



Contents lists available at ScienceDirect

Journal of Chromatography A

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



Development and optimization of a solid-phase microextraction gas chromatography–tandem mass spectrometry methodology to analyse ultraviolet filters in beach sand[☆]

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ARTICLE INFO

Article history:

Received 27 March 2018
Received in revised form 4 June 2018
Accepted 5 June 2018
Available online xxx

Keywords:

Emerging contaminants
Personal care products
UV filters
SPME
Experimental design
GC–MS/MS
Beach sand

ABSTRACT

A methodology based on solid-phase microextraction (SPME) followed by gas chromatography–tandem mass spectrometry (GC–MS/MS) has been developed for the simultaneous analysis of eleven multiclass ultraviolet (UV) filters in beach sand. To the best of our knowledge, this is the first time that this extraction technique is applied to the analysis of UV filters in sand samples, and in other kind of environmental solid samples. Main extraction parameters such as the fibre coating, the amount of sample, the addition of salt, the volume of water added to the sand, and the temperature were optimized. An experimental design approach was implemented in order to find out the most favourable conditions. The final conditions consisted of adding 1 mL of water to 1 g of sample followed by the headspace SPME for 20 min at 100 °C, using PDMS/DVB as fibre coating. The SPME–GC–MS/MS method was validated in terms of linearity, accuracy, limits of detection and quantification, and precision. Recovery studies were also performed at three concentration levels in real Atlantic and Mediterranean sand samples. The recoveries were generally above 85% and relative standard deviations below 11%. The limits of detection were in the pg g⁻¹ level. The validated methodology was successfully applied to the analysis of real sand samples collected from Atlantic Ocean beaches in the Northwest coast of Spain and Portugal, Canary Islands (Spain), and from Mediterranean Sea beaches in Mallorca Island (Spain). The most frequently found UV filters were ethylhexyl salicylate (EHS), homosalate (HMS), 4-methylbenzylidene camphor (4MBC), 2-ethylhexyl methoxycinnamate (2EHMC) and octocrylene (OCR), with concentrations up to 670 ng g⁻¹.

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1. Introduction

UV filters are substances added to personal care products (not only sunscreen products, but also lipsticks, moisturizing creams, make-up...) with the aim of protecting the skin against solar radiation. They are also found in plastics or furniture for photo protective purposes. They can enter the environment through domestic discharges, and recreational activities such as bathing or swimming in the sea, lakes or rivers. In the last years, the presence of these compounds in environmental waters has been reported

[1–3]. They are considered emerging pollutants and several studies evidence that organic UV filters may cause adverse effects like endocrine disruption [4–6]. In fact, due to their harmful effects, they are controlled in cosmetics by the European Regulation (EC) No. 1223/2009 (some of them are prohibited and other are restricted to a maximum concentration level) [7]. In the field of water policy, one of them, the 2-ethylhexyl methoxycinnamate (2EHMC), has recently been included in a monitoring EU Watch List for its consideration as a priority substance [8]. These compounds can be easily deposited on sand either applying the sunscreen on the beach or by direct contact of the person impregnated with the sunscreen with the sand. In addition, due to their relatively low solubility and high octanol–water partition coefficient (K_{ow}), UV filters are easily adsorbed on particulate matter, implying their likely occurrence in sand and sediments [1,9]. Concerning beach sand, the target matrix in the present study, the occurrence of

[☆] Selected paper from the 19th International Symposium on Advances in Extraction Technologies (ExTech 2017), 27–30 June 2017, Santiago de Compostela, Spain.

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UV filters has only been reported in one published paper [10], in which the compounds were extracted by dispersive liquid-liquid microextraction (DLLME) after a previous vortex-assisted extraction with acetone. In other studies, UV filters were extracted from other solid samples such as sediments and soils using different techniques such as: pressurized liquid extraction (PLE) [11,12], Soxhlet extraction [13], matrix solid-phase dispersion (MSPD) [14], pressurized hot water extraction–stir bar sorptive extraction (PHWE–SBSE) [15], microwave-assisted extraction (MAE) [9], ultrasound-assisted extraction [16], vortex extraction [17], and shaking [18].

To the best of our knowledge, the use of solid-phase microextraction for the determination of UV filters in this kind of solid environmental matrices has not been previously reported. However, there are studies that accomplish the extraction of UV filters by SPME [3,19–22] in water. SPME was also applied to other families of compounds in sediments such as dichlorobenzenes [23], perfluorinated alkylated substances [24], PAHs [25], musks [26], brominated flame retardants [27] and pyrethroids [28]. Therefore, SPME might offer a good option to extract UV filters from beach sand samples. SPME is an organic solvent free technique, providing a better environmental-friendly procedure than those previously reported. In addition, SPME usually achieves a high concentration factor, requires short extraction times, and it can be easily automated, providing high sample throughput [29].

In this study, we propose a methodology based on SPME–GC–MS/MS for the simultaneous analysis of eleven UV filters belonging to different chemical classes (benzophenone-derivatives, p-aminobenzoic acid derivatives, salicylates, cinnamates, and camphor derivatives) in beach sand. The analysis of sand samples collected in beaches from the Atlantic Ocean and the Mediterranean Sea confirms the widespread occurrence of these cosmetic ingredients in the environment.

2. Experimental

2.1. Chemicals, materials and samples

2-Ethylhexyl methoxycinnamate (2EHMC; 98.5%) was provided by Ehrenstorfer (Augsburg, Germany). 4-Methylbenzylidene camphor (4MBC; 99.8%) was obtained from Alfa Aesar (Karlsruhe, Germany). Benzyl salicylate (BS; >99%) and menthyl anthranilate (MA; 99.9%) were acquired from Fluka (Saint Louis, MO, USA). Octocrylene (OCR; 99.1%), ethylhexyl dimethyl PABA (EHPABA; 98%), ethylhexyl salicylate (EHS; >99%) and homosalate (HMS; 99.9%) were purchased from Sigma-Aldrich (Saint Louis, MO, USA). Isoamyl methoxycinnamate (IAMC; 96%), benzophenone-3 (BP3; 99.9%) and etocrylene (Eto; 99.7%) were supplied from TCI (Tokyo, Japan). Acetone and methanol were provided by Merck (Darmstadt, Germany) and Fluka Analytical (Steinheim, Germany), respectively. Commercial sea sand (200–300 μm grain size) was obtained from Scharlau (Barcelona, Spain); sodium chloride (NaCl) was acquired from Panreac (Barcelona, España). Milli-Q water was obtained in the laboratory with a purification system (Millipore). All solvents and reagents were of analytical grade.

Individual stock solutions of each compound were prepared in acetone or methanol in concentrations between 10 and 30 mg mL⁻¹. Mixtures in acetone were prepared to spike the sand samples (when required). Stock and working solutions were stored in a freezer at –18 °C protected from light.

Commercially available 65 μm polydimethylsiloxane-divinylbenzene (PDMS/DVB) and 85 μm polyacrylate (PA) fibres housed in manual SPME holders were purchased from Supelco (Bellefonte, PA, USA). The fibres were conditioned as recommended by the manufacturer, introducing them in the GC injection port

with carrier gas flow for 30 min at 250 °C (PDMS/DVB) and 280 °C (PA).

Sand samples were collected in the summer season (2017) from several beaches in the Atlantic Ocean coast: four samples from Galicia (NW Spain), three samples from the NW of Portugal, and one sample from Canary Islands (Spain). Other three samples were also taken from Mediterranean Sea beaches in Mallorca Island (Spain). The samples were collected about 1 m above the high tide level at 5 cm depth in 0.5 L amber glass bottles and stored at –18 °C until analysis. Three additional samples (Galicia, NW Spain) were taken in winter far from the seashore. These samples were supposed to be free of the target compounds, thereby offering an ideal material for performing the recovery study. The description of the samples (location and characteristics) is included in Table SM 1.

For method optimization and validation studies, the samples (0.5–2 g) were fortified with the target analytes. Spiking of samples was performed by the addition of acetone solutions containing the analytes (200 $\mu\text{L/g}$ sample) to achieve the desired concentration in the sample (0.01–50 ng g⁻¹). Then, the samples were kept at room temperature for at least 30 min, to allow solvent evaporation, before analysis. No differences were observed in the responses obtained for spiked samples analysed 30 min after the addition, and analysed several hours after the spike, in the same working day.

2.2. Solid-phase microextraction procedure

An aliquot of sand sample (0.5, 1 or 2 g, depending on the experiment) was placed in a 22 mL vial, and an accurate volume of Milli-Q water was added (1–10 mL). In some experiments, NaCl (20–40%) was also added. The vial was sealed with an aluminium cap furnished with PTFE-faced septa and immersed into a water bath maintained at 60 °C or 100 °C under magnetic stirring. After 5 min of sample equilibration, the corresponding SPME fibre, PDMS/DVB or PA, was immersed into the sample (direct immersion mode, SPME) or exposed to the headspace over the sample (headspace mode, HSPME) for 20–40 min. After extraction, the fibre was submerged in ultrapure water three times to extend its lifetime and to protect the chromatographic system. Finally, the fibre was retracted into the needle of the holder syringe, manually injected and immediately thermally desorbed at 260 °C in the GC injection port for 5 min, and GC–MS/MS analysis was carried out. To avoid carryover and memory effects, blank SPME procedure was periodically carried out. The optimal selected conditions were: 1 g of sand, 1 mL of Milli-Q water, PDMS/DVB fibre, headspace mode, 100 °C, and 20 min as extraction time.

2.3. GC–MS/MS analysis

GC–MS/MS analysis was performed using a Thermo Scientific Trace 1310 gas chromatograph coupled to a triple quadrupole mass spectrometer (TSQ 8000) and an IL 1310 autosampler from Thermo Scientific (San Jose, CA, USA). The GC–MS/MS parameters were previously optimized [3].

Separation was carried out on a 5% phenyl-arylene/95% dimethylpolysiloxane Zebron ZB–SemiVolatiles capillary column (30 m \times 0.25 mm i.d., 0.25 μm film thickness) supplied by Phenomenex (Torrance, CA, USA). Helium (purity 99.999%) was employed as carrier gas at a constant flow of 1.0 mL min⁻¹. The GC oven temperature was programmed from 100 °C (held 1 min) to 290 °C at 25 °C min⁻¹ (held 4 min). The injector temperature was 260 °C. The injector was operating in the splitless mode and programmed to return to the split mode after 1 min from the beginning of a run. The total run time was 13 min.

The mass spectrometer (MS) was operated in the electron impact (EI) ionization positive mode (+70 eV). The temperatures of the transfer line and the ion source were set at 290 and 350 °C,

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