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Deep eutectic solvent-based ultrasound-assisted dispersive liquid-liquid microextraction coupled with high-performance liquid chromatography for the determination of ultraviolet filters in water samples

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ABSTRACT

In the present study, a simple and rapid sample preparation method designated ultrasound-assisted dispersive liquid-liquid microextraction based on a deep eutectic solvent (DES) followed by high-performance liquid chromatography with ultraviolet (UV) detection (HPLC-UVD) was developed for the extraction and determination of UV filters from water samples. The model analytes were 2,4-dihydroxybenzophenone (BP-1), benzophenone (BP) and 2-hydroxy-4-methoxybenzophenone (BP-3). The hydrophobic DES was prepared by mixing trioctylmethylammonium chloride (TAC) and decanoic acid (DecA). Various influencing factors (selection of the extractant, amount of DES, ultrasound duration, salt addition, sample volume, sample pH, centrifuge rate and duration) on UV filter recovery were systematically investigated. Under optimal conditions, the proposed method provided good recoveries in the range of 90.2–103.5% and relative standard deviations (inter-day and intra-day precision, $n = 5$) below 5.9%. The enrichment factors for the analytes ranged from 67 to 76. The limits of detection varied from 0.15 to 0.30 ng mL^{-1}, depending on the analytes. The linearities were between 0.5 and 500 ng mL^{-1} for BP-1 and BP and between 1 and 500 ng mL^{-1} for BP-3, with coefficients of determination greater than 0.99. Finally, the proposed method was applied to the determination of UV filters in swimming pool and river water samples, and acceptable relative recoveries ranging from 82.1 to 106.5% were obtained.

1. Introduction

Overexposure to ultraviolet (UV) radiation has harmful effects on human health because it can cause several skin disorders, including sunburn, photoaging, photodermatosis and skin cancer [1]. With growing public awareness of these hazards, the demand for UV protection products containing UV filters has increased significantly in recent years [2]. Due to their frequent use in higher quantities, only organic UV filters were considered in this work. UV filters usually have single or multiple aromatic structures conjugated with different chemical groups such as carbonyl groups and double bonds [3]. These compounds, which can absorb UV radiation, are not only widely used in many cosmetic products such as sunscreen lotions, skin care, facial makeup and lip care products to avoid skin damage [4–6] but also in plastics, adhesives, paint and rubber to protect these products from UV degradation [7,8]. Because of their extensive use and physico-chemical properties, UV filters can be present in the environment at potentially harmful concentrations [9]. UV filters can reach surface waters via recreational activities such as sunbathing and swimming or through wastewater [10,11]. The lipophilic property of UV filters has also led to their accumulation in the environment (e.g., in biota and sediments) [12]. Furthermore, these compounds can cause serious problems due to their endocrine and developmental toxicity [13–15]. Particularly, benzophenones (BPs), one of the most commonly used groups of UV filters, have been reported as having genotoxic effects [16]. UV filters have been identified by the scientific community as emerging pollutants [17]. To evaluate the potential risks of UV filters, sensitive and reliable analytical methods are required. In the present study, 2,4-dihydroxybenzophenone (BP-1), benzophenone (BP) and 2-

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hydroxy-4-methoxybenzophenone (BP-3) were chosen as model analytes.

Due to the low concentration of UV filters in the environment, several sample preparation techniques were typically required to pre-concentrate the UV filters before instrumental analysis. Liquid phase microextraction (LPME), a solvent-minimized liquid-liquid extraction, provides relatively high enrichment factors for analytes. This technique has been widely used to extract UV filters from water samples for pretreatment purposes [5,12]. Dispersive liquid-liquid microextraction (DLLME), one of the most widely used LPME methods, has been developed with good repeatability, less extraction time, high recovery as well as a high enrichment factor [18,19]. In this technique, a mixture of extraction solvent (water-immiscible) and disperser solvent (water-miscible) was injected into a water sample, forming a cloudy solution [20]. The large contact area between the fine droplets of the extractant and the sample facilitates the mass transfer of the analytes into the extractant. The extraction equilibrium is quickly reached in DLLME. After the extraction is complete, phase separation is performed by centrifugation, and the analytes remain in the extractant [21]. However, the use of organic solvents as the extraction solvent and the consumption of disperser solvents may add to the environmental pollution burden. Currently, ionic liquids (ILs) with some significant advantages over organic solvents are considered as alternatives to conventional organic solvents [22]. Many studies have reported the application of ILs in the field of DLLME, especially imidazolium-based ILs [5,6,12,17]. However, the high price, complicated synthetic process and toxicity present disadvantages for imidazolium-based ILs [23]. Therefore, the selection of appropriate environmentally friendly green solvents is still a challenging task for the development of DLLME. To replace conventional disperser solvents, ultrasound has been introduced into DLLME. Ultrasound is a type of energy that can cause emulsion, homogenization and mass transfer between immiscible phases. In ultrasound-assisted DLLME (UA-DLLME), the extractant could be efficiently dispersed into fine droplets by the effect of ultrasound to accomplish extraction of target analytes [24]. In this study, UA-DLLME was used for the extraction of three types of UV filters from water samples.

Currently, deep eutectic solvents (DESs) are attracting great interest as alternatives to conventional organic solvents and ILs. DESs are eutectic mixtures of two or more compounds with the ability to associate with each other via hydrogen bonds [25]. Due to the self-association of hydrogen bond donors and acceptors, DESs have lower melting points than each of the individual components [26]. DESs may be considered cousins to ILs because they share similar solvent characteristics, such as negligible vapor pressure, wide liquid range, non-flammability, and good solubility for organic and inorganic compounds [27,28]. Moreover, most of the DESs are non-toxic, biocompatible and biodegradable [29]. The properties of DESs can also be tuned by changing the molecular structure, chemical nature and ratio of the individual components [30]. However, DESs differ from ILs since the former are not composed entirely of ions but, instead, of molecular components [26]. In addition, compared with ILs, DESs are less expensive and easier to prepare [31]. In many reports, DESs are typically prepared by simply mixing choline chloride (ChCl) with hydrogen bond donors, such as urea, carboxylic acids or polyols, without the need for solvents or complex purification steps [32]. Therefore, DESs have the potential to replace conventional organic solvents as well as ILs. However, DESs are generally hydrophilic because of their hydrogen bonding ability and can be easily dissolved in an aqueous environment [30]. This property restricts their applications for the separation and concentration of analytes dissolved in water. Therefore, extensive efforts should be devoted to the development of hydrophobic DESs.

In this study, hydrophobic DESs, consisting of a straight-chain monobasic acid and a quaternary ammonium salt, are presented. Trioctylmethylammonium chloride (TAC), which contains long carbon chains, was chosen as the hydrogen bond acceptor. Decanoic acid (DecA) was then chosen as the hydrogen bond donor because of its highly hydrophobic behavior and moderate ability to undergo hydrogen bonding interactions [30]. Few extraction procedures based on hydrophobic DESs have been reported for the determination of UV filters in water samples. Thus, the aim of this work is the utilization of hydrophobic DESs in UA-DLLME to extract UV filters from water samples. DESs were prepared with different molar ratios of TAC:DecA. To achieve the best extraction efficiency for DES-UA-DLLME, the main experimental factors that can affect the extraction, including the type of DES, the amount of DES, ultrasound duration, salt addition, sample volume, sample pH, and centrifuge rate and duration, were investigated in detail. Finally, the feasibility of the proposed method was evaluated in swimming pool and river water samples.

2. Experimental

2.1. Chemicals and reagents

The three organic UV filters, BP, BP-1 (pKa 7.72), and BP-3 (pKa 7.56), were purchased from the Aladdin Reagent Corporation (Shanghai, China). HPLC-grade methanol was obtained from Dikma Ltd. (Beijing, China). Ultrapure water was produced using a Milli-Q water purification system (Millipore, Bedford, MA, USA). TAC was supplied by the Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. DecA was acquired from Aladdin Reagent Corporation (Shanghai, China). Analytical-grade NaCl was purchased from Beijing Chemical Reagent Factory (Beijing, China).

A mixed standard solution of the three UV filters was prepared in methanol at 10 mg L^{-1} and stored at 4 °C. Water samples containing all the target analytes were prepared daily by spiking ultrapure water with the stock solutions. The concentration of the analytes in the samples for the optimization experiments was 100 ng mL^{-1}.

Two swimming pool water samples (1 and 2) were collected from two different swimming pools in Beijing, China. Two river water samples (1 and 2) were obtained from Xindian (Henan Province, China) and Beijing (China), respectively. The water samples were filtered through 0.45-μm membrane filters to remove suspended particulate matter and were stored at 4 °C before performing the extraction procedures.

2.2. Apparatus

Separation of the selected UV filters was performed on an Agilent 1260 HPLC equipped with a binary pump, an automated sample injector and a UV detector. A Waters X Select HSS C18 column (250 × 4.6 mm i.d., 5 μm) was used in reversed-phase mode. Additionally, a Spursil C18 guard column (10 × 2.1 mm i.d., 5 μm) was used in the chromatographic analysis. The injection volume was 10 μL and the column temperature was 25 °C. The mobile phase consisting of 70% methanol and 30% water was delivered at a flow rate of 0.7 mL min^{-1}. BP-1 and BP-3 were detected at a wavelength of 290 nm, and BP at 254 nm. A KQ3200DE ultrasonic water bath was supplied by Kunshan Ultrasonic Instrument Co., Ltd. (Kunshan, China) to emulsify the DES. A high-speed centrifuge was purchased from Anhui USTC Zonkia Scientific Instruments Co., Ltd. (Anhui, China) to separate the phases.

2.3. Preparation of hydrophobic DESs

The five DESs were synthesized as follows: mix TAC with DecA at different molar ratios (1:1 (DES_1), 1:2 (DES_2), 1:3 (DES_3), 1:4