Chromatographic Methods for the Determination of a Broad Spectrum of UV Filters in Swimming Pool Water

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Abstract

This paper describes an analytical approach based on Solid Phase Extraction (SPE) followed by analysis using liquid and gas chromatography coupled to mass spectrometry detectors for a simultaneous determination of 18 organic UV filters from water samples. Extraction method parameters were optimized: 250 ml of water sample loaded on Chromo-Bond C18 cartridges after adjustment to pH 4 and then eluted with acetonitrile. The mobile phase, the parameters of the mass spectrometer, as well as those of the ionization source were tested to enhance detection sensitivity. During method validation, the extracted target compounds showed good recoveries (> 68%) with acceptable values in terms of repeatability (CV_r) and reproducibility (CV_R), that were lower than 20%. The validated method was applied to different real water samples collected from different swimming pools located in Lebanon where nine UV filters among the eighteen targets compounds were detected at concentrations up to 1500 µg/L in some samples. Padimate-O and Octocrylene were detected frequently. This study represents the first available data on the occurrence of UV filter residues in swimming pool in Lebanon opening hence future perspectives to evaluate their degradation by-products and their toxicity on human health and marine ecosystem.

1. Introduction

The chemical groups that are used to block or absorb UV light are called UV filters. They are utilized as sunscreens and in other cosmetic products aiming at protecting the skin from the noxious effects of sun radiation. In addition, they have been used to produce some plastics, industrial products, vehicle maintenance products, and pesticides (Eriksson et al. 2008). Therefore, due to their extensive use, they have been detected at trace levels in different environmental samples such as rivers, lakes, drinking water, wastewater, fish, soil and sludge (Díaz-Cruz et al. 2012). These compounds can be released in the aquatic milieu (seas, lakes, and rivers) both directly, during sunbathing and swimming activities, and indirectly through wastewater (Gago-Ferrero et al. 2012). Moreover, according to the results of conducted toxicological studies, both in vitro and/or in vivo, it has been shown that some UV filters like: 2-ethylhexyl 4-methoxycinnamate (EHMC), 2-ethylhexyl 4-(dimethylamino) benzoate, homosalate (HMC), benzophenone 3 (BP-3), 3-(4-methylbenzylidene) camphor (4-MBC), octocrylene (OC), and butyl methoxydibenzoylmethane (BM-DBM) even at low concentrations, might affect the reproduction of fish by disturbing their endocrine activity (Blüthgen et al. 2014; Ozáez et al. 2016; Zhang et al. 2016; Quintaneiro et al. 2019). Consequently, UV-filters are considered as emerging contaminants nowadays with high concern rendering necessary the development of an analytical multiresidue method that allows their detection in the aquatic systems at trace levels. So far, previous studies reported the presence of organic UV filters in swimming pool waters (Lambropoulou et al. 2002) bathing and waste (Sakkas et al. 2003), surface waters (Fent et al. 2010), and seawater (Labille et al. 2020), sediments and sewage sludge (Cuderman and Heath 2007), human milk (Rainieri et al. 2017), plasma and urine (Kawaguchi et al. 2007; Klotz et al. 2019) .They report that UV-filters bioaccumulate in multiple environmental media even in aquatic organisms. Several compounds have been found at concentration up to 345 ng/L in lakes (Cuderman and Heath 2007), and benzophenone-4 (BP-4) at a concentration of 849 ng/L of in rivers (Rodil and Moeder 2008). In addition, EHMC was found in 15 drinking water samples collected from San Diego at 0.45 µg/L (Loraine and Pettigrove 2006).

The determination of UV-filters in water system at trace levels requires the uses of efficient extraction method that concentrate and enrichment the extract before their analysis by chromatographic techniques. Many analytical methods are previously published concerning the assessment of particular classes of UV-filter compounds in different aqueous matrices (Liu et al. 2010; Khalikova et al. 2018; Chisvert et al. 2018). Different sample preparations such as liquid–liquid extraction (LLE) (Tarazona et al. 2013), solid-phase extraction (SPE) (Silvia Díaz-Cruz et al. 2008) and solid-phase micro-extraction (SPME) (Negreira et al. 2009; Zhang and Lee 2012) were reported. LLE was the most frequently utilized method for aqueous samples. However, this method is a time-consuming, and laborious technique that requires large volumes of organic solvents. Many studies have substituted LLE method with SPE, since it allows to diminish significantly the utilisation of organic solvents. In most of these studies, UV filters were extracted from water through SPE using Oasis HLB and Chromo-Bond C18 as sorbent materials and were then analyzed by liquid chromatography coupled to tandem mass spectrometry

(LC-MS/MS) (Zenker et al. 2008). More recently, stir bar sportive and nonporous membrane-assisted extractions, as micro extraction techniques, have been also used. On the other hand, the analytical methods utilized to assess the UV filters in environmental matrices are mostly limited to chromatographic techniques, including gas chromatography (GC), and LC-MS/MS (Zhang and Lee 2011; da Silva et al. 2015; Kędziora-Koch and Wasiak 2018).

Different legislations were implemented to define the UV-filters compounds allowed to be present in sunscreen cosmetics whose aim is protecting the skin from solar harmful UV-light and avoiding or minimizing the damage on human health caused by this radiation. The European union, the United States and Japan have nowadays approved different compounds at different levels for authorized substances (Khalikova et al. 2018). Lebanon imports all their need for sunscreen from different area that open the probability to detect a wide variety of UV-filter substances in different environmental samples. In this context, target compounds chosen in this study aim at covering the mostly active ingredients present in the market for further assessment. To this end, the present study aims at developing a highly sensitive analytical method for the simultaneous assessment of 18 UV-filters in swimming pool water samples using the SPE technique and LC-MS/MS and GC/MS. The parameters altering extraction performance will be optimized, and the method will be validated before being applied to different swimming pool waters in Lebanon proving its suitability and performance.

2. Materials And Methods

2.1. Reagents Materials and Stock solutions

Oxybenzone, Dioxybenzone, Sulisobenzone, Octisalate, Ethylhexyl Methoxycinnamate, Isoamyl Methoxycinnamate, Octorylene, Padimate-O, Ethyl Hexyl Triazine, Ecamsule, Aminobenzoic acid, Cinoxate, Homosalate, Bemotrizinole, Drometrizole Trisiloxane, Avobenzone, Iscotrizinole and Hexyl Diethyl amine Hydroxybenzoyl Benzoate were of the highest available purity (> 98.5 %) and were purchased from Sigma-Aldrich (St. Louis, MO, USA). LC-MS grade acetonitrile (ACN), Dimethylformamide (DMF), methanol (MeOH), and Ethylenediaminetetraacetic acid disodium salt dihydrate (Na_2EDTA, 98.5%) were also purchased from Sigma-Aldrich (St. Louis, MO, USA). Deuterated benzophenone (benzophenone-d10) (BZ-d10)) 99% (Miamisburg, Ohio, USA) was purchased from Isotec and used as a surrogate to minimize possible deviations that occur during the SPE and GC injection processes. Benzoic d5 acid (BA d5) used as control for efficiency extraction in LC injections was from ISOTEC (Miamisburg, USA).

Ammonium Acetate was supplied by Merck and Formic acid, which was used for pH adjustment, was from BDH-Laboratory, England.

Deionized water with a resistivity of 18.2 $M\Omega \cdot cm^{-1}$ was obtained from Barnstead-Easy pure II from Thermo Fisher scientific (Hudson, USA). The cartridges for sample extractions were obtained from Waters technologies (Millipore, USA) for Oasis HLB (200 mg, 6 mL) and from Machery – Nagel (Germany) for Chroma bond C18 (200 mg, 3 mL).

Stock standard solutions were prepared in methanol except Bemotrizinol, Ethylhexyl Triazone and Iscorizinol in Dimethylformamide and stored in the dark at -15 . Working standard solutions of 1 mg/L were daily prepared with appropriate dilution in Acetonitrile and stored in the dark at -4 .

2.2. Liquid Chromatography/tandem mass spectrometry

An Agilent 1200 HPLC system (Agilent Technologies, USA) equipped with a reverse phase Zorbax Eclipse C8, with 3.5 um particles (2.1 mm × 100 mm) was used for the separation of the selected analytes from aqueous samples. The HPLC system was interfaced to an Agilent 6410 triple quadrupole mass spectrometry (Agilent Technologies) through an electrospray ionization source that was run in positive mode (ESI+). Capillary voltage (4000 V), temperature (350 °C), nebulizer pressure (20 psi) and gas flow rate (9 $L \cdot min^{-1}$) that constitute the MS/MS parameters were also optimized. The mobile phase of the system, composed of pure water and acetonitrile, was set at a flow rate of 0.3 mL/min and regulated according to a gradient elution consisted as follow (0 –0.5 min; 95:5 Water/ ACN, 0.5–10 min; 100% ACN and 15–20 min;

95:5 Water/ ACN). The necessary time for the analysis, the column temperature and the injection volume of the extract were set at 20.5 min, 35 °C, and 5 µL, respectively. The cone voltage and collision energy for each UV-filter product were optimized to give the highest abundance. One mg/L of standard solution was injected directly into the mass spectrometer to optimize the collision energy (CIV) and the fragmentor for each analyte.

2.3. Gas Chromatography/mass spectrometry

A GC Agilent technologies 6890N series (Agilent, Waldbronn, Germany) coupled to an Agilent single quadrupole mass spectrometry 5973N series (Santa Clara, CA, USA) was used for the analysis. The column used was an HP-5MS (Hewlett Packard, Palo Alto, CA, USA) capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). The oven temperature program was monitored as follow: a starting temperature of 100°C for 1 min; followed by a gradient increase of 25°C/min to reach 290°C. The total run time and the temperature of the injection port were 23.6 min and 250°C. The volume of the sampled to be injected into GC-MS following the spitless mode was 1 µL using the Helium as carrier gas flowed at 0.4 mL. min^{-1}. The electron impact (EI) ionization mode with 70 eV was applied within the mass spectrometry detector (MSD) with a temperature of ion source set at 230°C. Selective ion monitoring (SIM) mode was used to perform the analysis on MSD where one target and two or three qualifier ions were selected for each compound.

2.4. SPE procedure and samples pre-treatment

Ten water samples were collected in amber glass bottles, previously washed with acetone, methanol and Milli-Q water, from swimming pools situated in Beqaa (Lebanon) in 2019 during swimming period. Samples of 1 L each were placed in the glass bottle to which 100 mg of $Na_2S_2O_3$ were immediately added for neutralization of the chlorine and other chlorinating agents present in the samples, and for avoiding any reaction that might take place with the target compounds.

Once in the laboratory, the water samples were directly filtered through cellulose filters (pore size 0.45 µm) and conserved at 4 until analysis within the 48 h. SPE extraction was performed with a Visiprep SPE manifold (Supelco, Bellefonte, PA, USA). The experimental protocol consisted of conditioning the cartridge of Chromo Bond C18 (200 mg) at atmospheric pressure using acetonitrile (5 ml) followed by water adjusted at pH 4 with formic acid (5 ml). Afterwards, each water sample (250 ml) adjusted to pH 4 and supplemented with 10.375 ml of EDTA (250 mM) was doped with 15 µL from 1 ppm of the surrogate standard (BZ-d10, BA d5) to better control the quality of the extraction process and the daily performance of the method. The cartridge was then dried under vacuum for 1 hour. The compounds of interest were eluted, under atmospheric pressure, using acetonitrile (5 ml). Finally, nitrogen flow was used at 45°C to let the eluent evaporate that was reconstituted, in a 300 µL insert, with acetonitrile after the addition of 15 µL of atrazine D5 (0.5 ppm), used as internal standard for LC-MS/MS and GC-MS analysis.

2.5. Validation of the method

Blank water samples were used to assess the applicability of the optimized SPE-LC-MS/MS and SPE-GC/MS methods, before applying it to real water samples to determine their contamination levels with UV-filters. Table 2 shows the investigated parameters in terms of linearity, precision, instrumental limit of detection (ILD) and quantification (ILQ), and method detection limit (MDL). Blank water samples were fortified at 6 concentration levels (5, 10, 20, 40, 80, and 100 ng mL^{-1}) from which the linearity (Table 2) was assessed using the matrix-matched calibration curve. Four water samples were spiked with each analyte (30 ng) and analyzed in parallel to determine the repeatability of the methods. Fifteen µL of atrazine D5 (30 ng mL^{-1}) were added to each sample as internal standard. The evaluation of the intermediate precision (RSDi) was performed by analyzing the spiked water samples at different days. The repeatability was assessed within the same experiment, using the relative percentage recovery, by comparing the mean measured concentration with the fortified concentration of the samples. The lowest concentrations of each compound that shows a signal-to-noise for every target ion (m/z) equal or higher than 3 and 10 are defined as the instrumental limits of detection (ILD) and quantification (ILQ),

respectively. MDL of each compound, defined as signal to-noise ratio set at 3, was obtained after fortifying and analyzing blank water samples at low concentration.

To ensure the reliability of the results, procedures of quality assurance/quality control were applied. To this end, water samples were spiked with deuterated standards, as surrogate standard, before extraction. No spiked ultrapure water samples were considered as blank samples to exclude any cross-contamination during the process. To monitor the instrumental and the potential cross-contamination during LC-MS/MS detection, instrumental blank and a calibration solution were analyzed before and after each sample sequence. Twenty blank water samples, collected from different sources, were analyzed to check method selectivity and to verify the presence of potential interfering substances around the retention times of the compounds of interest.

The quantification of UV-filter compounds in real samples was achieved by comparing the analyte/internal standard peak area ratio from matrix-matched calibration curve to the analyte/internal standard peak area ratio in the analyzed samples.

3. Results And Discussion

3.1. LC-MS/MS analysis

All parameters were optimized by directly inject each standard at a level of 1 mg/L, prepared in acetonitrile, to identify the ionization mode for detection of all the analytes. In detail, among the 18 compounds, seven (4-Aminobenzoic Acid, Sulisobenzone, Avobenzone, Ecamsule, Bemotrizinole, Iscotrizinole, Ethylhexyl triazone) showed efficient ionization in ESI+. Afterwards, the precursor and the product ions for each compound were identified by optimizing the collision energy and the cone voltage. Consequently, the conditions of liquid chromatography were optimized. An Agilent Zorbax Eclipse XDB-C8 column was chosen for analyzing UV filters with particles size of 3.5 µm and a length of 100 mm. In addition, to optimize the mobile phase, a series of preliminary experiments were carried out, consisting of water and acetonitrile with formic acid at different concentrations (0.01%, 0.02%, 0.03%, 0.05%, and 0.1%) or with ammonium acetate (5mM) and water/methanol. Gradient elution with pure water and acetonitrile has been found to be the most efficient mobile phase for compounds analyzed in positive mode. This result can be related to the lower viscosity of the mixture of water / acetonitrile compared to water / MeOH, which reduce the pressure problems mostly frequent in liquid phase chromatography. Then, the intensities were better without additives (formic acid and ammonium acetate) for all compounds**.** The parameters of the drying gas temperature (250, 300 and 350°C) and the nebulizing gas pressure (5, 10, 15, 20 and 30 psi) were adjusted and the optimized intensities were established at 350 °C and 20 psi respectively. Multiple reaction monitoring (MRM) was utilized, and Table 1 shows the specific MS/MS parameters for the targeted compounds and their retention times.

3.2. GC-MS analysis

Data acquisition was done using the selected ion monitoring (SIM) and the full-scan modes. Full scan mode was selected with a wide range of m/z. Two monitored ions were chosen for each target compound, the first for confirmation while the second for quantitation, based on the scanning chromatograms of UV filter standards (**Table 1**).

3.3. Optimization of the extraction procedure

The SPE was chosen for extraction among the other extraction techniques. This technique is considered as the key step in sample pre-concentration due to its best extraction recovery and low solvent consumption rendering it the most utilized to extract pharmaceuticals compounds from aquatic samples. The filtration step did not influence the SPE extraction. Subsequently, the extraction process was assessed in terms of nature of sorbent, pH of sample, elution solvent and breakthrough volume.

3.3.1. Choice of cartridge type

The extraction efficacy of the SPE technique is highly affected by the type of the adsorbing material. For this reason, two different adsorbent materials were tested: Oasis HLB (200 mg) and Chromo Bond C18 (200 mg). Oasis HLB cartridge is constituted of two combined monomers, lipophilic divinylbenzene and hydrophilic N-vinylpyrrolidone , permitting the retention of polar and non-polar compounds (Khalikova et al. 2018). Moreover, this cartridge type has shown also a good performance in extracting acidic, neutral and basic compounds (Khalikova et al. 2018). Chromo Bond C18 is made by Silica material, permitting the retention polar and non-polar compounds (Khalikova et al. 2018). In this study, the results exhibited good extraction recoveries for all compounds with acceptable range (60–120%) using Chromo Bond C18 compared to Oasis HLB **(Fig.1)**. Moreover, the addition of EDTA salt, which act as metals chelates, in the water sample was studied. The **Fig.1** shows that the extraction recoveries of most of the UV-filter compounds were enhanced due to addition of EDTA salt. This result can be explained by the disruption of bonds between the studied target compounds and the metals presented in the water and by the decrease of the pH of the water samples allowing better retention of the compounds of interest on the cartridges.

3.3.2. Effect of pH

The adjustment of the pH of the water samples before being loaded into the cartridges consists another critical point of SPE procedure to be optimized. Therefore, the extraction efficiency of target compounds from adjusted water samples using formic acid was studied at four pH: 2, 4, 7 and 9. The adjusted water samples with pH 4 revealed the best extraction recoveries for all the target compounds **(Fig.2)**. The obtained results can be explicated by the fact that when increasing the pH, the target compounds acquired an ionization charge, which impar their interaction with the solid phase. Instead, when the pH becomes acidic, the ionic charge of the target compounds reduced, allowing then the obtention of best extraction recoveries.

3.3.3. Optimization of the elution solvent

Furthermore, to eluate the target compounds from the adsorbents, it is necessary to use a solvent whose interaction with compounds is higher than the adsorbents allowing then their desorption. Then, in order to choose the best elution solvent, three solvents were tested (MeOH 100%, ACN 100% and ACN / MeOH 60/40), the yields obtained in the case of MeOH 100% and ACN / MeOH 60 / 40 are between 40 and 50%, while with pure ACN the recovery increases up to 78% **(Fig.3)**. In the procedure of extraction, the pure acetonitrile was adopted due to the following reasons: it insured the highest recovery of all compound and a short evaporation time in the final step compared to the other eluents.

3.3.4. Optimization of breakthrough volume

Finally, a last experiment was carried out to assess the breakthrough volumes. It corresponds to the maximum volume, which can be percolated on an SPE cartridge without modifying the extraction yields. In this study, different sample volumes (100 mL, 250 mL, 500 mL and l L) were investigated. Samples were doped at the same concentration for all analytes (300 µg /L) and then extraction procedures were performed. As shown in **Fig.4**, the recoveries tended to decrease with a sample volume higher than 250 mL. For this reason, 250 mL has been selected as a sample volume to perform the extractions, thus a maximum enrichment.

3.4. Performance evaluation of our method

The developed method for the extraction of 18 UV filters in water samples was assessed for its analytical performance by evaluating the quality parameters (the linearity, precision, limit of detection (LOD) and limit of quantification (LOQ)) (**Table 2**). According to the optimum conditions, the method displayed good linearity with coefficients of determination (R^2) higher than 0.9 for all the UV filters studied in the 0.13- 400 µg/L range, and repeatability, considered as percentage relative standard deviations (RSD < 20%).

The minimum concentration of a target analyte detected in a spiked water sample with a signal-to-noise ratio (S/N) of 3 is defined as LOD. LOQ is the lowest concentration of a compound that can be quantified in a sample with acceptable precision under the stated operational conditions of the method. The concentration of target compound equivalenting to a S/N of 10 is considered as LOQ, that can be determined, from the less intense MRM transition calculated, using an extract of ultrapure water spiked at the 50 µg/L level. Calculated LOD were between 0.03 and 30 µg/L and calculated LOQ were between 0.13 and 60 µg/L. Then, water samples were spiked with low concentrations of UV filters to determine the MDL. Calculated MDL were between 2.5 and 50 ng/L.

3.5. Application to water samples from swimming pool

To assure the suitability of the validated method, 10 recreational water samples, collected from swimming pools located in the region of Bekaa in Lebanon were worked and alayzed (Al Rihâb, Bekaa Joy, Sunny Land, Al Tilal, Park Hôtel, Kadery, Water Park, Serenity, Shams Palace and Mountajaa Al Sharek). Nine out of the 18 target UV filters were detected in the analyzed samples (Dioxybenzone, Octorylene, Padimate-O, Ethylhexyl Methoxycinnamate, Iscotrizinol, Oxybenzone, Bemotrizinol and Isoamyl Methoxycinnamate). As showed in (**Fig.5**), Padimate-O is found in 90% of swimming pools at low concentrations: 1 to 20 ng/l. Others filters: Oxybenzone, Dioxybenzone, Isoamyl Methoxycinnamate and Bemotrizinol were detected at concentrations between 70 and 180 ng/L. The last category including Octocrylene, Ethylhexyl Methoxycinnamate and Iscotrizinol were showed in high concentration between 1500 and 3000 ng/L. Octocylene has been reported to be found in 75% of the studied swimming pools water. The presence of UV filters in swimming pool water samples varies according to the persistence of each filter in the light and its release in water.

4. Conclusion

A sensitive analytical method based on SPE followed by LC/MS/MS and GC/MS has been developed for the simultaneous determination of eighteen UV filters in water matrix. The parameters affecting pre-concentration step, the mobile phase, the parameters of the mass spectrometry for liquid and gas chromatography, and those of the ionization source have been all assessed and optimized. Moreover, the parameters of the SPE have also been evaluated. The optimized method demonstrated to be sensitive enough in detecting trace levels of UV filters allowing its application for environmental assessment studies. The best recoveries for all compounds were found when chromo bond C18 cartridges were used for extraction with acetonitrile as elution solvent. The method was satisfactory validated in terms of linearity, precision, repeatability and reproducibility. Its detection limits are between 2.5 and 50 ng/L with recoveries higher than 69% and RSD for repeatability and reproducibility values below 20 %. The validated method was applied to 10 samples collected from different swimming pools located in Bekaa region in Lebanon. Nine out of the 18 target UV filters were found in the analyzed samples. Padimate-O was detected in 90% of swimming pools at low concentrations ranged between 1 and 20 ng/l. Octorylene, Ethylhexyl Methoxycinnamate and Iscotrizinol were detected in high concentration between 1500 and 3000 ng/L. Our results reported here the first data for the occurrence of UV filters in swimming pools in Lebanon. Future studies are required to assess the presence of different UV filter compounds in swimming pools located in different regions in Lebanon. This study will be the building block for both long- and short-time applications. Shortly, it will contribute on the design of future monitoring programs of water quality assessment for water systems such as drinking water and wastewater. On the other hand, measuring the concentrations of these chemicals in water will help to guide future studies to deal with their removal using water treatment processes and to evaluate their eco- and cytotoxicity.

Declarations

Ethics approval and consent to participate

not applicable

Consent for publication

Not applicable

Availability of data and material

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to that the containing information could compromise the privacy of research participants.

Conflict of interest statement

All authors have approved the submission, and none declares any conflict of interest in the work performed or in the submission of the manuscript.

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Authors' contributions

Conception and design of study: Samia MOKH, Rania NASSAR, Mariam TAHA, Mohamad AL ISKANDARANI; acquisition of data Aitika BERRY, Raed EZZEDDINE, Mohamad AL ISKANDARANI; analysis and/or interpretation of data: Samia MOKH, Rania NASSAR, Mariam TAHA; drafting the manuscript: Samia MOKH, Rania NASSAR, Samah DOUMIATI, Mariam TAHA; revising the manuscript critically for important intellectual content: Mohamad AL ISKANDARANI.

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Code availability

Not applicable

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Tables

Table 1: LC/MS/MS and GC/MS Experimental parameters

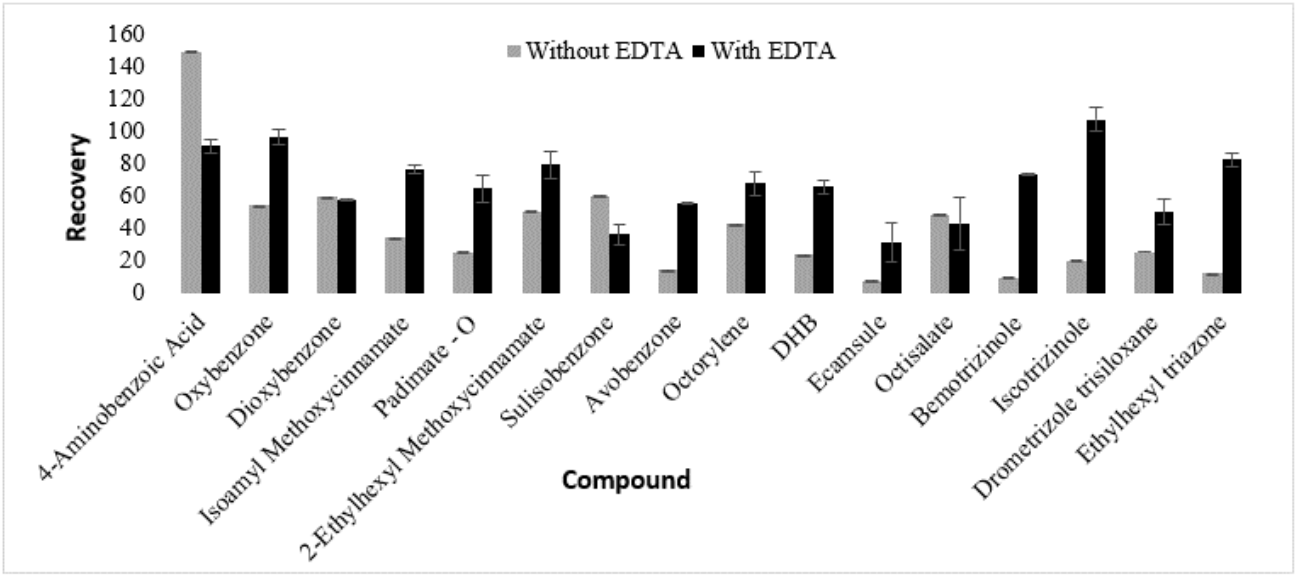
LC/MS/MS					
Compounds	Tr (min)	Precursor Ion	Fragmentor	Quantitative Ion/ CE	Qualitative Ion/CE
Benzoic acid d5 (BA d5)	3.2	126	80	82	
4-Aminobenzoic Acid	2.94	138	100	94/ 10	120/ 10
Sulisobenzone (BZ 4)	6.92	309.1	110	230.9/ 20	199/ 20
Avobenzone	12.67	311.1	80	161.1/ 20	135/ 20
Ecamsule	7.27	563.3	110	481/ 20	161.2/ 30
Bemotrizinole	17.87	628.4	100	516.2/ 30	404/ 30
Iscotrizinole	14.74	766.5	100	693.2/ 20	636.1/ 20
Ethylhexyl triazone	17.57	824	110	712/ 50	600/ 50
GC/MS					
Compounds	Tr (min)	Quantitative Ion		Qualitative Ion	
Benzophenone-d10 (surrogate)	6.85	110		82, 110, 192	
Octisalate	7.85	120		120, 138, 250	
Homosalate	8.28	138		138, 262, 120	
Oxybenzone (BZ3)	9	227		227, 151 ,228	
Cinoxate	9.1	178		250, 161, 178	
Isoamyl Methoxycinnamate	8.9	178		161, 178, 248	
Dioxybenzone (BZ 8)	9.7	121		121, 244, 151	
Padimate-O	10	165		277, 165, 148	
Ethylhexyl Methoxycinnamate	10.15	178		178, 161, 290	
Octorylene	12.25	204		204, 232, 360	
Drometrizole Trisiloxane	13.9	221		221, 369, 444	
DHB	17.47	397		382, 397	

Table 2: Performance and validation data of the analytical method

	R^2	LOQ (µg/L)	MDL (ng/L)	Recovery	Repeatability RSD %			Reproducibility RSD %		
					50 (µg/L)	100 (µg/L)	200 (µg/L)	50 (µg/L)	100 (µg/L)	200 (µg/L)
4-Aminobenzoic Acid	0.9994	3.40	50	86	10	7	1	12	17	11
Oxybenzone	0.9954	0.13	2.5	69	8	3	2	8	5	6
Dioxybenzone	0.9267	0.50	2.5	71	10	5	3	9	10	7
Isoamyl Methoxycinnamate	0.9792	6.50	5	94	8	3	1	12	13	6
Padimate - O	0.9948	0.08	1.25	106	8	4	4	9	4	3
2-Ethylhexyl Methoxycinnamate	0.9922	0.23	5	97	10	5	5	10	10	11
Sulisobenzone	0.9967	2.30	12.5	68	12	2	7	17	11	12
Avobenzone	1	0.50	2.5	98	10	2	4	9	14	7
Octorylene	0.9867	0.74	5	81	12	4	3	2	10	10
DHB	0.9978	0.40	5	83	9	6	2	12	11	5
Ecamsule	0.9957	6.25	50	94	6	4	4	3	10	13
Octisalate	0.9997	10.00	12.5	98	1	3	5	9	16	18
Bemotrizinole	0.9964	0.50	50	81	2	10	7	6	12	16
Iscotrizinole	0.9952	2.90	50	92	4	13	1	13	18	9
Drometrizole trisiloxane	0.9937	35.00	50	100	9	2	1	7	8	11
Ethylhexyl triazone	0.9948	60.00	50	97	8	3	2	8	10	16
Cinoxate	0.9966	12.05	10	98	4	3	4	5	7	15
Homosalate	0.9998	10.00	25	111	6	1	1	1	8	10

R2: Determination coefficient; LOQ: limit of quantification; MDL: Method detection limit; RSDr: Relative repeatability standard deviation; RSDi: Relative standard deviation for intermediate precision

Figures



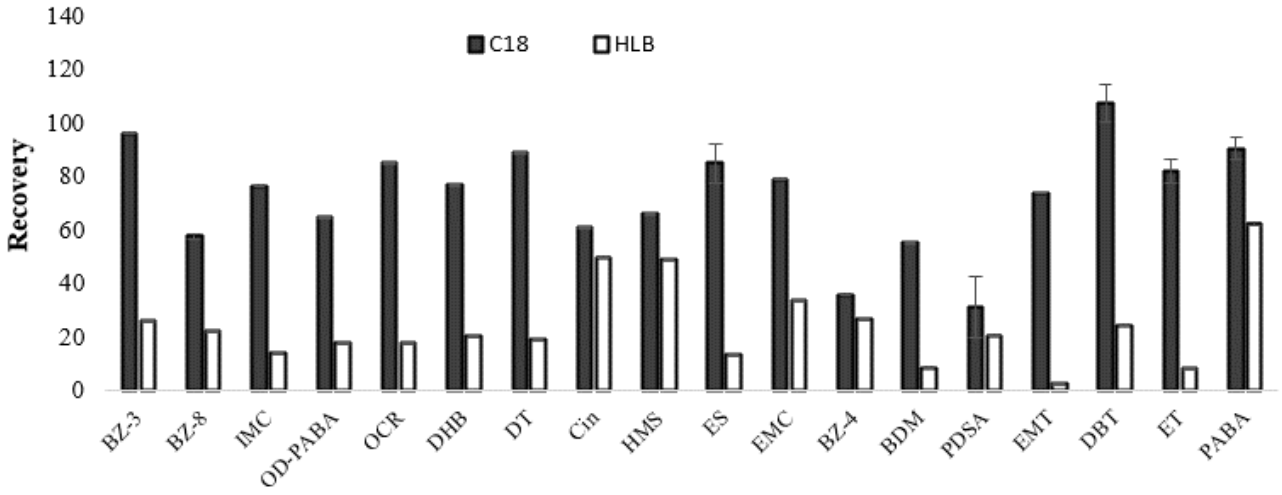


Figure 1

Chromo Bond C18 compared to Oasis HLB

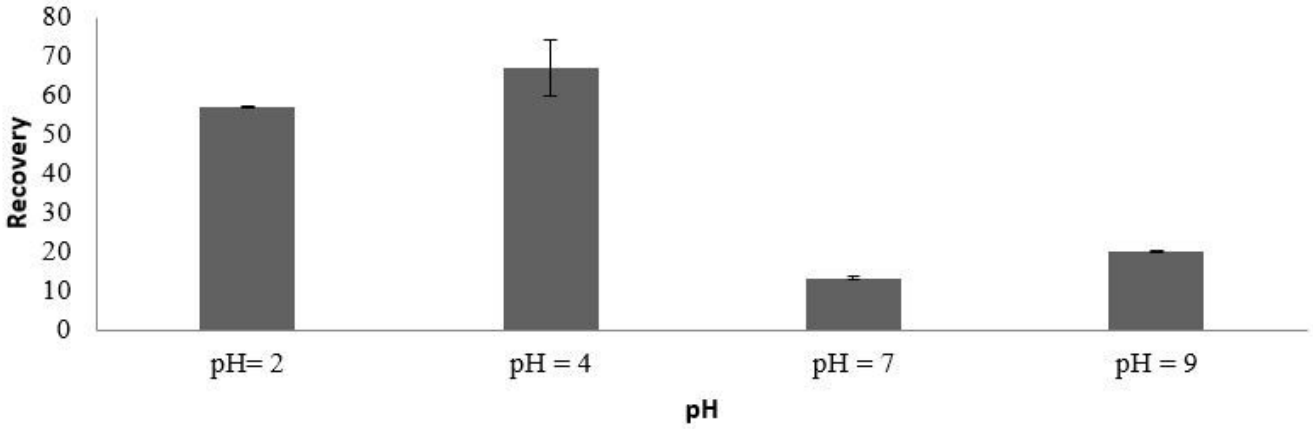


Figure 2

Extraction efficiency at different pH

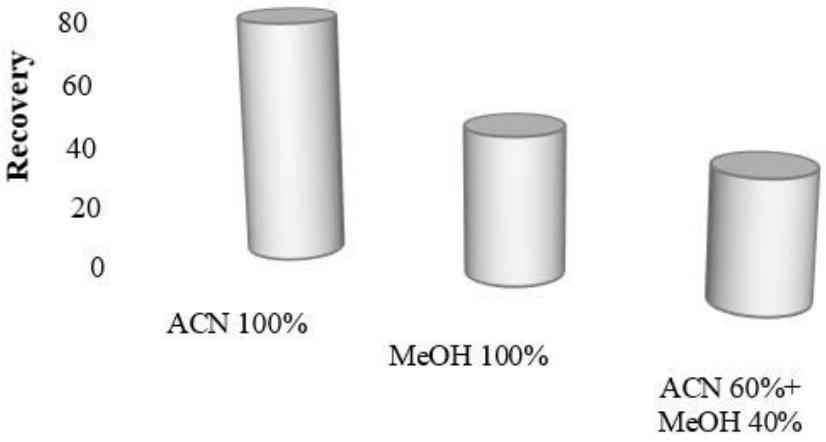


Figure 3

Effect of solvent on the average recovery of UV filters

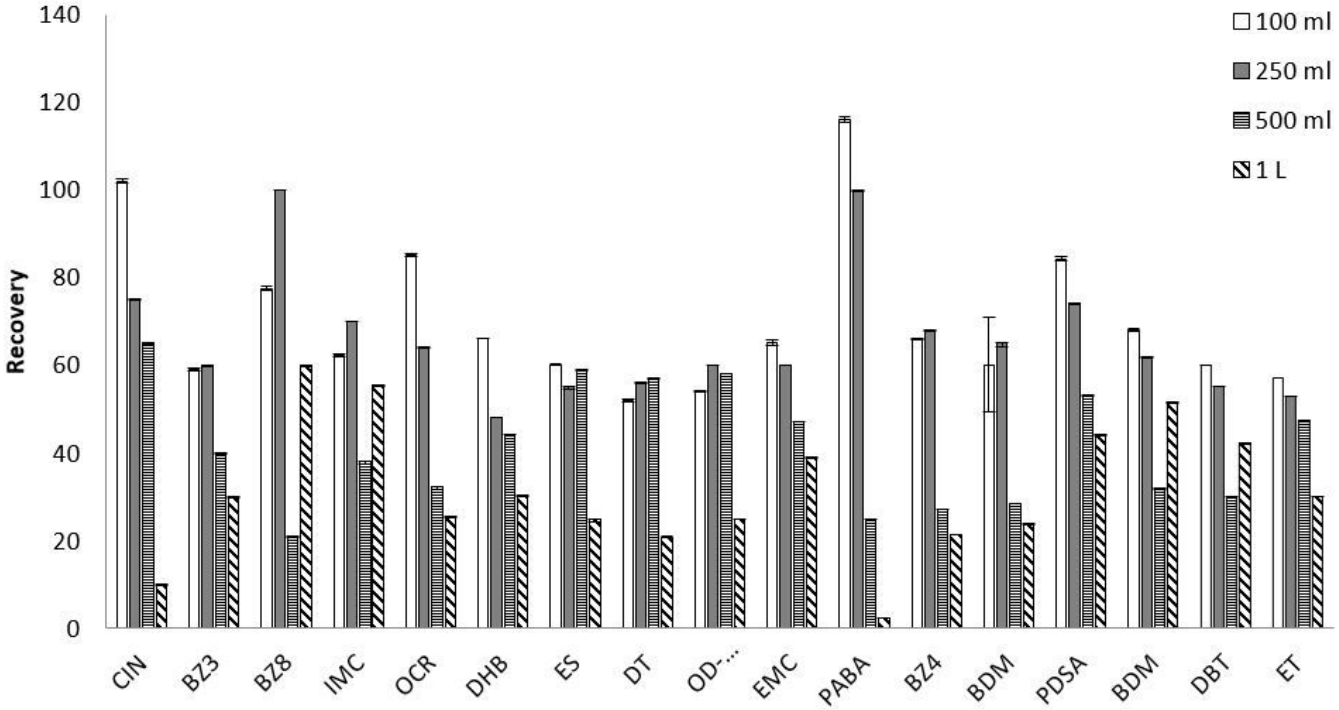


Figure 4

Effect of Breakthrough volume on recovery of UV filters

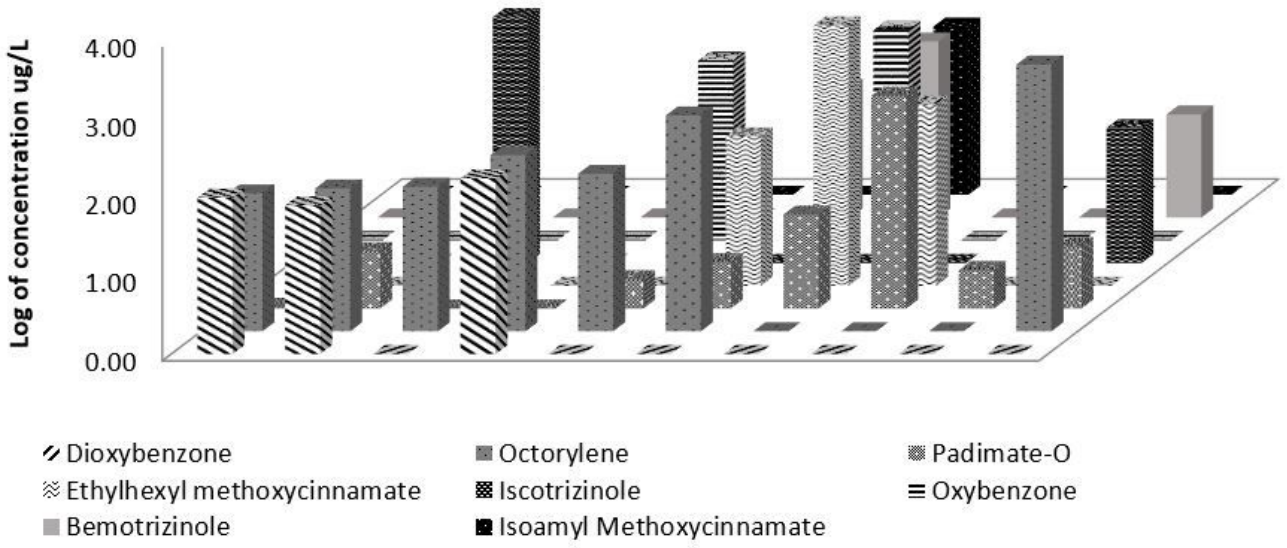


Figure 5

Log of concentrations of UV filters in water samples