Journal of Chromatography A, 1311 (2013) 1–10

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Determination of trace levels of benzophenone-type ultra-violet filters in real matrices by bar adsorptive micro-extraction using selective sorbent phases

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ARTICLE INFO

Article history:
Received 14 May 2013
Received in revised form 30 July 2013
Accepted 1 August 2013
Available online 7 August 2013

Keywords:
Floating sampling technology
BAμE
Sorbent phases
UV filters
Benzophenones
Real matrices

ABSTRACT

Bar adsorptive micro-extraction (BAμE), using selective sorbent phases, followed by liquid desorption in combination with high performance liquid chromatography–diode array detection (BAμE-LD/HPLC–DAD), is proposed for the determination of trace levels of four benzophenone-type UV filters (benzophenone, 2-hydroxy-4-methoxy-benzophenone, 2,4-hydroxybenzophenone and 4-hydroxybenzophenone) in real matrices. By comparing three polymers (P1, P2 and P3) and five activated carbons (AC1, AC2, AC3, AC4 and AC5) phases, P2 (a modified pyrrolidone polymer) and AC4 coatings showed much higher selectivity and capacity through BAμE, where the former offers multiple mechanisms of interaction and faster equilibrium kinetics. Assays performed on 25 mL of ultra-pure water samples spiked at the 8.0 μg/L level, yielded recoveries ranging from 76.6 ± 8.3% to 103.5 ± 6.4% depending on the sorbent phase used (P2 or AC4), under optimized experimental conditions. The analytical performance showed convenient detection limits (0.3–0.5 μg/L) and good linear dynamic ranges (1.0–24.0 μg/L) with remarkable determination coefficients ($r^2 > 0.9969$). Excellent repeatability was also achieved through intraday (RSD < 13.0%) and interday (RSD < 8.9%) experiments. By using the standard addition methodology, the application of the present analytical approach on sea water, wastewater, commercial cosmetic products and urine samples revealed good sensitivity, absence of matrix effects and the occurrence of levels of some benzophenones. The proposed methodology that uses nanostructured particles and operates under the floating sampling technology proved to be a sorption-based static micro-extraction alternative to monitor benzophenone-type UV filters in real matrices. Moreover, is easy to implement, reliable, sensitive, requiring low sample volume and the possibility to choose the most selective sorbent coating according to the target compounds involved.

1. Introduction

The daily exposure to sunlight and the awareness about the risks of it, has increase the use of personal care products containing ultra-violet (UV) filters, particularly in sunscreens, mainly due to bathing waters and swimming pool activities, but also in cosmetics, such as skin lotions, aftershaves, hair sprays, shampoos, lipsticks, as well as varnishes, clothes and food container plastics [1].

These substances action is made by blocking the penetration of harmful UV light, through the formation of a thin layer on the surface where the product is applied, protecting human skin but also several materials from strong exposure to harmful wavelengths from sunlight. In general, UV filters can have organic or inorganic nature, and are used in single or combination of both in cosmetics and sunscreens, to protect from UVA (400–320 nm), UVB (320–290 nm) and UVC (280–100 nm) light [2]. The organic UV filters action is based on absorption of UV light due to the single or multiple aromatic structures composition, while inorganic primary action is to scatter and reflect UV light, and if during this process no degradation occurs, UV filters continuously repeat all this procedure [3].

The main contamination sources of UV filters are environmental input from industrial wastewater discharges, bathing activities, laundering of clothes, human excretion after skin application and absorption, residues in packages, wastewater treatment plants and other applications, like car polishers, textiles and plastics [4]. Therefore, the persistence of these pollutants in the environment is of great concern with possible health effects on humans. According to some authors [1,5–8], UV filters have also demonstrated agonist

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0021-9673/$ – see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.chroma.2013.08.007

and antagonist activities, in particular the benzophenone-type, suggesting that they can induce ecotoxicological risk to humans and aquatic wildlife.

Once residues of UV filters can be found in water, wastewater and urine matrices at low concentration levels (parts-per-billion, μg/L), and in order to control the contents in some cosmetic formulations, sample enrichment procedures prior to chromatographic or hyphenated systems must be implemented [9–11]. Nowadays, the sorption-based approaches are the most used enrichment methods for the determination of low concentration levels of UV filters in environment and biological matrices, such as solid-phase extraction [4,9,10,12], solid phase micro-extraction (SPME) [13–15] and stir bar sorptive extraction (SBSE) [16–19], although some of them using undesirable derivatisation approaches.

Recently, our group have introduced a novel static micro-extraction technique, bar adsorptive micro-extraction (BAμE), which uses nanostructured materials that is a remarkable alternative for trace analysis of medium-polar to polar compounds in aqueous media [20]. This new analytical approach, which operates under the floating sampling technology, presents also a great advantage comparatively to other sorption-based methods (e.g. SBSE) [21], since allows to tune the most convenient sorbent phase (e.g. activated carbons (ACs), polymers (Ps), etc.) for each particular type of target compounds, which has shown high effectiveness in many applications [22–27].

The present contribution, aims to evaluate the performance of BAμE with liquid desorption prior to high performance liquid chromatography followed by diode array detection (BAμE-LD/HPLC–DAD), as an alternative analytical approach to monitor trace levels of four UV filters (benzophenone, 2-hydroxy-4-methoxy-benzophenone, 2,4-hydroxy-benzophenone and 4-hydroxy-benzophenone) in real matrices. The optimization of the analytical process, including the selectivity, interactions mechanism and equilibrium kinetics of the sorbent phases (five ACs and three Ps) tested, as well as, the influence of several experimental parameters is fully discussed. The validation and the application of the optimized methodology for the determination of trace levels of benzophenones in sea water, wastewater, urine and commercial cosmetics samples are also addressed.

2. Experimental

2.1. Standards, materials and samples

The solvents used were HPLC-grade methanol (MeOH, 99.8%) and acetonitrile (ACN, 99.8%) obtained from Fisher (UK) and pentane (*n*-C5, 99%) from Riedel-de-Haën (Germany). Sodium chloride (NaCl) was supplied from Merck (99.5%, Germany). Sodium hydroxide pellets were obtained from AnalaR (98.0%, BDH chemicals, UK). Hydrochloric acid 37% was supplied from Panreac (Spain). Ultra-pure water was obtained from Milli-Q water purification systems (Millipore, USA). The Ps phases supplied from Tecnocroma (Portugal) were P1 (styrene-divinylbenzene, particle size 100 μm, pore size 260 Å and surface area 500 m^2/g), P2 (modified pyrrolidone, particle size 33 μm, pore size 85 Å and surface area 800 m^2/g) and P3 (ciano, particle size 55 μm, pore size 70 Å and surface area 500 m^2/g), presenting all of them a pH stability between 1 and 14. The ACs provided by Salmon & Cia (Lisbon, Portugal) were AC1 (surface area 1500 m^2/g), AC2 (surface area 1100 m^2/g), AC3 (surface area 900 m^2/g), AC4 (surface area 1400 m^2/g) and AC5 (surface area 1400 m^2/g). Benzophenone (BP, >99.0%) was supplied by Fluka (Sigma–Aldrich, Germany). 2-Hydroxy-4-methoxy-benzophenone (HMB, 98%), 2,4-hydroxy-benzophenone (DHB, 99%) and 4-hydroxy-benzophenone (HBP, >99%) were supplied from Acros Organics (USA). Individual standard stocks of each benzophenone (1000 mg/L) were used to prepare the working standard mixtures prepared in MeOH, stored at −20 °C and renewed every month. Solutions of sodium hydroxide (0.1 M) and hydrochloric acid (5%) were used for pH adjustments. The sea water samples were collected in August 2011 (Costa da Caparica, Portugal). The wastewaters were obtained from Beirolas treatment plant (Lisbon, Portugal). The after shave and sun protection cosmetics were purchased from the local market. The urine sample was collected from a male volunteer of age 34 years.

2.2. Experimental setup

2.2.1. pH_{PZC} Determination

The ACs surface chemistry characterization was made by measuring the pH at the point of zero charge (pH_{PZC}) by reverse mass titration [28]. Samples having 1, 2, 6, 8 and 10% of each AC were prepared by mixing them with ultra-pure water in a glass bottle, bubbled and sealed under nitrogen flow to eliminate carbon dioxide. After a minimum of 24 h shaking at room temperature, the pH of the samples was measured. The final pH_{PZC} value is defined by the pH of the plateau equilibrium curve against the solid weight fraction. The pH was measured in a Metrohm 744 pH metre (Switzerland).

2.2.2. BAμE assays

The BAμE devices were lab-made prepared according to previous work [20] and cleaned with ultra-pure water before use. For powdered Ps, each bar had an average weight (Mettler Toledo, Switzerland) of 3.9 ± 0.3 mg for P1, 2.5 ± 0.2 mg for P2 and 4.5 ± 0.3 mg for P3. For the ACs, each bar had an average weight of 3.2 ± 0.3 mg for AC1, 2.8 ± 0.1 mg for AC2, 1.9 ± 0.2 mg for AC3, 1.8 ± 0.1 mg for AC4 and 1.7 ± 0.3 mg for AC5. Typical assays were performed in 25 mL of ultra-pure water spiked with appropriate amount of a standard working mixture to get 8.0 μg/L of concentration, followed by the introduction of the BAμE device, previously coated with powdered sorbent, into the sampling flasks. The assays were performed in a multipoint agitation plate (Variomag, Germany) at room temperature. In a first approach, several ACs and Ps sorbents were tested in order to evaluate the selectivity that reaches the best recovery yields. In general, these assays were performed under standard experimental conditions; extraction: 2 and 16 h (1000 rpm), 8.0 μg/L, pH 5.5; back-extraction: 1.5 mL mixture of ACN/MeOH (1:1, v/v) during 30 min under ultrasonic treatment. After selecting the best sorbent phase, systematic studies were performed for optimizing several parameters, in order to reach the best BAμE-LD efficiency for the sorbent phase selected. The extraction parameters studied were equilibrium time (1, 2, 3, 4 and 16 h), pH (2.0, 5.5, 8.0 and 11.0), agitation speed (750, 1000 and 1250 rpm), organic modifiers (MeOH: 5, 10 and 15%, v/v) and ionic strength (NaCl: 5, 10 and 15%, w/v). After extraction, the devices were removed from the samples with clean tweezes and placed into a 2 mL vial containing 1.5 mL of the stripping solvent, ensuring their total immersion prior to ultrasonic treatment (Branson 3510) at room temperature. For LD, *n*-C5, ACN, MeOH and mixtures of ACN/MeOH (1:1, v/v) were the stripping solvents tested. The back-extraction times tested under ultrasonic treatment were 5, 10, 15, 30, 45 and 60 min.

Subsequently, the stripping solvent was evaporated until dryness under a gentle stream of purified nitrogen (>99.5%) and reconstituted with 200 μL of MeOH, for which the vials were then sealed and placed on the auto-sampler for HPLC–DAD analysis. For the method validation experiments, 25 mL of ultra-pure water were spiked with 200 μL of the working standard mixture at the desired concentrations, under optimized experimental conditions. The application to real samples was performed with 25 mL of sea water and wastewater. For the after shave case, a 1:50,000 (v/v)