Talanta 81 (2010) 549–555

Contents lists available at ScienceDirect

Talanta

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

Ionic liquid-based single-drop microextraction followed by liquid chromatography-ultraviolet spectrophotometry detection to determine typical UV filters in surface water samples

Lorena Vidal [a], Alberto Chisvert [b,*], Antonio Canals [a,**], Amparo Salvador [b]

[a] Departamento de Química Analítica, Nutrición y Bromatología e Instituto Universitario de Materiales, Universidad de Alicante, P.O. Box 99, E-03080, Alicante, Spain
[b] Departamento de Química Analítica, Facultad de Química, Universitat de València, 46100 Burjassot, Valencia, Spain

ARTICLE INFO

Article history:
Received 1 October 2009
Received in revised form
17 December 2009
Accepted 21 December 2009
Available online 4 January 2010

Keywords:
UV filter
Single-drop microextraction (SDME)
Surface water
Ionic liquid
Liquid chromatography

ABSTRACT

A user-friendly and inexpensive ionic liquid-based single-drop microextraction (IL-SDME) procedure has been developed to preconcentrate trace amounts of six typical UV filters extensively used in cosmetic products (i.e., 2-hydroxy-4-methoxybenzophenone, isoamyl 4-methoxycinnamate, 3-(4′-methylbenzylidene)camphor, 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, 2-ethylhexyl 4-dimethylaminobenzoate and 2-ethylhexyl 4-methoxycinnamate) from surface water samples prior to analysis by liquid chromatography-ultraviolet spectrophotometry detection (LC-UV). A two-stage multivariate optimization approach was developed by means of a Plackett–Burman design for screening and selecting the significant variables involved in the SDME procedure, which were later optimized by means of a circumscribed central composite design. The studied variables were drop volume, sample volume, agitation speed, ionic strength, extraction time and ethanol quantity. Owing to particularities, ionic liquid type and pH of the sample were optimized separately. Under optimized experimental conditions (i.e., 10 μL of 1-hexyl-3-methylimidazolium hexafluorophosphate, 20 mL of sample containing 1% (v/v) ethanol and NaCl free adjusted to pH 2, 37 min extraction time and 1300 rpm agitation speed) enrichment factors up to ca. 100-fold were obtained depending on the target analyte. The method gave good levels of repeatability with relative standard deviations varying between 2.8 and 8.8% ($n = 6$). Limits of detection were found in the low μg L^{-1} range, varying between 0.06 and 3.0 μg L^{-1} depending on the target analyte. Recovery studies from different types of surface water samples collected during the winter period, which were analysed and confirmed free of all target analytes, ranged between 92 and 115%, showing that the matrix had a negligible effect upon extraction. Finally, the proposed method was applied to the analysis of different water samples (taken from two beaches, two swimming pools and a river) collected during the summer period.

1. Introduction

The intensity of solar UV radiation reaching earth has increased in recent years due to damage caused to the ozone layer. It is well-known that exposure to UV radiation in small amounts has a therapeutic effect on human health; however, it is also well-documented that over-exposure can promote harmful effects on human health, including skin cancer. The use of sunscreen cosmetic products containing UV filters, which mitigate the harmful solar radiation, may prevent or minimize the adverse effects of sunlight [1].

Nowadays, in order to achieve greater protection to solar radiation, UV filters are added not only to cosmetics to be used for sunbathing but also to daily cosmetic products, such as face day-creams, after-shave products, makeup formulations, lipsticks, shampoos, etc., thus resulting in an increase in the use of UV filters. Moreover, they can be found as additives in textiles, plastics, paints, car polishes, etc. [2].

This excessive use of UV filters has led to their presence in the aquatic environment and increased their potential for endocrine and developmental toxicity [3–5]. This fact has prompted that UV filters are considered emerging pollutants nowadays. These compounds can enter the aquatic environment directly from recreational activities, such as sunbathing and swimming in seas, lakes

* Corresponding author. Tel.: +34 96 354 49 00; fax: +34 96 354 44 36.
** Corresponding author. Tel.: +34 96 590 97 90; fax: +34 96 590 97 90.
E-mail addresses: alberto.chisvert@uv.es (A. Chisvert), a.canals@ua.es (A. Canals).

0039-9140/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2009.12.042

and rivers and also indirectly from showering, rinsing them off, washing clothes, etc., via wastewater treatment plants [2]. Levels observed in environmental waters are not far below the doses that cause toxic effects in animals [6,7].

In recent years, different publications have reported the determination of UV filters in water samples, thus showing it to be an area of growing interest [2,5–9]. Based on the literature, solid-phase based extraction techniques such as solid-phase extraction (SPE) [10–18], solid-phase microextraction (SPME) [19,20] and stir-bar sorptive extraction (SBSE) [21–23] have been widely used to extract UV filters from water samples for clean-up and preconcentration purposes. Other extraction techniques like liquid–liquid extraction (LLE) [24,25], membrane-assisted liquid–liquid extraction (MALLE) [26] and micelle mediated extraction-solvent back extraction [27] have also been used for this purpose.

SPE, SPME and SBSE use expensive materials, are time-consuming, usually have carry over effects and the last two in particular have long-time sorbent conditioning. On the other hand, in the case of LLE, the main disadvantages are the use of large amounts of potentially toxic and normally expensive organic solvents, it is time-consuming and samples require high manipulation. For this reason, miniaturization of the liquid–liquid extraction attempts to eliminate or minimize these drawbacks. In this sense, the single-drop microextraction (SDME) technique has been employed in a remarkable number of investigations during the last decade [28,29], and has been proven and consolidated as an interesting alternative to other microextraction techniques, like the frequently-used SPME. SDME stands out because it is simple to operate, fast, inexpensive, precise, sensitive, virtually solventless and environmentally friendly. In addition, it is characterized by its affordability, as it is not tied to any commercial source.

Usually, organic solvents such as octanol, cyclohexane, toluene, etc., have been used as acceptor phases in SDME. Nevertheless, in recent years, ionic liquids (IL), which are organic salts that are liquids at room temperature and have high boiling points, have been proposed for use in SDME [30–36]. IL have various advantages over traditional organic solvents, such as low vapour pressure, high stability, high viscosity, moderate dissolvability of organic compounds, adjustable miscibility and polarity, good extractability for different organic and inorganic compounds, as well as the possibility of using longer sampling time and larger droplet volume [37,38]. Nevertheless, it should be pointed out that despite these advantages, there are still few IL-based SDME applications but there is growing interest.

The aim of this paper is to develop a user-friendly, inexpensive, sensitive and environmentally friendly analytical method able to determine six typical UV filters extensively used in cosmetics, such as 2-hydroxy-4-methoxybenzophenone (also known as benzophenone-3 (BZ3)), isoamyl 4-methoxycinnamate (IMC), 3-(4′-methylbenzylidene)camphor (MBC), 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (also known as octocrylene (OCR)), 2-ethylhexyl 4-dimethylaminobenzoate (EDB) and 2-ethylhexyl 4-methoxycinnamate (EMC) in surface water samples. The chemical structures and other relevant data are shown in Table 1. The method is based on the use of an IL as extractant phase in SDME, carrying out both pre-concentration and clean-up steps. The method developed here was able to determine them at trace levels, employing common and inexpensive instrumentation, such as LC with UV spectrometric detector.

To our knowledge, there are no published methods based on SDME focusing on UV filter determination in water samples, and there is only one published paper where SDME has been used for UV filter determination [36]. This method, published by the same authors of the present manuscript, was developed to determine free BZ3 in urine from cosmetic users, and achieved good analytical performance.

2. Experimental

2.1. Apparatus

A LC system from Waters (Milford, MA, USA) equipped with a Waters 600E high-pressure pump, a Waters 996 diode array detector set at 313 nm and a 7725i Rheodyne valve injection (Rohnert Park, CA, USA) with 5 μL volume injection loop was employed. A personal computer equipped with a Milenium32 Waters program for LC system was used to process all chromatographic data. A Luna C_{18} column (250 mm × 4.6 mm I.D., 5 μm particle size) and a Luna C_{18} guard column (4 mm × 3 mm I.D., 5 μm particle size) both from Phenomenex (Torrance, CA, USA) were used for the separation of the target analytes.

A basic 20+ pHmeter from Crison (Alella, Spain) was used for the pH measurements.

2.2. Reagents and samples

2-Hydroxy-4-methoxybenzophenone (benzophenone-3 (BZ3)) 98% obtained from Aldrich (Steinheim, Germany), isoamyl 4-methoxycinnamate (IMC) 99.3% from Haarmann and Reimer (Parets del Vallés, Spain), 3-(4′-methylbenzylidene)camphor (MBC) 99.7% from Guinama S.L. (Valencia, Spain), 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (octocrylene (OCR)) >98% from F. Hoffmann-La Roche Ltd. (Basel, Switzerland) and 2-ethylhexyl 4-dimethylaminobenzoate (EDB) 99.8% and 2-ethylhexyl 4-methoxycinnamate (EMC) 99.8% both from Roig Farma S.A. (Terrasa, Spain) were used as standards. Standard stock solutions of each UV filter (500 mg L^{-1}) were prepared in ethanol. Multicomponent working standard solutions were freshly prepared daily by proper dilution of the ethanolic standard stock solutions with de-ionized water.

Acetic acid and ethanol, both LC-grade, from Scharlau Chemie (Barcelona, Spain), and de-ionized water (resistivity ≥ 18 MΩ cm) obtained from a water purification system (Milli-Q Biocel A10) supplied by Millipore (Billerica, MA, USA) were used to prepare the mobile phase for the LC system.

Synthesis-grade ionic liquids, 3-methyl-1-octylimidazolium hexafluorophosphate [C_8MIM][PF_6] and 1-hexyl-3-methylimidazolium hexafluorophosphate [C_6MIM][PF_6], were obtained from Green Solutions S.L. (Vigo, Spain).

Both hydrochloric and phosphoric acids, sodium hydroxide and sodium chloride all from Merck (Darmstadt, Germany) were used to adjust the pH and the ionic strength, respectively.

Surface water samples were collected from the River Turia, the Malvarrosa beach and an irrigation-channel, all in Valencia (Spain) during the winter, and used for the recovery studies. A preliminary analysis indicated that they were free of all target analytes. Other surface water samples from Bellreguard (Gandia, Spain) and Santa Pola (Alicante, Spain) beaches, a private swimming pool (Valencia, Spain), a public swimming pool (Alicante, Spain) and the River Xuquer (Valencia, Spain), collected in the summer season, were also analysed. All samples were collected in 250 mL Pyrex borosilicate amber glass containers with caps. They were stored in the dark at 4 °C and were analysed without previous filtration.

2.3. Proposed IL-SDME-LC-UV method

Twenty mL of each working standard solution or sample, adjusted to pH 2 and containing 1% of ethanol (v/v), was placed in 25 mL glass vials containing a miniaturized stirring bar (5 mm × 2 mm) from Cole Parmer (Vernon Hills, IL, USA).

A 3-mm-long polytetrafluoroethylene (PTFE) tube (0.8 mm I.D.; 1.6 mm O.D.) was fitted to the blunt needle tip of a 25 μL Hamilton (Bonaduz, Switzerland) syringe (model 1702), maximizing thus

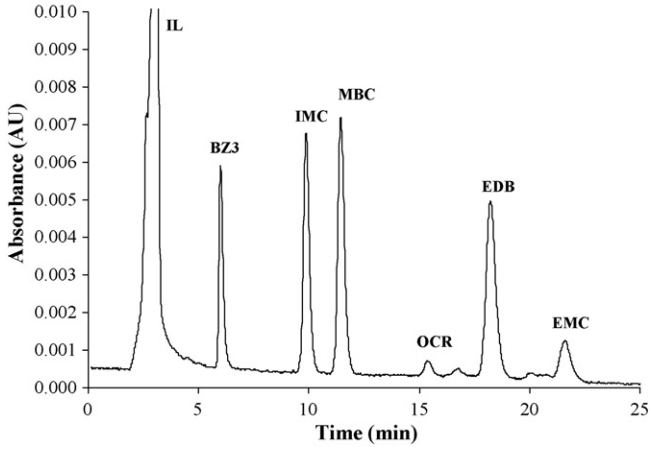


Fig. 1. Chromatogram of a standard solution (50 μg L^{-1}) subjected to the IL-SDME-LC-UV procedure (see Section 2.3 for details).

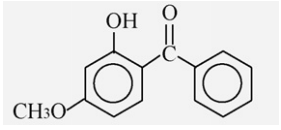
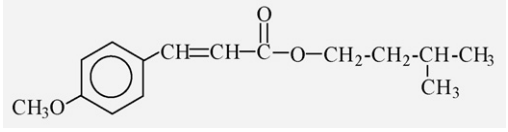
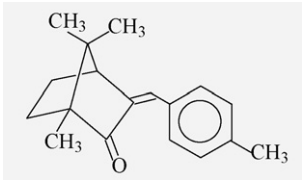
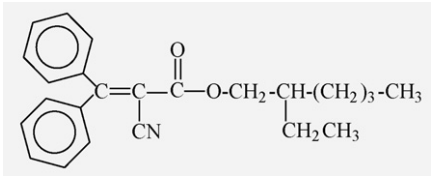
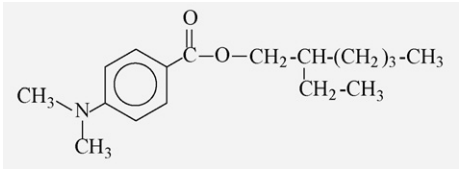
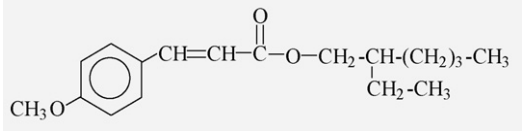
the contact area between the drop and the needle tip. The syringe, containing 10 μL of [C_6MIM][PF_6] as acceptor phase, was clamped above the vial and its needle was immersed in the sample. The plunger was depressed and a drop of the ionic liquid was exposed to the sample at room temperature for 37 min with magnetic stirring of 1300 rpm. After the extraction was accomplished, the acceptor phase was retracted into the syringe, the PTFE tube was removed, and finally the extract was injected into the LC system using isocratic ethanol:1% acetic acid 70:30 (v/v) as mobile phase at 1 mL min^{-1} flow rate. Fig. 1 shows a chromatogram of a standard solution containing 50 μg L^{-1} of the six UV filters extracted by SDME.

3. Results and discussion

3.1. Study of experimental variables involved in SDME

Different variables can affect the extraction yield in the SDME procedure and in most cases they are correlated. Therefore, their optimization through a multivariate approach could be of great interest. However, some of them might not have a significant effect and thus, they could be obviated, avoiding carrying out excessive

Table 1
Some relevant data about the six target analytes.

Name	CAS number	Structure	Log P_{ow}[a]	pK_a[b]
Benzophenone-3 (BZ3)	131-57-7		3.64	7.56
Isoamyl 4-methoxycinnamate (IMC)	71617-10-2		4.06	–
3-(4′-Methylbenzylidene)camphor (MBC)	36861-47-9		4.95	–
Octocrylene (OCR)	6197-30-4		7.53	–
2-Ethylhexyl 4-dimethylaminobenzoate (EDB)	21245-02-3		6.15	2.39[c]
2-Ethylhexyl 4-methoxycinnamate (EMC)	5466-77-3		5.66	–

[a] P_{ow} = octanol–water partition coefficient, obtained from SciFinder Scholar Database 2009.
[b] K_a = acidic constant, obtained from SciFinder Scholar Database 2009.
[c] Deprotonation of amino moiety (–$NH(CH_3)_2^+$).

experiments. In this respect, a screening step, prior to the optimization step, could be helpful in order to assess the significant variables involved in the analytical system under study.

In this case, based on the literature and our group's previous experience [34–36], the influence of eight variables, namely IL type, pH, drop volume, sample volume, ionic strength, stirring speed, extraction time and ethanol quantity, were studied in order to maximize the extraction yield of the six target analytes in the SDME procedure. In the first attempt to optimize these eight variables, a multivariate approach was tried; however, certain difficulties were encountered. On one hand, at basic pH, drop instability was notable and drop volumes higher than 8 μL fell. Thus, pH was not included in the multivariate approach. On the other hand, when IL [C_8MIM][PF_6] was used as extractant solvent, one of its impurities overlapped with BZ3, causing serious problems at low concentrations. Nevertheless, its extracting efficiency was compared with [C_6MIM][PF_6] by means of a univariate approach. The results obtained for these two variables (i.e., pH and IL type) are presented in greater detail below.

3.1.1. IL study

Two IL ([C_6MIM][PF_6] and [C_8MIM][PF_6]) were studied as extractant phases for SDME. For the study, 10 mL of a standard solution containing 500 μg L^{-1} of each target analyte was stirred at 750 rpm for 20 min using a 5 μL droplet volume. Results (not shown) revealed that the peak area for BZ3, IMC and MBC increased when the extractant phase was changed from [C_6MIM][PF_6] to [C_8MIM][PF_6], whereas it decreased for OCR, EDB and EMC. Moreover, as stated above, [C_8MIM][PF_6] showed one impurity overlapping with BZ3, furthermore it is more difficult to handle because of its higher viscosity. Therefore, in order to increase the sensitivity of the analytes showing the less peak area (i.e., OCR, EDB and EMC) and to avoid the drawbacks discussed above, [C_6MIM][PF_6] was selected as the extractant phase.

3.1.2. pH study

Different pH values, ranging from 0 to 10, were studied in order to evaluate its influence in the SDME process. For this study, 10 mL of a standard solution containing 500 μg L^{-1} of each target analyte was stirred at 750 rpm for 20 min using a 5 μL droplet of [C_6MIM][PF_6]. Results (not shown) revealed that similar peak areas were obtained for BZ3, IMC, MBC, OCR and EMC at the different studied pH. However, the best response for EDB was accomplished at pH values of 0 and 2. Therefore, pH 2 was selected for further experiments.

3.1.3. Study of other experimental variables by multivariate optimization

3.1.3.1. Screening step. When a large number of variables are involved, reduced factorial designs are employed for screening purposes in order to know which variables are significant. One particular case of these designs is the well-known Plackett–Burman design, which assumes that the interactions can be completely ignored and so the main effects can be calculated with a reduced number of experiments [39]. A saturated Plackett–Burman matrix with eleven variables (corresponding to six real variables and five dummy variables) was employed because of the large number of variables to be tested. The effects of dummy variables are used to estimate the experimental error used in the statistical interpretation [40]. For each variable, two levels were considered, which were chosen according to preliminary experiments. Thus, 5 and 10 μL for drop volume, 10 and 20 mL for sample volume, 0 and 20% (w/v) NaCl concentration for ionic strength, 0 and 750 rpm for stirring speed, 10 and 30 min for extraction time and 1 and 10% (v/v) for ethanol concentration were tested. The twelve experiments of the Plackett–Burman design were randomly carried out in order to nullify the effect of extraneous or nuisance variables, by using standard solutions (500 μg L^{-1}) and evaluating the sum of the areas of the six target analytes as a goal function for each experiment.

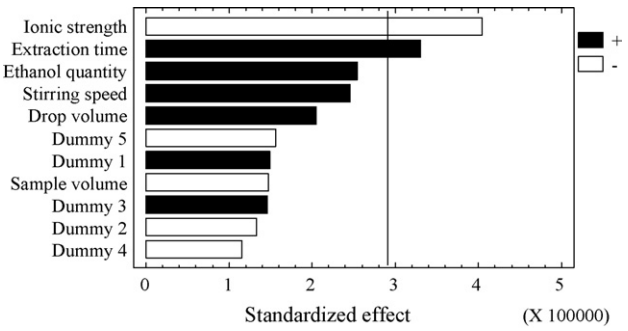


Fig. 2. Pareto chart of the main effects obtained from the Plackett–Burman design.

An ANOVA (analysis of variance) was used to evaluate the data and statistically significant effects were determined using a *t*-test with 90% probability [40,41]. The results were visualized using the main effect Pareto chart shown in Fig. 2. The bar length is proportional to the absolute value of the estimated main effect and a vertical reference line corresponding to 90% confidence interval is included. An effect which exceeds this vertical reference line may be considered significant with regard to the response. Furthermore, the positive or negative sign (corresponding to a black or white bar shading) reveals the cases when the response (i.e., sum of the areas of the filters) is enhanced or reduced, respectively, when passing from the lowest to the highest level set for the specific variable.

According to Fig. 2, ionic strength and extraction time are the significant variables having a negative and positive sign, respectively. The other variables show a non-significant effect. The stirring speed variable has a non-significant effect but it was included in the optimization step because of the previous experience, and it was the most significant variable in our previous work [36] focused on the determination of BZ3 in urine samples. The influence of the stirring speed and the significant variables will be discussed in depth in the following Section 3.1.3.2.

Fig. 2 also reveals that ethanol quantity has a positive non-significant effect upon extraction. This positive effect could be attributed to avoidance of target analyte adsorption by the glassware [22]. However, the use of 10% (v/v) of ethanol caused air bubble formation problems during the extraction process and resulted in drop instability. Since it is a non-significant variable, 1% of ethanol was selected in order to avoid this problem.

Drop volume showed a positive non-significant effect, which is due to the fact that the higher the drop volume, the higher the quantity of analyte extracted [31]. Therefore 10 μL of the extractant phase was selected for further work.

Sample volume had a negative non-significant effect upon extraction. In general, increasing the aqueous sample volume leads to an increase in the total amount of target analytes [31,35]. However, in this case there was a negative effect. This is due to the fact that with 20 mL the drop was maintained at the same distance from the solution surface as it was for 10 mL, in order to avoid the drop instability caused by stirring, and thus the distance between the drop and the stirring area was increased. This meant the analyte transfer to the drop was slower for 20 mL than for 10 mL sample volume. However, 20 mL of sample volume was finally chosen since drop instability was reduced and taking into account that this variable did not exert a significant effect.

Thus, based on the above-mentioned considerations, three variables were fixed (i.e., drop volume, 10 μL; sample volume, 20 mL and ethanol quantity, 1% (v/v)), and the other three were considered in the following optimization step.

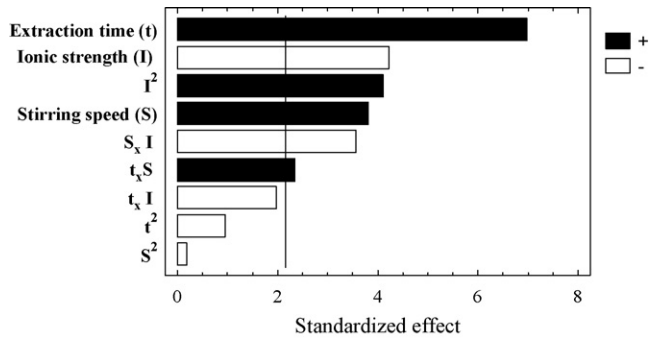


Fig. 3. Pareto chart of the main effects obtained from the circumscribed central composite design.

3.1.3.2. Optimization step. The second step is concerned with optimizing the values of the two significant variables (i.e., ionic strength and extraction time) plus stirring speed, in order to obtain the best response (in our case the extraction yield of UV filters, which is monitored by means of the LC peak area sum). Different experimental designs can be found in the literature, many of which are based on the so-called response surface designs. Box–Wilson or central composite design (CCD) is one of the most frequently-used response surface designs, which is constructed by several superimposed designs. It consists of a factorial design (2^k) augmented with ($2k$) star points, where k is the number of variables to be optimized, and with a central point, which can be run n times [39,42]. A circumscribed central composite design (CCCD) was employed, where the star points were located at $\pm\alpha$ from the centre of the experimental domain, which was situated in 0. In order to establish the rotatability and orthogonality of the experimental design, n was set at 9 and $\alpha = \sqrt[4]{2^k} = 1.682$ [39]. Therefore, the overall matrix of CCCD design involved twenty-three experiments. This design was used to optimize and evaluate the main effects, interaction effects, and quadratic effects. A 3-level design used is suitable for exploring quadratic response surfaces and constructing second-order polynomial models. In this study, the three variables considered were: extraction time (t), stirring speed (S) and sodium chloride concentration (ionic strength) (I). The low (−1), central (0), and high (+1) levels of these variables, as well as the location of their two star points were: 6, 15, 24 and 0, 30% (w/v) NaCl concentration for ionic strength, 600, 900, 1200 and 450, 1500 rpm for stirring speed and 10, 20, 30 and 3, 37 min for extraction time, respectively.

The data obtained were evaluated by an ANOVA, and the effects were visualized using Pareto chart (Fig. 3). As can be seen, the three variables considered were significant with 95% probability. Extraction time and stirring speed showed a positive effect, whilst ionic strength showed a negative effect upon extraction. Furthermore, examination of the quadratic effects, also shown in Fig. 3, reveal that the quadratic effect of ionic strength (I^2) was statistically significant, exhibiting a positive effect upon extraction. The interaction between stirring speed and ionic strength, and the interaction between extraction time and stirring speed showed a significant negative and positive effect, respectively.

Given that it is not possible to simultaneously plot the instrumental response as a function of all the variables controlling the extraction process, the effects of pairs of variables were considered separately. Accordingly, the plots shown in Fig. 4 are useful to graphically interpret the variation in the instrumental response as a function of each pair of independent variables. Thus, Fig. 4a shows the response surface obtained by plotting extraction time vs. stirring speed, whilst keeping a sodium chloride concentration of 15% (w/v), Fig. 4b shows the response surface developed for stirring speed and ionic strength, for an extraction time of 20 min, and finally, Fig. 4c shows the response surface obtained as a function of extraction time and ionic strength with the stirring speed fixed at 900 rpm. As can be seen, extraction time shows a positive effect upon extraction (Fig. 4a and c). Indeed, increasing the extraction time results in an increase in the total amount of analytes extracted, reaching a maximum at 37 min. As expected, stirring speed also shows a positive effect (Fig. 4a and b), since mass transfer is increased and thus extraction rate; however, stirring speed over 1300 rpm caused drop instability. In fact, values over 1500 rpm were not tested because they caused the drop to fall. Therefore, 1300 rpm was selected. On the other hand, ionic strength shows a negative effect (Fig. 4b and c), reaching a maximum when the sample is NaCl free, according to a previous publication [22]. It was assumed that apart from the salting-out effect, the presence of salt caused a second effect and changed the physical properties of the extraction film, thus reducing the diffusion rates of the analytes in the drop [43].

From this optimization study, the LC peak area sum for the six target analytes is expected to be maximized for a sample free of sodium chloride, extraction time reaching the value of 37 min and stirring speed reaching the value of 1300 rpm. Overall, summarizing the results of the preliminary studies, and both screening and optimization steps yield the following experimental conditions: sodium chloride concentration, 0%; extraction time, 37 min; stirring speed, 1300 rpm; pH, 2; ionic liquid type, [C_6MIM][PF_6]; drop volume, 10 μL; ethanol quantity, 1% (v/v); and sample volume, 20 mL.

It should be mentioned here that the overall optimum conditions were the same based on each individual analyte peak area.

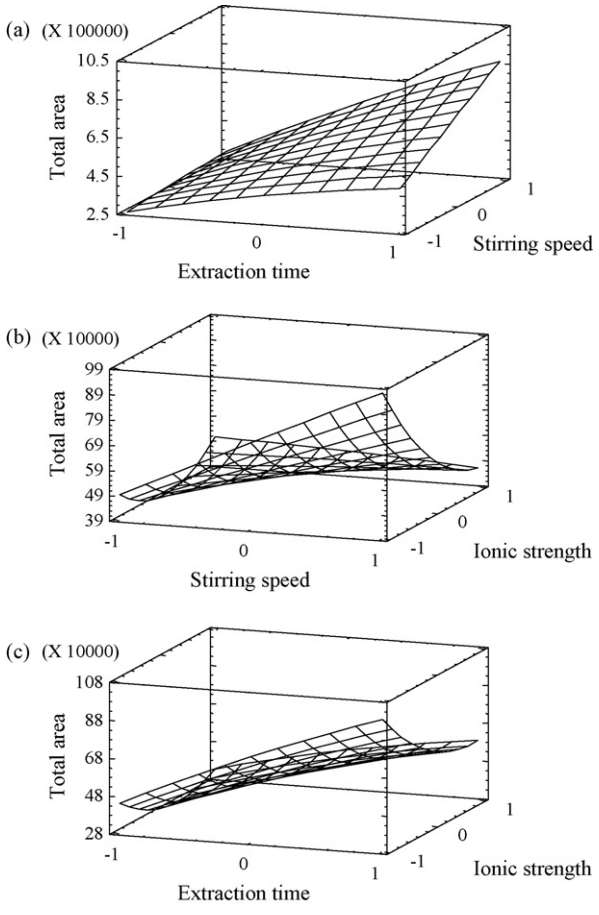


Fig. 4. Response surfaces using the circumscribed central composite design obtained by plotting: (a) extraction time vs. stirring speed (NaCl: 15%, w/v); (b) stirring speed vs. ionic strength (extraction time: 20 min); and (c) extraction time vs. ionic strength (stirring speed: 900 rpm).

Table 2
Main method parameters for the extraction of UV filters from surface water samples using the proposed IL-SDME-LC-UV method.

Analyte	Enrichment factor	Slope (μV s μg^{-1} L)[a]	Intercept (μV s)[a]	Correlation coefficient (r)[a]	Repeatability RSD (%)[b]	LOD (μg L^{-1})[c]	LOQ (μg L^{-1})[d]
BZ3	98	2610 ± 30	−2000 ± 3000	0.9997	2.8	0.11	0.37
IMC	32	1420 ± 20	4000 ± 2000	0.9994	2.9	0.16	0.53
MBC	48	5200 ± 60	−2000 ± 5000	0.9997	3.4	0.06	0.20
OCR	8	93 ± 4	1600 ± 300	0.9970	8.8	3.00	10.0
EDB	39	5140 ± 80	−4000 ± 6000	0.9995	4.1	0.07	0.23
EMC	14	2030 ± 50	−3000 ± 4000	0.9985	7.9	0.19	0.64

[a] Linear range: BZ3, IMC, MBC, EDB and EMC: 1–150 μg L^{-1} (number of calibration points = 5); OCR: 10–150 μg L^{-1} (number of calibration points = 4).
[b] Relative standard deviation (RSD); six replicate analysis of a standard solution containing 50 μg L^{-1}.
[c] Limit of detection (LOD) calculated using the $3S_b$ criterion, where S_b is the standard deviation of the blank.
[d] Limit of quantification (LOQ) calculated using the $10S_b$ criterion, where S_b is the standard deviation of the blank.

3.2. Analytical figures of merit of the proposed IL-SDME-LC-UV method

Quality parameters of the proposed method were evaluated under optimized conditions. The enrichment factors of the proposed procedure, defined as the ratio C_{IL}/C_a, where C_{IL} is the concentration of analytes in the IL phase after extraction and C_a is the original concentration of analytes in the aqueous phase, are shown for the six target analytes in Table 2. It ranged from 8 for OCR to 98 for BZ3. A calibration study was performed under optimized conditions by employing standard solutions of the six target analytes over concentration range of 1–300 μg L^{-1}. The calculated calibration curves gave a high level of linearity within 1–150 μg L^{-1} for BZ3, IMC, MBC, EDB and EMC, and within 10–150 μg L^{-1} for OCR. The correlation coefficients (r), ranged between 0.9970 and 0.9997, are also shown in Table 2. The repeatability of the proposed method, expressed as relative standard deviation (RSD), was evaluated by extracting six consecutive standard solutions (containing 50 μg L^{-1} of each target analyte) and was found to vary between 2.8 and 8.8% with a mean value of 5% (Table 2). Both limit of detection (LOD) and limit of quantification (LOQ) were estimated according to $3S_b$ and $10S_b$ criteria [44], respectively, where S_b is the standard deviation of the blank, by dividing these values by the slope of the calibration curve. As can be seen in Table 2, the LODs and LOQs values were found to be in the μg L^{-1} level ranging between 0.06 and 3.0 μg L^{-1} and between 0.20 and 10.0 μg L^{-1}, respectively. The LOD values obtained by the proposed IL-SDME-LC-UV method are generally higher than the LOD values obtained in most of the other previous works [10–27]. This fact is mainly due to the more sensitive detectors employed in those papers, such as the mass-spectrometry detector. Nevertheless, the extraction process described here is simpler, more economical and more ecological than most of the others, reported in previously published papers [10–27], since the extraction process is done with a drop of few μL by means of a conventional syringe, thus avoiding the use of large amounts of organic solvents, like in LLE and SPE, and avoiding the use of trademark material like in SPE, SPME and SBSE. Moreover, the feasibility of IL-SDME for extracting UV filters is clearly demonstrated.

In order to perform recovery studies, and thus evaluate matrix effects, river water, sea water and irrigation-channel water samples, collected during the winter, were spiked at 50 μg L^{-1} with each UV filter. As it was said before, all samples were initially analysed and were found to be free of all target compounds. Thus, three portions of each spiked sample were subjected to the IL-SDME-LC-UV procedure. Table 3 shows the relative recoveries obtained, determined by referring to a standard aqueous solution containing the same concentration level as the samples. Results show that relative recoveries ranged between 96 and 115% with a mean value of 100% for the river water sample, between 92 and 107% with a mean value of 96% for the sea water sample, and finally between 99 and 110% with a mean value of 104% for the irrigation-channel water sample. These results show there was no matrix effect on the developed IL-SDME-LC-UV method for the three different water samples, even for the sea water samples, which contained approximately 3.5% (w/w) salinity.

Table 3
Relative recoveries (±standard deviation) values obtained for the six target analytes in surface water samples.

Analyte	Relative recoveries ± standard deviation[a] (%)		
	River water	Sea water	Channel water
BZ3	96 ± 2	99 ± 2	99 ± 5
IMC	97 ± 1	92 ± 2	100 ± 7
MBC	98 ± 1	96 ± 1	100 ± 5
OCR	115 ± 16	92 ± 10	110 ± 12
EDB	96 ± 3	92 ± 3	103 ± 7
EMC	101 ± 10	107 ± 8	110 ± 14

[a] Spiking level: 50 μg L^{-1}; mean of three replicate analyses.

3.3. Application of the proposed IL-SDME-LC-UV method to the analysis of different surface water samples

Five different surface water samples, collected in the summer period, were analysed in triplicate using the developed IL-SDME-LC-UV method. These samples corresponded to two beaches, two swimming pools (one public and other one private) and one river. To our knowledge, sunbathing and swimming activities took place in all the surface water sampling sites, however it should be mentioned that only the public swimming pool water contained detectable quantities of two of the six UV filters studied, concretely IMC at 700 ± 300 ng L^{-1} and MBC below its limit of quantification. This fact contrasts with the sunbathing and swimming activities that take place in the studied space. It could be explained by the fact that beaches and rivers have water in movement, while on the other hand, not many people swim in the private pool. However, in a public swimming pool there are many people; mostly children, who are the greatest users of sunscreen cosmetics.

4. Conclusions

A sensitive method based on liquid chromatography with conventional UV detection is proposed to determine six UV filters at trace levels in surface water samples. A user-friendly and inexpensive methodology is developed, based on the use of an ionic liquid-based single-drop microextraction technique, which has proven useful to carry out both preconcentration and clean-up steps. Good figures of merit have been obtained, although the limits of detection could be improved by employing more sensitive detectors.

Acknowledgements

The authors would like to thank the Spanish Government (project nos. CTQ2005-09079-C03-01/BQU, CTQ2008-06730-C02-01, CTQ2006-00296/PPQ and CTQ2009-12709/PPQ), the Generalitat Valenciana (project nos. ACOMP/2009/144 and A-04/09) and "Vicerrectorado de Investigación, Desarrollo e Innovación" of University of Alicante (project no. GRE07-1J) for the financial support. L.V. also thanks "Vicerrectorado de Investigación, Desarrollo e Innovación" of University of Alicante and "DRAC programme" of Xarxa Vives d'Universitats for her fellowships.

References

[1] A. Chisvert, A. Salvador, UV filters in sunscreen and other cosmetics. Regulatory aspects and analytical methods, in: A. Chisvert, A. Salvador (Eds.), Analysis of Cosmetic Products, Elsevier, Amsterdam, 2007.
[2] D.L. Giokas, A. Salvador, A. Chisvert, Trends Anal. Chem. 26 (2007) 360.
[3] M. Schlumpf, P. Schmid, S. Durrer, M. Conscience, K. Maerkel, M. Henseler, M. Gruetter, I. Herzog, S. Reolon, R. Ceccatelli, Toxicology 205 (2004) 113.
[4] M. Schlumpf, S. Durrer, O. Faass, C. Ehnes, M. Fuetsch, C. Gaille, M. Henseler, L. Hofkamp, K. Maerkel, S. Reolon, B. Timms, J.A. Tresguerres, W. Lichtensteiger, Int. J. Androl. 31 (2008) 144.
[5] M.S. Díaz-Cruz, D. Barceló, Trends Anal. Chem. 28 (2009) 708.
[6] S.D. Richardson, T.A. Ternes, Anal. Chem. 77 (2005) 3807.
[7] S.D. Richardson, Anal. Chem. 79 (2007) 4295.
[8] A.M. Peck, Anal. Bioanal. Chem. 386 (2006) 907.
[9] M.S. Díaz-Cruz, M. Llorca, D. Barceló, Trends Anal. Chem. 27 (2008) 873.
[10] D.L. Giokas, V.A. Sakkas, T.A. Albanis, J. Chromatogr. A 1026 (2004) 289.
[11] T. Poiger, H. Buser, M.E. Balmer, P. Bergqvist, M.D. Müller, Chemosphere 55 (2004) 951.
[12] M.E. Balmer, H. Buser, M.D. Müller, T. Poiger, Environ. Sci. Technol. 39 (2005) 953.
[13] W. Li, Y. Ma, C. Guo, W. Hu, K. Liu, Y. Wang, T. Zhu, Water Res. 41 (2007) 3506.
[14] P. Cuderman, E. Heath, Anal. Bioanal. Chem. 387 (2007) 1343.
[15] R. Rodil, J.B. Quintana, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríguez, Anal. Chem. 80 (2008) 1307.
[16] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, Anal. Bioanal. Chem. 391 (2008) 1293.
[17] R. Rodil, J.B. Quintana, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríguez, J. Chromatogr. A 1216 (2009) 2958.
[18] R. Rodil, S. Schrader, M. Moeder, Rapid Commun. Mass Spectrom. 23 (2009) 580.
[19] D.A. Lambropoulou, D.L. Giokas, V.A. Sakkas, T.A. Albanis, M.I. Karayannis, J. Chromatogr. A 967 (2002) 243.
[20] N. Negreira, I. Rodríguez, M. Ramil, E. Rubí, R. Cela, Anal. Chim. Acta 638 (2009) 36.
[21] M. Kawaguchi, R. Ito, N. Endo, N. Sakui, N. Okanouchi, K. Saito, N. Seto, T. Shiozaki, H. Nakazawa, Anal. Chim. Acta 557 (2006) 272.
[22] R. Rodil, M. Moeder, J. Chromatogr. A 1179 (2008) 81.
[23] M. Kawaguchi, R. Ito, H. Honda, N. Endo, N. Okanouchi, K. Saito, N. Seto, H. Nakazawa, J. Chromatogr. A 1200 (2008) 260.
[24] H.-K. Jeon, Y. Chung, J.-C. Ryu, J. Chromatogr. A 1131 (2006) 192.
[25] T. Kupper, C. Plagellat, R.C. Brändli, L.F. de Alencastro, D. Gradjean, J. Tarradellas, Water. Res. 40 (2006) 2603.
[26] R. Rodil, S. Schrader, M. Moeder, J. Chromatogr. A 1216 (2009) 4887.
[27] D.L. Giokas, V.A. Sakkas, T.A. Albanis, D.A. Lambropoulou, J. Chromatogr. A 1077 (2005) 19.
[28] E. Psillakis, N. Kalogerakis, Trends Anal. Chem. 21 (2002) 53.
[29] L. Xu, C. Basheer, H. Lee, J. Chromatogr. A 1152 (2007) 184.
[30] J.-F. Liu, G.-B. Jiang, Y.-G. Chi, Y.-Q. Cai, Q.-X. Zhou, J.-T. Hu, Anal. Chem. 75 (2003) 5870.
[31] J.-F. Liu, Y.-G. Chi, G.-B. Jiang, C. Tai, J.-F. Peng, J.-T. Hu, J. Chromatogr. A 1026 (2004) 143.
[32] J.-F. Peng, J.-F. Liu, G.-B. Jiang, C. Tai, M.-J. Huang, J. Chromatogr. A 1072 (2005) 3.
[33] C.-L. Ye, Q.-X. Zhou, X.-M. Wang, Anal. Chim. Acta 572 (2006) 165.
[34] L. Vidal, E. Psillakis, C.E. Domini, N. Grané, F. Marken, A. Canals, Anal. Chim. Acta 584 (2007) 189.
[35] L. Vidal, C.E. Domini, N. Grané, E. Psillakis, A. Canals, Anal. Chim. Acta 592 (2007) 9.
[36] L. Vidal, A. Chisvert, A. Canals, A. Salvador, J. Chromatogr. A 1174 (2007) 95.
[37] C.F. Poole, J. Chromatogr. A 1037 (2004) 49.
[38] H. Zhao, S. Xia, P. Ma, J. Chem. Technol. Biotechnol. 80 (2005) 1089.
[39] R.H. Myers, D.C. Montgomery, Response Surface Methodology, Wiley, New York, 2002.
[40] Y.V. Heyden, K. Luypaert, C. Hartmann, D.L. Massart, J. Hoogmartens, J.D. Beer, Anal. Chim. Acta 312 (1995) 245.
[41] Y.V. Heyden, C. Hartmann, D.L. Massart, L. Michel, P. Kiechle, F. Erni, Anal. Chim. Acta 316 (1995) 15.
[42] R. Rodil, A. Carro, R. Lorenzo, M. Abuín, R. Cela, J. Chromatogr. A 963 (2002) 313.
[43] E. Psillakis, N. Kalogerakis, J. Chromatogr. A 907 (2001) 211.
[44] G. Ramis, M.C. García, Quimiometría, Síntesis, Madrid, 2001, p. 126.