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Expanding the application of stir bar sorptive-dispersive microextraction approach to solid matrices: Determination of ultraviolet filters in coastal sand samples

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ABSTRACT

This work describes a new method for the determination of organic compounds in solid samples based on the equilibrium desorption of the analytes in an aqueous phase followed by stir bar sorptive-dispersive microextraction (SBSDME). Sand samples, contaminated with UV filters due to bathing and recreational activities, were dispersed in an aqueous medium by using a coated stir bar with CoFe_2O_4 @oleic acid magnetic nanoparticles. The UV filters were physically desorbed from the surface of the sand particles and rapidly adsorbed on the hydrophobic coating of the nanoparticles, which were retrieved by means of their magnetism after stopping the stirring. In this manner, both preconcentration of the analytes and clean-up were simultaneously accomplished without the requirement of any additional sample preparation steps. After extraction, the analytes were desorbed in ethanol and then analyzed by gas chromatography-mass spectrometry (GC-MS). The main variables involved in the extraction process (i.e., sorbent amount, extraction time, pH and ionic strength) were studied to provide the best extraction efficiencies and maximum enrichment factors. Under the selected conditions, the figures of merit of the proposed method were evaluated providing limits of detection in the low ng g^{-1} range, enrichment factors between 23 and 80, and relative standard deviations (RSD%) below 14% for all the target analytes. Matrix effects were observed in real coastal sand samples and thus standard addition calibration was employed for quantification. The method was successfully applied to the analysis of UV filters in several coastal sand samples of different origin. This work expands the analytical potential of the novel SBSDMI approach to the determination of organic compounds in solid matrices.

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1. Introduction

Microextraction techniques play an important role in the sample preparation of environmental samples, since they allow for both enrichment of the analytes and clean-up to eliminate potentially interfering compounds in a single step. In this sense, in order to contribute to the development of new approaches, our group introduced a new hybrid microextraction approach termed stir bar sorptive-dispersive microextraction (SBSDME) [1] by using magnetic sorbents (e.g. magnetic nanoparticles (MNPs)) as extraction phases. This technique involves the addition of a coated stir bar

with a magnetic sorbent into a vial containing the sample. At low stirring rate, the sorbent remains in the stir bar and the extraction is similar to stir bar sorptive extraction (SBSE), whereas at higher stirring rates the sorbent is released and dispersed into the sample as in dispersive solid-phase extraction (DSPE). When the stirring is ceased, the magnetic sorbent returns to the stir bar without requiring an additional external magnetic field. Thus, the SBSDMI approach allows for lower extraction time than SBSE due to the dispersion of the sorbent and easier post-extraction treatment than DSPE since reduces the manual intervention. Then, the coated stir bar containing the extracted compounds can be desorbed in an appropriate solvent for further injection into a liquid chromatographic (LC) instrument [1,2], or directly thermally desorbed into a gas chromatographic (GC) system [3]. Up to now, this novel approach has only been applied to environmental water

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samples. Specifically, the analytical utility of this approach was demonstrated in the determination of lipophilic UV filters using lipophilic oleic acid-coated cobalt ferrite MNPs (CoFe_2O_4 @oleic acid MNPs) [1,3] and hydrophilic UV filters using a polar silica-coated cobalt ferrite-nylon 6 composite (CoFe_2O_4 @ SiO_2 -nylon 6) [2].

The analytical interest of organic UV filters in environmental samples lies in that these compounds have reached the environment by direct and indirect sources and are being accumulated in aquatic ecosystems [4]. Moreover, due to the lipophilic characteristics of some of these chemicals, solid samples such as soils, sediments, coastal sand, sewage sludge and even indoor dust have been shown to be an effective matrix for their accumulation [5]. Different *in vitro* and/or *in vivo* studies have demonstrated that some organic UV filters, even at trace levels, could cause hormonal disruption on the reproduction of fish [6,7] or malformations of fish [8]. For all these reasons, these compounds are considered as emerging contaminants without regulatory status. Hence, from an environmental point of view, there is a growing interest to develop analytical methods for their determination at trace levels and thus to estimate their bioaccumulation in these ecosystems.

Due to the low levels of UV filters in environmental samples, preconcentration techniques are usually employed to reach these values, and/or to eliminate some potentially interfering compounds, and therefore to achieve their determination. In this way, several methodologies for the determination of these emerging pollutants in environmental samples have been compiled in different reviews [9–12], but most are focused on the analysis of water samples. Regarding the scarce determination of UV filters in environmental solid samples, solid-liquid extraction with various organic solvents (by shaking, in consecutive steps) is usually the method of choice [13–17]. Other newer approaches, such as matrix solid-phase dispersion (MSPD) [18–20], microwave assisted extraction (MAE) [21,22] and, to a greater extent, pressurized liquid extraction (PLE) [23–28], have also been employed in order to accomplish faster, more efficient and lower solvent consumption extraction processes. An additional clean-up and/or preconcentration step is often performed on the extract due to the complexity of the solid matrix. This has been accomplished by means of solid-phase extraction (SPE) [13,15,16,22,25,26] or dispersive liquid-liquid microextraction (DLLME) [17]. However, some of these methods require specialized extraction devices and/or large amounts of organic solvents, even halogenated ones. On these grounds, the aim of this study is to expand the analytical applicability of the above mentioned SBS/DME approach to the trace determination of UV filters in solid matrices and improve some of the limitations of previous methods such as the consumption of organic solvents and analysis time. The main parameters involved in the extraction procedure were evaluated and optimized and it was then applied to four samples with satisfactory analytical features. In this way, the method could be useful for environmental surveillance purposes and bioavailability assessment.

2. Experimental

2.1. Reagents and samples

All reagents and solvents were obtained from major suppliers. 2-Ethylhexyl salicylate (ES) 99%, 2-hydroxy-4-methoxybenzophenone (benzophenone-3 (BZ3)) 98%, 2-ethylhexyl 4-methoxycinnamate (EMC) 99.8% and 2-ethylhexyl 4-(dimethylamino)benzoate (ethylhexyl dimethyl PABA (EDP)) 98% from Sigma-Aldrich (Steinheim, Germany); 3,3,5-trimethylcyclohexyl salicylate (homosalate (HS)) >98% from Merck (Darmstadt, Germany); isoamyl 4-methoxycinnamate

(IMC) 99.3% from Haarmann and Reimer (Parets del Vallés, Spain); 3-(4'-methylbenzylidene)camphor (MBC) 99.7% from Guinama S.L. (Valencia, Spain) and 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (octocrylene (OCR)) >98% from F.Hoffman-La Roche Ltd. (Basel, Switzerland) were used as standards. The chemical structures and selected relevant information are given in Table S1. Deuterated benzophenone (benzophenones- d_{10} (BZ- d_{10})) from Sigma-Aldrich (Miamisburg, OH, USA) was used as surrogate.

For the synthesis of cobalt ferrite coated with oleic acid nanoparticles, cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Acros Organics (New Jersey, USA) while oleic acid (90%) was obtained from Sigma-Aldrich.

HPLC-grade ethanol (EtOH) was purchased from Scharlau (Barcelona, Spain). Deionized water was obtained from a Connect water purification system provided by Adrona (Riga, Latvia). Sodium chloride (99.5%, analytical grade), ortho-phosphoric acid (85%, analytical grade) and sodium hydroxide (analytical reagent grade) that were used as ionic strength and pH regulators, respectively, were purchased from Scharlau (Barcelona, Spain). High purity helium (99.9999%) from Carbueros Metálicos S.A. (Paterna, Spain) was used as carrier gas in the GC-MS system.

Coastal sand samples were all collected from the shores of different beaches at different seasons of the year: Patacona beach (Valencia, Spain) in February 2017, El Saler beach (Valencia, Spain) in April 2017, Javea beach (Alicante, Spain) in June 2017 and Maspalomas beach (Canary Islands, Spain) in July 2017. Blank sand sample was collected away from the shore and out of summer season from Patacona beach. Blank sample was previously evaluated to confirm the absence of the studied UV filters. All samples were stored in the dark and dried at 50 °C overnight before sample analysis. No losses were observed at these gentle drying conditions, as previously demonstrated [17].

2.2. Apparatus and materials

An Agilent 1220 Infinity LC system comprised of a degasser, a quaternary pump, an autosampler, a thermostatted column oven and a UV/Vis detector was employed in the optimization of the main variables involved in the extraction step. Separations were carried out in a Purospher® 100 RP-18 (12.5 cm length, 4 mm I.D., 5 µm particle size) column (Merck). Twenty microliters of each extract were injected into the liquid chromatograph. The mobile phase, at 1 mL min⁻¹, consisted of EtOH and acetic acid 1% at a mixing ratio of 70:30 (v/v). The column temperature was maintained constant at 45 °C and the peak area was monitored at 325 nm for all the target analytes.

A Focus GC gas chromatograph coupled to a DSQ II mass spectrometry detector (operated in positive electron ionization mode at an ionization energy of 70 eV) from Thermo Fisher Scientific (Austin, TX, USA) was employed in the validation of the proposed method and the analysis of real samples.

A Basic 20 pH meter from Crison (Alella, Spain) was used for the adjustment of solutions pH. Magnetic stirring hotplates (Stuart Scientific, Staffordshire, United Kingdom) were used as stirrers in the extraction procedure, and NdFeB (45 MGOe) magnetic tumble stir cylinders (5 mm diameter x 10 mm long, nickel coated) from Supermanes S.L. (Sevilla, Spain) were used as stir bars for the extraction.

2.3. Synthesis of cobalt ferrite coated with oleic acid magnetic nanoparticles

The synthesis of the magnetic nanoparticles was performed by wet chemical co-precipitation according to an adapted protocol [29]. Briefly, 100 mL of a 0.4 M FeCl_3 aqueous solution and 100 mL of a 0.2 M CoCl_2 aqueous solution were mixed, and then 100 mL

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