



Stir bar sorptive-dispersive microextraction mediated by magnetic nanoparticles–nylon 6 composite for the extraction of hydrophilic organic compounds in aqueous media



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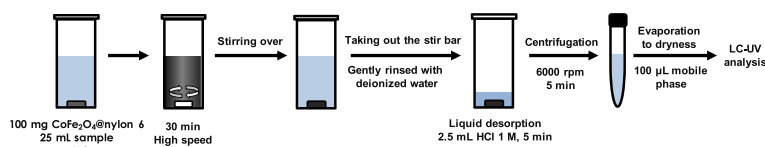
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HIGHLIGHTS

- SBSDME approach is extended for the extraction of hydrophilic compounds.
- SBSDME combines the advantages of SBSE and DSPE into a single approach.
- Magnetic nanoparticles–nylon 6 composite is used as sorbent material.
- The determination of hydrophilic UV filters in water is chosen as model application.
- The method has been developed and validated obtaining good analytical features.

GRAPHICAL ABSTRACT



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ABSTRACT

A new and sensitive analytical method based on the recently developed approach termed stir bar-sorptive dispersive microextraction (SBSDME) using a magnetic $\text{CoFe}_2\text{O}_4@\text{SiO}_2$ –nylon 6 composite as sorbent material is presented for the extraction of hydrophilic organic compounds. The simultaneous determination of four hydrophilic UV filters in environmental water samples has been chosen as a model analytical application due to the increasing awareness regarding the occurrence of sunscreen residuals in natural waters. The developed SBSDME approach combines the principles and benefits of stir bar sorptive extraction (SBSE) and dispersive solid phase extraction (DSPE) but allows for lower extraction time and easier post-extraction treatment. Moreover, most importantly, it enables the use of new magnetic materials that affords higher versatility and can be tailored to the needs of the analysis. The main experimental parameters involved in the SBSDME process (i.e. composite amount, extraction time, pH, ionic strength, desorption solvent and desorption time) were evaluated to provide the best enrichment factors. Under the optimized conditions, the method was successfully validated showing good linearity, enrichment factors between 105 and 145 depending on the analyte, limits of detection and quantification in the low ng mL^{-1} range (1.6 – 2.9 ng mL^{-1} and 5.4 – 9.6 ng mL^{-1} , respectively) and good intra- and inter-day repeatability ($\text{RSD} < 13\%$). The developed method was applied to the analysis of water samples of different origin (sea, river and swimming pool). Relative recovery values ranged between 90 and 115%, thus showing that the matrices under consideration do not affect the extraction process.

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1. Introduction

Sample preparation is one of the most important and critical steps of the analytical process. The importance of sample preparation is further emphasized in the determination of compounds at trace levels, since, on one hand, it is usually necessary to perform a preconcentration of the analytes, while on the other hand the samples often require a cleaning step to eliminate potentially interfering compounds. In this sense, extraction techniques, such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE), have played a fundamental role because they allow for both enrichment and separation in a single step. However, during the last years these traditional techniques are being progressively shelved in favor of the so-called ‘microextraction techniques’, which allow to obtain higher enrichment factors, to reduce the amounts of solvents and to generate significantly less wastes [1,2].

The introduction of solid-phase microextraction (SPME) in 1990 [3] as miniaturization of the traditional SPE constituted a major breakthrough in this field. This solventless technique, which is based on the sorption of the analytes in a coated fused silica fiber, became very popular due to its wide applicability. However, due to the low sorbent amount typically used ($\sim 0.5 \mu\text{L}$), the mass of analyte extracted is limited, and thus sensitivity could be negatively affected [4]. The stir-bar sorptive extraction (SBSE) technique [5], introduced a few years later and based on similar principles than SPME but using a coated magnetic stir bar, constituted another relevant example derived from the efforts to miniaturize SPE. In contrast to SPME, the sorbent amount used in SBSE (24–126 μL) is much larger than in SPME, which leads to higher amounts of analytes being extracted and thus achieving higher sensitivity [6–8]. However, the main drawback associated to SBSE is the low availability of commercial sorbents, mainly limited to polydimethylsiloxane (PDMS) and poly(ethyleneglycol) (PEG)-modified silicone. Thus, its applicability is mainly focused on the extraction of non-polar compounds [7,8]. To this respect, one of the most active trends is the development of new coatings in order to increase the versatility of this technique [7,8] or the development of alternative extraction approaches [8].

Dispersive solid phase extraction (DSPE) [9] is another promising miniaturized-SPE sample pretreatment technique. In DSPE, a SPE sorbent is dispersed in a sample solution containing the target analytes, thus maximizing the contact area between both donor and acceptor phases. After extraction, the sorbent containing the retained analytes is retrieved by centrifugation. This approach overcomes the versatility problem associated with SBSE, since a vast gamut of commercial sorbents is available [10]. In the last decade, magnetic nanoparticles (MNPs) coated with different sorbents have gained popularity as acceptor phases in DSPE [11], due to their higher specific surface area that speed up the extraction process, and their magnetic properties that allow their facile and fast retrieval by means of a strong magnet. The use of hybrid materials (i.e., composites) made of MNPs attached to polymers or carbon nanotubes is currently attracting great attention since the magnetic behavior of the MNPs and the high capability of sorption of the polymers (or of the carbon nanotubes) are jointly exploited [12,13].

Very recently, our research group introduced a new microextraction technique termed stir bar sorptive-dispersive microextraction (SBSDME) [14,15], where a magnetic stir bar coated with MNPs is placed into the sample. This novel technique aims to combine the principles of SBSE and DSPE, by acting as SBSE at low stirring rate, whereas at higher rate MNPs are detached and dispersed into the donor solution as in DSPE, returning to the magnetic bar when the stirring is stopped. In this manner, SBSMDME presents advantages over both SBSE (lower extraction time and

more versatile sorbents by using different coated MNPs) and DSPE (easier extraction and post-extraction treatment and minimum manual intervention). The analytical utility of this approach was demonstrated for the determination of lipophilic UV filters in water samples by using oleophilic CoFe_2O_4 @oleic acid MNPs [14,15].

With the aim of contributing to the development of new extraction approaches, the objective of this work is to show the versatility of SBSMDME for the extraction of highly polar compounds, such as hydrophilic UV filters (see Table 1), from environmental water samples. It should be pointed out that UV filters are considered as emerging pollutants due to the easy pathways to reach the aquatic environment and their potential harmful effects in the flora and fauna [16–18], and thus their determination presents a noticeable interest. However, the hydrophilic UV filters have a sulfonic moiety (see Table 1) that confers them a high solubility in water, which hinders their extraction. Nevertheless, the high affinity that sulfonated compounds exhibit to polyamides is well-known and it supposes the basis of dyeing of nylon with acid dyes [19,20]. In this sense, a CoFe_2O_4 @ SiO_2 -nylon 6 composite is proposed here as sorbent material in SBSMDME for the extraction of the target compounds. This composite is based on that previously presented by Valcárcel's research group for the extraction of polycyclic aromatic hydrocarbons [21] and bisphenol A [22] on the basis of π - π interactions and/or hydrogen-bonds.

Different published papers have been focused on the extraction, and subsequent determination, of different lipophilic UV filters from environmental water samples by using microextraction techniques [18,23,24]. However, as has been recently reviewed [24], some hydrophilic UV filters have been extracted from surface waters by SPE [25–28], but no publications dealing with their extraction using the high potential that microextraction techniques offer have been reported.

2. Experimental

2.1. Reagents and samples

Phenyldibenzimidazole tetrasulphonic acid (PDT) (disodium salt) > 99% from Haarmann and Reimer (Parets del Vallés, Spain), phenylbenzimidazole sulphonic acid (PBS) 99% from Guinama S.L. (Valencia, Spain), terephthalidene dicamphor sulphonic acid (TDS) (triethanolamine salt) 32% from L'Oreal (Paris, France) and benzophenone-4 (BZ4) 99.9% from Roig Farma S.A. (Terrassa, Spain) were used as standards. 1,2-naphthoquinone-4-sulfonic acid (NQ5) 95% from Sigma–Aldrich (Steinheim, Germany) was used as surrogate. The chemical structure and some relevant information are given in Table 1.

Cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) from Acros Organics (New Jersey, USA), tetraethylorthosilicate (TEOS) reagent grade 98% and nylon 6 pellets from Sigma–Aldrich (Steinheim, Germany), and formic acid from Fluka Chemika (Steinheim, Germany), were used for the synthesis of the CoFe_2O_4 @ SiO_2 -nylon 6 composite.

LC-grade ethanol (EtOH), hydrochloric acid 37% (reagent grade) and glacial acetic acid (extra pure) were obtained from Scharlau (Barcelona, Spain). The deionized water used in this work was produced from a Nanopure II water purification system provided by Barnstead (Boston, MA, USA). Analytical reagent grade sodium chloride 99.5% and ortho-phosphoric acid 85% from Scharlau were used as ionic strength and pH regulators, respectively.

Water samples were collected from Santa Ponsa beach (Majorca Island, Spain) in August 2011, Pinedo beach (Valencia, Spain) and Patacona beach (Valencia, Spain) in May 2013, a public swimming pool from Almudaina (Alicante, Spain) in July 2014 and Turia River (Valencia, Spain) in February 2015. All samples were collected in 1 L

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