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Development of stir bar sorptive-dispersive microextraction mediated by magnetic nanoparticles and its analytical application to the determination of hydrophobic organic compounds in aqueous media

Juan L. Benedé[a], Alberto Chisvert[a,*], Dimosthenis L. Giokas[b,**], Amparo Salvador[a]

[a] Departamento de Química Analítica, Facultad de Química, Universitat de València, 46100 Burjassot, Valencia, Spain
[b] Laboratory of Analytical Chemistry, Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece

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ABSTRACT

A novel microextraction technique combining the principles of stir bar sorptive extraction (SBSE) and dispersive micro-solid phase extraction (DμSPE) is presented. The main feature of the method is the use of a neodymium-core stirring bar physically coated with a hydrophobic magnetic nanosorbent. Depending on stirring speed, the magnetic sorbent either acts as a coating material to the stir bar, thus affording extraction alike SBSE, or as a dispersed nanosorbent medium for the collection and extraction of the target analytes, in close analogy to DμSPE. Once the stirring process is finished, the strong magnetic field of the stir bar prevails again and rapidly retrieves the dispersed MNPs. Alike SBSE, the stir bar is collected and the analytes are back-extracted by liquid desorption into an appropriate organic solvent, which is used for analysis. This enrichment technique is easy to prepare since it does not require special surface modification procedures, uses low volumes of non-toxic organic solvents and most importantly imbues SBSE with additional functionalities against a wide range of analytes (since nanosorbents with various coatings can be employed) while it affords additional merits to DμSPE in terms of extraction and post-extraction treatment. As proof-of-concept this new approach was applied to the determination of organic UV filters in seawater samples using oleic acid-coated cobalt ferrite ($CoFe_2O_4$@oleic acid) magnetic nanoparticles as sorbent material. The method showed good analytical features in terms of linearity, enrichment factors (11–148), limits of detection (low ng mL^{-1}), intra- and inter-day repeatability (RSD < 11%) and relative recoveries (87–120%).

1. Introduction

Sorption-based microextraction techniques such as solid-phase microextraction (SPME) [1], stir bar sorptive extraction (SBSE) [2] and dispersive solid phase extraction (DSPE) [3] constitute remarkable improvements of the traditional solid phase extraction (SPE) technique. They offer a wide variety of advantages such as simplicity, lower turnaround times, higher sample throughput, low sample volume requirements, use of small volumes of environmental benign and user friendly solvents, high degree of automation, etc. [4–9]. Although different in their application, all these techniques rely on the same principle: the trapping of solutes on a suitable sorbent which in turn is controlled by the partitioning coefficient of the solutes between the sorbent phase and the aqueous phase [4]. In SBSE, the sorption of the analytes takes places, usually, onto a film of polydimethylsiloxane (PDMS) which is coated on a magnetic stir bar whereas in SPME the analytes are adsorbed onto a fused-silica fiber coated with an appropriate sorbent layer. On the other hand, in DSPE analytes are adsorbed on the surface of micro or nanometer sized particles which are dispersed into the donor phase thus offering higher contact area.

Each of these techniques offer unique advantages [10–13] but they also have some drawbacks. SPME is a simple, high screening/high throughput method but it encounters problems related to robustness and reproducibility due to aging or sensitivity of the fiber. On the other hand, SBSE offers improved extraction efficiencies as compared to SPME, because the surface area of the stir bar is higher than that of the SPME fiber. However, only a few types of stir bar coatings are available, which limits its application to certain kinds of analytes. For this reason, over the last years a large amount

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* Corresponding author. Tel.: +34 96 354 49 00; fax: +34 96 354 44 36.
** Corresponding author. Tel.: +30 26510 08402; fax: +30 26510 08781.
E-mail addresses: alberto.chisvert@uv.es (A. Chisvert), dgiokas@cc.uoi.gr (D.L. Giokas).

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of research has been focused on the development of new coatings with high adsorption capacity, good regenerability and reusability [14,15], along with the development of novel approaches such as adsorptive microextraction techniques [16–18]. Nevertheless, extraction time is still long which reduces sample throughput. DSPE alleviates these drawbacks because dispersion increases considerably the contact area between the sorbent and the target compounds, thus affording reduced equilibrium time and improved extraction efficiencies [19]. However, the collection and post-extraction handling of the dispersed sorbent material is a multi-step and sometimes arduous undertaking [20–22] which jeopardizes the reproducibility of the analysis and the recovery of the analytes.

In the last years, the introduction of magnetic nanoparticles to DPSE procedures has offered a significant simplification along with enhanced enrichment factors due to the large surface-to-volume ratios of nanometer sized sorbents. In contrast to their non-magnetic analogs, magnetic nanoparticles can effectively be isolated by an external magnetic field without residual magnetization [23,24]. In this manner, the sorbent is rapidly and quantitatively retrieved and the target analytes can easily be eluted by means of liquid desorption with an appropriate solvent [25]. Additionally, MNPs can be conveniently coated with a large variety of chemicals (e.g. surfactants, polymers, highly hydrophobic substances, etc.) which confers multifunctional properties that enable their effective application in a large variety of different analytes (anions, cations, polar and non-polar organic compounds, etc.) [26,27]. To our knowledge, almost all studies employing magnetic nanosorbents [28–32] use external means (e.g. agitation by vortex or ultrasounds) to accomplish efficient dispersion of the MNPs since in the presence of a magnetic or metallic stirring bar, part of MNPs can adhere on it thus complicate both the collection and the elution procedure. Therefore, these external means could become impractical in case of having high volumes of sample to agitate unless specialized equipment is available (large vortex agitators, potent ultrasound sources, etc.).

In this work we introduce a new combined microextraction method relying on the principles of SBSE and DμSPE mediated by magnetic nanoparticles, termed as stir bar sorptive-dispersive microextraction (SBSDμE). The new method involves the convenient coating of neodymium-core magnetic stir bars with MNPs by means of physical methods (i.e. magnetism). Upon immersing the coated magnetic bar into a sample solution and as long as the stirring rate is maintained at low speed, magnetism is strong enough to retain MNPs resisting rotational (centrifugal) forces. Therefore, extraction is accomplished in a manner similar to SBSE. As stirring rate increases, the MNPs are dispersed into the aqueous solution, in close analogy to DSPE. When the stirring process is over, the strong magnetic field of the stir bar prevails again and rapidly retrieves the dispersed MNPs, without the requirement of an additional external magnetic field. In this manner, this enrichment technique takes into account the benefits provided by the stirring process and the dispersion of MNPs simultaneously. To prove its utility, eight of the most popular organic UV filters were extracted from aqueous sample solutions using the lipophilic oleic acid-coated cobalt ferrite ($CoFe_2O_4$@oleic acid) MNPs [28] as sorbent. The applicability of the method was examined in genuine seawater samples with satisfactory analytical features.

2. Experimental

2.1. Reagents

All reagents were procured 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 structure and some relevant information are given in Table S1. A stock solution containing 500 μg mL^{-1} all eight UV filters was prepared in ethanol. Working solutions (100–400 ng mL^{-1} for BZ3 and 10–50 ng mL^{-1} for the other UV filters), were prepared by appropriate dilution with doubly distilled water. Cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were purchased from Acros Organics (New Jersey, USA) while oleic acid (90%) was obtained from Sigma–Aldrich. HPLC-grade ethanol (EtOH), n-hexane (96%) and toluene (analytical-grade) were procured from Scharlau (Barcelona, Spain). The deionized water used in this work was obtained from a Nanopure II water purification system provided by Barnstead (Boston, MA, USA). Sodium chloride (99.5%, analytical grade) and ortho-phosphoric acid (85%, analytical grade) that were used as ionic strength and pH regulators, respectively, were purchased from Scharlau.

2.2. Genuine water samples

Prior to sampling all glassware was thoroughly cleaned by soaking in HNO_3:H_2O (50:50) and drying at 220 °C. Seawater samples were collected from the coastline of Western Mediterranean Sea: Santa Ponsa beach (Majorca Island, Spain) (Sample 1), Malvarrosa beach (Valencia, Spain) and Pinedo beach (Valencia, Spain) (Samples 2 and 3, respectively) in May 2013. All samples were collected in 1 L topaz glass bottles and stored in the dark at 4 °C. Before analysis the samples were left to reach room temperature.

To determine the total content of UV filters in the seawater samples (i.e. soluble fraction plus particulate fraction), 25 mL of unfiltered water samples were sonicated for 15 min to lixiviate the UV filters from particles following the procedure developed in our previous work [33].

2.3. Apparatus

An Agilent 1220 Infinity LC system comprised of a degasser, a quaternary pump, an autosampler, a thermostated column oven and a UV/vis detector was employed throughout the study. Separations were carried out in a LiChrospher® 100 RP-18 (12.5 cm length, 4 mm I.D., 5 μm particle size) column (Merck). A Basic 20 pH meter from Crison (Alella, Spain) was used for the adjustment of solutions pH. Magnetic stirrer hotplates (Stuart Scientific, Staffordshire, United Kingdom) were used as stirrers in the extraction procedure. A miVac DUO concentrator with miVac SpeedTrap from GeneVac (Ipswich, United Kingdom) was used for mild evaporation of the elution solvent (i.e. ethanol) to dryness.

2.4. Synthesis of cobalt ferrite coated with oleic acid nanoparticles

The synthesis of the magnetic nanoparticles was performed by wet chemical coprecipitation [34] by mixing 100 mL of a 0.4 M $FeCl_3$ aqueous solution and 100 mL of a 0.2 M $CoCl_2$ aqueous solution. Then, 100 mL of a 3 M sodium hydroxide aqueous solution were added dropwise under continuous stirring. Finally, 2 mL of oleic acid were added and the reaction mixture was heated to 80 °C for 1 h. The black precipitate product was slowly cooled to

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