images of the fibers are provided in Fig. S1 in Supplementary Material. The film thickness for PDMS and PDMS/DVB fibers determined using the same method by averaging 10 segment measurements was 98 ± 2 and 75 ± 2 μm, respectively. The coating lengths of PIL fibers were 13 mm for PIL1 and PIL2, and 12 mm for PIL3. These parameters were used for obtaining coating-volume-normalized responses of analytes. Normalized peak areas were obtained by dividing the responses obtained using each fiber coating by respective coating volumes.

2.3. Gas chromatography–mass spectrometry (GC–MS)

GC–MS analyses were conducted on a 6890N/5973N system (Agilent, USA) equipped with a DB-35ms column (30 m × 250 μm, 0.25 μm film thickness, Agilent, USA) under a constant helium flow of 1 mL min^{-1}. After extraction, analytes were desorbed from the coatings in the GC inlet for 5 min in *splitless* mode at 240 °C using a 0.75 mm I.D. SPME liner (Supelco, USA). The oven temperature was programmed from the initial 60 °C (held for 5 min) to 300 °C with a heating rate of 10 °C min^{-1}. Temperatures of the MS ion source, quadrupole, and interface were 230, 150, and 250 °C, respectively. Detection was conducted using an electron impact ionization at 70 eV employing the selected ion monitoring (SIM) mode. The MS program used for the detection of target pesticides in the SIM mode is provided in Table S2 in Supplementary Material. Epoxiconazole responses were measured as a sum of two peaks of isomers (enantiomers) [26]. Identification of the pesticides was carried out considering the retention time and the presence of the quantifier and qualifier ions of each analyte. For quantitative purposes, the peak area of the quantifier ion was employed. Typical chromatograms obtained using all studied fibers are given in Fig. S2 in Supplementary material.

2.4. HS-SPME procedure

During the optimization, 2.00 g of soil that was spiked with the standard solution of the pesticides to achieve a concentration of 100–500 ng g^{-1}, depending on the analyte, were placed in a 20 mL crimp-top headspace vial. A volume of 750 μL of ultrapure water or 35% (w/v) NaCl aqueous solution was added to study the extraction under common moist conditions of the soil and/or to study the effect of ionic strength. The vials were vigorously shaken for 1 min and were incubated for 30 min at 50–90 °C. HS-SPME extraction using different fibers (namely PDMS, PDMS/DVB, PIL1, PIL2, and PIL3) was then performed at 50–90 °C for 15–60 min, followed by thermal desorption in the GC–MS according to the conditions detailed in Section 2.2. All experiments were conducted in triplicates.

For the validation of the methodology, external standard calibration plots were constructed in the concentration range 25–1500 ng μL^{-1} for epoxiconazole and 5–300 ng μL^{-1} for the remaining analytes, and using the following optimized conditions: 2.00 g of soil, 750 μL of ultrapure water, incubation for 30 min at 90 °C, HS-SPME extraction at 90 °C for 60 min, and thermal desorption for 5 min at 240 °C for all studied fibers.

3. Results and discussion

3.1. Optimization of the methodology

3.1.1. Effect of water and salt addition

The addition of water to a solid sample is a common strategy used in HS-SPME to increase the extraction effectiveness of semi-volatile compounds [27]. The addition of water to the soil provides an enhancement in the desorption kinetics from the sample to the HS for nonpolar analytes due to increased polarity of the sample [28]. In this study, the effect of water was studied using PDMS fiber (Fig. 1A). The results indicated that the addition of water resulted in a 17–350 time increase in response, depending on the analyte for fluroxypyr, metribuzin, and oxyfluorfen, while the change in response of epoxiconazole was not significant according to the paired samples *t*-test ($p = 0.96$). The greatest effect of water addition was observed for oxyfluorfen (341–353 time increase in the extraction effectiveness), which was the analyte with the highest logarithm of octanol-water distribution coefficient (log K_{ow}) and Henry's Law constant value (Table S1).

The salting-out effect is often used in combination with water addition for enhancing the extraction effectiveness [27,29]. The addition of salt to the aqueous media can result in a decreased water solubility of analytes and the increase in a headspace-sample distribution constant. In this study, the salting-out effect was studied using PDMS coating fiber. The results (Fig. 1B) indicated an increase in responses for epoxiconazole and metribuzin by 24 and 45%, respectively. However, the effect of salting-out on responses of analytes was less pronounced compared to water addition. Thus, the HS-SPME extraction after the addition of water to the soil samples without the addition of salt was selected for further experiments.

3.1.2. Performance of studied fiber coatings at different extraction temperatures

Considering the low volatility of target analytes and the complexity of the sample matrix, the use of elevated extraction temperatures for HS-SPME is required in order to achieve acceptable responses. At elevated HS-SPME temperatures, the extraction effectiveness may be affected due to the decrease of the coating-air distribution constant [10]. In this study, the effect of the increase of extraction temperature from 50 to 90 °C on the response of analytes was evaluated using commercial (PDMS and PDMS/DVB) and PIL-based fiber coatings. The results (Fig. 2) revealed that the increase of extraction temperature to 90 °C resulted in a dramatic increase (10–58 times) of analytes' responses with nearly all studied fibers. This result implicates that the limiting process affecting the HS-SPME extraction for target pesticides is the desorption of analytes from the soil matrix. The decreased response was observed only for metribuzin when using 100 μm PDMS at 90 °C, likely due to the low affinity of the analyte to the coating. Despite having the greatest fiber thickness value, the 100 μm PDMS fiber provided the lowest responses for all target pesticides.

Taking into account the different film thickness values of the studied fiber coatings, normalized responses were obtained for studied pesticides by dividing the corresponding obtained peak areas by the volume of each fiber [30]. The normalized responses are also provided in Fig. 2. as patterned bars. For most target pesticides, the greatest normalized responses were obtained using PIL1 fiber based on an IL monomer comprised of the vinylbenzyl moiety and an imidazolium-based crosslinker. Normalized responses of epoxiconazole were 1.6–11 times higher when using PIL-based coatings with IL monomers containing vinylbenzyl moieties, which may indicate that these coatings are particularly sensitive for the extraction of this and similar triazole pesticides. For polar analytes, metribuzin, and fluroxypyr, the coatings based on IL monomers containing vinylbenzyl groups as well as the commercial PDMS/DVB coating provided 1.6–15 times higher extraction effectiveness compared to other studied coatings.

The increase in extraction effectiveness with temperature also resulted in better precision of the responses of pesticides with relative standard deviations (RSD) lower than 20% at 90 °C. The greatest precision for all analytes at these extraction parameters was obtained using the PIL1 coating (< 16%), owing to its lower thickness. Thus, the extraction temperature of 90 °C was selected as optimal for the rest of the experiments.

3.1.3. Performance of studied coatings at different extraction times

Another important extraction parameter affecting the speed and throughput of the method is the extraction time. To study the

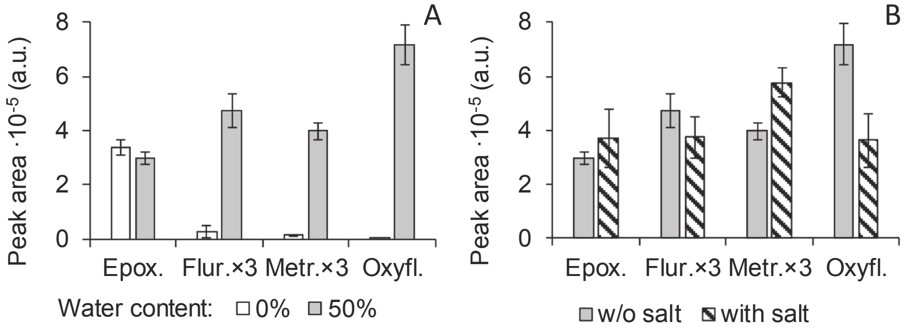


Fig. 1. Effect of water (A) and salt addition (B) on the HS-SPME response of analytes obtained with PDMS fiber. Experimental conditions (*n* = 3): 2.00 g of soil spiked with epoxiconazole at 500 ng g^{-1}, and remaining analytes at 100 ng g^{-1}, 750 µL of ultrapure water or 32% (*w*/*v*) NaCl aqueous solution, shaking (1 min), incubation (90 °C, 30 min), HS-SPME extraction (90 °C, 60 min), thermal desorption (240 °C, 5 min), and GC–MS. Abbreviations: Epox.: Epoxiconazole; Flur.: Fluroxypyr; Metr.: Metribuzin; and Oxfl.: Oxyfluorfen.

performance of studied coatings at 90 °C, the responses obtained with different fibers after 15, 30, 45, and 60 min extraction were evaluated (Fig. 3). For most evaluated coatings, the increased response was observed throughout the entire studied extraction time range. The strongest enhancements in the responses were observed for PIL3 and PDMS/DVB coatings. However, using these two coatings, equilibrium was not achieved for analytes over the studied time range. For PIL1 and PIL2 coatings, the response increments were 3–7 times lower, and equilibrium for metribuzin and oxyfluorfen was achieved in 30 and 45 min, respectively. This can be explained by lower coating thickness values of PIL1 and PIL2 fibers, which results in a faster equilibration of analytes between sample headspace and fiber coating due to the lower (at least theoretically) sorptive capacity. However, the PIL1 and PIL2 coatings, while providing faster extraction equilibrium, produced 1.3–17 times higher normalized responses for most analytes (Fig. S3 in Supplementary Material). The observed effect of coating thickness on response increments corresponds to an absorbent-type extraction process expected for PIL-based coatings and is in accordance with previously published methods using PILs for free fatty acids [31].

The results also indicated that PIL3 provide higher coating-

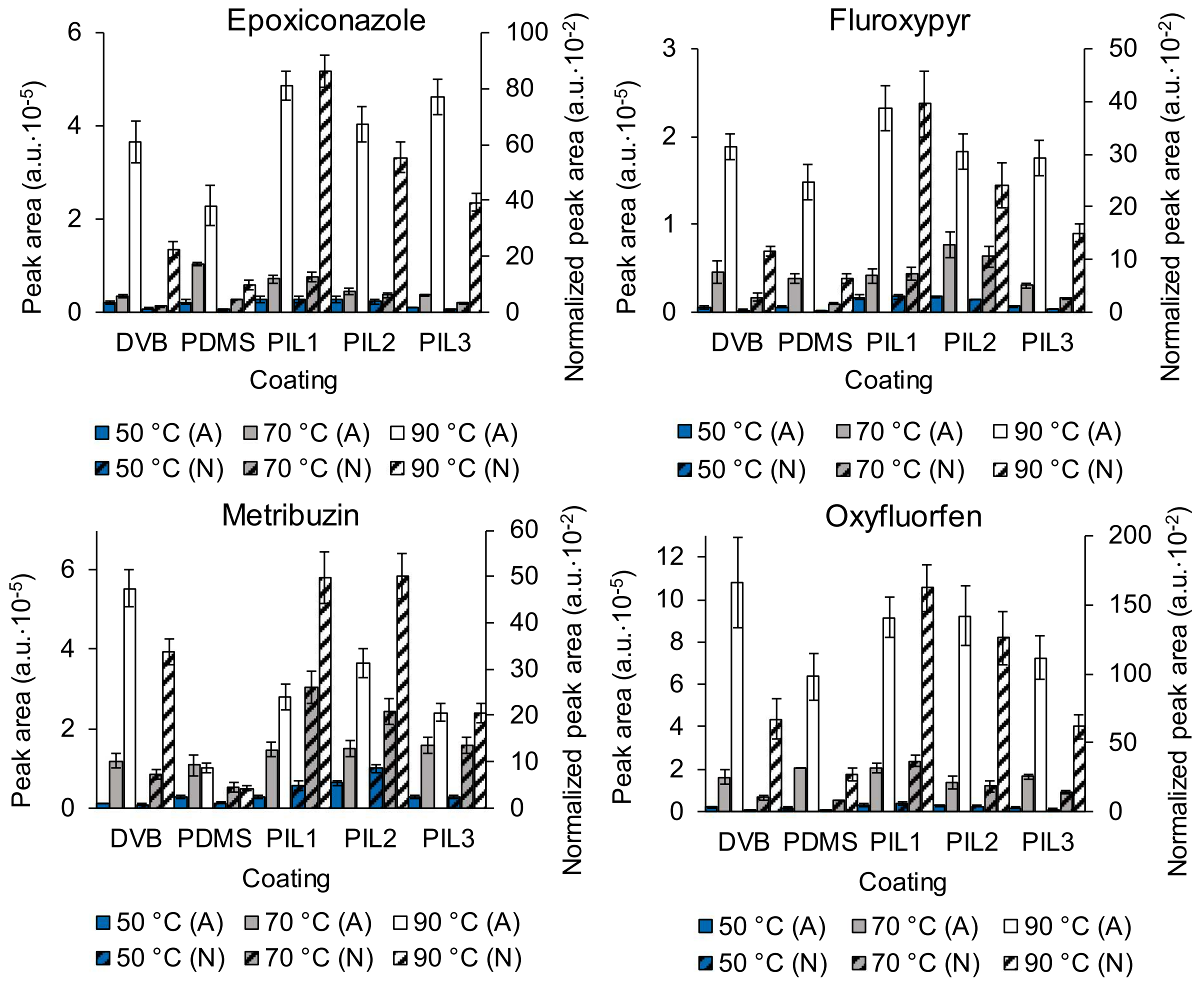


Fig. 2. Effect of extraction temperature on the HS-SPME response of analytes obtained using different fiber coatings. Solid fill bars represent the mean of the absolute peak areas obtained by three replicate extractions at 50, 70, and 90 °C, and are denoted in the figure legend with (A). The patterned fill bars located to the right for each coating represent the volume-normalized areas at the aforementioned temperature and are denoted in the legend with (N). Rest of experimental conditions (n = 3): 2.00 g of soil spiked with epoxiconazole at 500 ng g^{-1}, and remaining analytes at 100 ng g^{-1}, 750 µL of ultrapure water, shaking (1 min), incubation (for 30 min at 50–90 °C, respectively), HS-SPME extraction (50–90 °C, 30 min), thermal desorption (240 °C, 5 min), and GC–MS.

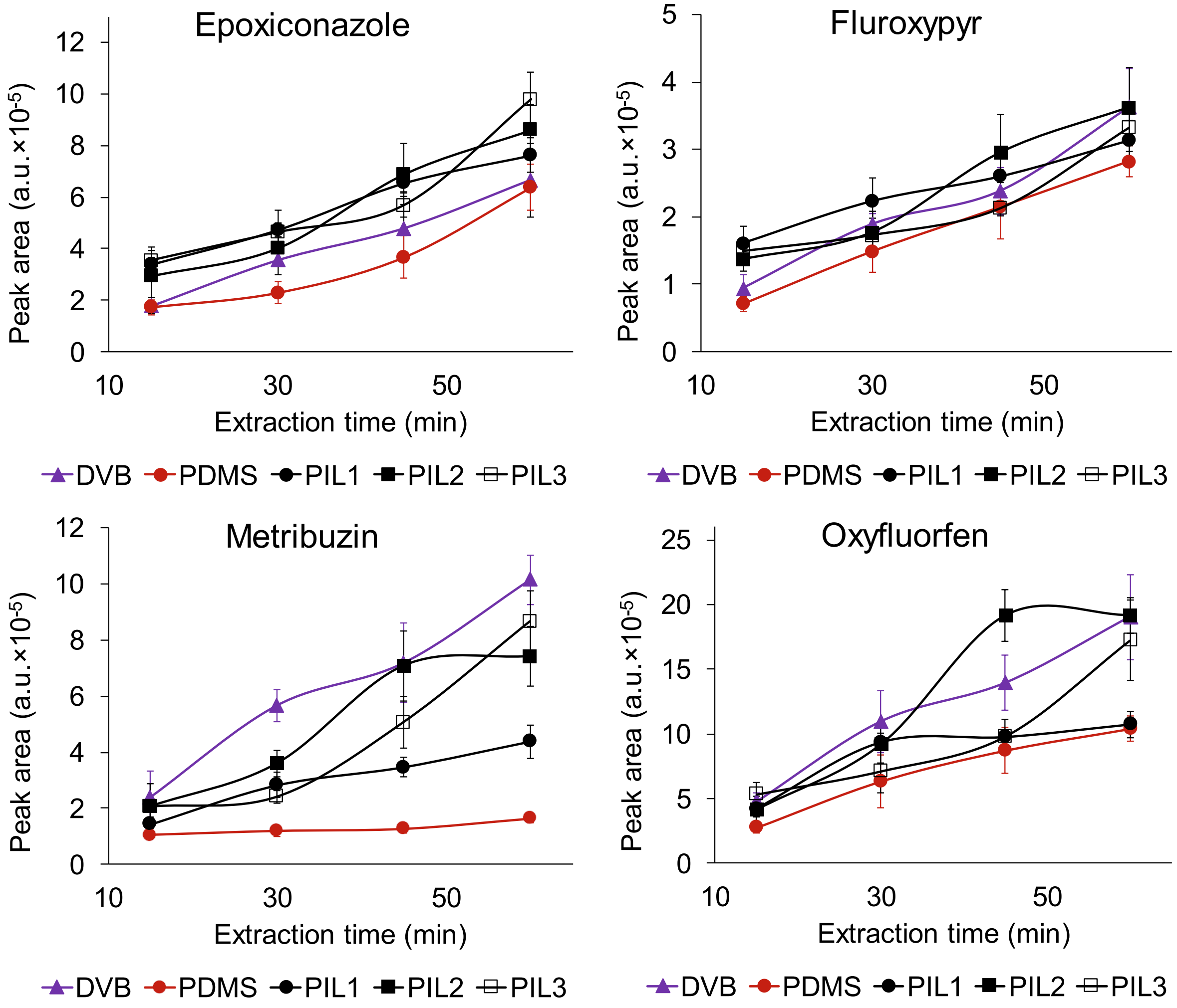


Fig. 3. Extraction time profiles obtained using different sorbent coatings. Experimental conditions (n = 3): 2.00 g of soil spiked with epoxiconazole at 500 ng g^{-1}, and remaining analytes at 100 ng g^{-1}, 750 µL of ultrapure water, shaking (1 min), incubation (90 °C, 30 min), HS-SPME extraction (90 °C, 15–60 min), thermal desorption (240 °C, 5 min), and GC–MS.

headspace distribution constants for target pesticides and can be used for a wider range of analyte concentrations, while PIL1 and PIL2 can be used to decrease the sampling time for analysis of residual concentrations of target pesticides.

An increase of the extraction time resulted in enhanced precision of responses for analytes using all coatings. PIL-based coatings provided more precise responses for epoxiconazole and oxyfluorfen even at shorter (30–45 min) extraction times, with RSDs < 18%. The most polar analytes, fluroxypyr and metribuzin had comparable precision between fibers with most RSDs ranging between 10 and 15%.

Based on these results, an extraction time 60 min provides a compromise between intensity and precision for all studied fibers and analytes and was selected for further experiments.

3.2. *Analytical performance of studied coatings*

The optimized HS-SPME parameters (at 90 °C for 60 min) were used to evaluate the analytical performance of each fiber via studying their linearity, accuracy, and sensitivity for quantification of target pesticides using a matrix-matched calibration approach with a soil that did not contain analytes. The results are presented in Table 2. The linearity studies were conducted in the range from 25 to 1500 ng g^{-1} for epoxiconazole, and from 5 to 300 ng g^{-1} for the remaining analytes. The optimized method provided linear calibration plots with R^2 values in the range from 0.982 to 0.999 for all studied coatings.

The sensitivity of the method with different fibers was evaluated using the calibration slopes. The obtained values ranged between (1.09 ± 0.05)·10^{-3} and (15.8 ± 0.07)·10^{-3} for PDMS, (1.44 ± 0.07)·10^{-3} - (27.7 ± 1.3)·10^{-3} for PDMS/DVB, (1.56 ± 0.04)·10^{-3} - (14.3 ± 0.5)·10^{-3} for PIL1, (1.38 ± 0.06)·10^{-3} - (16.5 ± 0.5)·10^{-3} for PIL2, and (1.38 ± 0.08)·10^{-3} - (18.4 ± 0.3)·10^{-3} for PIL3. The highest slopes were obtained when using PDMS/DVB and PIL3 coatings for most target pesticides. Despite PDMS being the thickest fiber, it provided lower slopes and regression coefficients for all target pesticides. This is likely due to a lower affinity of the fiber for these analytes. Relatively high background noise for metribuzin was obtained with PDMS due to its low molecular weight, which resulted in difficulties detecting this analyte at concentrations lower than 20 ng g^{-1}. The PIL1 fiber provided the highest sensitivity for epoxiconazole with a slope value higher than those obtained using the PDMS/DVB coating. Slopes obtained using the PIL3 coating for all target pesticides were close to the ones obtained using the PDMS/DVB coating. Considering the wide range of chemical compositions and molecular weights of analytes, this result shows the versatility of the PIL3 coating for the extraction of compounds of different nature.

The limits of detection (LODs) were estimated as concentrations that provide 3 signal-to-noise ratios. Low LODs were obtained, ranging between 0.2 and 2 ng g^{-1} for PDMS, 0.08–1 ng g^{-1} for PDMS/DVB,

Table 2
Analytical performance of the developed HS-SPME-GC–MS method using different sorbent coatings. The results refer to matrix-matched calibrations in a soil sample free of pesticides.

Coating	Calibration range (ng g^{-1})	(Slope ± standard deviation)·10^{-3}	R^2[a]	LOD[b] (ng g^{-1})
Epoxiconazole				
PDMS/DVB	25–1500	1.44 ± 0.07	0.9884	1
PDMS	25–1500	1.09 ± 0.05	0.9906	2
PIL1	25–1500	1.56 ± 0.04	0.9966	0.4
PIL2	25–1500	1.38 ± 0.06	0.9910	1
PIL3	25–1500	1.38 ± 0.08	0.9823	0.6
Fluroxypyr				
PDMS/DVB	5–300	4.3 ± 0.1	0.9944	0.2
PDMS	20–300	3.3 ± 0.2	0.9869	0.3
PIL1	5–300	3.25 ± 0.05	0.9986	0.1
PIL2	5–300	3.4 ± 0.1	0.9971	0.2
PIL3	5–300	3.8 ± 0.1	0.9932	0.2
Metribuzin				
PDMS/DVB	5–200	11.6 ± 0.5	0.9933	0.3
PDMS	20–200	1.47 ± 0.07	0.9935	2
PIL1	5–200	4.2 ± 0.1	0.9974	0.1
PIL2	5–200	7.3 ± 0.3	0.9933	0.2
PIL3	5–200	10.5 ± 0.6	0.9853	0.2
Oxyfluorfen				
PDMS/DVB	5–300	27.7 ± 1.3	0.9888	0.08
PDMS	5–300	15.8 ± 0.7	0.9904	0.2
PIL1	5–300	14.3 ± 0.5	0.9951	0.06
PIL2	5–300	16.5 ± 0.5	0.9971	0.1
PIL3	5–300	18.4 ± 0.3	0.9988	0.1

[a] Determination coefficient.
[b] Limit of detection, calculated as the concentrations that provide 3 signal-to-noise (S/N) ratios. S/N was measured in calibration standards with the lowest concentration of each analyte.

0.06–0.4 ng g^{-1} for PIL1, 0.1–1 ng g^{-1} for PIL2, and 0.1–0.6 ng g^{-1} for PIL3.

The accuracy of the method when using different coatings was studied by spiking the model soil samples with known concentrations of analytes. The spiked concentrations were 150 and 750 ng g^{-1} for epoxiconazole, and 30 and 150 ng g^{-1} for the remaining analytes. Table 3 summarizes the obtained recoveries. Acceptable recoveries were obtained for all fibers in the range from 79 to 121% for nearly all analytes. The greatest accuracy (83–114%) for all analytes was achieved using the PIL1-based fiber coating.

3.3. Comparison of the developed method with other known methods

The developed method using PILs was compared with other known methods for the determination of target pesticides in soil (Table S3 in Supplementary Material). Most GC-based methods use organic solvent extraction (with acetonitrile or methanol) followed by SPE [32,33], SPME [34] or QuEChERS [35] as extraction and clean-up step. With regards to the methods that used HPLC [7,26,36], most of them employed solvent extraction [7,26], microwave-assisted extraction [37,38] or QuEChERS [36,39,40] as sample preparation steps. Compared to the methods based on QuEChERS or solvent extraction, the proposed method provided 4–50 times lower detection limits for most analytes. In comparison to liquid-phase microextraction (LPME) based on solidification of floating organic drop that was applied for determination of metribuzin and three other triazine herbicides in soil [41], the proposed HS-SPME approach offers higher versatility of the extraction phase for different classes of analytes, lower LODs (0.1 ng g^{-1} *vs.* 1 ng g^{-1} in LPME-based method) and comparable extraction times. Furthermore, the proposed method provides better compliance with the principles of green analytical chemistry (GAC) [42], since it is faster, solvent-free, and reduces the number of required steps for preparing the sample.

3.4. Assessment of the green character of the proposed method

The shift towards greener analytical methods of analysis sets the task of evaluating the analytical procedures based on their green character, i.e., according to the principles of green analytical chemistry

Table 3
The relative recovery obtained after the analysis of spiked soil with the proposed HS-SPME method.

Coating	Concentration level 1			Concentration level 2		
	Spiked (ng g^{-1})	Measured ± SD[a] (ng g^{-1})	Recovery ± SD[a] (%)	Spiked (ng g^{-1})	Measured ± SD[a] (ng g^{-1})	Recovery ± SD[a] (%)
Epoxiconazole						
PDMS/DVB	150	165 ± 37	110 ± 22	750	603 ± 92	80 ± 15
PDMS	150	166 ± 41	110 ± 25	750	835 ± 198	111 ± 24
PIL1	150	140 ± 17	94 ± 12	750	765 ± 134	102 ± 17
PIL2	150	167 ± 22	111 ± 13	750	736 ± 135	98 ± 18
PIL3	150	133 ± 15	89 ± 11	750	667 ± 38	89 ± 6
Fluroxypyr						
PDMS/DVB	30	36 ± 3	121 ± 8	150	135 ± 12	90 ± 9
PDMS	30	32 ± 4	107 ± 12	150	159 ± 43	106 ± 27
PIL1	30	34 ± 4	114 ± 13	150	169 ± 16	112 ± 10
PIL2	30	34 ± 3	115 ± 8	150	155 ± 28	103 ± 18
PIL3	30	29 ± 4	96 ± 13	150	143 ± 22	95 ± 15
Metribuzin						
PDMS/DVB	30	26 ± 4	87 ± 17	150	103 ± 23	69 ± 22
PDMS	30	36 ± 7	120 ± 20	150	173 ± 33	116 ± 19
PIL1	30	26 ± 4	88 ± 14	150	124 ± 21	83 ± 16
PIL2	30	24 ± 3	82 ± 11	150	118 ± 20	79 ± 17
PIL3	30	24 ± 4	81 ± 15	150	119 ± 10	79 ± 8
Oxyfluorfen						
PDMS/DVB	30	25 ± 3	82 ± 12	150	126 ± 24	84 ± 19
PDMS	30	25 ± 4	84 ± 17	150	160 ± 32	107 ± 20
PIL1	30	28 ± 2	95 ± 6	150	151 ± 19	101 ± 12
PIL2	30	32 ± 5	108 ± 15	150	133 ± 25	89 ± 19
PIL3	30	25 ± 3	83 ± 11	150	128 ± 21	85 ± 16

[a] Standard deviation (n = 4, 95% confidence interval).

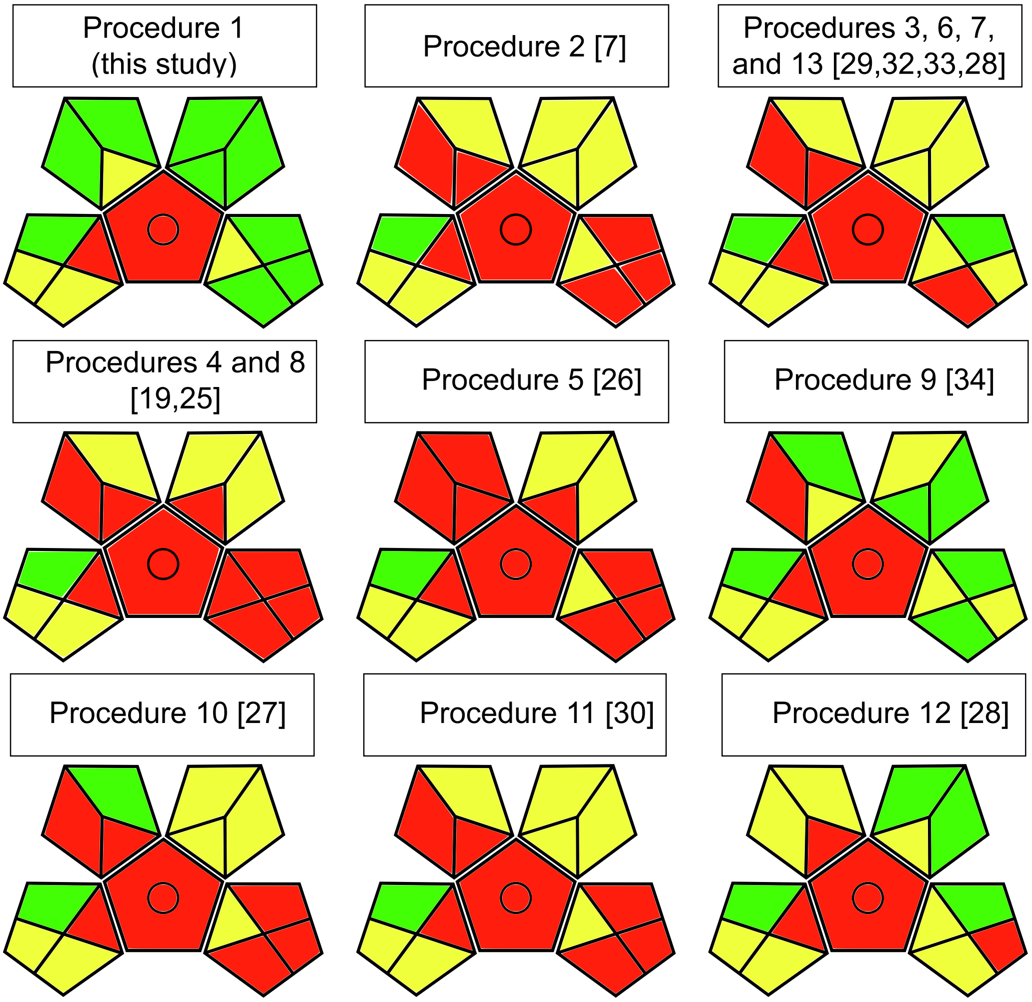


Fig. 4. GAPI assessment of the green profile of evaluated procedures for target pesticides in soil. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[42]. To compare the "greenness" of the proposed method with other reported methods, the two assessment tools: Analytical Eco-Scale [43] and Green Analytical Procedure Index (GAPI) [44] were employed.

The first method is based on calculating the Analytical Eco-Scale score of the analytical procedure by assigning penalty points (PPs) for the parameters that are not in agreement with the ideal green analysis that has a score of 100. This evaluation tool was applied for the proposed and 12 other methods reported for target analytes in soil (Table S4 in Supplementary Material). The highest score (94) was achieved for the method proposed in this study (procedure 1). The LPME-based method (procedure 9 [41]) is another greener approach with the Analytical Eco-Scale score 87. The lowest scores were obtained for the methods based on conventional solvent extraction (procedures 4 [26], and 8 [32]).

The GAPI tool provides a more detailed and visualized comparison of the methods based on fifteen parameters of sample preparation, reagents, solvents and instrumentation used in the analytical process. The results of the GAPI assessment of the evaluated methods correspond to the ones obtained using the Analytical Eco-Scale approach (Fig. 4). The procedures based on the same sampling and sample preparation techniques provide the same GAPI profiles. The two greenest procedures (1 and 9) are based on microextraction techniques, while the procedures involving solvent extraction have the least green profiles.

4. Conclusions

In this work, HS-SPME-GC–MS was applied for the determination of current-use pesticides (epoxiconazole, metribuzin, fluroxypyr, and oxyfluorfen) for the first time. The performance of PIL-based fiber coatings was evaluated in this application and compared with PDMS/DVB and PDMS commercial fiber coatings.

The optimum extraction was achieved when HS-SPME was conducted at 90 °C for 60 min using most of the studied fiber coatings. Decreased extraction effectiveness of analytes when increasing the extraction temperature up to 90 °C was not observed for almost all studied fiber coatings, except for when the PDMS coating was applied for the extraction of metribuzin. When using the PIL1 and PIL2 coatings containing vinylbenzyl moieties in the cationic component, the equilibrium extraction was reached for most analytes in 30 min and 45 min, respectively. For other coatings, equilibrium extraction was not observed for any of the analytes over the studied extraction time range. These results indicated that PIL1 and PIL2 could be used for the faster extraction of the selected pesticides at elevated temperatures while obtaining similar LODs than the most suitable commercial fiber for this determination, namely, PDMS/DVB.

Among the different PIL-based sorbent coating, PIL3 provides the highest extraction efficiencies for analytes, with affinity range close to PDMS/DVB, and the greatest versatility due to the possibility of using this fiber to extract both polar and non-polar pesticides.

The proposed method for quantification of current-use pesticides in soil provided the greatest results in greenness evaluations conducted using Analytical Eco-Scale and GAPI tools, even compared to other methods based on microextraction techniques, such as LPME.

Declaration of interest

The authors declare no conflict of interest.

CRediT authorship contribution statement

Dina Orazbayeva: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Jacek A. Koziel:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing - original draft, Writing - review & editing, Visualization, Supervision, Funding acquisition. **María J. Trujillo-Rodríguez:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing - original draft, Writing - review & editing, Visualization, Supervision. **Jared L. Anderson:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing - original draft, Writing - review & editing, Visualization, Supervision, Funding acquisition. **Bulat Kenessov:** Conceptualization, Methodology, Validation, Resources, Writing - review & editing, Supervision, Funding acquisition.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2020.104996.

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