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Online analysis of five organic ultraviolet filters in environmental water samples using magnetism-enhanced monolith-based in-tube solid phase microextraction coupled with high-performance liquid chromatography

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ABSTRACT

Due to the endocrine disrupting properties, organic UV filters have been a great risk for humans and other organisms. Therefore, development of accurate and effective analytical methods is needed for the determination of UV filters in environmental waters. In this work, a fast, sensitive and environmentally friendly method combining magnetism-enhanced monolith-based in-tube solid phase microextraction with high-performance liquid chromatography with diode array detection (DAD) (ME-MB-IT/SPME-HPLC-DAD) for the online analysis of five organic UV filters in environmental water samples was developed. To extract UV filters effectively, an ionic liquid-based monolithic capillary column doped with magnetic nanoparticles was prepared by *in-situ* polymerization and used as extraction medium of online ME-MB-IT/SPME-HPLC-DAD system. Several extraction conditions including the intensity of magnetic field, sampling and desorption flow rate, volume of sample and desorption solvent, pH value and ionic strength of sample matrix were optimized thoroughly. Under the optimized conditions, the extraction efficiencies for five organic UV filters were in the range of 44.0–100%. The limits of detection (S/N = 3) and limits of quantification (S/N = 10) were 0.04–0.26 μg/L and 0.12–0.87 μg/L, respectively. The precisions indicated by relative standard deviations (RSDs) were less than 10% for both intra- and inter-day variabilities. Finally, the developed method was successfully applied to the determination of UV filters in three environmental water samples and satisfactory results were obtained.

1. Introduction

Organic UV filters are a class of synthesized chemicals usually with single or multiple aromatic structures which strongly absorb a specific wavelength range of 280–315 nm (UVA) and 315–400 nm (UVB) [1,2]. As active ingredients, they are extensively used in many personal care products (PCPs) such as sunscreens, lipsticks and hair shampoos [3] for the purpose of protecting skin from adverse effect of ultraviolet radiation. Additionally, UV filters are added to polymeric materials and paints to improve their stability and prevent damaging photo-oxidation [4,5]. In order to avoid illegal or excessive use of UV filters and ensure the health of people, 25 organic compounds are currently limited by the European Union (EU) to be used in sunscreen products, with maximum individual concentration up to 10% (w/w) [6].

Undoubtedly, the widespread usage of UV filters may lead to their release into the aquatic environment. In fact, many of the compounds have been detected in a wide variety of water samples such as bathing waters [7], surface waters [8–10], wastewaters [11], and seawaters [12]. Concerns about the negative environmental impact of UV filters have been raised. Related toxicological studies have demonstrated that many UV filters can function as endocrine disrupters and exert estrogenic and anti-androgenic actions in various organisms [13,14]. Moreover, a study performed by Kunisue et al. [15] indicated that exposure to benzophenone type UV filters might result in oestrogen-dependent disease such as endometriosis in women. Hence, in view of the ecosystem and human health, more efforts should be made in the development of analytical methods that are convenient, accurate and efficient to detect UV filters in environmental water samples.

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Up to now, chromatographic analysis including high performance liquid chromatography with UV detector (HPLC-UV) [11,16], gas chromatography in combination with tandem mass spectrometry (GC–MS) [17] and liquid chromatography coupled to tandem mass spectrometry (LC–MS/MS) [18,19], has been the most common technique for the determination of UV filters in environmental waters. However, because of the complexity of sample matrices and the low concentration of targeted compounds, suitable sample preparation processes are necessary prior to the chromatographic analysis. So far, a variety of pretreatment techniques such as solid-phase extraction (SPE) [19], solid-phase microextraction (SPME) [11,17,20], stir bar sorptive extraction (SBSE) [21] stir bar sorptive-dispersive microextraction (SBSDME) [22] and dispersive liquid–liquid microextraction (DLLME) [23,24] are available to extract UV filters from aqueous samples. Among these techniques, SPME is a relatively simple and solventless approach developed by Pawliszyn and co-workers [25]. However, the problems of fragility, limited life-span and high cost are great challenges for SPME. As an alternative to SPME, in-tube SPME (IT-SPME) has attracted extensive attention due to its distinct advantages such as simple operation, easy automation and environmental friendliness. When online coupled to analytical instrument such as HPLC-UV and HPLC–MS, IT-SPME can realize continuous extraction, desorption and analysis, which not only improves the extraction sensitivity and precision but also greatly reduces the analytical time [26]. However, according to the study from Feng's group [27], low extraction efficiency could still be found in IT-SPME. In order to improve the extraction efficiency of IT-SPME, a new method named magnetism-enhanced monolith-based IT-SPME (ME-MB/IT-SPME) was developed in our group [28,29]. This method utilizes monolithic capillary column (MCC) doped with magnetic nanoparticles (MNPs) (MCC/MNPs) as extraction phase. When the MCC/MNPs is placed inside a magnetic coil, the MNPs can be induced to generate different magnetic field gradients by applying an external power supply. In this case, the diamagnetic analytes tend to be trapped in the region in which the field gradient is minimal, thus increasing the retention of the analytes inside the extractive medium [30]. These studies [28,29] well indicate that ME-MB/IT-SPME is a promising method to improve the extraction efficiency for the diamagnetic compounds.

Recently, Ionic liquids (ILs) have gained extensively attention in the field of sample preparation due to their peculiar characteristics such as low vapor pressure, high thermal stability and tunable physicochemical properties. Previous studies well demonstrate that ILs are ideal extractants for sample preparation [31]. In this work, a novel IL, 1-allyl-3-methylimidazoliumbis[(trifluoromethyl)sulfonyl]imide (AM) was first used as functional monomer to prepare MCC/MNPs. After that, the polymeric ionic liquid (PIL)-based MCC/MNPs (PIL-MCC/MNPs) was connected directly to the six-port valve and used as extraction medium of online ME-MB/IT-SPME-HPLC-DAD system. The conditions affected the extraction efficiency of ME-MB/IT-SPME were optimized thoroughly. Finally, the proposed method was successfully used for the online analysis of trace UV filters in environmental water samples.

2. Experimental

2.1. Chemicals

AM (98%) was purchased from ANPLE Laboratory Technologies Inc. (Shanghai, China). Ethylene dimethacrylate (ED) (97%) and 3-(trimethoxysilyl) propylmethacrylate (γ-MAPS) (95%) were supplied by TCI (Tokyo Kasei Kogyo Co., Japan). Azobisisobutyronitrile (AIBN) (97%, re-crystallized before use), 1-propanol (97%) and 1,4-butanediol (98%) were purchased from Shanghai Chemical Co. (China); $FeCl_3 \cdot 6H_2O$ (99%), $FeCl_2 \cdot 4H_2O$ (98%), tetraethylorthosilicate (TEOS) (98%) and PEG4000 was supplied from Xilong Chemical (Guangzhou, China). HPLC-grade acetonitrile (ACN) and methanol were purchased from Tedia Company (Fairfield, USA). Water used throughout the study was purified using a Milli-Q water purification system (Millipore, USA). Fused-silica capillary (320 μm i.d.) was got from Ruifeng Instrumental Co. (Hebei, China).

Five organic UV filters including 2-hydroxy-4-methoxybenzophenon (BP-3) (>99%), 3-(4-methylbenzylidene)camphor (4-MBC) (98%), 2-ethylhexyl 4-methoxycinnamate (EHMC) (98.5%), octyl dimethyl-p-aminobenzoate (OD-PABA) (98.4%) and octyl salicylate (OS) (98.6%) were purchased from ANPLE Laboratory Technologies Inc. (Shanghai, China).The basic properties of these diamagnetic compounds can be found in Supplementary material (Table S1). Individual stock solutions of five UV filters were prepared at a concentration of 1000 mg/L in methanol. The standard mixtures containing 100 mg/L of each compound were prepared by diluting individual stock solution in methanol. All solutions were stored at 4 °C and diluted with ultrapure water to give the required concentration.

2.2. Equipments and materials

The schematic of the online ME-MB/IT-SPME-HPLC-DAD system developed in this work is illustrated in Fig. 1. The whole system consisted of a ME-MB/IT-SPME segment, which included a Rheodyne 7725i high-pressure six-port valve (valve 1) (Cotati, CA, USA), two P230 II high pressure pumps (pump A and pump B) (Elite, Dalian, China) and a TPR-6405D DC power supply (Long Wei, Guangzhou, China), and a HPLC segment. The HPLC system was equipped with a Quater pump (pump C) (1260 Quat Pump), a Rheodyne 7725i high-pressure six-port valve (valve 2) with a 200 μL sample loop (Cotati, CA, USA) and a diode array detector (1260-DAD),

The morphologies of PIL-MCC/MNPs were investigated using transmission electron microscopy (TEM) (JEOL 2011 microscope, Japan) and scanning electron microscopy (SEM) (Philips, Eindhoven, Netherlands). Magnetic properties of the MNPs were studied by a PPMS-9 vibrating sample magnetometer (VSM) (QUANTOM, USA); elemental analysis (EA) was carried out on a PerkinElmer (Shelton, CT, USA) Model PE 2400. Fourier transform infrared spectroscopy (FT-IR) was performed on an Avatar-360 FT-IR instrument (Thermo Nicolet, Madison, WI, USA).

2.3. Chromatographic conditions

All chromatographic analyses were carried out on a Thermo Hypersil BDSC18 column (5 μm particle size, 250 mm × 4.6 mm i.d.). The mobile phase consisted of 0.1% (w/v) formic acid aqueous (solvent A) and methanol (solvent B). The optimized gradient elution program was as follows: 0–5 min, 10–70% B; 5–10 min, 70–90% B and kept for 4 min, 14–16 min, 90–10% B and kept for 4 min. The flow rate was 1.0 mL/min and the detection wavelength was set at 311 nm.

2.4. Preparation of PIL-MCC/MNPs

The PIL-MCC/MNPs was synthesized by an *in-situ* heat-initiated polymerization method. There were two steps, the first step was the preparation of modified MNPs and the procedure was the same as our previously reported [28]. In the second step, the polymerization mixture consisted of AM (175 mg), ED (175 mg), 1-propanol (315 mg), 1,4-butanediol (315 mg), AIBN (20 mg) and modified MNPs (25 mg), were mixed together and sonicated 20 min to get homogeneous reaction solution. The above polymerization solution was filled into the fused silica capillary column (20cm × 320 μm