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Vacuum-assisted sorbent extraction: An analytical methodology for the determination of ultraviolet filters in environmental samples

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ABSTRACT

Vacuum-assisted sorbent extraction (VASE) has been applied in combination with gas chromatography-mass spectrometry for the determination of UV filters in water samples. VASE is a variant of headspace extraction which was developed in conjunction with the sorbent pen (SP) technology. This technique combines the advantages of both stir-bar assisted extraction and headspace solid-phase microextraction. The SP traps allowed both reduced pressure in-vial extraction and direct thermal desorption via a unique gas chromatographic injection port. The main parameters that affect the performance of VASE, including both extraction and desorption conditions, were extensively optimized. Under optimum conditions, extraction required 10 mL of sample within 40 mL vials, pH 3.5, ~30 s of air-evacuation, 14 h incubation at 70 °C, stirring at 200 rpm, and a final water management step conducted at ~ −17 °C for 15 min. Optimal thermal desorption required preheating at 260 °C for 2 min followed by desorption at 300 °C for 2 min. The beneficial effect of reduced-pressure extraction was demonstrated by comparing the UV filter extraction time profiles collected using VASE to an analogous atmospheric pressure procedure, resulting in up to a 3-fold improvement under optimized conditions. The VASE methodology enabled simultaneous extractions using different SPs without compromising the method reproducibility, which increases the overall sample throughput. The method was characterized by low limits of detection, from 0.5 to 80 ng L^{-1}, and adequate reproducibility, with inter-SP and inter-day relative standard deviation lower than 14%. Tap and lake water was successfully analyzed with the proposed methodology, resulting in relative recoveries of spiked samples ranging between 70.0 and 120%.

1. Introduction

Ultraviolet (UV) filters are widely used components of everyday personal care products such as sunscreens, lotions, cosmetics, and shampoos [1]. These substances are added as ingredients to different formulations to protect the skin against both UVA and UVB radiation or to prevent degradation [2–4]. They are also added with the same purposes to adhesives or plastics, among other industrial products [3]. Due to their extensive use, UV filters are present in the aquatic environment at the nanogram per liter level [1,4]. In this medium, organic UV filters such as benzophenones, salicylates, cinnamates or aminobenzoates can be accumulated in suspended particles, sediments or sludge, as well as in the marine biota [1,5]. Furthermore, different toxicological studies have identified some UV filters such as benzophenone-3 (BP3) and octocrylene (OCR) as potential endocrine disrupting compounds (EDCs), which pose risks to human health [3,6], and they are considered contaminants of emerging concern due to their persistence [7]. Studies have also shown that BP3 and 2-ethylhexyl-4-methoxycinnamate (2EHMC) negatively affect ocean coral, leading to bleaching, genetic damage, increased mortality, and reduced ability to adapt to changing climates [8]. Existing regulations limit the use of UV filters in cosmetics [9], but there is no legislation controlling the levels present in water, even when some are considered as “hazardous to the aquatic environment” [10,11]. In recognition of these concerns, some regions such as Hawaii will ban the use of BP3 and 2EHMC in over-the-counter sunscreens starting in the year 2020 [12]. Therefore, the development of methods for UV filter determination is of great importance.

To detect trace-level UV filters in water, existing methodologies utilize a variety of extraction and preconcentration techniques followed by either high performance liquid chromatography (HPLC) or gas chromatography (GC) [13–16]. It is worth noting that 60% of the

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reported publications in the 2002–2017 period have used sorbent-based microextraction techniques [1]. Stir bar sorptive extraction (SBSE) and solid-phase microextraction (SPME) are the most widely employed techniques [1]. These two methods offer several advantages for monitoring UV filters and other organic compounds [17,18]. SBSE is effective for the extraction of non-polar compounds or species with medium polarity and high thermal stability, but its utility is limited for polar compounds as commercial stir bars are generally based on polydimethylsiloxane (PDMS) [18]. SPME can overcome the aforementioned limitation, although this technique is a non-exhaustive methodology [17]. Furthermore, SPME offers the possibility of performing the extraction procedure in different extraction modes. The vacuum headspace (HS)-SPME mode is especially beneficial for volatile and semivolatiles such as some organic UV filters that are characterized by low Henry's law constant (K_H) values [19], but this extraction mode has not yet been used for UV filters.

As an alternative approach to overcome the above limitations, this study examines a technique called vacuum-assisted sorbent extraction (VASE). By using commercialized sorbent traps called sorbent pens (SPs) and a headspace extraction environment, VASE combines the advantages of both SBSE and vacuum HS-SPME. The SPs are packed with a large quantity of extraction material (approximately 10 times the volume typically used for SBSE and approximately 500 times the volume typically used for SPME), which favors exhaustive extraction as in SBSE and other HS-extraction techniques [20]. At the same time, VASE operates at near equilibrium conditions, which improves reproducibility. To accelerate the extraction kinetics, reduce the sampling time, and extend the range of detectable compounds, in-vial extraction is performed in a reduced-pressure environment during VASE using a commercialized and leak-tight sealing system. The SPs are thermally desorbed via a unique GC injection port, followed by separation and detection by GC in combination with mass spectrometry (MS). Despite the advantages of this technique, there is only one reported study that uses VASE in food analysis, specifically for monitoring phenols in beer [21]. The present study reports the use of VASE in an environmental application, particularly the determination of UV filters in aqueous samples. This study also examines for the first time the beneficial effect of vacuum conditions for the extraction of UV filters.

2. Experimental

2.1. Chemicals, reagents, materials and samples

The studied analytes were nine UV filters, including three salicylates, two aminobenzoates, three cinnamates, and a benzophenone derivative. The analytes 2-ethylhexyl-salicylate (ES, ≥99.0%), homosalate (HS, pharmaceutical secondary standard), benzyl-salicylate (BS, ≥99.0%), benzophenone-3 (BP3, 98.0%), methyl-anthranilate (MA, 98%), 2-ethylhexyl-4-(dimethylamino)benzoate (EHPABA, 98.0%), etocrylene (Eto, 98.0%), 2-ethylhexyl-4-methoxycinnamate (2EHMC, 98.0%), and octocrylene (OCR, ≥98.0%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The relevant physicochemical properties of the UV filters are shown in Table S1 of the Supplementary Material (SM). The internal standards (ISs) octocrylene-(2-ethyl-d_5-hexyl-2,3,3,4,4,5,5,6,6-d_{10}) (OCR-d_{15}, ≥98.0% assay, and ≥97% of isotopic purity) and methyl salicylate (MS, ≥99.0%) were also obtained from Sigma-Aldrich. Individual stock solutions of all UV filters and ISs were prepared in acetone (99.0%, Sigma-Aldrich) at 2000 mg L^{-1} and 800 mg L^{-1} for OCR-d_{15}. Intermediate solutions containing all analytes or groups of analytes were prepared in acetone by dilution of the individual stock solutions at 0.5, 2, 5, or 150 mg L^{-1} in the case of the analytes, and 25, 130, or 150 mg L^{-1} in the case of the ISs. Working solutions were prepared by spiking appropriate amounts of the intermediate solutions into the sample or ultrapure water at concentrations ranging from 1 ng L^{-1} to 100 μg L^{-1}, depending on the experiment. The organic content of the working solutions was kept to 0.03% (v/v).

Ultrapure water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Sodium chloride (≥99.5%) was purchased from Fisher Scientific, Fair Lawn, NJ, USA). Sodium phosphate monobasic dihydrate (> 99%) was obtained from ACROS Organics (NJ, USA), and potassium phosphate monobasic (ACS reagent) from Sigma-Aldrich. Hydrochloric acid and sodium hydroxide (ACS reagents) were obtained from Fisher Scientific.

Tap and lake water were collected in Ames (IA, USA). The samples were stored in plastic bottles at 4 °C until analysis. Lake water was filtered using a 0.45 μm sterile syringe filter purchased from Corning Incorporated (Corning, Germany).

2.2. Instrumentation

A 7890B GC from Agilent Technologies (Santa Clara, CA, USA) equipped with a 5977 MS detector (single quadrupole) was employed in this study. A 5800 Sorbent Pen Desorption Unit (SPDU) from Entech Instruments (Simi Valley, CA, USA) was installed in the rear GC-inlet port. The SPDU was set for *split* injection (10:1 ratio) using the configuration described within the schematic shown in Fig. S1 of the SM. Inside the GC oven, the SPDU was connected via a T connector to a wide-bore Silonite™-coated pre-column (0.6 m L × 1 mm I.D.), which was connected to a HP-5ms ultra inert capillary column from Agilent Technologies (30 m L. × 0.250 mm I.D. × 0.25 μm of film thickness). Ultrapure helium was used as carrier gas at 1 mL min^{-1} (16.2 psi, 46.67 cm s^{-1} of average velocity). The GC separation was performed using the following temperature oven program: initially 100 °C for 3 min, 20 °C·min^{-1} ramp to 300 °C, and 2 min hold. The transfer line from the GC to the MS was kept at 280 °C. The MS was operated in electron ionization (EI) mode at 70 eV, employing gain factor mode and using 230 °C and 150 °C as the source and quadrupole temperatures, respectively. Data was acquired in single ion monitoring (SIM) mode. The identification of the UV filters was accomplished using the retention time and the presence and peak area ratio of two ions for each analyte (denoted as quantifier and qualifier ions). For quantitative purposes, the peak area of the quantifier ion was employed. Table S2 of the SM shows the MS ions, retention time and SIM segment program. All data was acquired using Mass Hunter Workstation software from Agilent Technologies version B.07.00. The SPDU was controlled using the 5800 SPDU software from Entech Instruments version 1.3.0.68.

2.3. Procedures

2.3.1. Vacuum-assisted sorbent extraction and desorption procedure

VASE is based on the use of commercialized vacuum-controlled sorbent traps called sorbent pens (SPs). HS SPs of Tenax® TA 35/60 model SP-HSP-T3560 from Entech Instruments were employed in this application. The SPs were comprised of a Silonite™-coated cylinder packed with 70 mg of Tenax® TA, which was chosen as the adsorbent due to its broad chemical coverage. The SPs were constructed with a micro septum-less seal (called a Micro QT™), enabling air-evacuation of the vial during the extraction, and a triple O-ring seal for directing gas flow and reducing the possibility of leaks (see Fig. S2 of SM).

The extraction and thermal desorption procedures were performed in six steps as shown in Fig. 1: (1) Vial preparation, (2) SP assembly, (3) air-evacuation, (4) VASE extraction, (5) water management, and (6) VASE thermal desorption. The extraction procedure was performed using vials with a total capacity of 20–60 mL, depending on the experiment. A volume of 1–40 mL of ultrapure water or sample (spiked with the UV filters or not spiked) was placed in vials from Environmental Sampling Supply (San Leandro, CA, USA). The ISs were spiked at a concentration of 20 μg L^{-1} for OCR-d_{15} and 2 g L^{-1} for MS. The pH was adjusted to 3.5–8.5 with 0.5 M HCl or 0.1 M NaOH. During experiments within Section 3.1.1, 3% (w/v) of NaCl, NaH_2PO4, or KH_2PO_4 was also added to the vial. The SPs were assembled onto the vials using cap liners for leak-tight sealing with 22 mm O.D. hole from

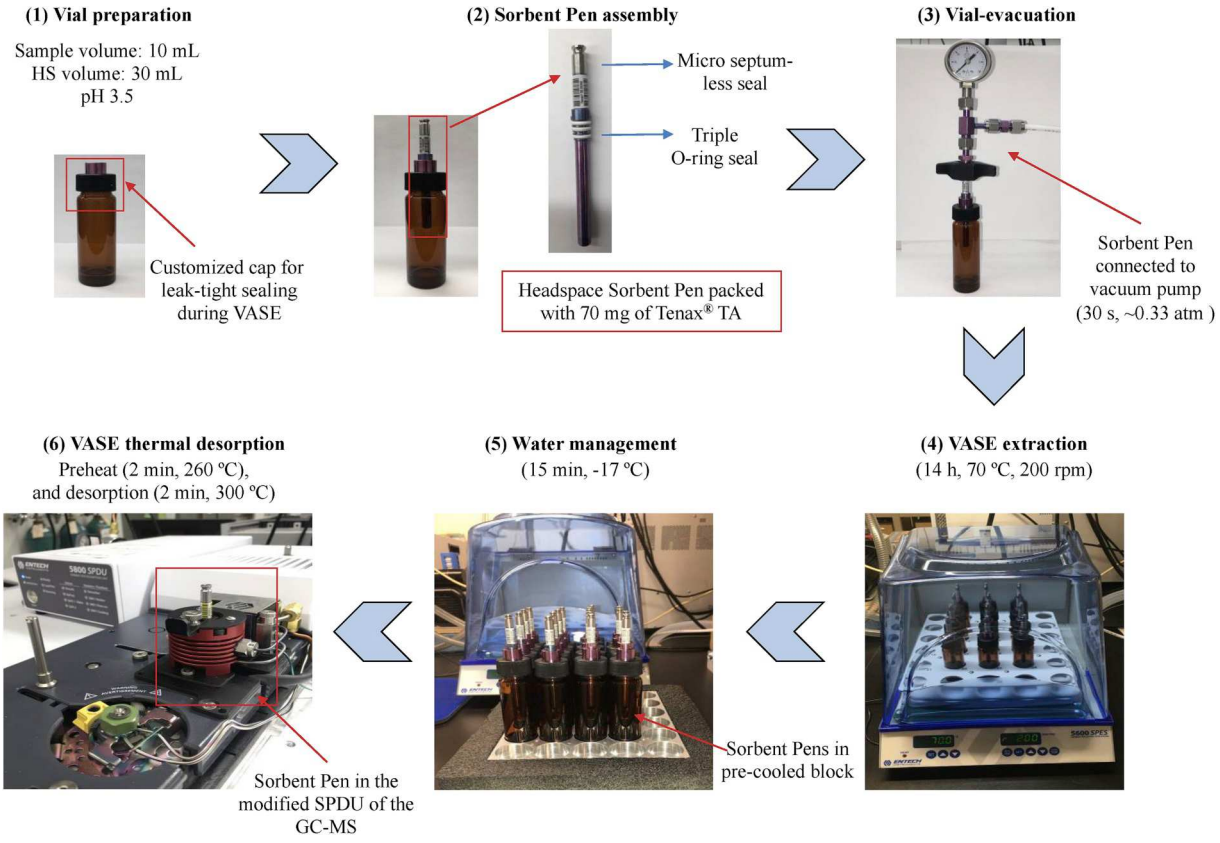


Fig. 1. Scheme of the VASE procedure at optimum conditions.

Entech Instruments, as in Fig. 1(2). After assembly, air-evacuation was performed by directly connecting the SP Micro QT™ to a vacuum pump for 30 s. The pressure read using a vacuum gauge was 0.33 atm. The vials were then placed on a 5600 Sorbent Pen Extraction System (SPES) from Entech Instruments where the extraction took place at controlled temperature (between 25 and 70 °C) using orbital agitation (between 30 and 200 rpm) for 1–24 h. A water management step was then performed for reducing water vapor and/or condensation in the extraction vial and the SP, which could lead to performance issues during desorption [20]. For the water management step, the SP-assembled extraction vials were placed in a pre-cooled block (~ −17 °C) for 2–35 min. The internal pressure of the vials was measured after this step to ensure that leak-tight conditions were achieved throughout extraction. The SPs were removed from the extraction vials and stored in leak-tight Silonite™-coated isolation sleeves until desorption. In the SPDU, each SP was subjected to a preheating step at 70–300 °C for 0.5–10 min, followed by desorption at 260–300 °C for 1–10 min. After desorption, the SPs were baked out at 280 °C inside the SPDU for the remainder of the GC run, followed by post-bake equilibration to 70 °C for 5 min. During the typical workflow, the SPs were stored in their isolation sleeves for the next round of experiments.

Under optimum conditions, the VASE method required 10 mL of sample in 40 mL vials, pH 3.5, air-evacuation for 30 s, extraction at 70 °C and 200 rpm for 14 h, water control step at ~ −17 °C for 15 min, and thermal desorption using preheating at 260 °C for 2 min followed by desorption at 300 °C for 2 min.

All experiments were performed in triplicate using different SPs. After use, the SPs were subjected to an extra bake-out conditioning step for 30 min at 300 °C under constant flow of nitrogen in a 3801 Sorbent Pen Thermal Conditioner (SPTC) from Entech Instruments.

2.3.2. Sorbent-assisted extraction and desorption procedure

Sorbent-assisted extraction (SAE) was performed employing an analogous approach to VASE but avoiding the air-evacuation and pressure control steps. Thus, the method required 10 mL of sample in 40 mL capacity vials, pH 3.5, extraction at 70 °C and 200 rpm for 0.5–24 h, water management step at ~ −17 °C for 15 min, and thermal desorption using preheating at 260 °C for 2 min followed by desorption at 300 °C for 2 min.

3. Results and discussion

3.1. Optimization of the VASE procedure

The main parameters that affect the extraction procedure including pH and ionic strength of the sample solution, sample and HS volume, extraction time, temperature, and stirring, water-control step time, and preheating and desorption time and temperature, were optimized using a factor-by-factor approach. Sensitivity and analysis time were considered in selecting the optimum conditions.

3.1.1. Effect of pH and ionic strength

Sample pH can affect the extraction efficiency of the VASE method as basic pH values can ionize those UV filters with ionizable groups, causing a decrease of the extraction efficiency [14]. For that reason, the pH was studied in the range between 3.5 and 8.5. As shown in Fig. S3 of the SM, the obtained results indicated that the extraction efficiency was lower at basic pH values for relatively less hydrophobic compounds with hydroxyl groups such as ES, HS, and BS. A dramatic decrease in the extraction efficiency was also observed for both Eto and BS when the pH was increased, likely due to the hydrolysis of the compound at basic pH values. On the other hand, there was not a significant change in the extraction efficiency at different pH values for BP3 and MA, and slightly higher extraction efficiency at pH 8.5 was observed for EHPABA, 2EHMC, and OCR. These latter results indicated that, with the exception of BS and Eto, controlling the sample pH is not essential for

the analysis of UV filters, and is in agreement with results from previous studies [11]. In view of the obtained results, a pH value of 3.5 was selected as optimum.

The addition of a salt can increase or decrease the amount of extracted analyte due to the salting out or salting in effects, respectively [17]. In some reported HS extraction methods for non-polar compounds, salting out is the most dominant effect [17]. In these cases, the addition of a kosmotropic salt decreases the analyte solubility, favoring their mass transfer to the HS and increasing extraction efficiency [22]. However, the salting in effect is also possible (i.e., an increase in aqueous phase analyte solubility resulting in a decrease in extraction efficiency). With these considerations, experiments were performed using 3% (w/v) of NaCl, NaH_2PO_4, and KH_2PO_4. Fig. S4 of the SM shows the obtained results. For comparison purposes, experiments in ultrapure water were also included. When the results obtained with different salts are compared, higher extraction efficiency was achieved using the salts based on $H_2PO_4^-$, a result that is in agreement with the general principles of the salting out effect that correlate with the Hofmeister series [22]. However, for seven of the ten analytes studied, the extractions using samples containing salt generally provided lower extraction efficiency compared to extractions of samples with no salt (ultrapure water), indicating that salting in was the dominant effect. In agreement with this observation, salting in has been observed in other studies determining UV filters [23]. The three analytes that were exceptions were BS, BP3, and Eto, for which the highest extraction efficiency was achieved using NaH_2PO_4. These results can be related to the relatively higher polarity of these analytes in comparison to the remaining UV filters (see Table S1 of the SM), which can alter the relative contribution of electronic repulsion and other hydrophobic effects [22]. In view of these results, no salt was added in the remaining experiments.

3.1.2. Effect of sample and headspace volume

Both the sample and the HS volume are important parameters to consider in HS-extraction procedures. In these applications, the phase ratio, defined as the ratio of the HS and initial volumes, is generally studied [11,20,24,25]. In general, the lower the phase ratio (i.e., the higher the sample volume and the lower the HS volume), the higher the extraction efficiency if the remaining of conditions (e.g., number of moles, type of vial, extraction phase position during the extraction, agitation, temperature, …) are held constant [11,20,24,25]. In this study, vials of different capacity (from 20 to 60 mL) were examined. The vials were filled with 1–40 mL of sample, with a HS volume between 19 and 39 mL, and were subjected to the entire VASE methodology. The maximum capacity of each vial was controlled to ensure that no sample splashed onto the outer surface of the SPs during extraction. The obtained results are shown in Fig. 2. The vial, sample and HS volumes, as well as the corresponding phase ratios are also indicated. Experiments **1** and **2** in Fig. 2 serve to compare the effect of the HS volume as the experiments contained the same amount of analyte. The comparison of these two experiments indicated no differences in extraction efficiency for ES, HS1, BS, HS2, MA, EHPABA, and 2EHMC, demonstrating independent from HS volume. For the remaining analytes (i.e., BP3, Eto, and OCR), higher extraction efficiency was observed in experiments **1**, as the theory predicts [11,20,24,25].

Experiments using 40 mL vials (experiments **2–5**) were beneficial for 8 of the 10 studied analytes as in these cases the sample volume increased. For BP3 and Eto, the extraction efficiency increased up to 4 mL (experiment **4**), and then slightly decreased from 4 to 10 mL. The use of sample volumes higher than 10 mL required increasing the vial size (i.e., from experiment **5** to experiment **6**). This change provided lower extraction efficiency than experiment **5** for BS, MA, EHPABA, 2EHMC, BP3, and Eto, no change in the extraction efficiency for OCR, and higher extraction efficiency for the remaining analytes. As mentioned above, results obtained from experiments **5** and **6** cannot be easily compared because the vials contained different quantities of analytes (by number of moles), volume-dependent differences in agitation, differences in the SP positioning within the HS, and other complicating factors. As a compromise, the conditions employed in experiment **5** (10 mL of sample in 40 mL vials) were selected as optimum.

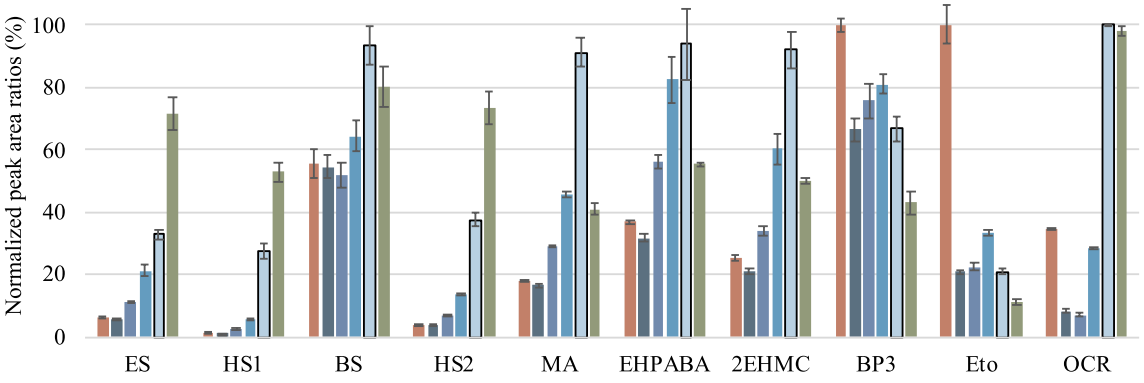
3.1.3. Effect of extraction conditions

The studied extraction parameters included temperature, stirring rate, and sampling time. In general, temperature can produce two competing effects during HS extraction. An increase in the temperature can favor the mass transfer of the analyte to the HS, thereby increasing the extraction efficiency. On the other hand, an excessive increase in the temperature can significantly reduce the analyte partition coefficients to the sorbent material due to the exothermic character of the extraction procedure [26]. With these considerations, the effect of extraction temperature was studied in the range between 25 and 70 °C. The results, shown in Fig. S5 of the SM, indicate that increasing the temperature had a positive effect for most analytes, especially for the most hydrophobic compounds (BP3, MA, Eto, EHPABA, 2EHMC, and OCR). The remaining four analytes exhibited a maximum extraction efficiency at 50 °C, and slight to no changes were observed at higher temperature. In view of these results, 70 °C was selected as the optimum temperature for further experiments.

Stirring during extraction can also accelerate the diffusion of analytes to the HS, increasing the extraction efficiency. For that reason, the effect of stirring rate using orbital agitation was studied in the range between 30 and 200 rpm. Values higher than 200 rpm were not examined to avoid the sample splashing onto the SPs. The results, shown in Fig. S6 of the SM, generally revealed an increase in the extraction efficiency when the stirring rate was increased for all analytes. Therefore, 200 rpm was selected as the optimum stirring rate.

The key factor during HS-extraction is the sampling time. Working near or under equilibrium conditions ensures higher extraction efficiency and better reproducibility than non-equilibrium conditions [17]. However, the time needed for achieving those conditions is usually very high. In order to accelerate the extraction kinetics, different approaches can be employed to increase the mass transfer of the analytes to the HS, which is often the limiting step in the extraction procedure [19,22]. Vacuum conditions can be used to increase extraction kinetics for analytes with low K_H values, such as the group of studied UV filters (see Table S1 of the SM) [19]. With these considerations, the influence of the extraction time in VASE was studied in the range between 1 and 24 h. The SP technology enabled the maintenance of a reduced pressure sampling environment for more than 24 h. To verify that vacuum conditions were beneficial in this application, experiments were performed using the same conditions employed in VASE but without the vial evacuation step (i.e., SAE). Fig. 3 shows the results obtained for representative UV filters using both VASE and SAE. The results for the remaining analytes are presented in Fig. S7 of the SM. Three different types of behavior were generally observed. Six of the ten analytes (i.e., MA, ES, HS2, HS1, EHPABA, and 2EHMC) exhibited an extraction time profile similar to the one observed for MA in Fig. 3. These analytes exhibited fast extraction kinetics up to 9 h, followed by a slower increase in the extraction from 9 to 24 h. On the other hand, polar UV filters such as BP3, BS, and Eto displayed slower extraction kinetics in the 24 h range studied. It is important to mention that the extraction efficiency obtained with VASE was considerably greater than for SAE for both groups of compounds, demonstrating the positive effect of working under vacuum conditions in this application. Finally, it is important to highlight that OCR exhibited extraction kinetics that differed from all other analytes, and vacuum was less important at longer extraction times. The unique extraction kinetics for OCR likely arise because the developed VASE methodology was not optimized for this specific compound, but instead for the larger group, and due to the unique physicochemical properties of OCR in comparison of the rest of UV filters (see Table S1 of the SM).

Extraction time profiles were also constructed using different



Experiment number	Volume (mL) Vial	Sample	Headspace	Phase ratio
1	20	1	19	19
2	40	1	39	39
3	40	2	38	19
4	40	4	36	9
5	40	10	30	3
6	60	40	20	0.5

Fig. 2. Effect of the sample and HS volume in VASE-GC-MS. Experimental conditions (n = 3): Spiked level of 15 μg L^{-1}; 1–70 mL sample in 20–125 mL vials; pH 3.5; extraction: 3 h, 70 °C, 200 rpm; water management: 35 min; desorption: preheating of 2 min, 260 °C, and desorption of 2 min, 300 °C, and GC-MS.

sample volumes (i.e., 4 mL and 10 mL), and different concentrations (15 and 100 μg L^{-1}). The results, shown in Fig. S8 of the SM, revealed that sample volume and concentration did not impact extraction kinetics, as has been previously demonstrated for other HS sampling techniques such as HS-SPME [17]. As a compromise between sensitivity and analysis time, an extraction time of 14 h was selected as optimum.

In order to further compare the extraction performance of VASE and SAE, extractions of 14 h at 70 °C and 200 rpm were performed at a low spiked level (0.010 μg L^{-1} for MA, 1 μg L^{-1} for BP3, Eto, and OCR, and 0.1 μg L^{-1} for the other analytes). Peak area ratios between 1.3 and 3.1 times higher were obtained for VASE, as shown in Fig. 4. The maximum and minimum differences between VASE and SAE were achieved for BS and MA, respectively. As theory predicts, the reduced pressure sampling conditions caused the greatest impact on those analytes with low K_H values (see Table S1 of the SM) [19]. However, the higher vapor pressure of MA (3.6 Pa *versus* $2.7 \cdot 10^{-2}$ Pa) facilitates their mass transfer to the HS in the case of SAE, resulting in minor differences between VASE and SAE. It is also important to mention that BP3 was only detected using VASE at the employed spiked level.

3.1.4. Effect of water-management

During VASE extraction, prolonged heating and stirring causes partial vaporization of the water sample in the evacuated sample vial. This effect is not desirable as the water vapor could be trapped on the SPs, causing backflushing and/or carry over due to the high expansion coefficient of water. This effect has been also observed in other HS extraction methods such as cryogenic HS-GC [20]. Water elimination by condensation, semipermeable membranes or chemisorption has been applied in these cases [20,27–29]. In this approach, water condensation was promoted by placing the vials after extraction in a pre-cooled block after extraction. The effect of this parameter was studied by cooling the vials at −17 °C for different periods of time, ranging from 2 to 20 min. The results indicated that a water-control step of 15 min was adequate for this application, while cooling times shorter than this value provided irreproducible results. During these shorter cooling times, condensed water was observed on the inner walls of the extraction vial.

3.1.5. Effect of desorption conditions

To ensure adequate desorption of the UV filters, split desorption (10:1) was used, and a 0.6 m long × 1.0 mm ID inert Silonite™ coated stainless steel pre-column was employed for connecting the SPDU to the analytical column. The pre-column acts as an expansion space during preheating and desorption, while the GC's native electronic pressure controller (EPC) controls splitting, which occurs after the pre-column. The effect of both the preheating and desorption conditions was subsequently studied.

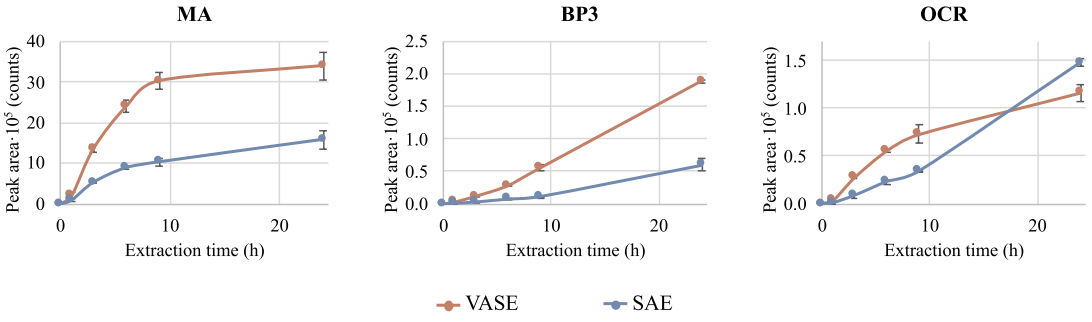


Fig. 3. Extraction time profiles obtained using VASE (in red) and SAE (in blue) for representative UV filters. Experimental conditions (n = 3): Spiked level of 15 μg L^{-1}; 10 mL sample in 40 mL vials; pH 4; extraction: 1–24 h, 70 °C, 200 rpm; water management: 15 min; desorption: preheating of 2 min, 260 °C, and desorption of 2 min, 300 °C, and GC-MS. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

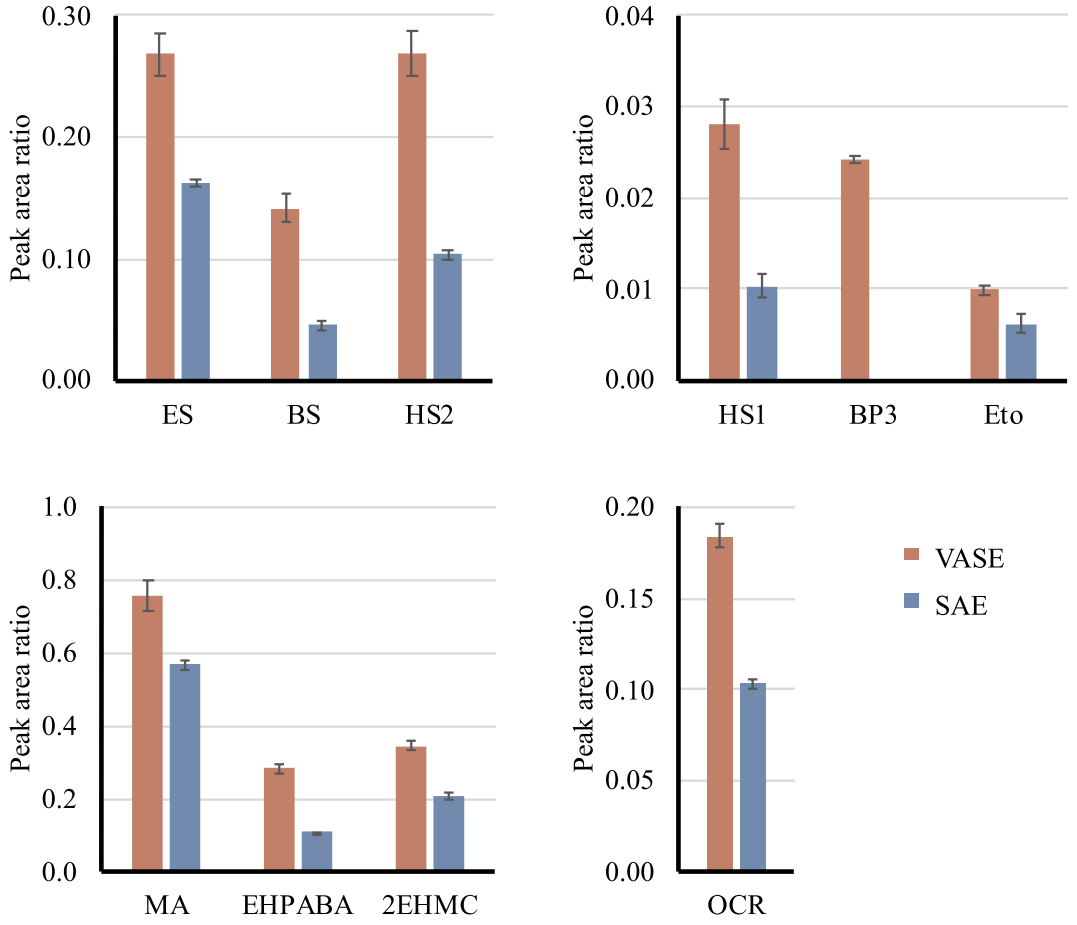


Fig. 4. Comparison of the extraction efficiency using VASE (in red) and SAE (in blue). Experimental conditions (n = 3): Spiked level of 0.010 μg L^{-1} for MA, 1 μg L^{-1} for BP3, Eto, and OCR, and 0.1 μg L^{-1} for the rest of analytes; 10 mL sample in 40 mL vials; pH 3.5; extraction: 14 h, 70 °C, 200 rpm; water management: 15 min; desorption: preheating of 2 min, 260 °C, and desorption of 2 min, 300 °C, and GC-MS. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Preheating corresponds to the first step of the desorption procedure. During this step, the SP was heated without flow and the GC was maintained in standby mode. The effect of both the preheating time and temperature was studied. Firstly, experiments were performed employing preheating temperatures ranging from 70 to 290 °C for 2 min (see Fig. S9 of the SM). In these experiments, a subsequent desorption step at 300 °C for 2 min was performed. The results showed an increase in the extraction efficiency up to 240 °C for HS1, BS, BP3, EHPABA, and 2EHMC, and up to 260 °C for ES, HS2, MA, and Eto. Beyond 260 °C, the extraction efficiency did not change or was found to slightly decrease. For OCR (which has the highest boiling point), the maximum extraction efficiency was achieved at 290 °C. The preheating time was studied from 0.5 to 10 min at 260 °C. In general, most analytes indicated an increase in the extraction efficiency up to 2 min, followed by a decrease at longer desorption times. For OCR, the extraction efficiency always increased with the preheating time, indicating a slower desorption pathway for this UV filter. In view of these results, a 2 min preheating time was selected as optimum. It is interesting to point out that modifications to the preheating also changed the retention time of MS, which was the first analyte to elute in the chromatographic run. A 0.06 min decrease in the retention time was observed when the preheating temperature increased from 70 to 120 °C (2 min of preheating), and a 0.09 min decrease of retention time from 0.5 to 2 min of preheating at 260 °C. The retention times of the remaining UV filters studied were not affected by changes in the preheating time as they eluted at longer desorption times. This observation suggests that MS is the only compound to significantly desorb during the preheating step.

With regard to the desorption step, the desorption temperature was studied from 260 to 300 °C for 2 min using the optimized preheating conditions (260 °C for 2 min). The results are provided in Fig. S10 of the SM. The data revealed an increase in the overall extraction efficiency of the method as the desorption temperature was increased, likely due to a decrease in the affinity of the analytes to the SP material at high temperatures. The exceptions were EHPABA and 2EHMC for which a slight decrease in the extraction efficiency was observed.

In a parallel study, the desorption temperature was varied from 260 to 300 °C for 2 min using mild preheating conditions (i.e., 70 °C for 2 min). These experiments were performed to further study the effect of the desorption temperature in the VASE method. The results, presented in Fig. S11 of the SM, showed that a combination of 70 °C of preheating and 260 °C of desorption caused the same effect than 260 °C and 300 °C of preheating and desorption, respectively. However, the last option was selected as optimal to avoid carry over between extractions. The desorption time was also studied from 1 to 10 min at 300 °C using a preheating step of 260 °C for 2 min. For performing these experiments, the GC oven program was modified as follows: initially 100 °C during 10 min (instead of 3 min as in Section 2.2), the temperature was then increased at 20 °C·min^{-1} up to 300 °C, and held for 2 min. The results, shown in Fig. S12 of the SM, revealed an increase in the extraction efficiency at longer desorption times for BS, BP3, MA, EHHPABA, 2EHMC, and OCR. For the remaining analytes, similar or better results were achieved at shorter desorption times. In addition, longer desorption times caused band broadening for the analytes eluting at the beginning of the chromatogram. In order to minimize the analysis time,

Table 1
Analytical performance of the VASE-GC-MS method.

UV filter	Working range ($\mu g \cdot L^{-1}$)	(Slope ± SD[a])·10^3	R[b]	$S_{y/x}$[c]·10^2	LOD[d] ($ng \cdot L^{-1}$)	Spiked level 1[e]	
						RSD intra-day[f] (%)	RSD inter-day[g] (%)
ES	0.01–1.0	2.0 ± 0.1	0.9923	10	4.0	6.1	7.6
HS1	0.01–1.0	0.11 ± 0.01	0.9921	0.61	4.0	10	14
BS	0.01–1.0	0.80 ± 0.04	0.9925	4.1	4.0	6.7	12
HS2	0.01–1.0	1.9 ± 0.1	0.9959	7.6	4.0	6.2	9.2
BP3	0.1–8.0	0.113 ± 0.003	0.9987	2.2	40	4.6	8.0
MA	0.001–0.1	142 ± 8	0.9919	74.4	0.5	3.5	12
Eto	0.2–10	0.014 ± 0.001	0.9999	0.1	60	9.7	9.7
EHPABA	0.01–1.0	9.5 ± 0.3	0.9976	29	4.0	8.7	13
2EHMC	0.01–1.0	5.3 ± 0.2	0.9965	15	4.0	11	14
OCR	0.2–10	0.17 ± 0.01	0.9961	5.9	80	4.5	6.9

[a] Standard deviation of the slope.
[b] Correlation coefficient.
[c] Standard deviation of the residuals (or error of the estimate).
[d] Limit of detection, determined experimentally.
[e] Spiked level: 0.010 $\mu g\,L^{-1}$ for MA, 1 $\mu g\,L^{-1}$ for BP3, Eto, and OCR, and 0.1 $\mu g\,L^{-1}$ for the rest of analytes.
[f] Relative standard deviation, calculated using 4 different SPs and performing extractions during the same day (n = 4).
[g] Relative standard deviation, calculated using 4 different SPs and performing extractions during 4 consecutive days (n = 16).

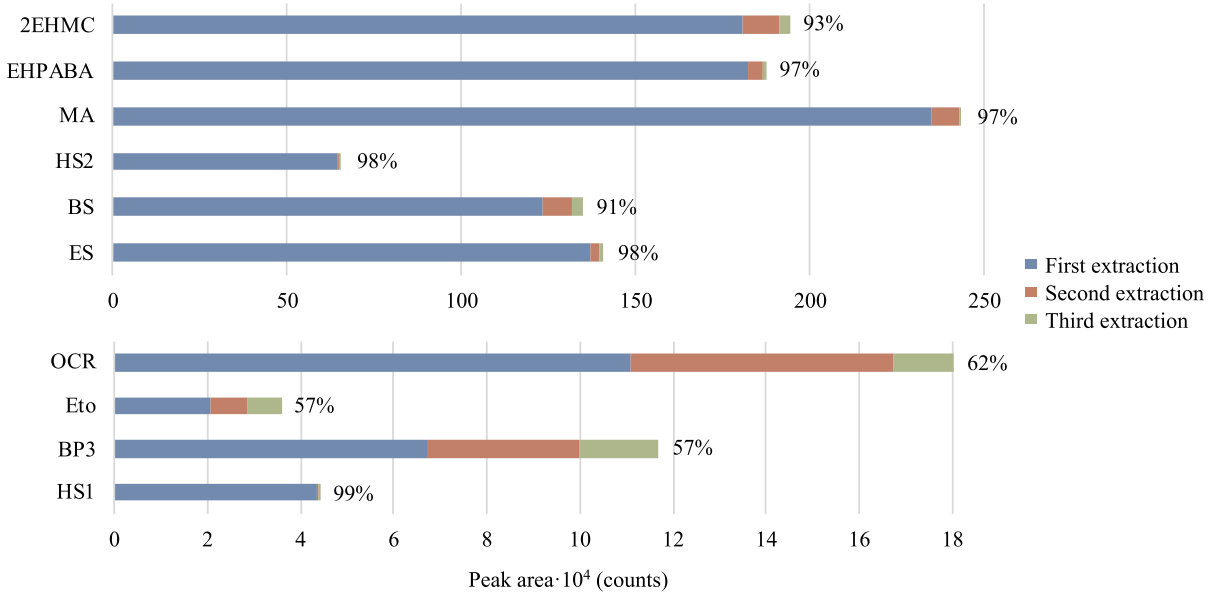


Fig. 5. Extraction efficiency obtained after performing three successive extractions of the same extraction vial using the VASE-GC-MS method under optimum conditions. The number following each bar corresponds to the percentage of analyte extracted in the first round of VASE (blue bars) with respect to the total amount of extracted analyte. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2 min was selected as the optimum desorption time, and the oven program described in Section 2.2. was employed.

3.2. Analytical performance of the VASE methodology

After optimization, the method was validated by developing the corresponding external calibration curves. Table 1 shows several figures of merit, including working range, sensitivity, correlation coefficient, limits of detection (LODs), and reproducibility. Wide working ranges were achieved ranging from 0.001 to 0.1 $\mu g\,L^{-1}$ for MA, 0.1–8.0 $\mu g\,L^{-1}$ for BP3, 0.2–10 $\mu g\,L^{-1}$ for Eto and OCR, and 0.01–1.0 $\mu g\,L^{-1}$ for the remaining analytes. The correlation coefficients were better than 0.9919 in all cases. The sensitivity of the method was evaluated as the calibration slopes, which ranged from (0.014 ± 0.001)·10^3 for Eto to (142 ± 8)·10^3 for MA. The LOD values were determined experimentally by performing successive extractions in which the UV filter spiked concentration was decreased until the obtained signal was 3 times higher than the signal-to-noise ratio. Low LOD values between 0.5 and 80 $ng\,L^{-1}$ were achieved.

The reproducibility of the method was evaluated as the relative standard deviation (RSD) by performing both intra-day (n = 4) and inter-day (n = 16 during 4 consecutive days) experiments at a low spiked level (0.010 $\mu g\,L^{-1}$ for MA, 1 $\mu g\,L^{-1}$ for BP3, Eto, and OCR, and 0.1 $\mu g\,L^{-1}$ for the remaining analytes). All experiments performed during both the method optimization and method validation were carried out using different SPs. The SPs were also re-used after cleaning in the SPTC. On the contrary, other HS-extraction techniques such as HS-SPME perform successive extractions of the same extraction material (i.e., the SPME fiber in the case in the cited example) [15]. Acceptable intra-day RSD values ranging from 6.9 to 14% were achieved, demonstrating high reproducibility even when different SPs are used for the same extraction.

To examine whether the developed VASE methodology allows for exhaustive UV filter extraction, successive extractions of the same vial were performed using the optimized VASE-GC-MS methodology. The results, shown in Fig. 5, indicated that exhaustive extraction was

Table 2
Comparison of different extraction methods that used GC-MS for the determination of UV filters.

Type of sample	Extraction method[a]/extraction material or solvent[b]	Reusability of the extraction phase	Possibility of simultaneous extractions	Extraction time	LOD[c] ($ng·L^{-1}$)	RSD[d] (%)	RR[e] (%)	Ref.
Tap and lake water	VASE/Tenax® TA	Yes	Yes	14 h	0.5–80	6.9–14	70.0–120	This work
Tap, lake and pool water	HS-SPME/PA and PILs	Yes	No	40 min	1.1–55	1.6–15	75.3–120	[15]
Sea, pool, river and spa water	DI-SPME/DVB/CAR-PDMS	Yes	No	45 min	0.060–8.2	3.0–18	79.9–106	[30]
River, lake and waste- water	SBSE/PDMS	Yes	Yes	3 h	0.2–63	4.0–16	77.0–125	[31]
River, sea, and pool water	SBSDμE/MNPs	No	Yes	40 min	13–148	2–19	80.0–116	[32]
River, tap, sea, and pool water	USAEME/Chloroform	No	Yes	15 min	0.22–25	2.3–11	69.6–110	[33]

[a] **DI:** Direct immersion, **HS:** Headspace, **SBSDμE:** Stir bar sorptive-dispersive microextraction, **SBSE:** Stir bar sorptive extraction, **SPME:** Solid-phase microextraction, **USAEME:** Ultrasound-assisted emulsification microextraction, and **VASE:** Vacuum-assisted sorptive extraction.
[b] **DVB/CAR-PDMS:** Divinylbenzene/carboxen-polydimethylsiloxane, **MIL:** Magnetic ionic liquid, **MNP:** Magnetic nanoparticle, **PA:** Polyacrilate, **PDMS:** polydimethylsiloxane, and **PIL:** Polymeric ionic liquid.
[c] Limit of detection.
[d] Relative standard deviation of spiked samples.
[e] Relative recovery of spiked samples.

Table 3
Relative recovery obtained after the analysis of spiked tap water and lake water with the VASE-GC-MS method.

Analytes	RR[a] (%)	
	Tap water	Lake water
ES	83.7	72.0
HS1	74.0	95.0
BS	91.8	70.0
HS2	81.5	75.9
BP3	80.8	nd[b]
MA	81.0	90.0
Eto	106	120
EHPABA	89.0	93.6
2EHMC	101	118
OCR	113	110

*Spiked level: 0.010 μg L^{-1} for MA, 1 μg L^{-1} for BP3, Eto, and OCR, and 0.1 μg L^{-1} for the remaining analytes.
[a] Relative recovery, calculated using 3 different pens and performing extractions during the same day (n = 3).
[b] None detected.

achieved after the first extraction for the majority of the UV filters, including ES, BS, HS1, HS2, MA, EHPABA, and 2EHMC. For these analytes, the first extraction represented 91–99% of the total peak area for the 3 successive performed extractions. This result indicates that VASE can be applied with quantitative purposes to large sample volumes (e.g., for further increasing the sensitivity of the method). On the contrary, non-exhaustive extraction procedures such as SPME can only be applied with quantitative purposes for low sample volumes [18]. With regard to the remaining analytes (BP3, Eto, and OCR), the second extraction in Fig. 5 was still significant, likely because these analytes had slower extraction kinetics (see Fig. 3 and Fig. S7 of the SM). The third extraction was very small for these analytes and only represented a 7–21% respect of the total peak area, depending on the analyte.

The VASE method was compared with other methods reported in the literature that employed GC-MS for the determination of UV filters, and the results are shown in Table 2 [15,30–33]. The VASE methodology provided similar LODs, RSDs, and RRs to both solid-phase and stir-bar microextraction methods [15,30–33]. With regards to the lifetime of the extraction sorbent, HS-extraction techniques such as VASE and HS-SPME [15] in general increased the lifetime of the extraction phase and could reduce the possibility of matrix effect in comparison to direct immersion techniques such as DI-SPME [30] and SBSE [31]. In terms of extraction time, VASE allowed for multiple extractions to be performed using different SPs without compromising the reproducibility of the method, in comparison to other extraction techniques, such as SPME, which often require the use of the same fiber for all samples [15,30]. This feature significantly increased the sample throughput of VASE. As an example, Fig. S13 of the SM compares the total analysis time needed for performing 1–60 extractions using the HS-SPME-GC-MS (according to the conditions of reference [15]) and VASE-GC-MS. During method development, the results indicated that HS-SPME is initially more efficient than VASE, but after approximately 25 extractions, both HS-SPME and VASE require the same extraction time. In routine analysis, the VASE throughput surpasses SPME as subsequent extractions are occurring while the previous set of samples is being analyzed in the GC-MS. At the same time, VASE could be considered a slower technique than SBSE [31], a method that also allows for simultaneous extractions with different stir bars. However, it is important to point out that the continuous contact of the extraction phase in the stir with the vial glass normally reduces the lifetime of the stir bar and could cause reproducibility problems. Furthermore, extra steps of conditioning are in general required in SBSE to prevent carry over (i.e., 15 min per stir bar in Ref. [31]) In VASE, SP conditioning can be required (as in this application), but it is not a general requirement [21].

3.3. Analysis of real samples

The developed method was applied for the analysis of two real water samples (tap water and lake water). No analytes were detected in any of the studied samples, which is an encouraging finding due to the possible endocrine disruptive character of some of the studied UV filters [3]. To study the matrix effect that these samples exert in the methodology, the VASE-GC-MS method was applied for the analysis of spiked samples. Table 3 shows the obtained relative recovery (RR) values. Acceptable RR values were achieved for both spiked samples, ranging from 74.0 to 113% and 70.0–120% for tap water and lake water, respectively. The exception was BP3, which was not detected in the spiked lake water. For this analyte, the matrix effect was significant, probably because optimal conditions for BP3 were not applied (i.e the addition of NaH_2PO_4, and the use of longer sampling times, see Fig. S4 of the SM and Fig. 3, respectively).

4. Conclusions

VASE has been applied for the determination of a group of organic UV filters in water samples. The developed VASE technology used commercialized SP traps containing Tenax® TA, which are specially designed for both reduced pressure in-vial extraction and direct thermal desorption via a customized GC inlet.

The data obtained in this study demonstrated that reduced pressure conditions can be maintained for more than 24 h during VASE without loss of vacuum. The extraction kinetics of the studied UV filters was accelerated by the application of vacuum, apart from OCR at longer extraction times. When VASE and the analogous procedure at atmospheric pressure (SAE) are compared, the extraction efficiency of VASE was between 1.3 and 3.1 times higher at the selected optimum sampling time (i.e., 14 h).

The developed VASE methodology was sensitive and allowed for low LODs, ranging from 0.5 to 80 ng L^{-1}. The intra-day RSD, evaluated during 4 consecutive days employing different SPs, was lower than 14% for all analytes studied. The capability to perform reliable analysis with different SPs makes the VASE workflow as efficient as many competing techniques, as the extraction of one set of samples can be performed concurrently with the desorption of another set. Exhaustive extraction was achieved for most analytes within 14 h, with the exception of BP3, Eto, and OCR, which exhibited slower extraction kinetics. VASE-GC-MS was successfully applied for the analysis of spiked tap water and lake water, with RR values between 70.0 and 120%, which demonstrates the reliability of the method for analyzing UV filters in the presence of a complex matrix background.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2019.120390.

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