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Development of an analytical methodology based on fabric phase sorptive extraction followed by gas chromatography-tandem mass spectrometry to determine UV filters in environmental and recreational waters

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ABSTRACT

A novel method based on fabric phase sorptive extraction (FPSE) followed by gas chromatography-tandem mass spectrometry (GC-MS/MS) has been validated for the simultaneous determination of 11 UV filters (ethylhexyl salicylate, benzyl salicylate, homosalate, benzophenone-3, iso-amylmethoxycinnamate, 4-methylbenzylidenecamphor, methyl anthranilate, etocrylene, 2-ethylhexylmethoxycinnamate, 2-ethylhexyl *p*-dimethylaminobenzoate, and octocrylene), in natural and recreational waters. Major experimental parameters affecting FPSE procedure have been optimized to obtain the highest extraction efficiency. Different types and sizes of sol-gel coated FPSE media, sample volume, extraction time, and type and volume of desorption solvent were evaluated. The optimal conditions involved the use of a (2.0 × 2.5) cm^2 FPSE device with PDMS based coating for the extraction of 20 mL of water for 20 min. The quantitative desorption of the target compounds was performed with 0.5 −1 mL of ethyl acetate. The method was satisfactorily validated in terms of linearity, precision, repeatability and reproducibility. Recovery studies were performed at different concentration levels in real water matrices to show its suitability, obtaining mean values about 90% and satisfactory precision. LODs were at the low ng L^{-1} in all cases. Finally, the validated FPSE-GC-MS/MS method was applied to different real samples, including environmental water (lake, river, seawater) and recreational water (swimming-pool), where 8 out of the 11 studied compounds were detected at concentrations between 0.12-123 μg L^{-1}. FPSE is proposed as an efficient and simple alternative to other extraction and microextraction techniques for the analysis of UV filters in waters. Since no matrix effects were observed, quantification could be carried out by conventional calibration with standard solutions, without the need to perform the complete FPSE procedure, thus allowing a higher throughput in comparison with other microextraction techniques.

1. Introduction

UV filters are a class of chemical compounds employed in cosmetic and personal care products, especially in sunscreen formulations, to protect consumers against the harmful UV radiation. They are considered as emerging pollutants (EPs) and can enter the aquatic environment both indirectly, by domestic and industrial discharges and wastewater treatment plant (WWTP) effluents, or directly from the personal care products employed during recreational aquatic activities, especially in summer [1,2].

Although UV filters are not included in European monitoring water policy programs, their occurrence has been reported in natural waters such as lakes, rivers, wastewaters, and in recreational waters such as swimming-pools or sea bathing areas [1–3]. Several toxicological studies suggest that some UV filters present high bioaccumulation in animal and human tissues, and in the

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environment. Some authors classify several of them as endocrine disruptors, which represents a potential risk for the human health and for the aquatic media [4–6].

The determination of UV filters in the aquatic environment requires the use of extraction techniques capable to concentrate the analytes, since they should be monitored at trace concentration levels in waters. Traditionally, liquid-liquid extraction (LLE), and solid-phase extraction (SPE) have been the most employed extraction techniques to determine organic pollutants in water. However, these extraction procedures, especially LLE, require large volume of organic solvents, with the consequent generation of high volume of waste, and both involve several steps which imply a long time to prepare the sample. New trends for extracting classical and emerging pollutants are focused on the development of microextraction procedures, allowing efficient extraction, and avoiding the drawbacks of the classical procedures. In this way, several microextraction techniques such as solid-phase microextraction (SPME), ultrasound-assisted emulsification microextraction (USAEME), dispersive-liquid liquid extraction (DLLE), or stir-bar sorptive extraction (SBSE), among others, have been proposed for the determination of UV filters in water [7–14]. In SBSE, the amount and surface of extraction phase is much higher than in SPME (~50–250 times) and consequently, a higher extraction sensitivity would be expected. However, this technique does not offer anticipated advantages over SPME [15], mainly due to the slow mass transfer. Considering the need of both higher sorbent loading as well as larger surface area to increase sensitivity without prolonging extraction time, thin-film microextraction (TFME) was introduced by Prof. Pawliszyn [16]. This new format of SPME has demonstrated higher extraction sensitivity compared to SBSE [17]. TFME provides higher enrichment factor and matrix compatibility in comparison with other equilibrium approaches.

Few years ago, in 2014, Kabir and Furton developed the fabric phase sorptive extraction (FPSE), that can be considered as a variety of TFME, which combines the extraction mode of SPME (equilibrium extraction) and SPE (exhaustive extraction) into a single technology platform [18]. FPSE employs natural or synthetic fabric substrates, chemically coated with an ultra-thin coating with sol-gel organic-inorganic hybrid sorbent as the extraction media. Among the current available sorbent based sorptive microextraction techniques, FPSE is the only one that uses a permeable substrate to accelerate the extraction equilibrium, reducing the extraction time [19]. One of the main advantages of FPSE is its high primary contact surface area (PCSA), which allows efficient and fast extraction of the analytes from the sample, as well as quantitative fast desorption. The flexibility of the FPSE device allows also its direct insertion into the original samples from different backgrounds without previous modification. The amount of solvent required for quantitative desorption is low, which enables a high pre-concentration factor required for environmental analysis [19,20]. In addition, both TFME and FPSE are resistant to particulate clogging and contamination due to their open bed nature.

FPSE has been successfully employed for the determination of heavy metals, alkylphenols, brominated flame retardants, pesticides, plasticizers, pharmaceuticals, and preservatives or UV-stabilizers (benzotriazoles) in water samples [20–22]. However, to the best of our knowledge, it has not been applied for the determination of non-polar UV filters usually employed in cosmetic formulations and personal care products, excluding benzophenone-3. FPSE has been typically employed prior to liquid chromatography coupled to ultraviolet (LC-UV) detection, or tandem mass spectrometry (LC-MS/MS) [20]. However, gas chromatography-tandem mass spectrometry (GC-MS/MS) is a very suitable option after FPSE extraction, for the determination of non-polar or low polar compounds, such as most of the UV filters found in the aquatic environment. Besides, the use of MS/MS provides the required analytical selectivity and sensitivity for environmental analysis.

The main goal of this work is the development of a highly sensitive analytical methodology based on FPSE-GC-MS/MS to simultaneously determine 11 non-polar UV filters in different natural and recreational water samples. After the optimization of the most critical experimental parameters affecting extraction, the method was validated and applied to different environmental and recreational waters demonstrating its suitability.

2. Materials and methods

2.1. Chemicals and reagents

The studied UV filters, their CAS numbers, purity, suppliers, and partition octanol/water coefficients (log K_{OW}) are summarized in Table S1. Acetone, ethyl acetate, methanol and acetonitrile were supplied by Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Ultrapure water MS grade was purchased from Scharlab (Barcelona, Spain). Sodium thiosulphate ($Na_2S_2O_3$) was provided by Panreac (Barcelona, Spain). The FPSE devices coated with sol-gel polydimethylsiloxane (sol-gel PDMS), sol-gel poly (caprolactone-dimethylsiloxane-caprolactone) block copolymer (sol-gel PCAP-PDMS-PCAP), and sol-gel Carbowax 20 M (sol-gel CW 20 M) have been kindly supplied by Prof. Kabir. The preparation of the sol-gel FPSE media is described in Section 2.3.

Individual stock solutions of each UV filter were prepared in methanol following supplier recommendations. Further dilutions and mixtures were prepared in acetone, to perform sample fortification studies, and ethyl acetate, to accomplish method calibration since this solvent was the one employed for FPSE device desorption. 2,4,6-trichlorobiphenyl (PCB-30), supplied by Dr. Ehrenstorfer (Augsburg, Germany) was employed as internal standard. All solutions were stored in amber glass vials and protected from light at ¬20 °C. All solvents and reagents were of analytical grade.

2.2. Sampling and sample treatment

Different types of environmental water samples (lake, river and seawater), and recreational water samples (swimming-pool) were collected (summer 2018). Five hundred mL were placed in a glass bottle and immediately 0.5 mL of methanol were added to prevent the adsorption of the compounds on the collecting bottle glass. For the swimming-pool water samples, 50 mg of $Na_2S_2O_3$ were added to neutralize chlorine and other chlorinating agents present in the samples, and to avoid the reaction with the target studied compounds. The samples were stored at 4 °C and protected from light until analysis.

2.3. Preparation of sol-gel sorbent coated fabric phase sorptive extraction membrane

Preparation of sol-gel sorbent coated FPSE membrane involves several distinct steps: (a) selection of a suitable fabric substrate; (b) cleaning and surface treatment of the fabric substrate to maximize its sorbent loading capacity; (c) designing the sol solution in order to maximize the selectivity towards the target analytes present in different complex sample matrices including environmental water, food, biofluids; (d) optimization of sol-gel sorbent coating process to ensure appreciable sorbent loading; and (e) conditioning, aging and cleaning of sol-gel sorbent coated FPSE membrane. Commercial Muslin cotton fabric (100% cellulose) was selected as the substrate for sol-gel sorbent coating. Prior to the sol-gel sorbent

coating, the fabric substrate needs a thorough cleaning to remove residual finishing chemicals and other unwanted dust and particles accumulated on its surface during its self-life. In addition, chemical treatment of the fabric is needed to maximize the accessible hydroxyl functional groups that anchor the growing sol-gel sorbent network during the sol-gel sorbent coating process. The detailed fabric cleaning and surface treatment process is described elsewhere [19,23]. Briefly, a 150 cm^2 (15 cm × 10 cm) piece of Muslin cotton fabric was soaked and cleaned with water and subsequently treated with 1.0 M NaOH solution for 1 h at room temperature. The fabric was then washed with water several times and treated with 0.1 M HCl for 1 h. The cleaned and chemically treated fabric was then dried in an inert atmosphere for 12 h and subsequently stored in an airtight container until used for sol-gel sorbent coating.

Sol solution design primarily involves selection of a polymer (organic or inorganic), a sol-gel precursor, a solvent system, a catalyst and water. Since the organic/inorganic polymer plays the most significant role in the sorbent selectivity, selection of an appropriate polymer is the key to a successful sorbent design. Considering the broad polarity range of the selected UV filters (log K_{ow} values range from 3.6 to 7.8), three sol-gel sorbents were designed which include sol-gel PDMS (nonpolar), sol-gel PCAP-PDMS-PCAP (medium polar) and sol-gel CW 20 M (polar). All sol solutions were prepared using methyl trimethoxysilane (MTMS) as the sol-gel precursor, trifluoroacetic acid (TFA) as the sol-gel acid catalyst, a mixture of acetone and methylene chloride (50:50, v/v) as the solvent system, and deionized water as the hydrolytic agent. The molar ratio between sol-gel precursor, organic/inorganic polymer, acetone, methylene chloride, TFA and water were optimized and maintained at 1:0.004:1.94:2.3:0.75:3 for sol-gel PDMS, 1:0.07:1.94:2.3:0.75:3 for sol-gel PCAP-PDMS-PCAP, and 1:0.0071:1.94:2.3:0.75:3 for sol-gel CW 20 M.

The preparation of sol solution and sol-gel coating process have been described in detail elsewhere [18,19,23]. Sol-gel sorbent coating was carried out for 4 h. Subsequent to the sol-gel coating, the coated fabric was air dried for 1 h and kept in a desiccator for 12 h to dry the solvent and aging the sol-gel sorbent network. Finally, the sol-gel sorbent-coated FPSE membrane was rinsed with methylene chloride: acetone (50:50, v/v) mixture under sonication for 30 min. The cleaned FPSE membrane was air dried for 1 h and stored in an airtight container until its application in analyte extraction.

2.4. Fabric phase sorptive extraction procedure

First, the sol-gel sorbent coated FPSE media was conditioned for its use by immersing into 2 mL of a mixture of methanol/acetonitrile (50:50, v/v) for 5 min to remove any undesirable impurities from the material. Afterwards, it was rinsed by immersing in 2 mL of ultrapure water for 3 min, eliminating the residues of organic solvents and then, it was immersed in a 22 mL glass vial containing the water sample and a metallic nail. The vial was sealed, and the sample was magnetically stirred. The FPSE device remained submerged and turning at the top of the vial during the selected extraction time. In this step, the sorption of the target analytes by the sorbent takes place. Afterwards, the FPSE device was removed from the vial and left to dry at room temperature on a watch glass and then, it was brought in contact with ethyl acetate to accomplish solvent desorption. Desorption was performed for 3 min using a vortex stirrer (Velp Scientifica, Italy). Finally, the organic extract was directly injected in the chromatographic system, and GC-MS/MS analysis was carried out. The FPSE procedure is graphically summarized in Fig. S1. In addition, a real picture showing the film position in the vial has been included.

After the optimization of the experimental parameters (see Section 3.3), the final FPSE conditions implied the use of a 5 cm^2 (2.0 × 2.5 cm) FPSE device with PDMS based sol-gel coating to extract 20 mL of water for 20 min. Desorption of the analytes is achieved with 0.5 mL or 1 mL of ethyl acetate. In all cases, the solvent contained 5 μg L^{-1} of PCB-30 (internal standard). Procedure blanks were systematically performed, by applying the optimized FPSE procedure to 20 mL of ultrapure water, to evaluate the presence of contamination and memory effect for the target compounds.

The FPSE media can be reused for further extractions after reconditioning and drying at room temperature, as it was previously described (first paragraph in this section).

2.5. GC-MS/MS analysis

The GC-MS/MS analysis was carried out employing a Thermo Scientific Trace 1310 gas chromatograph coupled to a triple quadrupole mass spectrometer (TSQ 8000) with an autosampler IL 1310 from Thermo Scientific (San Jose, CA, USA). Separation was performed on a Zebron ZB-Semivolatiles (30 m × 0.25 mm i.d. × 0.25 μm film thickness) obtained from 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), and to 290 °C at 25 °C min^{-1} (held 6 min). The total run was 15 min. Injection volume was 1 μL, injector temperature was set at 260 °C and pulsed splitless mode (200 kPa, held 1.2 min) was employed for injection.

The mass spectrometer detector (MSD) 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 °C, and 350 °C, respectively. The filament was set at 25 μA and the multiplier voltage was 1460 V. Selected Reaction Monitoring (SRM) acquisition mode was implemented monitoring 2 or 3 transitions per compound (see Table S2) for an unequivocal identification of the target UV filters. The system was operated by Xcalibur 2.2, and Trace Finder™ 3.2 software.

The instrumental GC-MS/MS conditions were optimized for a satisfactory separation and identification of the 11 studied UV filters. These conditions were adapted from previous studies [10].

3. Results and discussion

3.1. Mechanism of extraction and working principle of FPSE

As a new generation sample preparation technique, FPSE presents the most comprehensive improvements in the current state-of-the-art of sample preparation technologies. The areas of improvement delivered by FPSE include: (a) highly reproducible sorbent coating process using sol-gel coating technology with tunable selectivity parameter; (b) exploitation of an active substrate with distinct role in the selectivity and extraction efficiency; (c) flexibility in extraction mode; (d) integration of the extraction mechanism of two major but opposing sample preparation technologies, solid phase extraction (SPE) and solid phase microextraction (SPME); and (e) development of new sorbent phases for FPSE which are exclusively used either in SPE (e.g., C8, C18) or SPME (e.g., PDMS, PEG).

Unlike commercial solid sorbent-based extraction and microextraction techniques that utilize pristine polymers such as PDMS/PEG or ligands such as C8/C18, physically immobilized on an inert substrate, FPSE has adopted sol-gel coating technology as a chemical coating process that not only provides highly reproducible and chemically bonded sponge-like porous sorbent in the form of ultrathin coating, but also allows fine tuning the sorbent selectivity by employing one or more suitable sol-gel precursor(s). In the current

study, MTMS is used as the sol-gel precursor, which by its methyl pendant group compliments to the overall selectivity of the FPSE membrane and exerts London dispersion type intermolecular interaction towards the analytes. It is important to note that the selectivity and extraction efficiency of pristine polymer e.g., PDMS and sol-gel PDMS are not the same. Pristine PDMS used in SPME, SBSE and TFME is a highly viscous, liquid like polymer [24] that extracts analytes via absorption. As the analyte enter the coating, it continues migrating deeper into the core until it reaches the core. Due to the high viscosity of the sorbent, analyte migration is a slow process that results in prolonged extraction equilibrium time. As such, significantly higher PDMS loading in SBSE has not improved the extraction efficiency of SBSE over SPME significantly. The chemical integration of PDMS into the silica network using sol-gel synthesis results in a new material with substantially improved material properties including thermal, chemical and solvent stability and sponge-like porous architecture. S. Lakade et al. [25] compared the extraction efficiency of different sol-gel FPSE sorbent coatings with two commercially available SBSE phases and demonstrated the performance superiority of FPSE over SBSE. In addition, the use of chemical coating process in FPSE ensures remarkably improved coating reproducibility, resulting in superior batch-to-batch reproducibility.

Contrary to the conventional sample preparation techniques, FPSE is the only sample preparation technique that utilizes an active substrate (cellulose, polyester, fiberglass) with its hydrophilic or hydrophobic surface property. The substrate chemically binds to the growing sol-gel network via surface hydroxyl functional groups during sol-gel synthesis. The substrate, by its hydrophilic or hydrophobic surface property, exerts affinity towards the aqueous samples or the analytes to bring them closer to the sorbent so that the sorbent can interacts with the analyte via plethora of intermolecular interactions implanted into the sorbent including London dispersion, hydrogen bonding, dipole-dipole interactions.

3.2. Characterization of sol-gel PDMS coated FPSE membrane

During the FPSE method development experiments, sol-gel PDMS coated FPSE membrane was identified as the most efficient sorbent for the selected UV filters among all three sorbent coatings tested which include sol-gel PDMS, sol-gel PCAP-PDMS-PCAP and sol-gel CW 20 M. All sorbent coatings were created on 100% cotton cellulose substrate. Subsequently, sol-gel PDMS coated FPSE membrane was characterized using (a) Fourier-Transform Infrared Spectroscopy (FT-IR); (b) Scanning electron microscopy (SEM); and (c) assessment of sorbent loading and sol-gel coating reproducibility by gravimetric analysis.

3.2.1. Fourier-transform infrared spectrocopy (FT-IR)

Fig. S2 presents the FT-IR spectra of the sol-gel precursor, MTMS (a), inorganic polymer, polydimethyl siloxane (b) and sol-gel PDMS coated FPSE membrane (c) [19,23,26,27]. FT-IR spectra for MTMS demonstrats Si—OCH_3 bond at 2840 cm^{-1}, 1190 cm^{-1} and 1077 cm^{-1}; Si—CH_3 bond at 1267 cm^{-1} and 837 cm^{-1}. FT-IR spectra of PDMS demonstrates the presence of Si—O—Si bonds at 1011 cm^{-1}, Si—CH_3 bonds at 1258 cm^{-1} and 864 cm^{-1}, and asymmetric CH_3 strething in Si—CH_3 at 2961 cm^{-1}. FT-IR spectra representing sol-gel PDMS sorbent coated FPSE membrane reveals characteristics peaks at 3333 cm^{-1}, 2903 cm^{-1}, 1315 cm^{-1}, and 1012 cm^{-1} which correspond to O—H, C—H, and C—O stretching and C—H bending vibration, respectively. Several bands simultaneously appear in sol-gel PDMS coated FPSE membrane, PDMS and/or MTMS spectra (e.g., asymmetric CH_3 stretching in Si—CH_3 at ~2963 cm^{-1}, CH3 deformation in Si—CH_3 at ~1250 cm^{-1}, ~864 cm^{-1}) which are indicative of the successful integration of MTMS precursor and PDMS polymer into the sol-gel PDMS network. Substantial decrease in OH absortion band at 3333 cm^{-1} in sol-gel PDMS coated FPSE membrane compared to uncoated cellulose fabric (Fig. S2) may be attributed to the chemical inclusion of sol-gel PDMS network to the cellulose substrate via condensation during the sol-gel reaction.

3.2.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) images presented in Fig. S3 sheds light on the surface morphology of uncoated cellulose fabric and the sol-gel PDMS coated FPSE membrane. The SEM images reveal that uncoated cellulose fabric is constructed with bundles of microfibrils woven in such a way that it possesses well structured macropores. The macropores remain intact even after the sol-gel PDMS coating. These throughpores of FPSE membrane allow flowing the sample matrix freely without requiring any positive or negative pressure (as in the case of solid phase extraction bed) during the analyte extraction process and bring the analyte close to the extraction sorbent for rapid sorbent-analyte interactions, resulting in faster extraction kinetic and near exhaustive extraction. These throughpores mimics solid phase extraction (SPE) bed with its flow-through extraction mechanism which are absent in convention microextraction techniques including SPME, SBSE and TFME. As such, FPSE integrates both the SPME (equilibrium driven extraction, direct immersion SPME mode) and SPE (flow through extraction mode, exhaustive extraction).

SEM was also carried out to assesss the thickness of sol-gel PDMS sorbent coating. The SEM images are presented in Fig. S4. The average thickness of uncoated cellulose fabric was measured as 312 μm (Fig. S4a) and the average thickness of sol-gel PDMS coated FPSE membrane was measured as 220 μm (Fig. S4b). The cellulose micro fibrils are loosely oriented in uncoated cellulose fabric. However, the sol-gel PDMS sorbent coating behaves like a spongy and porous glue and orients the cellulose micro fibrils in a more condensed and organized state, resulting in substantially reduced average thickness. The SEM image also reveals homogeneous and thin PDMS sorbent coating around the cellulose micro fibrils. It should be noted that the spongelike porous architecture of sol-gel sorbent allows rapid permeation of the sample matrix containing the target analytes and results in shorter extraction equilibrium time. Due to the same porous archtecture, organic solvent permeates rapidly through the sol-gel sorbent and exhaustively excavenges the extracted analytes in few min. As a result, FPSE does not require solvent evaporation and sample reconstitution which are integral processes in SPE.

3.2.3. Sorbent loading and coating reproducibility evaluation via gravimetric analysis

Batch-to-batch coating reproducibility is one of the major challenges in sorbent based sorptive extraction and microextraction techniques including SPE, SPME or SBSE. The poor batch-to-batch reproducibility of these sample preparation techniques primarily stems from the sorbent coating processes. In order to mitigate this burgeoning issue, FPSE uses sol-gel coating process which is a highly controllable chemical coating process. Due to the superior control of sol-gel process over conventional physical sorbent coating process, FPSE ensures higher coating reproducibility and identical sorbent loading. In order to asses the sorbent loading and coating reproducibility, 5 individual batches of sol-gel PDMS coated FPSE membrane were prepared (15 cm × 10 cm). The sorbent loading was calculated via gravimetric method by substracting the mass of sol-gel PDMS coated FPSE membrane from the mass of uncoated fabric. The sol-gel PDMS sorbent loading was 4.56 mg cm^{-2} with coefficient of variance 2.5%.

3.3. Optimization of the FPSE procedure

Several experimental FPSE parameters were maintained constant, such as the extraction temperature, agitation, elution time and solvent. The temperature was set at 25 °C to avoid loss of the analytes during the FPSE procedure. Agitation under magnetic stirring was employed during the extraction procedure since an increase in the kinetic favors the equilibrium in a shorter time, and the elution time was fixed at 3 min. As elution solvent, ethyl acetate was selected for its low polarity, since the target UV filters present a non-polar character, and for its compatibility with the chromatographic (GC) system [28].

To obtain the highest extraction efficiency, several experimental parameters that might affect the extraction and solvent desorption have been evaluated. In this way, the sol-gel coating, the FPSE device size, the sample volume, the extraction time, and the elution volume were studied. Table 1 summarizes the different parameters studied.

3.3.1. Effect of the sol-gel coating

The interaction between the target analytes and the sol-gel coating is one of the most critical parameters to obtain an effective extraction. Three sol-gel coatings of different polarities were evaluated for the extraction of the target UV filters from the water samples: sol-gel polydimethylsiloxane (sol-gel PDMS), sol-gel poly (caprolactone-dimethylsiloxane-caprolactone) block copolymer (sol-gel PCAP-PDMS-PCAP), and sol-gel Carbowax 20 M (sol-gel CW 20 M). Experiments were performed employing a (2.0 × 2.5) cm^2 FPSE device to extract 10 mL of spiked ultrapure water (0.2 μg L^{-1}). Extraction time was 20 min, and the solvent volume was 0.5 mL (see detailed procedure in the Section 2.4). As can be seen in Fig. 1, the highest chromatographic responses were obtained employing sol-gel PDMS as coating for the 11 UV filters studied, whereas sol-gel PCAP-PDMS-PCAP offered the lowest responses for all the compounds, being some of them (HMS and 4MBC) hardly extracted with this coating. These results are in concordance with those reported in the literature, in which PDMS is the most useful coating for the extraction of non-polar UV filters from aqueous samples by other microextraction techniques such as SBSE, probably due to its highly lipophilic nature [7]. Therefore, further experiments were performed employing sol-gel PDMS coating.

3.3.2. Effect of the FPSE device size

One of the major drawbacks of most of the microextraction tecnhiques is the primary contact surface area (PCSA). The PCSA is the part of the surface area of the extraction media, which can be available for direct interaction with the analytes during the extraction procedure, and it can affects the kinetics and thermodinamics of the extraction procedure [19]. In this case, if the amount of extraction phase is low, as well as the PCSA, the extraction could be not efficient. On the other hand, if the amount of extraction phase and the contact area are higher, the extraction should be more efficient.

Two different sizes were evaluated for the FPSE device (sol-gel PDMS coating): 1 cm^2 (1.0 × 1.0 cm), and 5 cm^2 (2.0 × 2.5 cm). Larger sizes were not evaluated because they were not operationally feasible considering the sample volume and vial size. Under these conditions, and as previously indicated, the amount of phase and the contact surface area increase by a factor of 5 whereas the surface area-to-extraction phase volume ratio is kept constant. In both cases, 20 mL of ultrapure water spiked at 0.5 μg L^{-1} were employed, and the extraction time was 20 min. Desorption was performed with 0.5 mL of ethyl acetate. Fig. 2a represents the chromatographic response obtained for the studied compounds. As can be seen, the use of the larger size offered more efficient extraction for all the analytes, being the responses between 2-3 times higher compared with the 1 cm^2 (1.0 × 1.0 cm) FPSE media. In fact, exhaustive extractions employing (2.0 × 2.5) cm^2 are achieved (see Section 3.4), whereas with the smallest FPSE device size, extractions were not quantitative.

Table 1
Experimental parameters optimized for the FPSE procedure.

Experimental parameters	Levels
Sol-gel coating	PDMS, PCAP-DMS-CAP, CW-20
FPSE device (size/cm^2)	(1.0 × 1.0), (2.0 × 2.5)
Sample volume (mL)	5, 10, 20, 50, 100
Extraction time (min)	10, 20, 40
Desorption volume (mL)	0.5, 1

3.3.3. Effect of the sample volume

Considering the thermodynamic process, the amount of analytes extracted in any microextraction system and, therefore, the extraction efficiency, is expected to increase with the increase of the sample volume, until the sample volume becomes significantly larger than the product of the distribution constant and volume of the coating. At this point, larger volumes of sample do not improve the extraction efficiency [29]. In non-equilibrium systems the volume will also affects the kinetic of the process [19].

Several water sample volumes were tested: 5, 10, 20, 50, and 100 mL. Experiments were performed in all cases employing a 5 cm^2 (2.0 × 2.5 cm) sol-gel PDMS coated FPSE media (spiked water 0.5 μg L^{-1}). The extraction time was 20 min. Chromatographic responses for the different studied water sample volumes are represented in Fig. 2b.

For most compounds, the responses increased with the volume up to 20 mL. Higher volumes resulted in a decrease on the chromatographic response. It might be attributed to kinetic reasons suggesting a slower transfer of analytes between the phases for larger sample volumes. Larger volumes also imply a change in the vial size, the headspace volume and the agitation conditions. All these modifications may affect the kinetic of the extraction procedure. Therefore, 20 mL of water was the selected volume to perform extraction.

3.3.4. Effect of the extraction time

In a microextraction procedure, it is important to evaluate the time required to reach the equilibrium when extracting the analytes from the water samples. However, it is also important to take into account the productivity and the throughput; therefore, the time should be the lowest as possible, but without compromising the extraction efficiency. Considering the chromatographic run time (see experimental section), an extraction time of 20 min was initially selected. Besides, a shorter and a longer time, 10 min and 40 min, were included in the FPSE optimization. Results are shown in Fig. 3a, and as can be observed, 10 min offered the lowest responses for some compounds. For other UV filters (IAMC, 4MBC, MA and 2EHMC), the results obtained at the three evaluated times were equivalent. On the other hand, no significant difference was observed between 20 and 40 min, indicating that the extraction procedure is fast, and after 20 min exhaustive extraction was achieved employing 20 mL of sample (see Section 3.4). Therefore, since the objective is to obtain an efficient and high throughput methodology, 20 min was selected as the optimum extraction time.

3.3.5. Effect of the solvent desorption volume

Since the UV filters included in this work are non-polar, a low polar solvent such as ethyl acetate was selected as desorption solvent. This solvent has demonstrated good performance for the

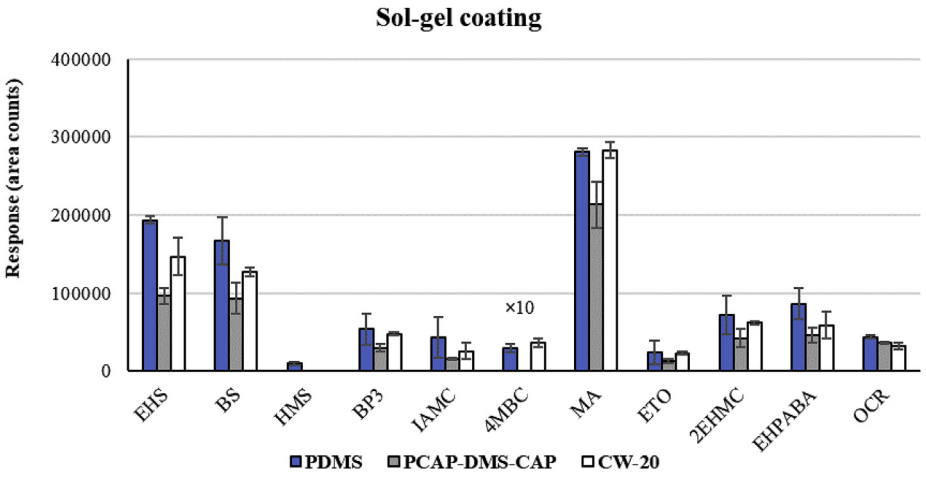

Fig. 1. Chromatographic response for the target compounds with the different sol-gel coatings tested.

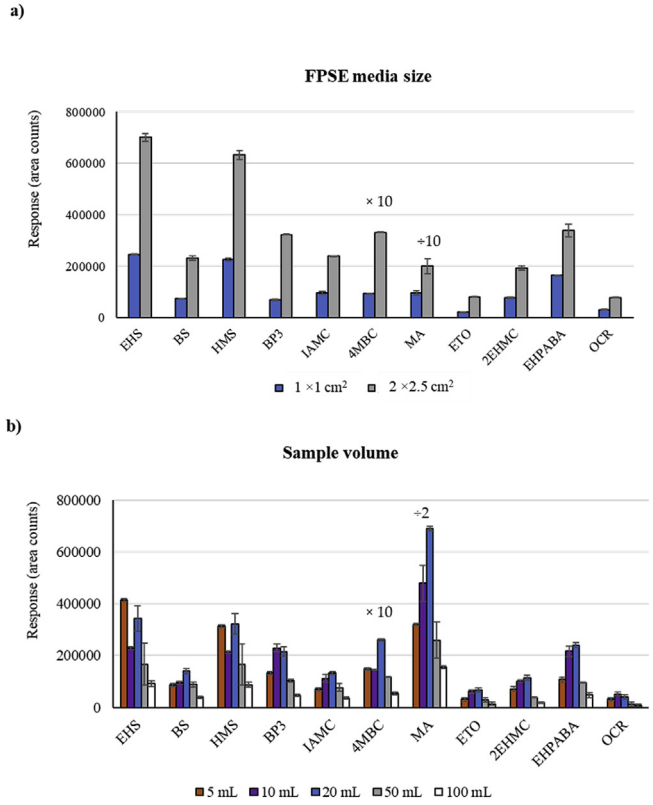

Fig. 2. Chromatographic response of the target compounds for **a)** the different FPSE media sizes evaluated and **b)** the different sample volumes evaluated.

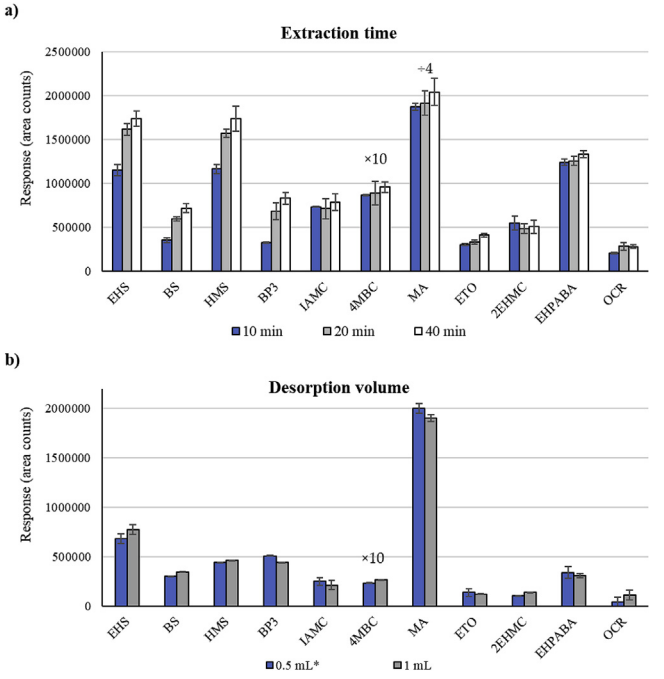

Fig. 3. Chromatographic response of the target compounds for **a)** the extraction time tested and **b)** the desorption volumes evaluated. *Response multiplied by 0.5 for a better visualization.

extraction of UV filters in other kind of matrices such as cosmetics, as well as satisfactory chromatographic analysis [28]. Two different desorption volumes were evaluated: 0.5 mL and 1 mL. The experimental conditions involved the use of a 5 cm^2 (2.0 × 2.5 cm) sol-gel PDMS FPSE device, 20 mL of water sample (spiked at 0.2 μg L^{-1}), and a extraction time of 20 min.

The obtained results expressed as chromatographic responses are shown in Fig. 3b. In all cases, responses for 0.5 mL were double than those obtained for 1.0 mL. However, for a better visualization, responses for 0.5 mL were multiplied by 0.5 in Fig. 3b. Therefore, the use of the low volume, 0.5 mL, allows obtaining an enrichment factor of up to 40 (20 mL of sample, 0.5 mL of extract) in case of quantitative extraction. However, to avoid the use of glass inserts for GC injection, 1 mL of solvent was selected, although 0.5 mL can be used to increase sensitive when necessary.

3.3.6. *Stability of the FPSE device*

The stability of the target compounds sorbed in the FPSE device was also evaluated. With this purpose, the FPSE procedure was carried out under the optimal conditions, and the chromatographic responses were compared with the obtained performing the elution of the analytes after 24 h. Results revealed that the studied UV filters remain sorbed on the FPSE device 24 h after extraction from the water sample (see Fig. S5). This offers a great advantage since having stability of the compounds in the FPSE media allows in-situ extraction, which is a convenient option for environmental

analysis, permitting subsequent desorption in the laboratory up to 24 h after the extraction.

3.4. FPSE-GC-MS/MS performance

After method optimization, the selected experimental FPSE conditions for the analysis of the 11 studied UV filters involve the use of a 5 cm^2 (2.0 × 2.5 cm) FPSE device coated with PDMS for the extraction of 20 mL of water for 20 min. Desorption was performed with 1 mL of ethyl acetate, although it can also be succesfully carried out with 0.5 mL solvent.

The FPSE-GC-MS/MS method was validated in terms of linearity, accuracy, repeatability, reproducibility, and limits of detection (LODs) were calculated. Method performance parameters are summarized in Table 2. Calibration standards were prepared in ethyl acetate covering a concentration range between 0.2 and 200 μg L^{-1} with ten levels (0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, 200 μg L^{-1}). Each level was injected at least three times. The method exhibited a direct proportional relationship between the concentration of each UV filter and the chromatographic response, obtaining determination coefficients (R^2) higher than 0.9913 in all cases. Instrumental method precision was evaluated within a day (n = 3), and among days (n = 6) at different levels. Relative standard deviation (RSD) values for 10 μg L^{-1} are shown in Table 2 showing mean values about 7%.

Limits of detection (LODs) were calculated as the compound concentration giving a signal-to-noise ratio of three (S/N = 3), employing for that spiked water samples at low concentration levels, once FPSE-GC-MS/MS was carried out. For the compounds detected in the procedure blanks (EHS and OCR), LODs were calculated as the concentration corresponding to the signal of the blanks plus three times its standard deviation. LOD values are shown in Table 2 and as can be seen, they were at the low ng L^{-1} level.

To show the suitability of the proposed methodology for the extraction and analysis of different water matrices, recovery studies were carried out employing ultrapure water, two different environmental waters, river water and seawater, and a recreational water (swimming-pool). In all cases, recovery studies were performed at two different concentration levels: 0.5 and 5 μg L^{-1}. For quantitative purposes, the concentration in the samples was calculated using the calibration curves in ethyl acetate (see Table 2) and considering the enrichment factor that would be obtained in case of complete extraction. This theoretical enrichment factor is defined as the ratio of the analyte concentration in the extract to the concentration in the sample, and it is equivalent to the ratio of the sample volume to the solvent volume. In some cases, some of the analytes were initially found in the non-spiked real samples and, in those cases, initial concentrations were taken into account to calculate the recoveries. Recovery studies were performed by triplicate employing in each case different FPSE devices. Results for ultrapure water and mean values for the real samples are summarized in Table 2, and individual recovery values for ultrapure, river, sea, and swimming-pool water are shown in Fig. 4. In all cases, good accuracy was obtained, with recovery values between 75-115%, excluding 4MBC in the river, and 2EHMC for the swimming-pool water at the low spiked concentration level. The RSD values for the FPSE membrane reproducibility were in general lower than 12%. Matrix effects were not observed. The recoveries can be considered quantitative, and the extraction procedure exhaustive, avoiding the need to perform the complete FPSE procedure for quantification purposes. This supposes a great advantage, allowing a high analytical throughput with a simplified methodology.

Table 3 shows a comparison between the proposed methodology and other analytical methodologies based on microextraction techniques for the determination of UV filters in waters. As can be seen, the extraction time required for FPSE is quite lower than those reported in the literature. Besides, LODs values are similar, or even lower than those reported for the determination of UV filters in waters employing microextraction techniques such as SPME, SBSE or BAμE (bar-adsorptive microextraction) [8,30–33]. In addition, most of these methods are not exhaustive requiring to perform the whole process (extraction and analysis) to obtain the calibration curve, and including some of them further steps, such as evaporation and reconstitution of the extract. The proposed method provides quantitative extraction for all the target analytes, therefore calibration can be easily performed using solvent standards prepared in ethyl acetate.

3.5. Application to real samples

Once the FPSE-GC-MS/MS method was validated, it was applied to the analysis of real water including environmental waters, lake, river and seawater, and recreational water from swimming-pools. Results are shown in Table 4.

The quantification of the real samples was performed by external calibration employing standard solutions of the studied

Table 2
Method performance. Coefficient of determination (R^2), linear range, precision, recoveries, and limits of detection (LODs).

UV filter	R^2	Linear range (μg L^{-1})	Precision, RSD (%)		Recoveries, %				LODs (ng L^{-1})
			Intra-day[a]	Inter-Day[b]	Ultrapure water		Real samples (mean values)		
					0.5 μg L^{-1}	5 μg L^{-1}	0.5 μg L^{-1}	5 μg L^{-1}	
EHS	0.9988	0.2–200	5.1	7.6	109 ± 5	100 ± 2	73 ± 10	106 ± 5	0.68
BS	0.9974	0.55–200	9.5	8.1	97 ± 4	98 ± 5	98 ± 3	98 ± 4	1.6
HMS	0.9979	2–200	0.40	10	113 ± 4	105 ± 5	96 ± 1	101 ± 3	2.2
BP3	0.9913	2–200	9.2	12	98 ± 13	110 ± 7	94 ± 8	88 ± 15	4.5
IAMC	0.9979	0.5–200	8.0	12	79 ± 10	99 ± 8	78 ± 12	77 ± 6	1.5
4MBC	0.9982	2–200	1.5	15	108 ± 16	93 ± 5	85 ± 20	108 ± 8	2.0
MA	0.9994	0.5–200	2.4	1.8	99 ± 7	110 ± 3	77 ± 2	98 ± 2	2.1
ETO	0.9998	0.2–200	5.8	14	76 ± 5	105 ± 7	77 ± 2	86 ± 11	0.020
2EHMC	0.9974	1–200	1.0	5.1	85 ± 9	75 ± 5	82 ± 23	68 ± 6	0.013
EHPABA	0.9986	0.5–200	9.7	12	101 ± 5	100 ± 6	81 ± 5	107 ± 2	0.12
OCR	0.9987	0.5–200	4.0	1.7	119 ± 19	110 ± 4	105 ± 9	86 ± 6	3.3

[a] n = 3.
[b] n = 6.

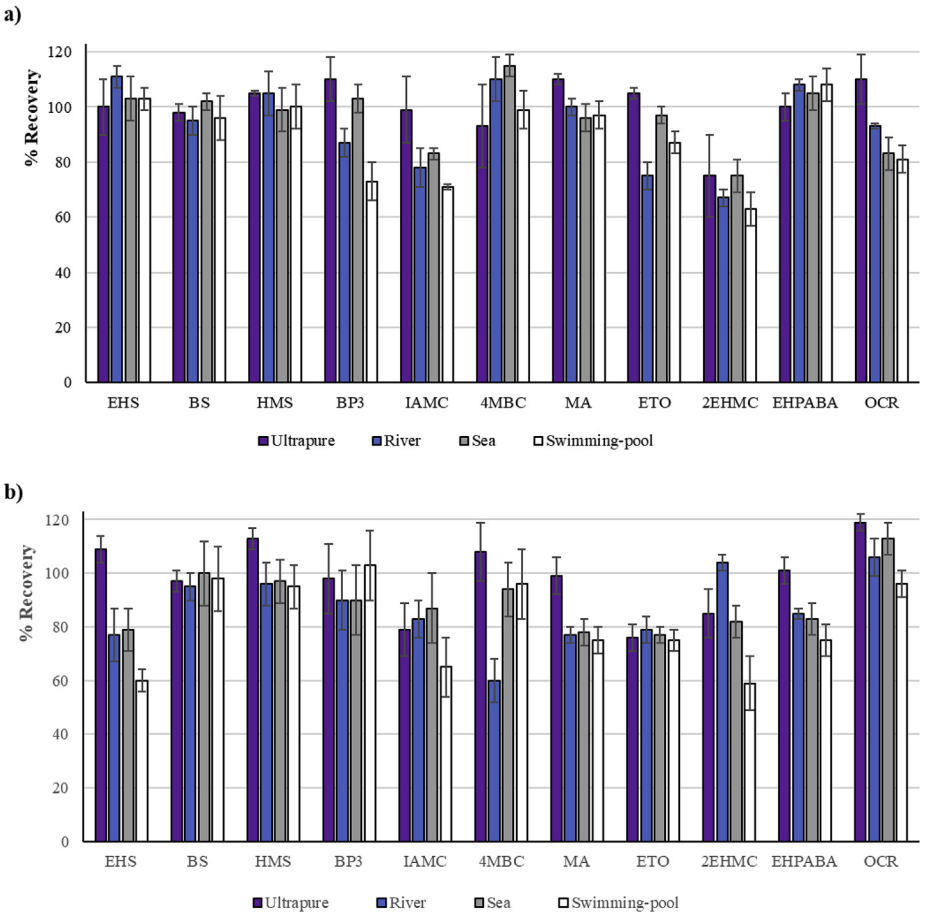

Fig. 4. Recoveries (%) obtained for ultrapure, river, sea and swimming-pool waters at a spiked level of **a)** 5 μg L^{-1} and **b)** 0.5 μg L^{-1} for the 11 UV filters.

Table 3
Comparison of the proposed FPSE-GC-MS/MS method with other reported methods based on microextraction for the analysis of UV filters in water.

UV filters	Extraction technique	Sample volume (mL)	Extraction time (min)	Analysis	LODs (ng L^{-1})	Ref.
EHS, BS, HMS, IAMC, BP3, 4MBC, MA, ETO, EHPABA, 2EHMC, OCR, BMDM, DRT, DHHB	(HS)-SPME	10	20	GC-MS/MS	0.07–12	[8]
BP3, EHPABA, 2EHMC, EHS, HMS, IAMC, 4MBC, OCR	DLLE	5		GC-MS	10–30	[30]
BP3, EHPABA, 2EHMC, EHS	(DI)-SPME	15	45	LC-UV	30–64	[31]
BP3, BP10, EHPABA, 2EHMC, EHS, HMS, 4MBC	SBSE	100	300	GC-MS	0.01–12	[32]
BP1, BP3	BAμE	25	240	LC-UV	300–500	[33]
EHS, BS, HMS, IAMC, 4MBC, MA, ETO, EHPABA, 2EHMC, OCR	USAEME	10	15	GC-MS/MS	0.08–9.7	[10]
EHS, BS, HMS, BP3, IAMC, 4MBC, MA, ETO, 2EHMC, EHPABA, OCR	FPSE	20	20	GC-MS/MS	0.01–4.5	This work

Table 4
Concentration (μg L^{-1}) of the studied UV filters in the analyzed samples.

UV filter	Lake	River	Seawater	Swimming-pool	Children's swimming-pool
EHS	40 ± 3		17 ± 4	4.4 ± 0.5	19 ± 1
BS	0.14 ± 0.02		0.42 ± 0.05		0.12 ± 0.02
HMS	0.46 ± 0.10		0.13 ± 0.08	2.4 ± 0.2	8.4 ± 0.4
IAMC			87 ± 20	0.14 ± 0.03	
4MBC	19 ± 1				2.0 ± 0.1
ETO	0.13 ± 0.01				
2EHMC	0.92 ± 0.05	0.28 ± 0.04	23 ± 5	0.19 ± 0.05	0.80 ± 0.11
OCR	123 ± 7	2.3 ± 0.2	0.39 ± 0.06	6.4 ± 0.4	62 ± 0.3

compounds in ethyl acetate, since the extraction was complete and no matrix effect was observed. The internal standard, PCB-30, was added to the calibration standards as well as the desorption solvent of the FPSE procedure to correct the possible volume variability before the analysis. In all cases, the chromatographic response of the PCB-30 was equivalent both in the spiked samples, real samples and calibration curve. Therefore, it was used as an additional measure to control the procedure but internal standard (IS)

correction was not necessary.

Eight of the 11 target UV filters were detected in the analyzed samples. Two of them, 2EHMC, and OCR, were found in all the analyzed samples, demonstrating the relationship between the use of cosmetics and personal care products and the presence of these compounds, since 2EHMC and OCR are the two UV filters most employed, especially in sunscreen formulations [34]. EHS and HMS were detected in 4 out of the 5 analyzed samples; BS has been found in 3 samples, whereas IAMC and 4MBC were detected in 2 samples and ETO in the lake sample. Fig. 5 shows a FPSE-GC-MS/MS reconstructed chromatogram for the lake sample, where seven UV filters were detected, highlighting the presence of OCR at a concentration level higher than 120 μg L^{-1}. Regarding the swimming-pool water samples, the children's pool contains 6 UV filters, in comparison with the 5 found in the other analyzed sample. Besides, in the children's pool, the concentration was higher for all compounds, up to one order of magnitude in the case of OCR. This is probably due to the lower water volume and the larger number of users.

4. Conclusions

An analytical method based on FPSE-GC-MS/MS has been developed for the first time for the simultaneous determination of 11 UV filters in different water samples. The main parameters affecting extraction efficiency such as the type of sol-gel coating, the FPSE device size, sample volume, extraction time and elution volume were evaluated. The optimal extraction conditions comprised the use of 5 cm^2 (2.0 × 2.5 cm) of sol-gel PDMS coated FPSE media for the extraction of 20 mL of water in 20 min. After extraction, quantitative desorption of the target compounds was achieved with 0.5 or 1 mL of ethyl acetate in a vortex stirrer for 3 min.

The method was satisfactory validated in terms of linearity, precision, repeatability and reproducibility. Recovery studies were also performed at two different concentration levels in real environmental and recreational water matrices, obtaining values between 80-110% for most of the target compounds, and RSD values lower than 13%.

The validated method was applied to different real samples, including natural water systems (lake, river, seawater) and recreational waters (swimming-pool), where 8 out of the 11 studied compounds were detected in many of the samples at levels above 10 μg L^{-1} in some cases, which evidences the entry of these compounds into the aquatic environment.

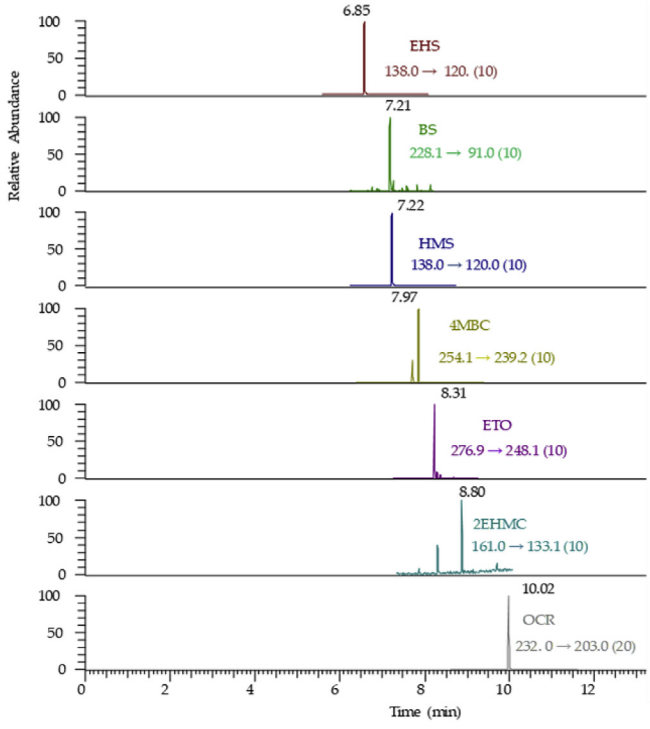

Fig. 5. SRM reconstructed chromatogram of the lake water containing 7 target compounds.

Author contribution section

Maria Celeiro: Data curation, methodology, validation, writing-original draft, and writing - review & editing; **Ruben Acerbi**: Data curation, investigation and methodology; **Abuzar Kabir**: Investigation, conceptualization and supervision; **Kenneth G. Furton**: Investigation, conceptualization and supervision; **Maria Llompart**: Conceptualization, formal analysis, funding acquisition, project administration, resources, and supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.acax.2019.100038.

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