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Micro-solid phase extraction based on oxidized single-walled carbon nanohorns immobilized on a stir borosilicate disk: Application to the preconcentration of the endocrine disruptor benzophenone-3

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ABSTRACT

A novel micro-solid-phase extraction approach is presented. It consists of a borosilicate disk with oxidized single-walled carbon nanohorns (o-SWNHs) immobilized in its pores. The o-SWNH disk is placed in the screw of a portable drill that allows the extraction unit to be stirred inside the sample. The technique was applied to the extraction of benzophenone-3 from swimming pool water samples, followed by its determination with ultrahigh performance liquid chromatography with photodiode array detection. The variables affecting extraction were optimized, and the method was characterized in terms of linearity, limit of detection (0.16 μg L^{-1}) and precision (the relative standard deviation is lower than 11.9 %). The enrichment factor is as high as 1379 and it involves an absolute recovery of 68.9 %. Relative recoveries are close to 90%. The method is likely to represent a new approach towards microextraction of organic species using this nanomaterial.

1. Introduction

Extraction and stirring integrated techniques have been in a continuous evolution [1] since the proposal of stir bar sorptive extraction (SBSE) [2] in 1999. However, few are the designs whose configurations can be adapted to perform on-site sampling [3]. SBSE shares the same general principles of solid phase microextraction (SPME) [4,5] but it uses higher volume of extracting phases [6] which increases the overall extraction capacity. Off/on-site SBSE has been successfully accomplished by attaching the stir bar to a homemade miniature battery-operated portable electric stirrer [7]. This new configuration is very convenient to install, remove and replace the stir bar. Moreover, the coating loss by friction, which occurred frequently in conventional SBSE system, is avoided. Rotated-fiber and rotated-membrane samplers are also designed for field water sampling [8]. The commercially available fibers or membranes are coupled to a battery-operated drill which permits their stirring. Rotated-membranes use a higher volume of extracting phase and thus the extraction efficiency is improved. However, the rotated-fiber also provides some advantages, such as the easy introduction of the fiber into the gas chromatograph after the extraction. A more convenient fiber-retracted SPME device was also designed for field sampling [9].

Thin film microextraction (TFME) [10] was proposed as a new geometry for SPME in 2004. In TFME, a sheet of flat film with high surface area-to-volume ratio is used as extraction phase. With this configuration, the volume of the extraction phase increases while the thickness of the coating remains constant or it is even thinner. TFME has been investigated as sample preparation tool in many fields and it can easily conduct on-site sampling by using an electronic drill [11].

The exceptional properties of nanoparticles (NPs), specially their high superficial area and the variety of interactions, make them useful tools in extraction procedures. Single-walled carbon nanohorns (SWNHs) are a new type of carbon nanomaterial related to single-walled carbon nanotubes (SWCNTs) but with a conical shape [12]. Despite the potential of SWNHs, few are the references which describe their use for analytical purposes [13–17] probably due to their scarce commercialization. To date, the extraction/stirring devices that use nanoparticles as extracting material are the so-called carbon nanotube assisted pseudo-stir bar solid/liquid microextraction [18], carbon nanotube-assisted pseudo-stir bar hollow fiber solid–liquid-phase microextraction [19] and magnetically confined hydrophobic nanoparticles [20,21]. However, none of them can be easily adapted to perform on-site sampling or extraction.

Solid phase extraction disks based on the use of carbon nanomaterials have been proposed in the last years to extract organic compounds from large-volume environmental water samples. In these proposals, the disk is formed by passing a suspension of SWCNTs [22,23] or multiwalled CNTs [24] through a polymeric filter where the NPs are retained. In this paper, the chemical immobilization of SWNHs

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into borosilicate disks is proposed to build a new extraction/stirring integrated technique. The mechanical resistance and easy functionalization of borosilicate disks, which has been recently evaluated by our research group [25], make them exceptional support in this type of extractions. The novel proposal, that works under the micro-solid phase extraction principles, has been practically evaluated by using the determination of benzophenone-3 (BP-3) in swimming pool water samples as model analytical problem. BP-3 is widely employed in sunscreens as it belongs to the group of ultraviolet (UV) filters, which are considered to be potential endocrine disrupting substances [26]. The increased use of these compounds would lead to environmental pollution as well as adverse health effects. For these reasons, UV-filters should be monitored in natural waters and efficiently sample preconcentration steps are required. To the best of our knowledge, this is the first method based on SWNHs and focused on the determination of BP-3 in water samples.

2. Experimental

2.1. Reagents and samples

All the reagents were of analytical grade or better. BP-3 (2-hydroxy-4-methoxybenzophenone) was purchased from Sigma-Aldrich (Madrid, Spain). Stock standard solution was prepared in acetonitrile (Sigma-Aldrich) at a concentration of 1 g/L and stored at 4 °C in the dark. Working standards were prepared on a daily basis by rigorous dilution of the stock in Milli-Q water (Millipore Corp., Madrid, Spain) or acetonitrile as required. Sodium chloride from Sigma-Aldrich was used in the optimization process.

Borosilicate filter disks (20 mm in diameter and pore size in the range of 16–40 μm), purchased from ROBU (Glasfilter-Geraete GmbH, Germany), were used as inert support for the immobilization of o-SWNHs. SWNHs, obtained from Carbonium S.r.l. (Padua, Italy), present purity better than 90% and lengths in the range from 40 to 50 nm with diameters between 4 and 5 nm. The synthesis of borosilicate disks with immobilized SWNHs required the use of hydrogen peroxide, sulfuric acid, sodium hydroxide, 3-aminopropyltriethoxysilane (APTS), N-3(dimethylaminopropyl)-N-ethyl-carbodiimidehydrochloride (EDC·HCl), glutaraldehyde (GA), sodium borate, N,N′-dimethylformamide (DMF) and anhydrous acetone. All of these reagents were purchased from Sigma-Aldrich, acetone excepted (Panreac, Barcelona, Spain).

Different swimming pool water samples from Córdoba, Spain, were analyzed. The samples were collected in amber-glass bottles without headspace and stored in the dark at 4 °C until their analysis. Filtration or pH adjustment was not required prior to the extraction process.

2.2. Apparatus

Chromatographic analyses were carried out on a Waters-AcquityTM Ultra Performance LC system (Waters Corp., Madrid, Spain) using an Acquity UPLC® BEH C_{18} column (1.7 μm particle size, 2.1 mm × 100 mm) maintained at 45 °C. The mobile phase consisted of (A) water and (B) acetonitrile at a flow rate of 0.5 mL/min using a gradient elution program. The initial composition was fixed at 40 % B, the percentage being increased to 60% in 5 min. The injection volume was 5 μL with partial loop with needle overfill mode. The separated analytes were determined by using a PDA eλ (extended wavelength) Detector (Waters) at 290 nm. System control was achieved with Empower software.

A JEOL JSM 6300 scanning electron microscopy (Isaza, Alcobendas, Spain) was also used to obtain the micrographs of the borosilicate disk before and after the immobilization of the o-SWNHs. Micrographs were acquired in the Central Service for Research Support (SCAI) of the University of Córdoba.

2.3. Synthesis of the borosilicate disks with immobilized SWNHs

The functionalization of the borosilicate disk consists of several and well defined steps.

2.3.1. Activation and functionalization of the borosilicate disk

First of all, the borosilicate disk was activated by its immersion in a sulfuric acid: hydrogen peroxide (2:1, v/v) solution for 150 min at 100 °C, the solution being renewed every 30 min in order to avoid losses due to evaporation. The activated disk was washed with Milli-Q water up to neutral pH and dried in an oven at 80 °C for 12 h.

In a second step, the borosilicate disk was introduced in NaOH 1 M solution for 30 min under continuous stirring at 500 rpm. After that, the disk was washed with Milli-Q water up to neutral pH and dried in an oven at 80 °C for 12 h.

In a third step, amine groups were introduced in the disk by using a 2% v/v APTS solution prepared in anhydrous acetone. The solution, in close contact with the disk, was stirred at 500 rpm for 15 min and the disk was finally washed with Milli-Q water (10 min) and methanol (10 min) in order to eliminate the excess of APTS.

In a fourth step, the borosilicate disk was introduced in 10% v/v GA solution prepared in a 50 mM borate buffer at pH 9.0. After stirring the solution during 60 min at 500 rpm, the disk was washed with Milli-Q water (10 min) and dried in an oven at 80 °C for 12 h.

2.3.2. Oxidation of SWNHs

First of all, 10 mg of pure SWNHs was accurately weighted in a glass vial. Subsequently, the nanomaterial was functionalized by using microwave energy (800 W, 10 min) [27] introducing oxygenated functional groups on the nanoparticle surface, which could facilitate their dispersion in polar media. The functionalized solid was dispersed in 50 mL of Milli-Q water and then stirred for 60 min in an ultrasonic bath. The dispersion was centrifuged (J.P. Selecta, Barcelona, Spain) at 10,000 rpm for 15 min to remove potential non-functionalized material, thus improving the reproducibility between dispersions. The dispersion was filtrated through a 0.5 μm polytetrafluorethylene tape (Miarco, Valencia, Spain) which was previously conditioned with methanol. The oxidized SWNHs (o-SWNHs) recovered were sonicated in methanol (20 mL) to remove them from the tape and they were finally dried in an oven at 40 °C for 12 h. This procedure was repeated three times in order to obtain an amount of 10 mg of o-SWNHs.

2.3.3. Immobilization of o-SWNHs on the activated borosilicate disk

The activated borosilicate disk was placed in a 25-mL glass beaker containing 20 mL of a EDC·HCl (0.01 g) solution in DMF and 10 mg of o-SWNHs. The disk was maintained in close contact with this dispersion for 3 h under a N_2 stream. Finally, the disk was washed with Milli-Q water and methanol to remove the non-immobilized o-SWNHs. The washing step was repeated twice.

Fig. 1 shows the micrographs obtained for the bare borosilicate disk (Fig. 1A) and the borosilicate disk with the o-SWNHs immobilized on its pores (Fig. 1B) at different magnifications. As it can be seen in Fig. 1B, the surface of the borosilicate disk presents a rough aspect due to the immobilization of the o-SWNHs over the pores of the disk. Attending to the size of the roughness of the disk, it corresponded with the diameter of the dahlias of the o-SWNHs. These results are in agreement with those obtained by using hollow fiber as support [15].

The coupling of the o-SWNHs to the extraction device is depicted in Fig. 2. The synthesized borosilicate disk with immobilized o-SWNHs (Fig. 2A) was finally pierced with a screw and adapted to a rotating metallic axle (Fig. 2B). The modified axle was finally integrated in a drill (Fig. 2C) to make feasible its stirring (Fig. 2D).