



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



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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 ([VImC₁₀][SS]) and 1,12-di(3-vinylbenzylimidazolium) dodecane distyrenesulfonate ([VBlm]₂C₁₂][2SS]), 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 $\mu\text{g L}^{-1}$. 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 $\mu\text{g L}^{-1}$. 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 $\mu\text{g L}^{-1}$ and as high as 5 $\mu\text{g L}^{-1}$.

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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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 ([VImC₁₀][SS]) and 1,12-di(3-vinylbenzylimidazolium) dodecane distyrenesulfonate ([VBIm)₂C₁₂][2SS]), 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%), avobenzene (BMDM) (≥99.0%), acrylonitrile (99.0%), 1,12-dibromododecane (98.0%), 1-vinylimidazole (≥99.0%), 1-chlorododecane (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 (LiNTf₂) 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 ([VImC₁₀][Cl]), 1-vinyl-3-decylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([VImC₁₀][NTf₂]), 1,12-di(3-vinylbenzylimidazolium) dodecane dichloride ([VBIm)₂C₁₂][2Cl]) and 1,12-di(3-vinylbenzylimidazolium) dodecane dibis[(trifluoromethyl)sulfonyl]imide ([VBIm)₂C₁₂][2NTf₂]) were synthesized according to previously published procedures [22,32,33]. The preparation of 1-vinyl-3-decylimidazolium styrenesulfonate ([VImC₁₀][SS]) was carried out in a similar manner to a previously reported method [28] by mixing [VImC₁₀][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)₂C₁₂][2SS]) was synthesized by the same method as the monomer using a molar ratio of

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