Ionic liquids-based nanoemulsion for assisted by ultrasound liquid–liquid microextraction of UV-filters in water samples

Cintia J. Fernandez [a], Natalia A. Gomez [a], Gerardo M. Oresti [b], Claudia E. Domini [a,*], Marcos Grünhut [a,*]

[a] INQUISUR (UNS-CONICET), Departamento de Química, Universidad Nacional del Sur, Bahía Blanca, Argentina
[b] INIBIBB (UNS-CONICET), Departamento de Biología, Bioquímica y Farmacia, Universidad Nacional del Sur, Bahía Blanca, Argentina

ARTICLE INFO

ABSTRACT

Organic UV filters can contaminate various bodies of water such as streams, rivers, and seas, and as such, they have been identified as emerging contaminants of relevance in aquatic ecosystems. Therefore, the detection and determination of these compounds at low concentrations from an environmentally friendly perspective are necessary. In this work, an ionic liquids based nanoemulsion for the ultrasound assisted liquid–liquid micro-extraction (ILs-NE/US-LLME) of benzophenone-3, octocrylene, octisalate and octinoxate in different water bodies was reached. The material was based on a mixture of the ionic liquids 1,3-didecyl-2-methylimidazolium chloride and 1-butyl-3-methylimidazolium hexafluorophosphate, and the surfactant Triton X-100. The microextraction process was assisted by ultrasound and was performed using 475 μL of extractant solvent and 10.0 mL of sample, and an optimal preconcentration factor of 100 was achieved. The detection was performed by HPLC-UV in less than 5 min for all analytes. Low detection limits (lower than 2.0 μg L^{-1}) and an optimal precision (RSD lower than 6.7 %) were obtained for the four UV filters. Different water samples (pool, stream, river, sea and a simulated sample) were analyzed and satisfactory recovery values were obtained in all cases (82–119 %). The method was fast (15 min^{-1}) and it presented an optimal value of greenness (0.50) according to the AGREE metric. The extractant material was easily synthesized using a minimum amount of materials. The chromato-graphic procedure for separation and detection of the analytes was simple and fast. Moreover, the method was more environmentally friendly compared to previous work reported in the literature.

1. Introduction

UV organic filters are a reason for attention since they are considered emerging pollutants [1]. In recent years, the use of pharmaceutical and personal care products (PPCPs) containing this kind of compound has increased significantly due to the awareness of skin care to sunlight exposure to avoid diseases, such as skin cancer. Moreover, UV organic filters are also used in paints, plastics, and adhesives to prevent their degradation due to sun exposure [2]. Thus, the increasing use of PPCPs and materials containing these compounds leads to their accumulation in the environment and living organisms [3]. In this sense, UV organic filters can contaminate different water bodies, such as streams, rivers and seas as a result of aquatic recreational activities or due to poor wastewater treatment [4]. In a recent study, D'Amico et al. found traces of sunscreen agents in the snow at the North Pole, including benzophenone-3, octocrylene, ethylhexyl methoxycinnamate and

ethylhexyl salicylate, which had never been identified in Arctic snow before [5,6]. The results showed that the presence of emerging con-taminants in remote areas could be attributed to the role of long-range atmospheric transport. Moreover, the distribution of some of these contaminants varied with altitude. For example, octocrylene and benzophenone-3 were more abundant on glacier tops where they must have travelled from lower latitudes transported by atmospheric circulation.

Adverse effects caused by UV organic filters on aquatic organisms have already been detected, such as alteration in endocrine and hor-monal system functions. Effects on the endocrine system of fish and bioaccumulation in zebrafish (Danio rerio) [7], algae [8], as well as in larvae and embryos of marine invertebrates, [9] have been reported.

One of the most used techniques to determine UV organic filters is the chromatographic technique. In particular, high-performance liquid chromatography (HPLC) provides a satisfactory separation when

---

determining UV filters in environmental samples [10]. However, extraction and preconcentration steps previous to chromatographic analysis must be performed due to the low concentrations of these contaminants in this kind of samples [11]. Liquid-liquid extraction (LLE) is widely utilized for detecting various analytes in low concentrations, both organic and inorganic, due to its simplicity, stability, reproducibility, and low cost. However, the traditional LLE method often necessitates the use of large amounts of potentially toxic organic solvents and is time-consuming. To address these drawbacks, liquid–liquid microextraction (LLME) has been developed as a miniaturized version of LLE. LLME offers advantages such as ease of operation, high enrichment factors, low cost, and reduced use of toxic organic solvents [12]. Considering the principles of green chemistry, the development of an environmentally friendly and non-toxic solvent is essential in LLME techniques [13]. Consequently, several green solvents have emerged, such as deep eutectic solvents [14] and ionic liquids [15].

Ionic liquids (ILs) are organic salts that are in the liquid state at room temperature, and represent an alternative to replace the conventional organic solvents to extract and preconcentrate metal ions [16] and organic analytes [17], among others. These solvents present good physical properties, such as low volatility, high viscosity, excellent stability, and good solubility of both organic and inorganic compounds [10]. Moreover, the combination of ILs with surfactants to form nanoemulsions (NEs) can improve the efficiency and selectivity of the extraction procedure [18]. NEs are a kinetically stable clear dispersion of two immiscible phases, oil phase and water phase, in combination with surfactant molecules. Small particles or droplets, with a size range of 5–200 nm usually comprise the dispersed phase [19]. On the other hand, ultrasound has been implemented to improve the extraction process [20] because this energy is able to increase the contact between the drops of both aqueous and extractant phases achieving a good emulsification and homogenization of the extractant in the sample. In addition, a greater mass transfer of the analytes to the dispersed phase has also been observed [21].

This work proposes the extraction and preconcentration of the UV filters benzophenone-3 (2-hydroxy-4-methoxy benzophenone), octocrylene (2-ethylhexyl 2-cyano-3,3-diphenylacrylate), octisalate (2-ethylhexyl salicylate) and octinoxate (octyl-p-methoxycinnamate) from different water samples, such as pool, stream, river and sea through the liquid–liquid microextraction technique assisted by ultrasound energy and using as extracting material a new nanoemulsion based on a mixture of two ionic liquids (short and long chain) and a non-ionic surfactant.

2. Material and methods

2.1. Reagents and solutions

All solutions were prepared using analytical grade reagents and ultrapure water (18 MΩ cm^{-1}). The organic UV filters benzophenone-3 (BZ3), octinoxate (OMC), octocrylene (OCR) and octisalate (EHS) were obtained from Parafarm (Argentina). Stock solutions (1000 mg L^{-1}) of each UV filter were prepared by dissolving the appropriate quantity of each analyte in 5.00 mL of methanol (Dorwil, Argentina). Standard solutions were obtained by appropriate dilutions of the stock solution with methanol. The ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF6), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF4), 1,3-didecyl-2-methylimidazolium chloride ([DDmim]Cl) and 1-decyl 3-methylimidazolium chloride ([Dmim]Cl), and the surfactant Triton X-100 (TX-100) were acquired from Merck (Germany). The buffer solution (pH = 2.0) was obtained by mixing solutions 0.20 mol L^{-1} of boric acid (Cicarelli, Argentina), 0.20 mol L^{-1} of acetic acid (Cicarelli, Argentina), and 0.20 mol L^{-1} of phosphoric acid (Cicarelli, Argentina) in appropriate proportions. Sodium chloride (Cicarelli, Argentina) and hydrochloric acid (Anedra, Argentina) were used to adjust the ionic strength and pH of the samples, respectively. HPLC-grade ultrapure acetonitrile (UVE, Argentina) was used for the

chromatographic procedure.

2.2. Apparatus and software

A Sonics Vibra Cell model VCX 130 ultrasonic probe (USA) provided by a titanium probe tip (9.5 mm diameter, 20 kHz frequency and 130 W nominal power) was used for the extraction process. The quantification of the UV filters was carried out in an Agilent model 1260 Infinity HPLC system (USA) with a UV detector equipped with an Eclipse Plus C18 reverse phase column (3.5 μm spherical particles coated with octadecylsilane, 100 × 4.6 mm) provided by Agilent (USA). An Adwa model AD32 conductivity meter (Hungary) and an Orion model 710 A pH meter (USA) with Orion Ross® model 81–02 electrode (USA) were used for conductivity and pH measurements, respectively. In addition, an Arcano model DTL80 centrifuge (China) and a Hanna magnetic stirrer model HI 190 M (USA) were used during the analytical procedure. Average droplet size (Z) and polydispersity index (PdI) were measured by dynamic light scattering (DLS) using a Malvern Zetasizer Nano Series instrument (UK) and calculated by the Zetasizer 7.13 software (UK) using the time correlation function. The experimental design data processing was performed using the Statgraphics Plus 5.1 program (USA).

2.3. Preparation and characterization of the extractant material

The ionic liquids based nanoemulsion (ILs-NE) used as extractant material was prepared by mixing 2.0 mL of the [DDmim]Cl (2.0 g%) with 5.6 mL of a mixture containing [Bmim]PF6 (4.7 g%) and Triton X-100 (6.9 g%) under constant stirring for 5.0 min. The dispersed system was analyzed by the DLS technique in order to obtain the Z and PdI values. For this, a 10-fold dilution of the ILs-NE in ultra-pure water was performed. Then, the sample was magnetically stirred for 5.0 min and the measurements were carried out at 25 °C, in an optical quality 4.0 mL borosilicate cell and at 90° angle. Moreover, the turbidity or phase separation of the material was evaluated by visual inspection during a period of seven days at room temperature (25 °C).

2.4. Extraction and preconcentration procedure

The extraction and preconcentration of the UV filters (BZ3, OMC, OCR and EHS) were carried out by an ionic liquids based nanoemulsion for the ultrasound assisted liquid–liquid microextraction (ILs-NE/US-LLME). 10.0 mL of sample (or standard) were placed in a plastic centrifuge tube and then 500 μL of buffer solution (0.20 mol L^{-1}; pH = 2.0), 475 μL of ILs-NE and NaCl up to a final concentration of 1.0 % were added. Immediately after, the ultrasound probe was inserted into the tube and sonicated at 117 W for 150 s (40 s ON and 20 s OFF). During this period of time, the cloud point was reached and the analytes migrated from the aqueous phase to the NE fine droplets. Upon completion of sonication, the extractant material was quickly centrifuged at 3500 rpm for 120 s and the phases were separated. Then, the phase containing the analytes was dissolved in methanol up to a final volume of 100 μL to decrease the viscosity and achieve a sufficient volume to the HPLC analysis without a significant dilution of the analytes. A schematic diagram of the procedure is shown in Fig. 1.

2.5. Experimental design

A saturated Plackett-Burman experimental design was used to identify the significant variables that affect the extraction of the UV-filters [22]. This design allows evaluating up to N-1 factors, where N is the number of experiments, with two levels for each variable studied (low and high). In our case, a total of twelve experiments were carried out of which six correspond to independent parameters or real factors (NaCl concentration, ultrasound time, ultrasound cycles, ultrasound power, extractant concentration and centrifuge time) and five to fictitious factors or dummies. The experiments were performed randomly to
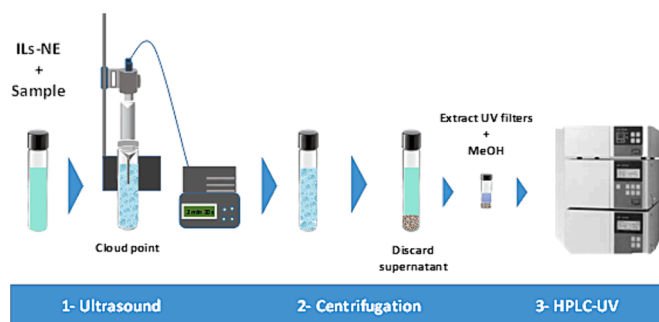
Fig. 1. Schematic representation of the extraction, preconcentration and detection procedure of UV filters using ionic liquids based nanoemulsion for the ultrasound assisted liquid–liquid microextraction (ILs-NE/US-LLME).

reduce the effect of unknown variables and/or systematic errors. The values of the real factors studied in low (−) and high (+) levels can be seen in Table S1. Once the significant variables were selected, a full-factorial experimental design was carried out in order to obtain the optimal value for each variable in the extraction process. All experiments were performed using 10.0 mL of a synthetic sample containing the UV-filters in a concentration of 20.0 µg L^{-1}.

2.6. Chromatographic procedure

The quantification of the UV filters in the different analyzed samples was carried out by the HPLC technique. Gradient elution of acetonitrile and ultrapure water was used as the mobile phase starting at a ratio of 90:10 (v/v) to 10:90 (v/v) at 7 min, and controlled by activating quaternary pumps at 40 °C. The flow rate was 0.50 mL min^{-1} and the volume of the sample injected was 20 µL. The detector operated at λ = 307 nm. Under these conditions, tailless and well-resolved chromatographic peaks were obtained for each analyte.

2.7. Samples

Pool, stream, river and sea water samples were analyzed by the proposed methodology considering the probable presence of the studied UV-filters. Sample A and sample B were collected in the region of Bahía Blanca, Buenos Aires province, Argentina. Sample A was obtained from a private pool (38° 41 '46″ S, 62° 13′ 1″ W), while sample B was collected from the Sauce Chico stream (38° 42 '8″ S, 62° 27′ 27″ W). On the other hand, sample C and sample D were collected in the region of Viedma, Río Negro province, Argentina. Sample C was obtained from Río Negro river (40° 47′ 59″ S, 62° 59′ 51″ W), while sample D was collected in El Cóndor sea coast (41° 3′ 30″ S, 62° 50′ 12″ W). Fig. S1 shows the geographical location of the sampling sites with their respective coordinates. Additionally, a simulated sample (sample E) was prepared in the laboratory by application of a commercial sunscreen (Dermaglós SOLAR FPS 50) on the hands of a volunteer and exposed to the sun for 40 min. Then, the volunteer rinsed their hands in 1.8 L of distilled water. This sample was considered for further analysis. All samples were filtered using a Whatman quantitative paper filter (pore size: <2 µm) to eliminate the solid material suspended, and were stored at 4 °C in amber glass bottles until analysis.

3. Results and discussion

3.1. Preparation and characterization of the extractant material

Different ILs, such as [Bmim]PF₆, [Bmim]BF₄, [DDmim]Cl and [Dmim]Cl were tested to obtain an optimal extractant material. The ILs [Bmim]PF₆ and [Bmim]BF₄ present short carbon chains (n = 4), while [DDmim]Cl and [Dmim]Cl present long carbon chains (n = 10).

However, [Bmim]PF₆ and [Bmim]BF₄ are lipophilic, and both present a good affinity by the organic UV-filters. The ILs were combined in different proportions and in the presence of surfactant (TX-100), and evaluated taking into account the ability to form the cloud point, the possibility of separating the extractant phase after sonication, and the extraction efficiency of the analytes. A total of eight extractant materials (EM1-EM8) were tested (Table S2), and an extractant material formed by 2.0 g% of [DDmim]Cl (n = 10), 4.7 g% of [Bmim]PF₆ (n = 4) and 6.9 g% of Triton X-100 was selected. Since it was possible to form the cloud point, a good separation of extracting-aqueous phases was achieved, and good relative recovery percentages for all the UV-filters were obtained.

On the other hand, the extractant material was transparent and stable over time with no evidence of turbidity or separation of phases, suggesting the formation of a NE. This fact was confirmed by DLS, a technique that makes it possible to determine the size distribution and obtain the PdI, which is the ratio of standard deviation to mean droplet size. PdI values between 0.10 and 0.25 indicate a narrow size distribution whereas a PdI > 0.50 indicates a very broad distribution. As shown in Fig. S2, the extractant material exhibited a Z value of 14.9 nm and a lower value of PdI (0.24). This finding indicated that the NE tended to approach monodispersion and become stable systems due to the uniformity in the drops.

3.2. Chromatographic method

A chromatogram corresponding to a sample containing the four UV-filters is shown in Fig. 2. As it can be seen, retention times of 1.50 min for BZ3, 3.16 min for OMC, 3.52 min for OCR and 4.45 min for EHS were obtained in each case. It is important to note that the time of analysis was lower than 5.0 min, contributing to minimization of both energy and solvent consumption. The subsequent quantification of the analytes was carried out by the univariate method using the area of the corresponding chromatographic peak as the analytical signal. Additionally, the chromatograms of a sample (C) and of this sample spiked with the four filters at a concentration of 20 µg L^{-1} are shown in Fig. S3.

3.3. Optimization

Once the extractant material was established, an exploratory analysis of some variables related to the extraction process was carried out. The optimization of the variables was performed using as response the extraction recovery (ER%) defined as (Eq. (1)):

$$ER\% = \frac{n_{EP}}{n_0} \times 100\% = \left(\frac{C_{EP} \times V_{EP}}{C_0 \times V_0}\right) \times 100\% \qquad (1)$$

where n_0 is the total amount of the analyte and n_{EP} is the total amount of the analyte that was extracted in the extractant phase, C_{EP} corresponds to the concentration of the analyte in the extractant phase and V_{EP} to the volume of this phase, C_0 is the initial concentration of the analyte in the sample and V_0 the volume of the sample solution. C_{EP} was calculated from calibration curves obtained for each analyte using HPLC methodology.

3.3.1. Preliminary assays

The effect of the temperature during the phase separation step was studied. In particular, the extraction at low temperature was evaluated to verify if a solid phase is formed and it facilitates the separation of the extractant material containing the analytes from the sample, as is reported by [23,24]. For this, the extraction at low temperature (0.5–1 °C) was performed using an ice bath and compared with an extraction at room temperature (25 °C). In both cases, the extractant phase was easily separated from the sample, and the recovery results were similar. Thus, in our case it was not necessary to cool the extract during the separation process.

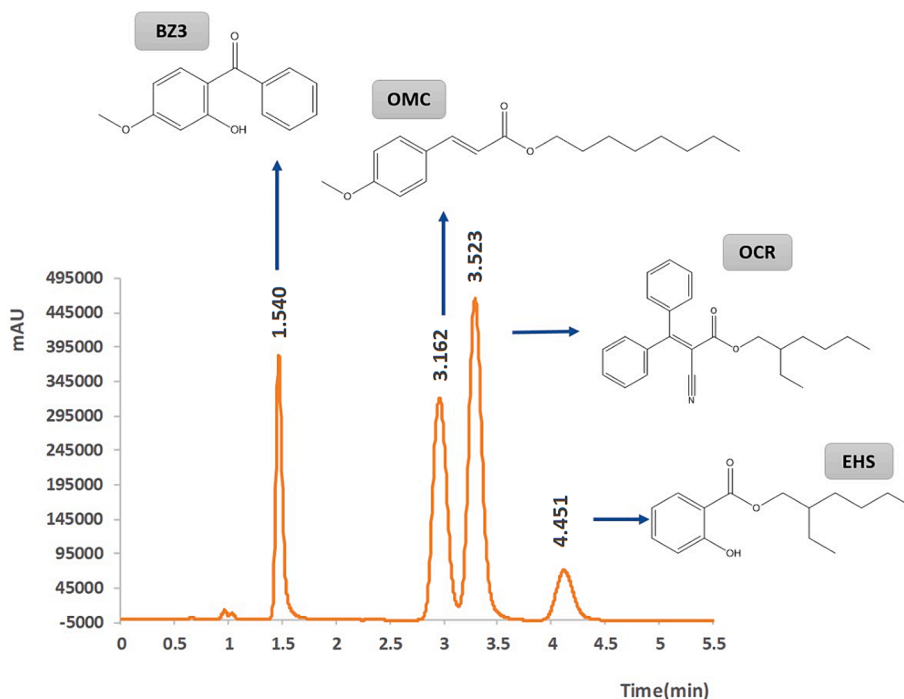On the other hand, the effect of the pH during the extraction process

Fig. 2. Chromatogram corresponding to the separation of the four studied UV filters by HPLC. Retention times of 1.50 min for benzophenone-3 (BZ3), 3.16 min for octyl-p-methoxycinnamate (OMC), 3.52 min for 2-ethylhexyl 2-cyano-3, 3-diphenyl acrylate (OCR) and 4.45 min for ethylhexyl salicylate (EHS) were achieved. The molecular structure of each organic UV filter is also shown.

was studied in the range 3.0–6.0 due to the fact that in this range the UV filters are not ionized. In particular, BZ3 (pKa = 7.56) and EHS (pKa = 8.13) are weak acids that would facilitate the migration to the oily phase of the extractant material if they are in a neutral form [25,26].

As it can be seen in Fig. 3, a more efficient extraction for all the UV-filters was obtained at pH 3.0, which was in accordance with previously reported studies [27].

3.3.2. Experimental design

3.3.2.1. Plackett-Burman. As mentioned in section 2.5, NaCl concentration (g%), ultrasound time (s), ultrasound cycles (s/s), ultrasound power (W), ILs ratio and centrifuge time (s) were studied in two levels (low and high). Significance of the variable effects were evaluated using a test-t. The effect value of the variable was compared with a critical effect (E_{crit}), obtained with a standard error estimated using the dummies and a t value (2.571). Effects higher than their corresponding E_{crit} were considered as significant [28]. The Pareto charts plotted in Fig. 4 show the variable effects (represented by bars) and the E_{crit} values (vertical lines) for each UV-filter. In the case of BZ3, the only significant variable was the ultrasound time at high level (210 s). For OMC, OCR
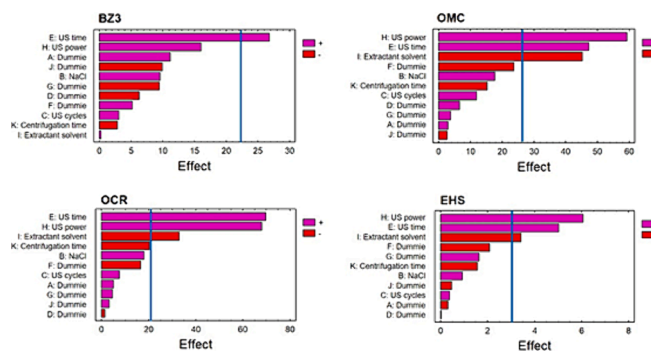

Fig. 3. Effect of the pH in the extraction process of BZ3, OMC, OCR and EHS.

Fig. 4. Paretto charts corresponding to the Plackett-Burman experimental design. The critical effects (E_{crit}) were 22.2 for BZ3, 28.7 for OMC, 20.9 for OCR and 3.09 for EHS.

and EHS the variables ultrasound time and power at high level (210 s and 117 W, respectively) and ILs ratio at low level (0.3:1) were significant. On the other hand, NaCl concentration, ultrasound cycles and centrifugation time were not significant at the studied levels. Based on these results, only the variables ultrasound time and ILs ratio were selected to continue with the optimization study since ultrasound power was fixed at 117 W, the maximum power value at which the ultrasound probe operates. The response surface corresponding to the selected variables are shown in Fig. 5 and the statistical data are showed in Table S3.

3.3.2.2. Full-factorial. According to the results obtained in the Pluckett-Burman design, the variables ultrasound time and ILs ratio were studied using a two-level full factorial design (2^2). Thus, a total of four experiments in triplicate were performed. The ultrasound time was evaluated between 150 s (low level) and 240 s (high level), and the ILs ratio was considered between 0.2 DDmimCl:1.0 BmimPF₆ (low level) and 0.36 DDmimCl: 1.0 BmimPF₆ (high level). Fig. 6 shows the effect of each
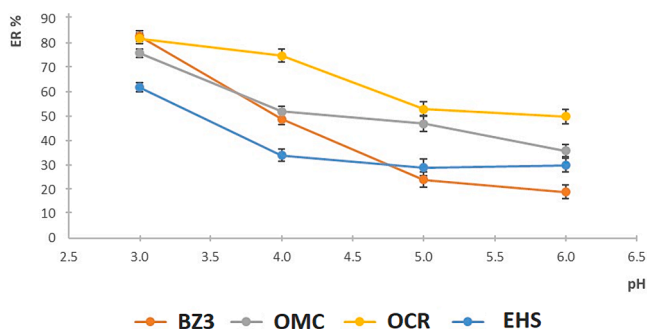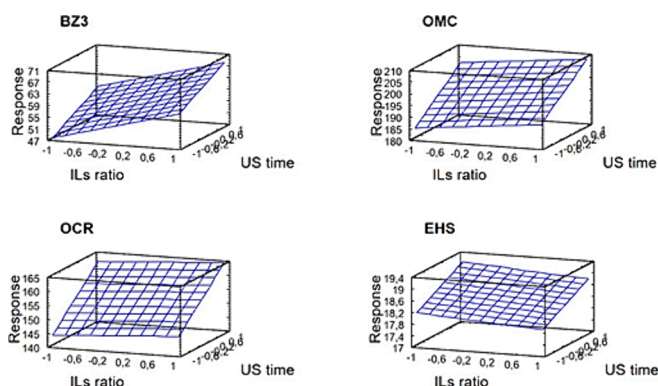
Fig. 5. Estimated response surfaces corresponding to the selected variables (ultrasound time and ILs ratio) for the four UV filters by application of the Plackett-Burman experimental design.
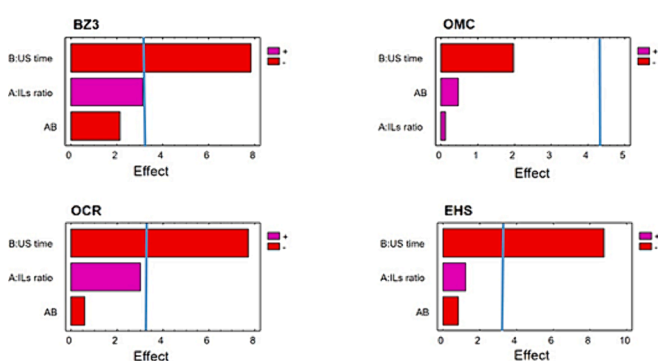

Fig. 6. Paretto charts corresponding to the full-factorial experimental design. The critical effects (E$_{crit}$) were 3.2 for BZ3, 4.25 for OMC, 3.23 for OCR and 3.18 for EHS.

variable and their interaction for the four UV filters. The optimal values for ultrasound time was 150 s and for ILs ratio a relation of 0.36 DDmimCl: 1.0 BmimPF$_6$ (Fig. 7). In the case of the ultrasound time, a longer time probably generates an increase in temperature that decreases the extraction efficiency. For ILs ratio, the higher ratio contains a greater amount of long chain IL (DDmimCl), which also contributes to a better extraction of lipophilic UV filters.

3.4. Analytical performance

Table 1 shows the figures of merit of the proposed method. As it can be seen, a wide linearity interval between 2.0 and 50.0 µg L^{-1} was
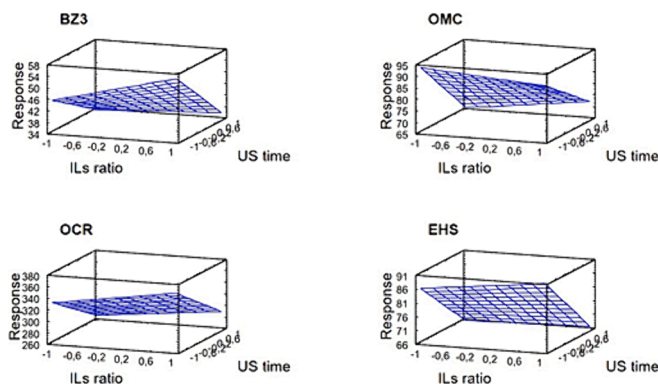

Fig. 7. Estimated response surfaces (ultrasound time and ILs ratio) for the four UV filters corresponding to the full-factorial experimental design.

Table 1
Statistic values and analytical performance of the proposed ILs-NE/US-LLME method.

	BZ3	OMC	OCR	EHS
Calibration Curve				
Intercept	25.786 ± 2.720	1.332 ± 0.680	7.929 ± 2.398	4.958 ± 0.663
Slope (L µg^{-1})	5.086 ± 0.109	3.160 ± 0.063	14.257 ± 0.082	1.011 ± 0.023
R^2	0.998	0.998	0.999	0.998
Analytical performance				
Linearity interval (µg L^{-1})	6.0–50.0	2.5–50.0	2.0–50.0	6.5–50.0
LOD (µg L^{-1})	1.6	0.64	0.5	1.9
LOQ (µg L^{-1})	5.3	2.1	1.7	6.4
Extraction efficiency (%)	93	100	96	94
Preconcentration factor		100		
Inter-day precision[a] (RSD%)	5.1	4.3	4.2	6.5
Intra-day precision[b] (RSD%)	5.3	5.4	3.7	6.7

[a] n = 5.
[b] n = 5; k = 3.

obtained for OCR and 2.5 and 50.0 µg L^{-1} was obtained for OMC, while a slightly smaller intervals were obtained for BZ3 (6.0–50.0 µg L^{-1}) and EHS (6.5–50.0 µg L^{-1}). Moreover, limits of detection (LODs) and limits of quantification (LOQs) were calculated as 3*(s/S) and 10*(s/S), respectively, where s corresponds to the standard deviation of the regression equation and S to its slope [29]. Intra-day precision and inter-day precision were expressed as percentage of relative standard deviation (RSD%). Intra-day precision was calculated from five replicates (n = 5) of solutions containing a concentration of 20 µg L^{-1} of each UV-filter while inter-day precision was calculated from replicates (n = 5) made on 3 different days (k = 3). In all cases, the RSDs% were lower than 7.0 %, which was satisfactory. Finally, the preconcentration factor (PF) was 100 and it was calculated as the ratio between the final concentration of each analyte in the extractant phase (C$_{EP}$) at the end of the extraction and the initial concentration of the analyte in the sample (C$_0$) (Eq. (2)):

$$PF = C_{EP}/C_0 \qquad (2)$$

3.5. Analysis of samples

In order to evaluate the applicability of the proposed method, four water samples from different origins were analyzed (section 2.7). No residues of BZ3, OMC, OCR and EHS were found in the selected samples above the LODs of the method. In the case of the simulated sample (sample E), concentrations of 25.1, 18.6, 26.2 and 22.7 µg L^{-1} of BZ3, OMC, OCR and EHS were found, respectively (Table 2).

On the other hand, the accuracy of the proposed method was evaluated by a recovery study. Thus, all samples (A-E) were spiked at two concentration levels (7.0 µg L^{-1} and 20.0 µg L^{-1}) by adding the corresponding volumes of standard solutions of each UV-filter. Then, the fortified samples were treated as described, and the extract introduced into the HPLC system for their analysis. The relative recovery (RR%) was calculated as (Eq. (3)):

$$RR\% = \left(\frac{C_{cal} - C_{real}}{C_{add}} \right) \times 100 \qquad (3)$$

where C$_{cal}$ is the concentration of the analyte found in the fortified sample, C$_{real}$ is the concentration of the analytes in the real sample, and C$_{add}$ is the known concentration of the standard added to the sample. As it can be seen in Table 2, the results of the recovery study ranged from

Table 2
Sample analysis and recovery study by applying the proposed ILs-NE/US-LLM procedure.

Sample	C_{add} (µg L^{-1})	BZ3		OMC		OCR		EHS	
		C_{cal}[a] (µg L^{-1})	RR%	C_{cal}[a] (µg L^{-1})	RR%	C_{cal}[a] (µg L^{-1})	RR%	C_{cal}[a] (µg L^{-1})	RR%
A	0	n.d.	–	n.d.	–	n.d.	–	n.d.	–
	7.0	5.9 ± 0.8	84.6	6.5 ± 0.7	92.2	6.4 ± 0.5	91.4	6.1 ± 0.5	87.5
	20.0	20.1 ± 1.8	100.5	20.0 ± 0.8	99.8	21.8 ± 1.3	108.9	16.6 ± 1.9	83.0
B	0	n.d.	–	n.d.	–	n.d.	–	n.d.	–
	7.0	6.5 ± 0.3	92.6	6.2 ± 0.3	88.9	6.8 ± 0.3	97.5	7.0 ± 0.2	100.1
	20.0	21.0 ± 1.7	104.9	17.2 ± 0.7	85.8	19.9 ± 2.2	99.3	18.9 ± 2.5	94.5
C	0	n.d.	–	n.d.	–	n.d.	–	n.d.	–
	7.0	6.3 ± 0.9	90.4	6.2 ± 0.9	88.5	6.1 ± 0.5	87.1	6.9 ± 0.3	99.2
	20.0	18.5 ± 1.3	92.7	19.1 ± 0.2	95.3	20.0 ± 2.4	99.8	19.7 ± 1.0	98.4
D	0	n.d.	–	n.d.	–	n.d.	–	n.d.	–
	7.0	7.7 ± 0.8	110.2	8.0 ± 1.0	114.5	7.2 ± 1.1	103.2	7.0 ± 0.3	100.2
	20.0	16.4 ± 1.9	81.9	23.7 ± 1.3	118.7	20.8 ± 0.6	104.2	21.4 ± 2.2	106.8
E	0	25.1 ± 1.9	–	18.6 ± 0.6	–	26.2 ± 0.4	–	22.7 ± 1.0	–
	7.0	32.3 ± 5.8	103.5	26.5 ± 3.7	113.1	37.8 ± 0.5	119.9	29.3 ± 1.8	93.6
	20.0	44.6 ± 4.0	97.6	38.4 ± 1.4	99.0	47.7 ± 2.4	107.5	40.2 ± 4.6	87.5

A: private pool; B: Sauce Chico stream; C: Rio Negro river; D: El Cóndor sea coast; E: simulated sample; C_{add}: known concentration added to the sample; C_{cal}: concentration of the analyte found in the fortified sample; n.d.: no detected; RR%: relative recovery.

[a] The samples were analyzed in triplicate (n = 3) and the standard deviation is indicated.

81.9 to 110.2 % for BZ3, 85.8 to 118.7 % for OMC, 87.1 to 119.9 % for OCR and 83.0 to 106.8 % for EHS. These values were satisfactory, demonstrating the capacity and the versatility of the method to be applicable to complex samples even when they have a high ionic strength, as is the case with sea water samples.

3.6. Comparison and advantages of the proposed method

Different methods for the extraction and determination of different UV filters are presented in Table 3. The comparison was performed in terms of different analytical parameters, such as, extraction and detection times, preconcentration factor (PF), precision, recovery percentages and limit of detection (LOD). The proposed ILs-NE/US-LLME method

presented the lowest time of analysis per sample, which was 10 min (including extraction and detection times) in comparison to the other cited works, which varied from 16 to 108 min [30]. Moreover, the PF (100) was comparable with other methods that use ionic liquids as extractant material [31]. Although other methods (non-ionic liquid based) showed higher PF values, a high volume of sample (50 mL) [32] and a long time of analysis (higher than 50 min) were necessary for the preconcentration process [30,33]. Moreover, optimal accuracy, precision and LODs were obtained by the proposed method. So, recoveries were comparable to other methods based on LLME [10,33,34] and cloud point extraction [32], and were better than works based on solid phase microextraction [30]. In the case of precision and LODs, the obtained values, less than 7.0 % and 2.0 µg L^{-1} for the different UV-filters, were

Table 3
Comparative table of the proposed ILs-NE/US-LLME method with different works for determination of UV chemical filters in water samples.

UV filters	Sample	Volume (mL)	Method	Extraction (min)	Detection (min)	PF	RR%	Repeatability (RSD%)	LOD (µg L^{-1})	Ref.
BZ3, DHB, BZ8, THB	Sea	5	DLLME-GC–MS	3	53	83	65–222	5.6–6.2	0.032–0.050	[33]
BZ, HMB, DHMB	Pool, lake, waste	5	UDSA-IL-DLLM	6	10	125	92–120	1.0–1.8	0.20–1.30	[34]
BZ3, OMC, E232, E6300, E9020	Tap, pool, lake	50	CPE HPLC-UV	30	20	500	95–102	not reported	0.14–1.27	[32]
BZ3, MBC, OCR, EDB, EHS, HMS	Pool, sea	3.5	In-syringe MSA-DLLME-HPLC	5.5	12	25	86–114	4.0–6.0	0.08–12.0	[10]
BZ3, BS, OMC, EDB, EHS, ETO, OCR, HMS, BMDM	Tap, pool, lake	10	DI-SPME	75–98	12	200–300	54–124	not reported	0.1–5.0	[30]
BZ3, OCR, OMC, EHS	Pool, stream, river, sea	10	ILs-NE/US-LLME	4.5	5	100	80–118	4.2–6.5	0.64–1.90	This work

BZ3: 2-hydroxy-4-methoxybenzophenone; DHB: 2,4-dihydroxybenzophenone; BZ8: 2,2-dihydroxy-4-methoxybenzophenone; THB: 2,3,4-trihydroxybenzophenone; BZ: benzophenone; E232: 2-phenylbenzimidazol-5-sulfonic acid; E6300: 3-(4-methylbenzyldene)-camphor; OMC: octyl p-methoxy cinnamate; E9020: 1-(4-*tert*-butylphenyl)-3-(4-methoxyphenyl)1,3 propanedione; MBC: 3-(4methylbenzylidene)-camphor; EDB: 2-ethylhexyl-4-dimethylaminobenzoate; EHS: ethylhexyl salicylate; HMS: homosalate; OCR: 2-ethylhexyl-2-cyano-3,3-diphenylacrylate; BS: benzyl-salicylate; ETO: etocrylene; BMDM: avobenzone; DLLME-GC–MS: dispersive liquid–liquid microextraction followed by gas chromatography-mass spectrometry; UDSA-IL-DLLME: Up-and-down shaker-assisted ionic-liquid-based dispersive liquid–liquid microextraction; CPE HPLC-UV: cloud point extraction coupled with high-performance liquid chromatography and UV detector; In-syringe MSA-DLLME-HPLC: in syringe magnetic stirring assisted-dispersive liquid–liquid microextraction coupled with high-performance liquid chromatography; DI-SPME: direct immersion solid-phase microextraction; ILs-NE/US-LLME: ionic liquids based nanoemulsion for the ultrasound assisted liquid–liquid microextraction; PF: preconcentration factor; RR%: relative recovery; RSD%: relative standard deviation.

comparable to the cited works.

3.7. Green approach

The greenness of the proposed method was evaluated by applying the AGREE [35]. This methodology provides an analytical greenness estimation calculator based on the twelve principles of the green analytical chemistry (GAC). Fig. S4 shows the colored pictogram corresponding to the proposed ILs-NE/US-LLME method and other chromatography-based methods. As it can be seen, a numerical value of 0.50 was obtained for the proposed method, complying with 9 of the 12 total principles of green chemistry. Points 3, 5 and 10 were not green (red in color), and this was related to the fact that the detection equipment operates in an off-line position (point 3), the method is manual and not miniaturized (point 5), and the reagents were not obtained from natural sources (point 10). However, the obtained value was acceptable and higher than other chromatographic methods to determine UV filters in water samples. In such cases, the values differ significantly from the ideal value of greenness (ideal value = 1). This is mainly due to the points detailed in Table S4, which highlights the use of derivatizing agents [36–38], a greater number of steps in sample treatment [39], the use of a chromatograph coupled to a mass detector which implies a higher energy consumption [40], the use of a large volume of sample [32], a greater amount of reagents with high toxicity, and a high time of analysis [40,41]. Then, although low LODs were obtained and several analytes were simultaneously determined, scores lower than 0.34 were obtained by the AGREE metric.

4. Conclusion

The combination of two ionic liquids with different polarities and a surfactant in low concentration allowed the synthesis of a nanoemulsion capable of extracting and pre-concentrating from water samples four lipophilic UV filters which are currently considered emerging contaminants. The extractant material was easily synthesized and the chromatographic procedure for separation and detection of the analytes was simple and fast. The analytical performance of the method was satisfactory, and some aspects were improved with respect to other reported methods. The method was appropriate for the analysis of different kinds of water samples including pool, stream, river, and sea water. In comparison to other chromatographic methodologies, the proposed method presented a lower environmental impact.

CRediT authorship contribution statement

Cintia J. Fernandez: Formal analysis, Investigation, Writing – original draft. **Natalia A. Gomez:** Formal analysis, Investigation, Writing – original draft. **Gerardo M. Oresti:** Investigation. **Claudia E. Domini:** Conceptualization, Funding acquisition, Investigation, Supervision. **Marcos Grünhut:** Conceptualization, Funding acquisition, Investigation, Supervision, Writing – review & editing.

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.

Data availability

Data will be made available on request.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2024.111007.

References

[1] C. Juliano, G.A. Magrini, Cosmetic ingredients as emerging pollutants of environmental and health concern. A mini-review, Cosmetics 4 (2017) 11, https://doi.org/10.3390/cosmetics4020011.

[2] J. Kockler, M. Oelgemöller, S. Robertson, B.D. Glass, Photostability of sunscreens, J. Photochem. Photobiol. C 13 (2012) 91–110, https://doi.org/10.1016/j.jphotochemrev.2011.12.001.

[3] C. Yücel, H. Ertaş, F.N. Ertaş, I. Karapinar, Development of a solid phase microextraction gas chromatography tandem mass spectrometry method for the analysis of UV filters, Microchem. J. 200 (2024) 110247, https://doi.org/10.1016/j.microc.2024.110247.

[4] H. Zhao, D. Wei, M. Li, Y. Du, Substituent contribution to the genotoxicity of benzophenonetype UV filters, Ecotoxicol. Environ. Saf. 95 (2013) 241–246, https://doi.org/10.1016/j.ecoenv.2013.05.036.

[5] M. D'Amico, A. Gambaro, C. Barbante, E. Barbaro, L. Caiazzo, M. Vecchiato, Occurrence of the UV-filter 2-Ethylhexyl 4-methoxycinnimate (EHMC) in Antarctic snow: First results, Microchem. J. 183 (2022) 108060, https://doi.org/10.1016/j.microc.2022.108060.

[6] M. D'Amico, R. Kallenborn, F. Scoto, A. Gambaro, J.C. Gallet, A. Spolaor, M. Vecchiato, Chemicals of Emerging Arctic Concern in north-western Spitsbergen snow: Distribution and sources, Sci. Total Environ. 908 (2024) 168401, https://doi.org/10.1016/j.scitotenv.2023.168401.

[7] K.L. Kinnberg, G.I. Petersen, M. Albrektsen, M. Minghlani, S.M. Awad, B.F. Holbech, H. Holbech, Endocrine-disrupting effect of the ultraviolet filter benzophenone-3 in zebrafish, Danio rerio, Environ. Toxicol. Chem. 34 (2015) 2833–2840, https://doi.org/10.1002/etc.3129.

[8] R. Rodil, M. Moeder, R. Altenburger, M. Schmitt-Jansen, Photostability and phytotoxicity of selected sunscreen agents and their degradation mixtures in water, Anal. Bioanal. Chem. 395 (2009) 1513–1524, https://doi.org/10.1007/s00216-009-3113-1.

[9] H. Falfushynska, E.P. Sokolov, K. Fisch, H. Gazie, D.E. Schulz-Bull, I.M. Sokolova, Biomarker-based assessment of sublethal toxicity of organic UV filters (ensulizole and octocrylene) in a sentinel marine bivalve Mytilus edulis, Sci. Total Environ. 798 (2021) 149171, https://doi.org/10.1016/j.scitotenv.2021.149171.

[10] M. Rezaee, Y. Assadi, M.R.M. Hosseini, E. Aghaee, F. Ahmadi, S. Berijani, Determination of organic compounds in water using dispersive liquid-liquid microextraction, J. Chromatogr. A 1116 (2006) 1–9, https://doi.org/10.1016/j.chroma.2006.03.007.

[11] S. Bahar, R. Zakerian, Speciation of Fe(II) and Fe(III) by using Dispersive Liquid-Liquid Microextraction and Flame Atomic Absorption Spectrometry, J. Braz. Chem. Soc. 23 (2012) 944–950, https://doi.org/10.1590/S0103-50532012000500021.

[12] X.L. Xu, B. Wang, Y.W. Liu, W.X. Li, J.Y. Wu, H. Yuan, D. Chen, In-pipette-tip natural-feather-supported liquid microextraction for conveniently extracting hydrophobic compounds in aqueous samples: A proof-of-concept study, Microchem. J. 185 (2023) 108274, https://doi.org/10.1016/j.microc.2022.108274.

[13] D. Yang, Y. Wang, J. Peng, C. Xun, Y. Yang, A green deep eutectic solvents microextraction coupled with acid-base induction for extraction of trace phenolic compounds in large volume water samples, Ecotox. Environ. Safe 178 (2019) 130–136, https://doi.org/10.1016/j.ecoenv.2019.04.021.

[14] A. Jouyban, M.A. Farajzadeh, M.R.A. Mogaddam, F. Khodadadeian, M. Nemati, M. Khoubnasabjafari, In-situ formation of a hydrophobic deep eutectic solvent based on alpha terpineol and its application in liquid-liquid microextraction of three β-blockers from plasma samples, Microchem. J. 170 (2021) 106687, https://doi.org/10.1016/j.microc.2021.106687.

[15] A. Akhtar, T.G. Kazi, H.I. Afridi, J.A. Baig, M. Khan, Simultaneous preconcentration of toxic elements in eye makeup products through single drop ionic liquid based non-dispersive microextraction method using narrow glass column: Multivariate application, Microchem. J. 157 (2020) 104963.

[16] C.J. Fernandez, C.E. Domini, M. Grünhut, A.G. Lista, A soft material for chromium speciation in water samples using a chemiluminescence automatic system, Chemosphere 196 (2018) 361–367, https://doi.org/10.1016/j.chemosphere.2017.12.178.

[17] M.L. Polo-Luque, B.M. Simonet, M. Valcárcel, Ionic liquid combined with carbon nanotubes: a soft material for the preconcentration of PAHs, Talanta 104 (2013) 169–172, https://doi.org/10.1016/j.talanta.2012.10.025.

[18] S.A. Arain, T.G. Kazi, H.I. Afridi, M.S. Arain, A.H. Panhwar, N. Khan, F. Shah, A new dispersive liquid-liquid microextraction using ionic liquid based microemulsion coupled with cloud point extraction for determination of copper in serum and water samples, Ecotoxicol. Environ. Saf. 126 (2016) 186–192, https://doi.org/10.1016/j.ecoenv.2015.12.035.

[19] P. Shah, D. Bhalodia, P. Shelat, Nanoemulsion: A pharmaceutical review, Syst. Rev. Pharm. 1 (2010) 24–32.

[20] J.L. Benedé, A. Chisvert, A. Salvador, D. Sánchez-Quiles, A. Tovar-Sánchez, Determination of UV filters in both soluble and particulate fractions of seawaters by dispersive liquid-liquid microextraction followed by gas chromatography-mass spectrometry, Anal. Chim. Acta 812 (2014) 50–58, https://doi.org/10.1016/j.aca.2013.12.033.

[21] B. Sajjadi, S. Asgharzadehahmadi, P. Asaithambi, A.A.A. Raman, R. Parthasarathy, Investigation of mass transfer intensification under power ultrasound irradiation using 3D computational simulation: A comparative analysis, Ultrason. Sonochem. 34 (2017) 504–518, https://doi.org/10.1016/j.ultsonch.2016.06.026.

[22] X. Guo, W. Jiang, D. Du, X. Shang, Plackett-Burman experimental design of modified wood ceramics for ammonia nitrogen removal from water and response optimization of the modified wood ceramic's comprehensive performance, Ceram. Int. 49 (2023) 11612–11622, https://doi.org/10.1016/j.ceramint.2022.12.008.

[23] K. Zhang, S. Li, Y. Wang, J. Fan, G. Zhu, Air-assisted liquid-liquid microextraction based on solidification of floating deep eutectic solvent for the analysis of ultraviolet filters in water samples by high performance liquid chromatography with the aid of response surface methodology, J. Chromatogr. A 1618 (2020) 460876, https://doi.org/10.1016/j.chroma.2020.460876.

[24] D. Ge, G. Zhong, X. Zhou, E. Dai, Y. Wang, Elevated temperature-assisted surfactant-enhanced emulsification microextraction based on solidification of a floating organic drop for the determination of UV filters in water samples by high-performance liquid chromatography coupled to a diode array detector, J. Iran. Chem. Soc. 17 (2020) 499–506, https://doi.org/10.1007/s13738-019-01785-1.

[25] P.P. Zhang, Z.G. Shi, Q.W. Yu, Y.Q. Feng, A new device for magnetic stirring-assisted dispersive liquid–liquid microextraction of UV filters in environmental water samples, Talanta 83 (2011) 1711–1715, https://doi.org/10.1016/j.talanta.2010.11.076.

[26] L. Vidal, A. Chisvert, A. Canals, A. Salvador, Sensitive determination of free benzophenone-3 in human urine samples based on an ionic liquid as extractant phase in single-drop microextraction prior to liquid chromatography analysis, J. Chromatogr. A 1174 (2007) 95–103, https://doi.org/10.1016/j.chroma.2007.07.077.

[27] I.P. Román, A. Chisvert, A. Canals, Dispersive solid-phase extraction based on oleic acid-coated magnetic nanoparticles followed by gas chromatography-mass spectrometry for UV-filter determination in water samples, J. Chromatogr. A 1218 (2011) 2467–2475, https://doi.org/10.1016/j.chroma.2011.02.047.

[28] B. Dejaegher, Y.V. Heyden, Experimental designs and their recent advances in set-up, data interpretation, and analytical applications, J. Pharm. Biomed. Anal. 56 (2011) 141–158, https://doi.org/10.1016/j.jpba.2011.04.023.

[29] D.L. Massart, B.G. Vandeginste, L.M. Buydens, P.J. Lewi, J. Smeyers-Verbeke, S. D. Jong, Handbook of chemometrics and qualimetrics, Elsevier Science Inc., 1998.

[30] J. An, J.L. Anderson, Determination of UV filters in high ionic strength sample solutions using matrix-compatible coatings for solid-phase microextraction, Talanta 182 (2018) 74–82, https://doi.org/10.1016/j.talanta.2018.01.052.

[31] S. Li, S. Cai, W. Hu, H. Chen, H. Liu, Ionic liquid-based ultrasound-assisted dispersive liquid-liquid microextraction combined with electrothermal atomic absorption spectrometry for a sensitive determination of cadmium in water samples, Spectroc. Acta Pt. B-Atom. Spectr. 64 (2009) 666–671, https://doi.org/10.1016/j.sab.2009.05.023.

[32] D.L. Giokas, V.A. Sakkas, T.A. Albanis, D.A. Lampropoulou, Determination of UV-filter residues in bathing waters by liquid chromatography UV-diode array and gas chromatography-mass spectrometry after micelle mediated extraction-solvent back extraction, J. Chromatogr. A 1077 (2005) 19–27, https://doi.org/10.1016/j.chroma.2005.04.074.

[33] I. Tarazona, A. Chisvert, Z. León, A. Salvador, Determination of hydroxylated benzophenone UV filters in sea water samples by dispersive liquid-liquid microextraction followed by gas chromatography-mass spectrometry, J. Chromatogr. A 1217 (2010) 4771–4778, https://doi.org/10.1016/j.chroma.2010.05.047.

[34] Y.C. Ku, M.I. Leong, W.T. Wang, S.D. Huang, Up-and-down shaker-assisted ionic liquid-based dispersive liquid-liquid microextraction of benzophenone-type ultraviolet filters, J. Sep. Sci. 36 (2013) 1470–1477, https://doi.org/10.1002/jssc.201201108.

[35] F. Pena-Pereira, W. Wojnowski, M. Tobiszewski, AGREE-Analytical GREEnness metric approach and software, Anal. Chem. 92 (2020) 10076–10082, https://doi.org/10.1021/acs.analchem.0c01887.

[36] J.W. Wu, H.C. Chen, W.H. Ding, Ultrasound-assisted dispersive liquid–liquid microextraction plus simultaneous silylation for rapid determination of salicylate and benzophenone-type ultraviolet filters in aqueous samples, J. Chromatogr. A 1302 (2013) 20–27, https://doi.org/10.1016/j.chroma.2013.06.017.

[37] C. Yücel, H. Ertaş, F.N. Ertaş, I. Karapinar, Determination of UV Filters in Surface Water by VA-DLLME-SFOD Technique Coupled with GC-MS/MS, Clean-Soil Air Water 50 (2022) 2100246, https://doi.org/10.1002/clen.202100246.

[38] H.K. Jeon, Y. Chung, J.C. Ryu, Simultaneous determination of benzophenone-type UV filters in water and soil by gas chromatography–mass spectrometry, J. Chromatogr. A 1131 (2006) 192–202, https://doi.org/10.1016/j.chroma.2006.07.036.

[39] H. Çabuk, O. Kavaracı, Magnetic retrieval of a switchable hydrophilicity solvent: fast homogeneous liquid–liquid microextraction for the determination of benzophenone-type UV filters in environmental waters, Int. J. Environ. Anal. Chem. 102 (2022) 2569–2585, https://doi.org/10.1080/03067319.2020.1757088.

[40] M.G. Pintado-Herrera, E. González-Mazo, P.A. Lara-Martín, Environmentally friendly analysis of emerging contaminants by pressurized hot water extraction-stir bar sorptive extraction-derivatization and gas chromatography-mass spectrometry, Anal. Bioanal. Chem. 405 (2013) 401–411, https://doi.org/10.1007/s00216-012-6453-1.

[41] M. Celeiro, R. Acerbi, A. Kabir, K.G. Furton, M. Llompart, 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, Anal. Chim. Acta 4 (2020) 100038, https://doi.org/10.1016/j.acax.2019.100038.