Talanta 182 (2018) 74–82

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of UV filters in high ionic strength sample solutions using matrix-compatible coatings for solid-phase microextraction

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ARTICLE INFO

Keywords:
Polymeric ionic liquids
Solid-phase microextraction
Double-confined polymer
Ultraviolet filters
High performance liquid chromatography

ABSTRACT

A double-confined polymeric ionic liquid (PIL) sorbent coating was fabricated for the determination of nine ultraviolet (UV) filters in sample solutions containing high salt content by direct immersion solid-phase microextraction (DI-SPME) coupled to high-performance liquid chromatography (HPLC). The IL monomer and crosslinker cations and anions, namely, 1-vinyl-3-decylimidazolium styrenesulfonate ([$VImC_{10}$][SS]) and 1,12-di (3-vinylbenzylimidazolium) dodecane distyrenesulfonate ([$(VBIm)_2C_{12}$] 2[SS]), were co-polymerized to create a highly stable sorbent coating which allowed for up to 120 direct-immersion extractions in 25% NaCl (w/v) solution without a decrease in its extraction capability. Extraction and desorption parameters such as desorption solvent, agitation rate, extraction time, desorption solvent volume, and desorption time were evaluated and optimized. The analytical performance of the styrenesulfonate anion-based PIL fiber, PIL fiber containing chloride anions, and a commercially available polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber were compared. Coefficients of determination (R^2) for the styrenesulfonate anion-based PIL fiber ranged from 0.995 to 0.999 and the limits of detection (LODs) varied from 0.1 to 5 μg L^{-1}. The developed method was successfully applied in real water samples including tap, pool, and lake water, and acceptable relative recovery values were obtained. The lifetime of the PIL fiber containing chloride anions as well as the PDMS/DVB fiber were considerably shorter than the PIL fiber containing the styrenesulfonate anion, with both fibers showing a notable decrease in reproducibility and significant damage to the sorbent coating surface after 40 and 70 extractions, respectively. The R^2 values for the chloride anion containing PIL fiber were at or higher than 0.991 with LODs ranging from 0.5 to 5 μg L^{-1}. For the PDMS/DVB fiber, R^2 values ranged from 0.992 to 0.999 and LODs were found to be as low as 0.2 μg L^{-1} and as high as 5 μg L^{-1}.

1. Introduction

Personal care products (PCPs) refer to a wide range of substances including cosmetics, disinfectants, and plasticizers that are used in everyday lives [1,2]. Ultraviolet (UV) filters are a well-known class of ingredients found in cosmetic products such as sunscreens, lotions, and lipsticks, as well as plastics, adhesives, and paints [3,4]. A combination of UV filters is added to the aforementioned products to protect skin from two types of solar radiation (UV-A and UV-B) [3,5] or to prevent UV degradation of materials [4]. Studies have indicated that UV filters can accumulate directly or indirectly in environmental water sources from recreational activities (sea, lake, swimming pool) or industrial discharge [5]. However, many compounds belonging to the UV filter family are now considered emerging contaminants due to their ecotoxicity and possible endocrine disrupting characteristics [6,7].

In an attempt to monitor and control the level of UV filters in water sources, a number of analytical methods have been developed over the past decade focusing on the detection of these compounds in the environment. As the trend in analytical chemistry moves towards miniaturized and automated sampling processes [8], many newly introduced methods for the detection of UV filters are based on microextraction techniques. Liquid-phase microextraction (LPME) is among the most widely-used methods for the extraction of UV filters and includes single-drop microextraction (SDME) [6,9], hollow fiber liquid phase microextraction (HF-LPME) [10], stir bar dispersive liquid microextraction (SBDLME) [11] and conventional or ultrasound-assisted dispersive liquid-liquid microextraction (DLLME or UA-DLLME, respectively) [12–15]. The aforementioned LPME methods employ various solvents to preconcentrate the target UV filters from water samples. Organic solvents such as tetrachloroethylene and chloroform are common extraction solvents for DLLME methods, and often these methods require disperser solvent volumes up to 1 mL to successfully perform the extraction.

Sorbent-based microextraction techniques that further reduce the

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https://doi.org/10.1016/j.talanta.2018.01.052
Received 24 November 2017; Received in revised form 18 January 2018; Accepted 19 January 2018
Available online 20 February 2018
0039-9140/

use of organic solvents are an alternative to LPME. Several sorbent-based microextraction techniques have been reported for UV filter monitoring, such as solid-phase microextraction (SPME) [3,4,16] and stir bar sorptive-dispersive microextraction (SBSDME) [17]. These methods have utilized polymerized sorbent materials or magnetic nanoparticles (MNPs) as an extraction phase. Ionic liquids (ILs) and deep eutectic solvents (DESs) are widely utilized as alternative solvents in various LPME techniques in order to reduce toxic organic waste [18]. ILs are a non-molecular class of solvents with melting points at or below 100 °C [19]. Their physicochemical characteristics such as low vapor pressure, variable solvent miscibility, viscosity, and high stability have resulted in the application of various ILs as extraction solvents in a few reported LPME studies regarding UV filters [6,9–11,20]. Unlike LPME methods, the use of IL-based sorbents has not been explored in SPME for the determination of UV filters. Polymeric ionic liquids (PILs) not only possess physicochemical characteristics inherent to ILs, but they can also be incorporated as sorbent coatings for SPME [21]. The tunability of ILs allows for the structural modification of PIL sorbent coatings for selective analyte extractions as well as for a specific mode of analysis (i.e., headspace or direct-immersion) [21]. PIL-based sorbent coatings have been applied in SPME for the determination of a wide variety of analytes including polycyclic aromatic hydrocarbons (PAHs) [22,23], fatty-acid methyl esters (FAMEs) [24], phthalate esters (PAEs) [25], and amines [26,27]. However, the possibility of anion exchange has often been considered as a major drawback for PIL-based sorbent coatings when performing direct-immersion sampling from very complex sample matrices. As the counteranion within the PIL is not chemically bound, anion exchange can occur between the PIL sorbent coating and the sample matrix, ultimately changing the chemical properties of the sorbent material. [26]. For this reason, headspace extraction mode (HS-SPME) has most often been employed when using PIL-based fibers [28]. However, the use of HS-SPME is limited when extracting large molecules and paired with high-performance liquid chromatography (HPLC).

In 2012, a double-confined IL polymer was introduced by Qiu et al. where ILs containing polymerizable anions, namely, *p*-styrenesulfonate and 2-acrylamido-2-methylpropane sulfonic acid (AMPS), were utilized to copolymerize the cation and the counteranion onto the silica surface for multi-mode chromatography [29]. Shortly thereafter, a double-confined PIL-based SPME sorbent coating was reported [28]. Similar to the previous work, the *p*-styrenesulfonate counteranion was copolymerized along with the IL cation onto a stainless-steel surface to create a robust and stable sorbent coating material [28]. In comparison to the same IL containing the bromide counteranion, it was proven not only that the copolymerized fiber exhibited no anion exchange capabilities, but it could also be used in a sample solutions containing high salt content using the direct immersion (DI-SPME) mode. More recently, the *p*-styrenesulfonate anion has been applied in monolith SPME [30] and hollow fiber SPME (HF-SPME) [31] for the analysis of endocrine disrupting chemicals from aqueous samples and estrogens from milk samples, respectively. This type of copolymerized PIL-based sorbent coating can overcome the ion-exchange tendency that PIL coatings inherently face, expanding the types of sample matrices in which these coatings can be used.

In this work, an IL monomer and crosslinker, namely, 1-vinyl-3-decylimidazolium styrenesulfonate ([$VImC_{10}$][SS]) and 1,12-di(3-vinylbenzylimidazolium) dodecane distyrenesulfonate ([$(VBIm)_2C_{12}$] 2[SS]), are reported for the first time as double-confined PIL-based SPME sorbent coatings for the extraction of 9 UV filters in high ionic strength sample solutions using DI-SPME. Unlike the previously reported studies where only the IL monomer was utilized to create double-confined PIL fibers, this study utilized both the IL monomer and crosslinker to fabricate the sorbent coating. In addition, fibers with significantly thicker films were constructed using a highly reproducible, reliable, and consistent photo-initiated polymerization process. The copolymerization of monomer and crosslinker cations and anions yielded a fiber with extended lifetime compared to other PIL-based and commercial SPME fibers when used in sample solutions with high salt concentration. The developed SPME method was coupled to HPLC with UV detection. The analytical performance of the copolymerized PIL-based fiber was compared with another PIL-based fiber containing the chloride counteranion and a commercially available polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber. This method demonstrates that the copolymerized PIL-based fiber can be successfully applied in DI-SPME for the extraction of various UV filters in a sample solution containing high ionic strength.

2. Experimental

2.1. Materials and reagents

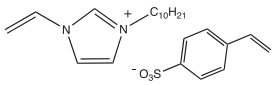
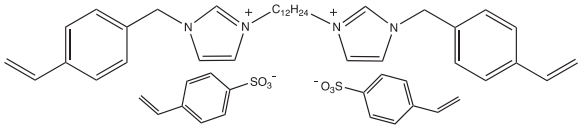
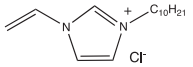
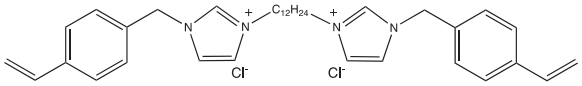
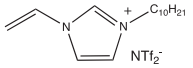
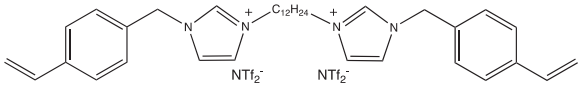
Oxybenzone (BP3) (98.0%), benzyl-salicylate (BS) (≥99.0%), 2-ethylhexyl 4-methoxycinnamate (EMC) (98.0%), 2-ethylhexyl 4-(dimethylamino)benzoate (EPP) (98.0%), 2-ethylhexyl salicylate (ES) (≥99.0%), etocrylene (ETO) (98.0%), octocrylene (OCR) (≥98.0%), homosalate (HS) (≥99.0%), avobenzone (BMDM) (≥99.0%), acrylonitrile (99.0%), 1,12-dibromododecane (98.0%), 1-vinylimidazole (≥99.0%), 1-chlorodecane (98.0%), vinyltrimethoxysilane (VTMS) (98.0%), and 2-hydroxy-2-methylpropiophenone (DAROCUR 1173) (> 96.0%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Acetonitrile, acetone, methanol, ethyl acetate, and isopropanol with purities equal to or higher than 99.0% were also purchased from Sigma Aldrich. Lithium bis[(trifluoromethyl)sulfonyl]imide ($LiNTf_2$) was purchased from SynQuest Laboratories (Alachua, FL, USA). Sodium chloride and hydrogen peroxide (30.0%, w/w) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Sodium *p*-styrenesulfonate hydrate (> 93.0%) was purchased from Tokyo Chemical Industries (Tokyo, Japan). Nitinol wire (128 μm in diameter) was purchased from Nitinol Devices & Components (Fremont, CA, USA). All solutions were prepared with ultrapure water (18.2 MΩ cm) produced by a Milli-Q water filtration system (Millipore, Bedford, MA, USA). PDMS and PDMS/DVB fibers were obtained from Supelco (Bellefonte, PA, USA).

Individual stock solutions of the nine analytes were prepared at 5000 mg L^{-1} in methanol, with exception of EPP, ES, and BMDM, which were prepared at 1000 mg L^{-1}. A working solution containing all nine analytes was prepared at 200 mg L^{-1} in methanol. The sample solution was prepared fresh by spiking an appropriate amount of stock solution into ultrapure water or a 25% NaCl (w/v) aqueous solution. The amount of organic solvent in aqueous sample solution was kept at 0.1% (v/v) at all times.

2.2. Synthesis of polymeric ionic liquids (PILs)

A total of six different monomers and crosslinkers were synthesized for PIL sorbent coatings, as shown in Table 1. The ILs 1-vinyl-3-decylimidazolium chloride ([$VImC_{10}$][Cl]), 1-vinyl-3-decylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([$VImC_{10}$][NTf_2]), 1,12-di(3-vinylbenzylimidazolium) dodecane dichloride ([$(VBIm)_2C_{12}$] 2[Cl]) and 1,12-di(3-vinylbenzylimidazolium)dodecane dibis[(trifluoromethyl) sulfonyl]imide ([$(VBIm)_2C_{12}$] 2[NTf_2]) were synthesized according to previously published procedures [22,32,33]. The preparation of 1-vinyl-3-decylimidazolium styrenesulfonate ([$VImC_{10}$][SS]) was carried out in a similar manner to a previously reported method [28] by mixing [$VImC_{10}$][Cl] with an aqueous solution of sodium *p*-styrenesulfonate at 1:1.1 M ratio. The solution was stirred overnight at room temperature in darkness. Afterwards, the product was extracted with ethyl acetate (5 mL × 5) and washed with ultrapure water. An aqueous silver nitrate (1 M) solution was used to test the existence of [Cl^-] in the aqueous phase. Ethyl acetate was removed by rotary evaporation and the product dried under vacuum. The crosslinker 1,12-di(3-vinylbenzylimidazolium) dodecane distyrenesulfonate ([$(VBIm)_2C_{12}$] 2[SS]) was synthesized by the same method as the monomer using a molar ratio of

Table 1
Structures and approximate film thickness of all fibers employed in this study.

	Structure	Approximate film thickness (μm)
Fiber 1		83[a]
		
Fiber 2		148[a]
		
Fiber 3		128[a]
		
Fiber 4	PDMS	100
Fiber 5	PDMS/DVB	60

[a] Sorbent coating thickness was measured and estimated by SEM imaging.

1:2.1 of $[(VBIm)_2C_{12}]$ 2[Cl] and the aqueous solution of sodium *p*-styrenesulfonate, respectively. The ^{1}H NMR spectral data for all monomers and crosslinkers used in the study are shown in Figs. S1-S6.

2.3. Fiber fabrication

Modification of the nitinol fibers was performed according to previously published studies [21,34,35]. A mixture of ILs comprised of monomer and crosslinker (50% weight of the monomer) was homogenized and DAROCUR 1173 was added. The amount of DAROCUR 1173 was kept at 5% of the IL mixture (w/w) for styrenesulfonate-based PIL fibers and at 3% for all other PIL fibers. The coating mixture was placed on a hotplate under low heat, and 1 μL of methanol was added to promote homogenization. The mixture was coated onto the modified nitinol surface and the coated fibers were placed in the UV chamber for 2 h.

2.4. Instrumentation

Synthesized ILs were characterized by collecting ^{1}H NMR spectra in deuterated dimethyl sulfoxide using a Bruker DRX 500 MHz nuclear magnetic resonance (NMR) spectrometer (Billerica, MA, USA). A RPR-100UV reactor purchased from Southern New England Ultraviolet Company (Bradford, CT, USA) was used for UV-initiated polymerization of PILs. UV lamps with a wavelength of 360 nm were used for $[NTf_2^-]$ based PILs whereas 254 nm was used for $[SS^-]$ and $[Cl^-]$ based PILs. The film thickness of PIL based fibers were studied with FEI Quanta-250 scanning electron microscope (SEM).

Chromatographic separations were performed with a Shimadzu LC-20A HPLC system (Tokyo, Japan) consisting of a manual injector, a DGU-20A_3 degasser, two LC-20AT pumps, and a SPD-20 UV/Vis detector. All separations were carried out using a Restek Ultra II C18 column (250 mm × 4.6 mm, 5.0 μm, State College, PA, USA). Ultrapure water and acetonitrile (mobile phase A and B, respectively) were utilized as mobile phases for the separation of all compounds. A gradient separation was started with 80% B and increased to 100% in 3 min, followed by a 10 min isocratic hold. Detection of all analytes was achieved at 310 nm except for BMDM, which was monitored at 254 nm. A representative chromatogram after the extraction using Fiber **1** is shown in Fig. S7.

An Agilent 1260 Infinity HPLC with a binary pump and a diode array detector (DAD) coupled to an Agilent 6230B Accurate Mass Time of Flight (TOF) mass spectrometer with an electrospray ion (ESI) source (Santa Clara, CA, USA) was used for LC-MS analysis. Separation of analytes was carried out using a Restek Ultra II C18 column (250 mm × 4.6 mm, 5.0 μm) prior to MS analysis. Conditions of ESI-MS were as follows: nebulizing gas, 35 psi; drying gas (N_2) flow rate, 9 L min^{-1}; drying gas temperature, 350 °C; capillary voltage, 3500 V; spectra scan rate, 1 spectrum s^{-1}.

2.5. Optimization

Parameters including desorption solvent, agitation, extraction time, desorption solvent volume, and desorption time were investigated. The desorption solvent parameter was first optimized for all 5 fibers employed in this study as it was shown in the previous study to have low dependency on other parameters [35]. Salt concentration optimization was performed only with Fiber **1**, and the remaining parameters were optimized for both Fiber **1** and the PDMS/DVB fiber. Fiber cleaning time was investigated to ensure fast and efficient cleaning of the fibers post-extraction.

2.6. Solid-phase microextraction procedure

All fibers were pre-conditioned in ultrapure water for 2 min prior to extraction. An aliquot of 10 mL of ultrapure water or 25% NaCl solution (w/v) was placed in a 10 mL amber vial, and the sample solution was stirred for 1 min to promote pre-equilibration. DI-SPME was performed by subjecting the fiber directly into the sample solution for 60 min (commercial fibers) or 75 min (PIL fibers) at room temperature. A small magnetic stir bar was added and the sample solution was stirred at a constant stir rate of 900 rpm (commercial fibers) or 700 rpm (PIL fibers). Following extraction, the fiber was exposed to the optimal volume of desorption solvent for 10 min (PIL fibers) or 15 min

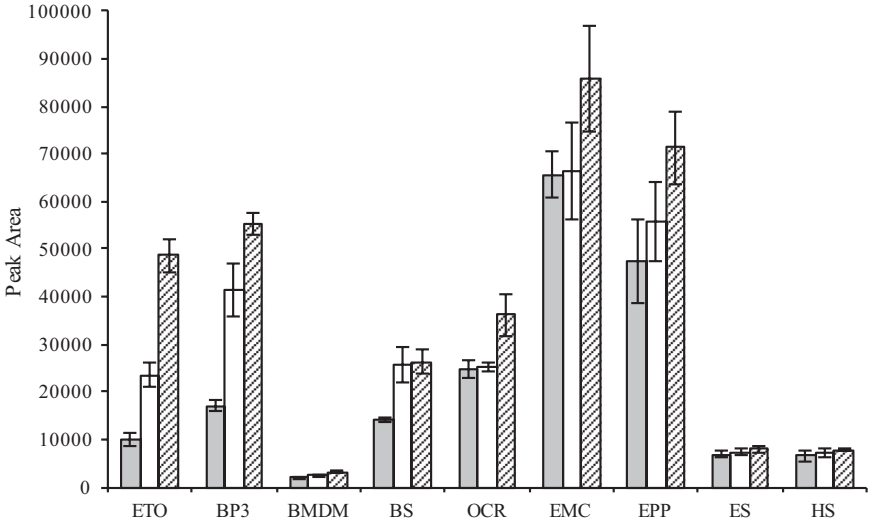


Fig. 1. Comparison of extraction efficiencies based on peak area using Fiber **1** at different NaCl concentrations: (▭) 0% NaCl, (▭) 10 % NaCl, and (▨) 25% NaCl (w/v). Experimental conditions (n = 3): analyte concentration: 200 μg L^{-1}; extraction time: 30 min; stir rate: 500 rpm; desorption solvent: methanol; desorption time: 15 min; desorption volume: 40 μL.

(commercial fibers). Then, 20 μL of the desorption solvent was subjected to HPLC. The fiber was washed in ultrapure water for 2 min to remove any salt adsorbed onto the sorbent coating surface, followed by a 5 min wash in methanol.

2.7. Method validation

The analytical parameters including linear range, limits of detection (LODs), and relative recovery were determined using the Fiber **1**, Fiber **2**, and the PDMS/DVB fiber. A calibration curve containing a minimum of five concentration levels was constructed for each analyte. The LODs were determined at a signal-to-noise ratio of 3 (S/N = 3). Tap water was collected after running the tap for 5 min. Pool water was collected from a local outdoor swimming pool (Ames, IA, USA). Lake water was collected from Oak Grove Beach (Johnston, IA, USA) and was used as a real sample to evaluate relative recovery. The collected lake water was passed through nylon filters (0.45 μm) before extraction. For all water samples, NaCl was added to make an aqueous salt solution containing 25% NaCl (w/v).

3. Results and discussion

3.1. Sorbent coating selection for procedure optimization

The three PIL-based fibers examined in this study are composed of the same cationic structures but with different anions (Table 1). PIL-based fibers containing [NTf_2^-] or [Cl^-] anions have been utilized in several studies for the extraction of polar and non-polar analytes [22,27,32,35]. PILs containing the styrenesulfonate anion have been applied in techniques such as HF-SPME [31] and SPME [28,30] coupled to HPLC and GC, though they have not been studied extensively in microextraction techniques to date. Fiber **1** reported in this study contains the styrenesulfonate as a counteranion in both IL monomer and crosslinker and possesses a higher ratio of aromatic moieties compared to the other commonly used PIL sorbent coatings (i.e., Fibers **2** and **3**). Furthermore, copolymerization of the anion results in a fiber with higher stability, mainly overcoming unwanted anion exchange between the matrix component and the fiber sorbent coating, as reported in a previous study [28]. Among the many factors that affect extraction efficiencies, the addition of salts to the analytical sample can often increase extraction efficiencies in SPME through the salting out effect [36]. However, addition of salt is generally discouraged in DI-SPME mode as the salt or other matrix components cause the fiber coatings to be easily damaged, thus reducing the fiber lifetime [36]. Employment of double-confined fibers can overcome this inherent weakness and expand the class of matrices in which DI-SPME can be performed. In order to explore the stability and performance of the styrenesulfonate anion within the sorbent coating in sample solutions containing high ionic strength, one PIL-based fiber (Fiber **1**) and one commercially available fiber (PDMS/DVB) were selected for optimization. Subsequently, the analytical performance of Fiber **1**, Fiber **2**, and the PDMS/DVB fiber were evaluated and compared.

3.2. Optimization of extraction and desorption parameters

3.2.1. Desorption solvent optimization

The desorption solvent was optimized individually for all five fibers. Fig. S8 (a-e) shows the effectiveness of methanol, acetonitrile, and acetone when used as desorption solvents for each fiber. Methanol and acetone resulted in comparable peak areas for most analytes using Fiber **1** and the PDMS/DVB fiber (Fig. S8a and S8d, respectively). However, BMDM was not detected when acetone was used as desorption solvent with the PDMS/DVB fiber (Fig. S8d). Considering these results, methanol was chosen as the optimal desorption solvent for Fiber **1** and the PDMS/DVB fiber. As for the remaining PIL-based fibers (Fibers **2** and **3**), the highest peak areas were observed for most of the analytes using acetone as desorption solvent (Fig. S8b and S8c). The PDMS fiber exhibited the most dissimilar results compared to the other fibers with acetonitrile being the optimal desorption solvent for all 9 analytes (Fig. S8e).

3.2.2. Extraction/desorption optimization using Fiber 1

Extraction and desorption parameters including salt concentration, sample agitation rate, extraction time, desorption volume, and desorption time were examined using a factor-by-factor method. To examine the effects of ionic strength in the extraction of UV-filters using Fiber **1**, a series of extractions were performed in aqueous sample solutions containing 0%, 10%, and 25% NaCl (w/v). As shown in Fig. 1, an increase in the ionic strength of the sample solution increased the peak areas of all analytes. Addition of NaCl to the sample solution was especially favorable for the extraction of ETO and BP3, showing a sharp rise in peak areas as the salt concentration increased from 0% to 10% NaCl (w/v) and again from 10% to 25% NaCl (w/v). Though the maximum peak areas were observed for all analytes when 25% NaCl (w/v) sample solution was used, the effect of ionic strength was much less pronounced for BMDM, ES, and HS. Therefore, an aqueous sample solution of 25% NaCl (w/v) was used for all subsequent experiments.

Performing the extraction under proper agitation conditions can not only accelerate diffusion of analytes from the sample to fiber coating, but it can also affect the equilibration time of the extraction system

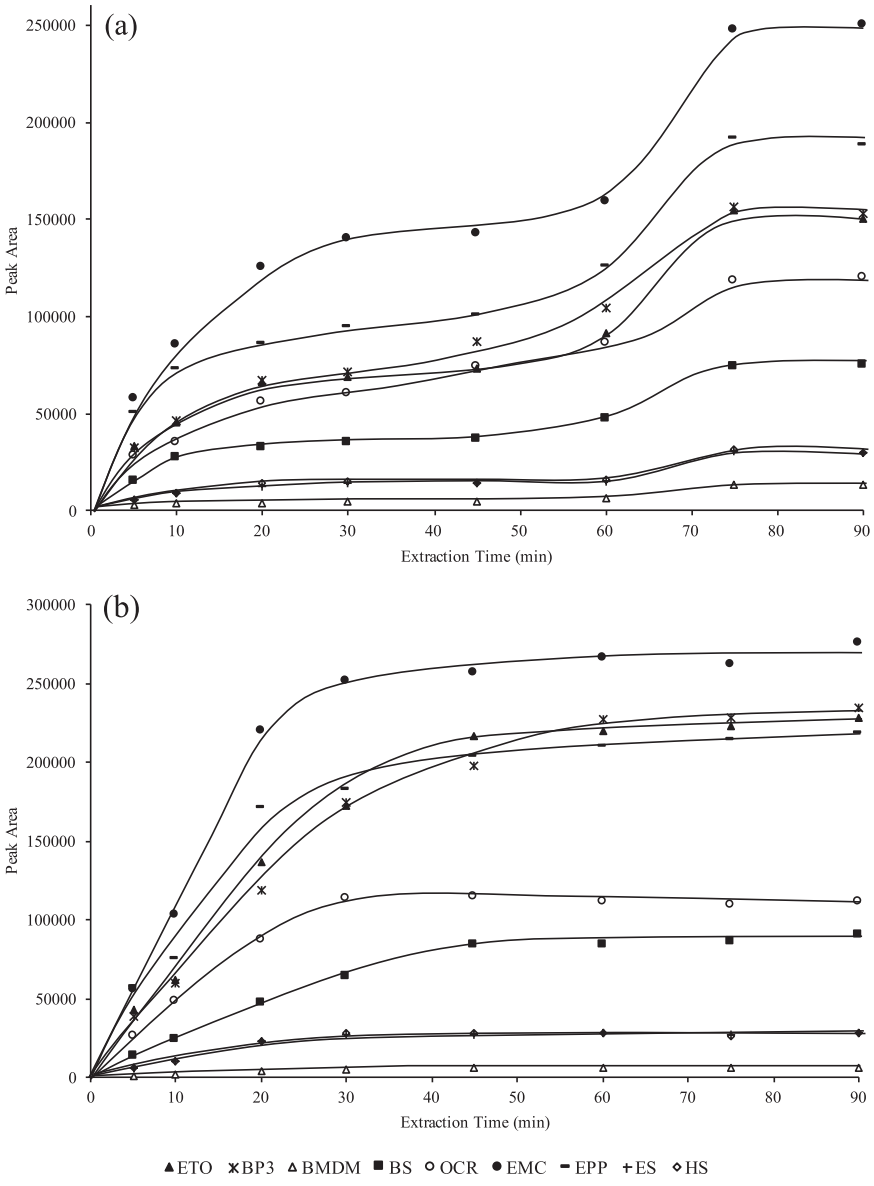


Fig. 2. Sorption time profile of (a) Fiber **1** and (b) PDMS/DVB fiber. Experimental conditions (n = 3): analyte concentration: 200 μg L^{-1}; salt concentration: 25% NaCl (w/v); stir rate: 700 rpm (Fiber 1) and 900 rpm (PDMS/DVB); desorption solvent: methanol; desorption time: 15 min; desorption volume: 40 μL.

[37]. A total of 4 different agitation rates ranging from 300 to 900 rpm were tested using Fiber **1**. Increased peak areas were observed for all analytes as the stir rate increased up to 700 rpm, as shown in Fig. S9a. Further enhancements in the stir rate to 900 rpm resulted in comparable peak areas to 700 rpm. However, the relative standard deviation (%RSD) values increased from 4.2% to 11.2% at 700 rpm to 8.2% – 16.5% at 900 rpm. Consequently, 700 rpm was chosen as the optimal stirring rate for the PIL fibers.

Even though SPME is a non-exhaustive extraction method [38], obtaining quantitative and precise results is possible when sampling is performed under non-equilibrium conditions [37]. Though many methods may shorten the sampling time in order to increase sample throughput, maximum sensitivity is usually achieved when the extraction system has attained equilibration [39]. The extraction time was varied from 0 to 90 min to generate a sorption-time profile using Fiber **1**, as shown in Fig. 2a. A steady increase in peak areas was observed up to an extraction time of 20 min with a relatively steep increase being observed from 60 to 75 min. No significant difference was observed when the extraction time was further increased to 90 min, indicating that the equilibrium was reached for the target analytes by 75 min. Therefore, an extraction time of 75 min was used for all subsequent experiments.

A challenge in liquid desorption procedures is determining the minimum amount of solvent that can desorb the highest amount of target analytes, as a large sample volume can lead to significant extracolumn dispersion during the separation process, causing peak broadening [40]. Desorption volume was optimized by using 30, 40, and 50 μL of methanol. Fig. S10a shows that based on the peak areas observed, an increase in the desorption solvent volume resulted in a higher mass of extracted analyte. The analytes EMC and EPP were most influenced by the desorption solvent volume, showing a significant improvement in peak areas when the desorption volume increased from 40 to 50 μL. Given these results, 50 μL of methanol was applied as the desorption volume for the PIL-based fibers.

Desorption time was optimized by performing static desorption in organic solvent for 5, 10, and 15 min Fig. S11a shows that static desorption at 5 min was not sufficient to desorb the target analytes from the fiber. When the time was increased to 10 min, a significant increase in extraction efficiency was observed for all analytes. However, no statistically substantial changes were observed when the desorption time was increased from 10 to 15 min. Based on these results, a desorption time of 10 min was chosen as the optimal parameter.

3.2.3. Extraction/desorption optimization using the PDMS/DVB fiber

The same extraction and desorption parameters were optimized for the PDMS/DVB fiber using a factor-by-factor method, with the exception of salt concentration. Unlike Fiber **1**, a high agitation rate was beneficial for all analytes when extractions were performed using the PDMS/DVB fiber (Fig. S9b). A steep rise in extraction efficiency was observed from 700 to 900 rpm without a decrease in precision. Therefore, 900 rpm was selected as the optimal stir rate for the PDMS/DVB fiber. A sorption-time profile was also generated for the PDMS/DVB fiber using extraction times ranging from 0 to 90 min (Fig. 2b). The analytes BMDM, OCR, ES and HS reached a relatively fast equilibrium at around 30 min, whereas ETO, BP3, BS, EMC, and EPP required 45–60 min in order to attain equilibration. For maximum sensitivity of all analytes, 60 min was used as the extraction time for all subsequent experiments.

Fig. S10b shows the influence of desorption solvent volume for the PDMS/DVB fiber. In contrast to the results obtained with Fiber **1**, a lower desorption solvent volume of 30 μL yielded higher peak areas for all analytes except EPP, which showed no significant difference between desorption solvent volumes of 30 and 40 μL. Moreover, longer desorption time was more effective for most of the analytes when the PDMS/DVB fiber was used, as shown in Fig. S11b. Considering these results for the PDMS/DVB fiber, 30 μL and 15 min were selected as optimal parameters for desorption solvent volume and time, respectively.

3.3. Assessment of analyte carryover

Carryover or memory effect is often not considered as a major concern in SPME unless the concentration of analytes is low where trace amounts of analytes sorbed on the fiber from a previous extraction can affect the equilibrium between the fiber coating and the sample solution [41]. Many studies that have coupled SPME to liquid chromatography perform multiple desorption steps or flush the desorption chamber in order to eliminate the carryover effect [42–44]. To minimize analyte carryover, the fiber cleaning time was optimized prior to evaluating the analytical performance of Fiber **1**. After the initial desorption in 50 μL of methanol, the fiber was washed with methanol for 2, 3, and 5 min under stirring. The washed fiber was then immersed in 50 μL of fresh methanol for a second desorption step, and the desorption solvent subjected to HPLC analysis. As can be seen in Fig. S12, analyte carryover was greatly reduced by increasing the fiber wash time from 2 to 3 min. When the wash time was increased to 5 min, no peaks were detected for most of the analytes. Therefore, the fiber cleaning time was reduced from 20 min to 5 min for all subsequent analyses.

3.4. Fiber to fiber comparison of extraction efficiencies

Following the extraction of the target analytes using all 5 fibers employed in this study, the extraction efficiency of all fiber was estimated by two methods: direct comparison of peak areas of analytes and the normalized peak areas. The normalized peak areas were calculated by the ratio between peak areas and the approximate film thickness of each fiber measured by SEM (see Table 1). Fig. 3 shows the obtained results. The approximate film thickness of Fiber **1** was higher than the PDMS/DVB fiber, and similar peak areas were found for analytes such as ETO and BP3 (Fig. 3a). Higher peak areas were observed for all other analytes using Fiber **1**. These results are also demonstrated by the LODs, which show that similar or lower LOD values were obtained with Fiber **1** compared to the PDMS/DVB fiber for most analytes. Normalized peak areas (Fig. 3b) show that the extraction efficiencies of the target analytes for Fiber **1** and the PDMS/DVB fiber are much more similar under the normalized condition, with exception of ETO and BP3. Additionally, Fiber 1 exhibited outstanding reproducibility compared to other fibers with %RSD values falling below 5.0%. Fibers **2** and **3** were the least favorable in the extraction of the target analytes. The PDMS fiber exhibited fair extraction capabilities of ETO and BP3. However, normalized peak areas for all other analytes were much lower than those of Fiber **1** and the PDMS/DVB fiber.

3.5. Detection of UV filters using HPLC-ESI-TOF

The detection of UV filters has most often been accomplished with gas chromatography (GC) [15], gas chromatography-mass spectrometry (GC-MS) [12–15,17], gas chromatography-tandem mass spectrometry (GC-MS/MS) [3,4], and liquid chromatography-tandem mass spectrometry (LC-MS/MS) [45–47]. The use of LC coupled to time-of-flight (TOF) mass spectrometry with electrospray (ESI) ionization was considered for the detection of the target UV filters. Detailed LC-TOF instrumental parameters are included in Section 2.4. The same extraction procedure was carried out using Fiber **1** and the desorption solvent was diluted to 80 μL for the injection using an autosampler. The injected sample was detected using a diode array detector (DAD) and subsequently analyzed by TOF-MS. As shown in Fig. S13, detection of the target analytes was proven to be difficult when TOF-MS was used in comparison to when DAD was used as a detection method. A relatively high extracted ion chromatogram (EIC) signal was obtained for BS and EPP compared to other analytes, whereas the analytes EMC and ES were not detected after the extraction was performed at 200 $\mu g\,L^{-1}$. Considering these results, HPLC with UV detection was employed for all subsequent analytical performance studies.

3.6. Analytical performance and recovery study

The analytical performance of Fiber **1**, Fiber **2**, and PDMS/DVB fiber was evaluated by carrying out extractions at a series of spiked concentration levels. All extractions for the analytical performance evaluation were completed in 25% aqueous NaCl solution (w/v). Table 2 lists the figures of merit for the 9 analytes extracted using Fiber **1**, Fiber **2**, and the PDMS/DVB fiber. Different linear ranges were obtained by constructing five- to seven-point calibration curves. Limits of detection (LODs) were acquired by decreasing the spiked analyte concentration until a signal-to-noise ratio of 3 (S/N = 3) was achieved using UV detection. Coefficient of determination values (R^2) for Fiber **1** ranged from 0.995 to 0.999, and the LODs varied from 0.1 to 5 $\mu g\,L^{-1}$. Good reproducibility at the LODs was observed with the % RSD values ranging from 1.8% to 11.6%. For Fiber **2**, R^2 values differed from 0.991 to 0.999, with LODs ranging from 0.5 to 5 $\mu g\,L^{-1}$. Values of %RSD at or below 13.9 were obtained at LODs. The PDMS/DVB fiber resulted in R^2 values varying from 0.992 to 0.999. Comparable LODs to Fiber **1** were acquired, with their values being as low as 0.2 $\mu g\,L^{-1}$ and as high as 5 $\mu g\,L^{-1}$. Acceptable reproducibility was also obtained using the PDMS/DVB fiber with %RSD values at or below 10.4%.

To evaluate the applicability of the fibers in real samples, relative recoveries were assessed in water samples that may be likely to contain the target analytes. Three different water samples were tested including tap water, pool water, and lake water. The tap and pool water were collected and NaCl was added to make up a 25% aqueous NaCl solution (w/v). The salt was added to the lake water after the collected lake water sample was passed through 0.45 μm filters. No observable peaks were detected for most analytes except for EMC, which was detected below the LOD using Fiber **1** when the real samples were analyzed without analyte spiking. Table 3 shows the relative recovery values and the standard deviation of the 9 UV filters from each water sample at 10 $\mu g\,L^{-1}$ using Fiber **1**, Fiber **2**, and the PDMS/DVB fiber. For Fiber **1**, the relative recovery of the target analytes from tap water ranged from 93.2% to 106.4%, whereas they varied from 82.2% to 111.4% from the pool water. Lake water recovery values were as low as 66.6% and as high as 118.5%. For Fiber **2**, the average relative recovery values were found to range from 73.1% to 111.0% in tap water. Additionally, recovery from the pool water ranged from 72.7% to 106.8% and from 70.1% to 112.6% in lake water. For the PDMS/DVB fiber, a relative

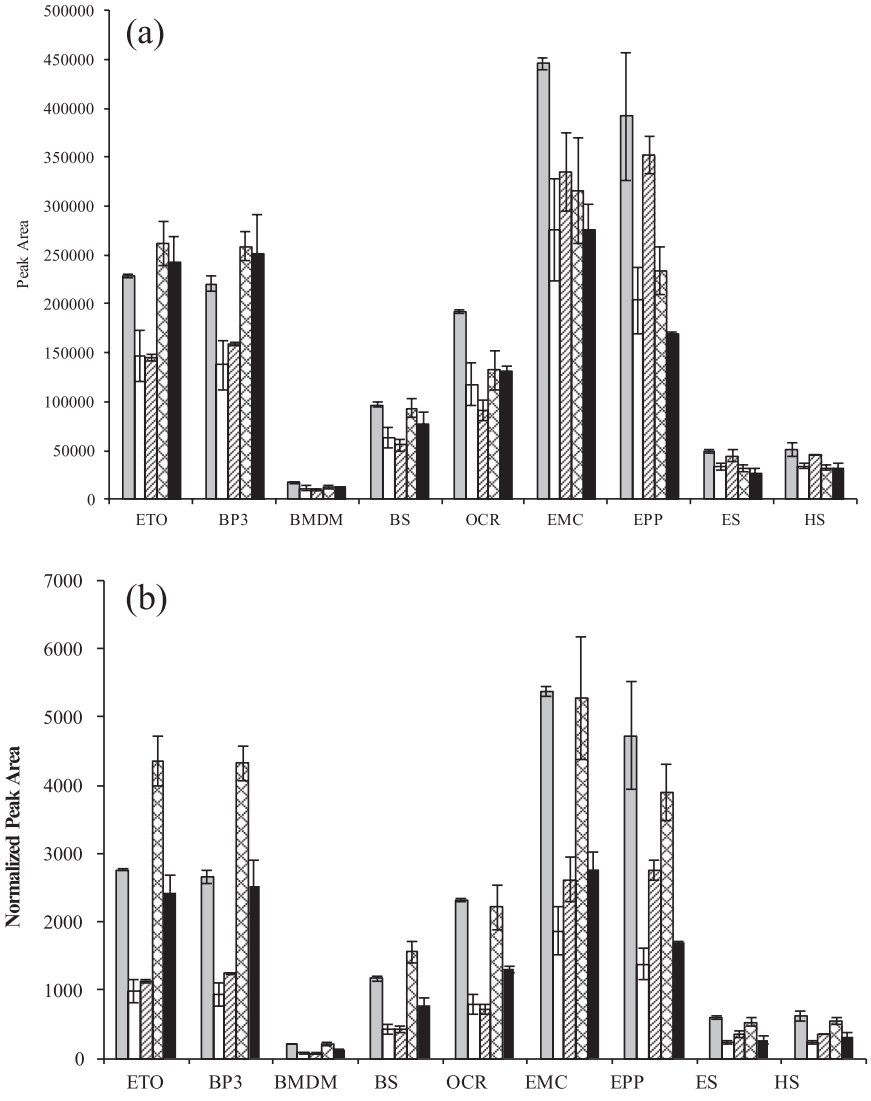


Fig. 3. Comparison of peak areas after three replicate extraction/desorption cycles using all fibers (a) without normalization and (b) after normalization by the approximate film thickness of each fiber (see Table 1 for the approximate film thicknesses). ( ) Fiber **1**, ( ) Fiber **2**, ( ) Fiber **3**, ( ) PDMS/DVB, and ( ) PDMS fiber. Experimental conditions for Fibers 1, 2, and 3 (n = 3): analyte concentration: 200 μg L^{-1}; salt concentration: 25 % NaCl (w/v); extraction time: 75 min; stir rate: 700 rpm; desorption solvent: methanol (Fiber 1) and acetone (Fibers 2 and 3); desorption time: 10 min; desorption volume: 50 μL. Experimental conditions for the PDMS and PDMS/DVB fibers (n = 3): analyte concentration: 200 μg L^{-1}; salt concentration: 25 % NaCl (w/v); extraction time: 60 min; stir rate: 900 rpm; desorption solvent: methanol (PDMS/DVB) and acetonitrile (PDMS); desorption time: 15 min; desorption volume: 30 μL.

Table 2
Figures of merit for the 9 analytes extracted using Fiber **1**, Fiber **2**, and the PDMS/DVB fiber.

Analyte	Acronym	Linear range (μg L^{-1})			R^2			LOD (μg L^{-1})			%RSD[c] (n = 3)		
		Fiber **1**[a]	Fiber **2**[a]	PDMS/DVB[b]	Fiber **1**[a]	Fiber **2**[a]	PDMS/DVB[b]	Fiber **1**[a]	Fiber **2**[a]	PDMS/DVB[b]	Fiber **1**[a]	Fiber **2**[a]	PDMS/DVB[b]
Ethyl 2-cyano-3,3-diphenylacrylate	ETO	1–100	2–200	1–100	0.997	0.995	0.998	0.5	1	0.2	8.5	6.2	6.9
Oxybenzone	BP3	1–150	2–200	0.5–100	0.995	0.997	0.999	0.2	1	0.2	11.6	7.1	7.0
Avobenzone	BMDM	10–150	10–200	10–200	0.998	0.991	0.992	5	5	5	10.1	11.4	5.5
Benzyl-salicylate	BS	1–150	5–200	2–100	0.998	0.998	0.999	0.5	2	1	5.6	8.9	9.2
Octocrylene	OCR	1–150	2–100	2–100	0.999	0.999	0.999	0.5	1	1	7.1	13.9	5.6
2-Ethylhexyl 4-methoxycinnamate	EMC	0.2–100	1–100	0.5–100	0.998	0.998	0.998	0.1	0.5	0.2	7.7	10.7	9.8
2-Ethylhexyl 4-(dimethylamino)benzoate	EPP	.5–100	2–100	1–100	0.998	0.997	0.993	0.2	1	0.5	4.5	7.4	10.4
2-Ethylhexylsalicylate	ES	5–150	5–200	5–200	0.998	0.996	0.999	2	2	2	4.1	9.4	7.4
Homosalate	HS	5–150	5–200	5–200	0.995	0.999	0.997	2	2	2	1.8	4.6	7.9

[a] Experimental conditions: Salt concentration: 25% NaCl (w/v); Stir rate: 700 rpm; Extraction time: 75 min; Desorption solvent: methanol; Desorption volume: 50 μL; Desorption time: 10 min.

[b] Experimental conditions: Salt concentration: 25% NaCl (w/v); Stir rate: 900 rpm; Extraction time: 60 min; Desorption solvent: methanol; Desorption volume: 30 μL; Desorption time: 15 min.

[c] % Relative standard deviation calculated at LOD.

Table 3
Relative recoveries of the target analytes from real samples using Fiber **1**, Fiber **2**, and the PDMS/DVB fiber.

Analyte	% Relative recovery ± SD (n = 3)[a,b]								
	Fiber **1**			Fiber **2**			PDMS/DVB		
	Tap	Pool	Lake	Tap	Pool	Lake	Tap	Pool	Lake
ETO	106.4 ± 3.7	86.8 ± 4.0	109.0 ± 7.4	76.4 ± 1.5	86.7 ± 3.4	89.9 ± 5.8	100.3 ± 6.9	122.7 ± 9.3	120.5 ± 16.1
BP3	98.3 ± 4.8	111.4 ± 6.1	118.5 ± 16.9	109.6 ± 2.6	102.8 ± 11.3	112.6 ± 15.2	97.7 ± 3.4	110.3 ± 9.6	103.5 ± 15.0
BMDM	93.1 ± 6.0	99.9 ± 4.3	108.2 ± 7.3	95.7 ± 8.7	87.8 ± 11.3	70.1 ± 14.8	85.2 ± 3.3	78.9 ± 9.2	54.5 ± 13.2
BS	94.2 ± 9.8	87.2 ± 2.7	84.9 ± 9.3	111.0 ± 6.9	99.3 ± 6.8	95.2 ± 11.0	97.5 ± 7.6	89.1 ± 12.3	112.2. ± 8.6
OCR	102.3 ± 5.4	83.9 ± 5.6	72.5 ± 6.1	87.9 ± 5.5	91.4 ± 2.0	77.4 ± 3.8	97.2 ± 2.1	82.0 ± 10.4	69.1 ± 4.0
EMC	98.5 ± 3.1	99.1 ± 10.8	117.9 ± 8.2	102.6 ± 8.1	106.8 ± 8.8	92.7 ± 11.0	96.0 ± 2.7	99.6 ± 11.4	76.8 ± 6.6
EPP	97.1 ± 6.6	82.5 ± 7.7	83.0 ± 17.3	73.1 ± 3.6	72.7 ± 3.5	70.7 ± 1.6	107.6 ± 6.1	98.1 ± 17.3	73.2 ± 7.2
ES	97.5 ± 5.8	82.2 ± 5.7	66.6 ± 15.0	89.5 ± 3.2	79.3 ± 3.0	74.4 ± 7.3	101.7 ± 7.4	107.8 ± 16.9	68.3 ± 10.8
HS	96.3 ± 3.5	96.0 ± 10.0	88.3 ± 15.3	94.6 ± 6.6	94.3 ± 12.5	81.0 ± 15.9	103.1 ± 6.7	123.7 ± 10.1	77.9 ± 11.2

[a] Concentration of all analytes at 10 μg L^{-1}.
[b] All extractions performed in 25% NaCl sample solution (w/v) at optimal conditions.

recovery of 85.2–107.6% was obtained from tap water, 78.9–123.7% from pool water, and 54.5–120.5% from lake water. Matrix effects were relatively more significant for Fiber **2** and the PDMS/DVB fiber when the pool and the lake water were used as sample matrices.

Table S1 shows a comparison of analytical performance obtained using Fiber **1** with other reported microextraction methods for the determination of UV filters coupled to HPLC with UV detection. The number of analytes used in the previously reported studies were equal to or less than six UV filters, whereas a total of nine UV filter compounds were determined using this method. The LOD values were comparable to those of the existing methods. The developed DI-SPME method utilized a sample solution containing the highest salt content, demonstrating the robustness of the PIL-based SPME sorbent coating and its possibility to be applied in other complex matrices.

Approximately 120 DI-SPME extractions were performed in 25% NaCl aqueous sample solution (w/v) using Fiber **1** without a loss of reproducibility or extraction efficiency. Fig. S14 shows a representative SEM image of the Fiber **1**, Fiber **2**, and Fiber **3** sorbent coatings. Fiber **2** was replaced after 40 extractions. The PDMS/DVB fiber was replaced after approximately 70 extractions in the high salt sample solution using DI mode, due to observable damage to the fiber surface and a clear decrease in reproducibility. Overall, Fiber **1** exhibited acceptable relative recovery values with good precision from the real water samples, proving that the double-confined PIL-based fiber containing phenyl groups (and π − electron capability) within the crosslinker and anion possesses higher stability compared to other PIL-based fibers or commercially available fibers, while also not being prone to undergoing ion-exchange with matrix components.

4. Conclusions

In this work, a double-confined PIL-based sorbent coating composed of both IL monomer and crosslinker was successfully constructed using a UV-initiated polymerization process, and was applied for the determination of nine UV filters in sample solutions containing high salt concentrations using DI-SPME coupled to HPLC. The analyte-enriched desorption solvent was directly injected to HPLC for the separation of analytes. When an aqueous solution containing NaCl (25%, w/v) was used as a sample matrix, Fiber **1** exhibited the best extraction efficiencies and highest stability compared to Fiber **2** and the PDMS/DVB fiber. Low parts-per-billion level LODs were achieved with good reproducibility, and the fibers were applied in three different real samples including tap, pool, and lake water for the evaluation of relative recovery.

The co-polymerization of IL cations and anions resulted in a robust sorbent coating compatible with high salt solutions, overcoming the inherent drawback of limited matrix choices for SPME when DI extraction mode is used. Fiber **1** was used for approximately 120 extraction/desorption cycles without a loss of extraction efficiency, exhibiting a much longer lifetime compared to the PDMS/DVB fiber. The double-confined sorbent coatings such as Fiber **1** greatly expands the types of possible matrices for DI-SPME while providing the capability of structural tuning of the PIL. Future work with the double-confined sorbent coatings are focused on biological or environmental applications which require sampling from complex matrices.

Acknowledgments

The authors acknowledge funding from the Chemical Measurement and Imaging Program at the National Science Foundation (Grant number CHE-1709372).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2018.01.052.

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