Review

Application of Liquid Chromatography for the Analysis of Organic UV Filters In Environmental and Marine Biota Matrices

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Application of Liquid Chromatography for the Analysis of Organic UV Filters in Environmental and Marine Biota Matrices

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Abstract: Sunscreens are topical preparations containing one or more compounds that protect humans from ultraviolet (UV) light. This review focuses on analytical methods, particularly liquid chromatography, aimed at identifying and determining UV filters (UVFs) in environmental and marine biota matrices. A literature review was done using NIH (PubMed and Medline), FDA and EPA databases, Google Scholar, and Federal Regulations. This retrospective literature review is focused on the last five years. UVFs quantification in environmental and biological matrices showed a wide array of methods where liquid chromatography is predominant. The scientific literature identified a large variety of analytical methodologies that are compared in this review, to evaluate the better results in terms of limits of quantification and the possibility to identify as many analytes as possible simultaneously.

Keywords: UV filters; sunscreens; liquid chromatography; environmental matrices; marine biota

1. Introduction

UV filters (UVFs) are a group of chemicals characterized by their capacity to absorb the UV radiation, like UVA (280–315 nm), UVB (315– 400 nm) or both of them (UVA and UVB) [1].

They can also be distinguished into organic and inorganic ones: organic filters are compounds with single or multiple aromatic structures, capable only of absorbing the UV radiation, while inorganic filters can reflect and scatter it [2,3].

Due to their ability to absorb UV radiation, they are frequently used in sunscreens and personal care products to prevent solar-induced human skin damage [4].

Moreover, they are not only used in cosmetics, but also in adhesives, rubber, and materials for food containers in order to reduce UV degradation [5]. In fact, they can efficiently prolong the service life of materials, delaying UV degradation and oxidative processes [6]. Recent studies demonstrated that the direct contact between these materials and food, allows the migration of UVFs into the food and, in turn, into the human body through food intake [7–9]. In fact, also if it is well known that the principal route of human exposure to UVFs present in sunscreen products is the direct dermal contact through skin permeation (direct way), humans can be exposed to these chemicals also by ingesting fish and seafood, or beverages in contact with packaging materials containing UVFs as stabilizers (indirect way) [7,8].

Given their large use, in recent decades, the safety of UVFs for humans and the environment has raised concern in the scientific community.

Experimental evidence demonstrates that large quantities of UVFs are released into the environment and can accumulate in environmental and marine biota matrices [10–13], thus entering the food chain [14–16]. Moreover, many studies confirmed the presence of organic UVFs in several human biological samples [17–19].

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Because of their hydrophobicity and poor degradation, UVFs are able to accumulate in several matrices leading to important negative effects, including endocrine-disrupting ones [20]. Different types of UVFs can differently contribute to give health toxicity [21].

To avoid their inappropriate or excessive exposure, the Scientific Committee on Consumer Safety approved the margin-of-safety estimation (MoS) to assess the health risk derived by UVFs. This estimation can be determined for a single substance from different exposure routes or for multiple substances to estimate the combined risk [22]. In fact, the combined risk depends both on the concentration of different UVFs in sunscreen products and on human exposure routes [23]. To evaluate their widespread in the environment and potential adverse effects on ecosystems and human health, it is important to quantify UVFs not only in cosmetics and biological samples but also in environmental matrices. Therefore, it is important to develop efficient analytical methods to simultaneously identify and quantify these compounds. To date, most of the publications focus on the study of benzophenone-3 (BP-3) and its metabolites in biological matrices [24]. Among the chromatographic techniques, liquid chromatography shows to be the technique of choice for the separation and quantification of UVFs [25,26].

The aim of this review is to provide a comprehensive overview about the analytical methods, available in the literature over the last five years, focusing on the application of liquid chromatography for the analysis of organic UVFs in environmental and marine biota matrices. A recent review already reported an excursus of analytical methods for the determination of organic UVFs in cosmetics and human samples [26].

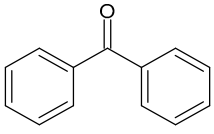
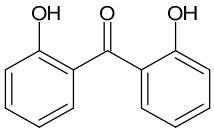
Currently, a total of around 45 organic UVFs are globally registered for cosmetic use in the European Union (EU), Canada, USA, China and Japan. The EU limited the use in sunscreen products to one inorganic (titanium bioxide) and 26 organic UVFs [27]. In Canada, the UVFs for human use registered by Health Canada include two inorganic chemicals (zinc oxide and titanium dioxide), and 19 organic chemicals [28]. The Food and Drugs Administration (FDA) authorizes in USA a total of 16 UVFs, including two inorganic compounds [29]. The Chinese regulation permits the use of 26 sunscreens [30] vs. the 27 ones permitted in Japan [31]. The permitted maximum concentration in cosmetics ranges from 2 to 25%. Recently, the EU have reduced the allowed limit of BP-3 from 10% to 6% in sunscreens and to 0.5% in cosmetics [32]. Given their toxicity, some countries have recently prohibited the use of some sunscreens as BP-3 and octinoxate [33,34].

2. Analytical methods for the analysis of organic UVFs

Among synthetic UVFs, we can find different classes of compounds, like benzophenones, dibenzoyl methane derivatives, benzotriazoles, cinnamates, salicylates, crylenes, PABA derivates, camphor and triazine derivatives (Table 1).

In this review, we want to analyze the most recent liquid chromatographic methods aimed at identifying and quantify different organic UVFs according to their chemical structural class.

Table 1. Classification and chemical structures of investigated organic UVFs.

Classes	Chemical name	INCI name	Code	Chemical structure
BENZOPHENONES	Benzophenone	Benzophenone	BP	
	2,4-Dihydroxybenzophenone	Benzophenone -1	BP-1	

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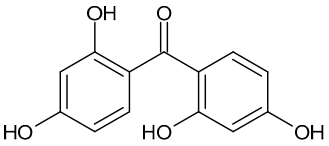
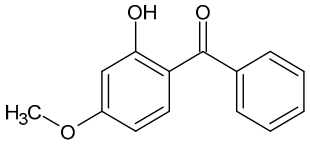
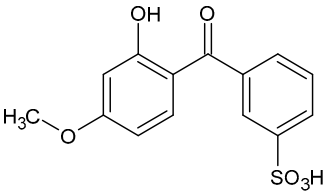
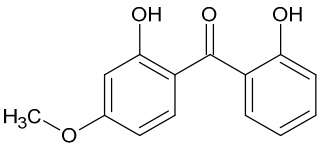
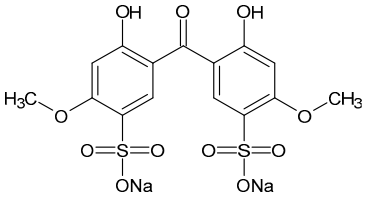
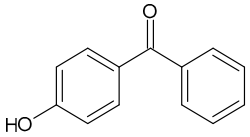
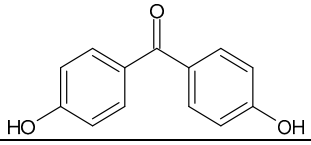
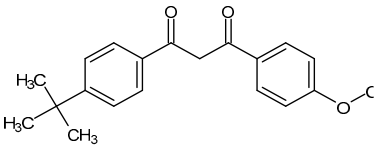
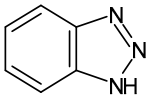
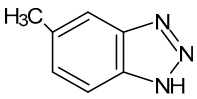
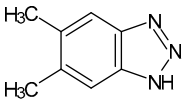
	2,2',4,4'-Tetrahydroxy benzophenone	Benzophenone -2	BP-2	
	2-Hydroxy-4-methoxy benzophenone (Oxybenzone)	Benzophenone -3	BP-3	
	2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid (Sulisobenzone)	Benzophenone -4	BP-4	
	2,2'-Dihydroxy-4-methoxybenzophenone	Benzophenone -8	BP-8	
	2,2'-Dihydroxy-4,4'-dimethoxybenzophenone-5,5'-disulfonic acid disodium salt	Benzophenone -9	BP-9	
	4-Hydroxybenzophenone		4-HBP	
	4,4′-Dihydroxybenzophenone		4,4′-DHBP	
DIBENZOYL METHANE DERIVATIVES	4-tert-Butyl-4'-methoxy-dibenzoylmethane	Avobenzone	AVO	
BENZOTRIAZOLES	1H--Benzotriazole	Benzotriazole	1HBT	
	5-Methyl-1H-benzotriazole		MeBT	
	5,6-Dimethyl-1H-benzotriazole		DMeBT	

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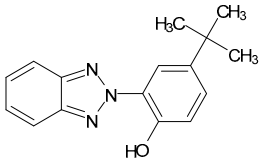
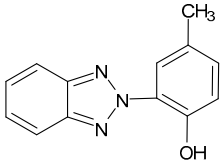
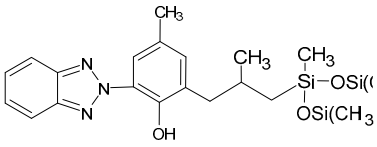
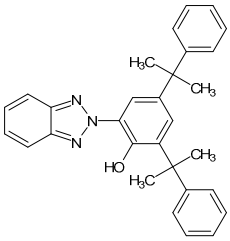
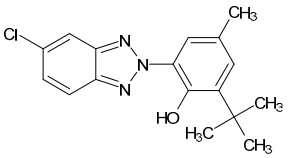
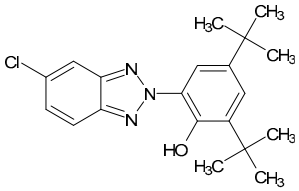
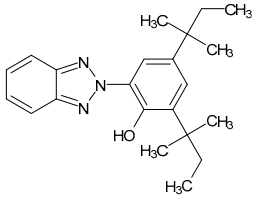
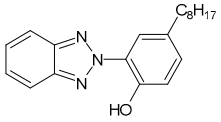
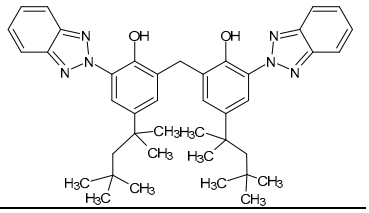
2-(5-tert-Butyl-2-hydroxyphenyl) benzotriazole		TBHPBT	
2-(2'-Hydroxy-5'-methylphenyl) benzotriazole	Drometizole	UV-P	
2-(benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[methyl-bis(trimethylsilyloxy)silyl] propyl] phenol	Drometizole trisiloxane	DTS	
2-[2-Hydroxy-3,5-bis (1,1-dimethylbenzyl) phenyl] benzotriazole		UV-234	
2-(2′-Hydroxy-3′-tert-butyl-5′-methylphenyl)-5-chlorobenzotriazole	Bumetrizole	UV-326	
2-(2′-Hydroxy-3′,5′-di-tert-butylphenyl)-5-chlorobenzotriazole		UV-327	
2-(2′-Hydroxy-3′,5′-di-tert-amylphenyl) benzotriazole		UV-328	
2-(2′-Hydroxy-5′-(1,1,3,3-tetramethylbutyl) phenyl) benzotriazole	Octrizole	UV-329	
Methylene bis-Benzotriazolyl tetramethyl butylphenol	Bisoctrizole	UV-360	

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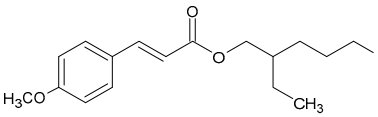
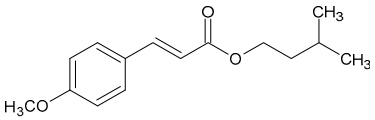
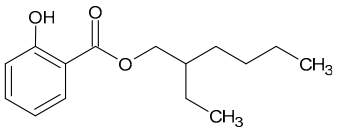
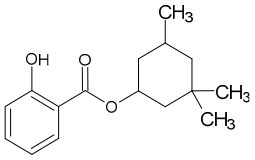
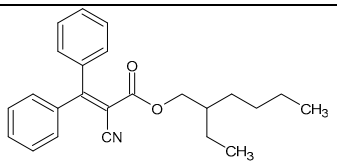
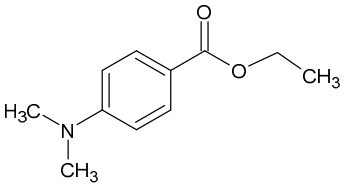
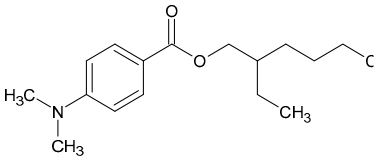
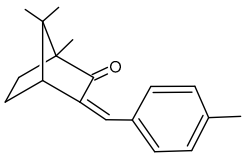
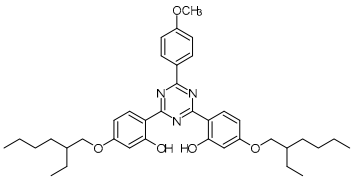
CYNNAMATES	2-Ethylhexyl 4-methoxy cinnamate (Octyl methoxy cinnamate)	Octinoxate	EMC	
	Isoamyl 4-methoxycinnamate	Amiloxate	IMC	
SALYCILATES	2-Ethylhexyl salicylate	Octisalate	EHS	
	3,3,5-Trimethylciclohexyl salicylate Homomethyl salicylate	Homosalate	HMS	
CRYLENES	2-Ethylhexyl 2-cyano-3,3-diphenyl acrylate	Octocrilene	OCR	
PABA DERIVATES	Ethyl-4-(dimethyl-amino) benzoate		EtPABA	
	2-Ethylhexyl 4-(dimethyl-amino) benzoate (Padimate-O)		ODPABA	
CHAMPHOR DERIVATIVES	4-Methylbenzylidene camphor		4-MBC	
TRIAZINE DERIVATIVES	Bis-ethylhexyloxyphenol methoxyphenyl triazine (Bemotrizinol)		BEMT	

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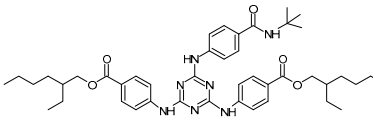
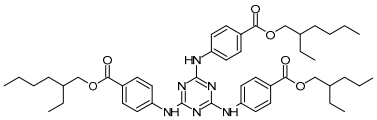
Diethylhexyl butamido triazone (Iscotrizinol)	BDT	
Ethylhexyl triazone	EHT	

2.1. Benzophenones

Benzophenones (BPs) are one of the most diffused families of UVFs. Chemically, they are dibenzoyl methane derivatives that belong to the aromatic ketone category. The main drawbacks to the use of benzophenones as UVFs are concern about their safety, as aromatic ketones are more difficult to detoxify than esters, and their solid state, which impairs their solubilization in cosmetic formulations. They are in fact usually used in combinations with solubilizers [35].

Given their high lipophilicity, they can easily penetrate the dermis and bio-accumulate in the human body. Numerous studies confirmed their presence in a variety of biological samples [36,37]. BPs have been shown to act as endocrine disruptors [38,39]. They have also been associated to skin irritation in the form of contact dermatitis and photoallergic reactions [40].

Among BPs, twelve of them, from benzophenone-1 (BP-1) to benzophenone-12 (BP-12), are commercially used as UVFs, as well as some of their photodegradation and metabolization products [41,42]. BP-3 is the most commonly used [43]; after the application of sunscreens, it is transformed into BP-1. For this reason, both BP-3 and BP-1 are considered main markers of exposure [42,44].

Considering their increasing diffusion, BPs have been the topic of numerous investigations in both environmental and marine biota fields.

2.1.1. Environmental matrices

Water was shown to be the most investigated matrix between those that could be used to study BPs' widespread in the environment, including drinking water, freshwater, seawater and groundwater.

In 2019, an on-line solid phase extraction followed by liquid chromatography coupled to tandem mass spectrometry method (SPE-LC-MS/MS) was applied to determine BP-1, BP-2, BP-3, BP-8, 4-HBP, 4,4'-DHBP and other UVFs in river water and sediments from the Evrotas River in Greece [45]. During this study, samplings were conducted according to the recommended guidelines on chemical monitoring of river water and sediment from the Directive 2000/60/EC [46]. Samples were analyzed following the method by Gago-Ferrero et al. [47]. The separation was achieved using a C18 (50 × 2.0 mm, 5 μm) column with a mobile phase, consisting of water and acetonitrile (ACN), both with 0.1% formic acid. Positive ionization (PI) mode was selected for the MS/MS detection. Under the optimized chromatographic conditions, the method showed low limits of quantification (LOQs) for river water and sediments. BP-3 was the most frequently detected UVF (in 88% of investigated samples), with high concentrations ranging from 0.2 to 2031 ng/L; three of its metabolites (BP-1, 4-HBP and 4,4'-DHBP) were also detected with average concentration of 50 ng/L.

In the same year, Força-Lima et al. reported an efficient sampling methodology with a semipermeable membrane device for the extraction and preconcentration of some organic UVFs (between them BP and BP-3) from swimming pool waters [48]. The analytical determination was performed using high performance liquid chromatography with diode array detection (HPLC-DAD) using a C18 column (150 x 4.6 mm, 4 μm). Chromatographic separation was carried out in isocratic elution mode (ACN and phosphate buffer solution 0.01 M, pH = 3.5). BP and BP-3 were monitored at 204 nm. Analysis by UV-DAD showed higher limits of detection (LODs) than tandem mass spectrometry, for both analytes. The extraction performance of the extraction device was also verified

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through the BPs determination in swimming pool water and obtaining recovery percentages in the range of 74.9–98.5%.

An LC-MS analysis was optimized by Horricks et al. [49] for the determination of BP-3 widespread in seawater of Grenada, West Indies, using a C18 column (30 x 2mm, 5µm), with water and methanol with 0.1% formic acid as mobile phase. LODs and LOQs of the method were not reported. Percent recovery was reported between 107–121%. BP-3 was detected in 60% of seawater samples with a mean concentration of 0.046 µg/L.

In analytical fields, significant efforts are continually being carried out to develop new methodologies that improve the performance of extraction methods from environmental matrices. The main goal, in sample preparation, is to design stationary phases for dealing with the retention of polar and apolar analytes simultaneously. An attempt to improve the selectivity or specificity toward target analytes was developed by Kharbouche et al., using a solid phase extraction (SPE) with silica-based mesoporous, functionalized with cyanopropyl groups for the determination of BP-1, 4-HBP, and 4,4′-DHBP in river and swimming-pool waters [50]. The quantification of these emerging contaminants in water was carried out using LC-MS/MS in both PI and negative ionization (NI) modes. For the chromatographic separation, a C8 column (2.1 mm × 100 mm, 1.8 µm) with 0.1% formic acid (PI) or 5mM ammonium formate (NI) and methanol as mobile phase were used. The recoveries for 4,4′-DHBP and BP-1 were between 61.9 and 66.8%, while for 4-HBP were higher than 83.2%. The intraday relative standard deviation (RSD%) values were in the range of 6.0 and 15.5%. All BPs were detected in swimming pool water, but at concentrations lower than their LOQs. Conversely, in the river water sample, none of the investigated BPs was detected.

Mallappa Gopal et al. (2020) developed a liquid chromatography linear ion-trap tandem mass spectrometer method (LC-MS/MS) for the investigation and quantification of BP-1, among other 11 pharmaceuticals and personal care products, in water samples collected from Arkavathi river (India). [51]. The samples were pretreated with SPE. Analytes were resolved by a C18 column (150 mm x 4 mm, 5 µm) and a mobile phase consisting of methanol and ammonium acetate (5 mM, pH 5.8). All target analytes were quantified in NI. The results were compared with other studies existing in the literature. Generally, the determination of pharmaceuticals in water by ion trap is scarce, due to lack of sensitivity in comparison with triple quadrupole mass spectrometers [52,53]. This LC-MS/MS method proved to be sensitive and reliable. The Oasis HLB sorbent used to preconcentrate water samples proved recoveries ranging from 68.86 % to 90.72 %. Data for precision was within the satisfactory limit of 15%, according to adopted guidelines [54].

The study of Cadena-Aizaga et al. analyzed the occurrence of 8 organic UVFs (including BP-3) in seawater from three beaches on Gran Canaria Island (Spain) and in three wastewater treatment plants [55]. The UVFs determination was carried out by SPE-LC-MS/MS, in PI mode, using a C18 column (50 × 2.1 mm, 1.7 µm), and methanol/water with 0.1% (v/v) formic acid as mobile phase. LOD and LOQ values were in order of ng/L for both seawater and wastewater. The extraction recoveries range was 78.9-99.3%. Intraday and interday precision ranged between 0.02% and 13.0%. BP-3 was the most recurrent compound in the seawater samples (frequency detection of 83%) with concentration ranges from 0.16 to 20.5 µg/L. Also, in wastewater, it was present in all samples, with loads ranging from 200 to 903 µg/d/1000 inhabitants.

In 2021, Fisch et al. conducted a study to identify BP-1, BP-3, BP-4 and 4,4′-DHBP in the coastal waters of the Delta Pearl River (China) [56]. LC-MS/MS analysis was carried out using a C18 column (50 x 2.1 mm, 2.6 µm) with a mobile phase consisting of water and methanol, with each 0.1% acetic acid and formic acid, respectively. The ionization was achieved in both PI and NI mode. LODs and LOQs for target compounds ranged between 0.01 and 2.4 ng/L. Average recovery percentages were good for all investigated BPs except for BP-3 (33%). The other mean recoveries were 85% (BP-1), 89% (BP-2), 99% (BP-4), and 76% (4,4′-DHBP). The 4 UVFs were detected with a detection frequency of 40-100% in a concentration range from 1.3 to 24.3 ng/L.

BP-1, BP-2, BP-3, BP-4, BP-8, 4-HBP,and 4,4′-DHBP were also investigated in seawater and sediments along the coast of Mahdia (Tunisia), using an SPE-LC-MS/MS method [57]. The performance of the applied method was previously validated by Gago-Ferrero et al. [47,58]. The

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chromatographic separation was achieved on a C18 (50 × 2.0 mm, 5 μm) with methanol and 0.1% formic acid or 5mM ammonium formate as mobile phases. MS/MS detection was performed in PI mode for all BPs except for BP-4, which, being an aromatic sulfonic acid, with a very strong acidic character, solely can be ionized under NI mode [59]. Recoveries were between 70 and 110%, with good reproducibility. BP-3 was present in all water samples with concentrations in the range from 16.4 to 66.9 ng/L. In sediments, neither BPs were found.

Another SPE-LC-MS/MS method for the determination of 18 UVFs in swimming pool water was performed by Mokh et al. in 2022 [60]. The authors reported a SPE extraction followed by two different analytical methods: LC-MS/MS for BP-4 analysis, and GC/MS for determination of BP-3 and BP-8. For liquid chromatographic analysis, a C8 column (2.1 × 100 mm, 3.5 μm) with gradient elution with pure water/ACN was used. The MS/MS was achieved in PI. Recovery for BP-4 was 68% and RSD for repeatability values were below 20%. The method has proven to be sensitive enough in detecting traces of BP-4.

Recently, Brown et al. tested a unified method to quantify eight UVFs (between them BP-3, BP-4 and BP-8) by SPE-LC-MS/MS, in both NI and PI modes using polarity switching [61]. The chromatographic separation was performed using a C18 column (2.1 mm ×50 mm, 1.8 μm), in gradient elution with water and ACN (0.05% formic acid). The validated method resulted in accuracies ranging from 97 to 104%. The method was applied to chlorinated outdoor pool waters in Winnipeg (Canada).

Beside to water matrix, several authors investigated soils and sediments to monitor the widespread of BPs in the environment.

Votani et al. presented a new approach, named On-line Extraction (OLE), coupled to liquid chromatography for the analysis of BP-3 and other organic UVFs from complex solid samples [62]. Specifically, they replaced the sample loop of a conventional LC injection valve by an extraction vessel consisting of an empty guard column filled with the solid sample. Upon injection, the mobile phase flows through the extraction vessel and accomplishes the dynamic extraction of the analytes assisted by the high pressure developed in the LC system. The eluted analytes are then directly transferred to the LC column for separation and analysis. In this manner, the on-line analysis is accomplished without the need for additional sample pretreatment; steps such as cleaning, solvent exchange, filtration and drying of the extracts are no longer required [63]. The extraction and LC analysis were performed in a Shimadzu LC system equipped with a UV/Vis detector. Peak area was monitored at 285 nm for all analytes. The chromatographic separation was performed in a thermostated (40 °C) C18 column (250 mm x 4.6 mm, 5 μm) using methanol/ water (75/25) as mobile phase. The method was optimized for the extraction of hydrophobic UV filters from spiked soil and sediment samples yielding recoveries between 59 and 117%, which are comparable to those reported from more advanced sample preparation methods.

2.1.2. Biota marine matrices

The already cited study of Díaz-Cruz et al. reported an SPE-LC-MS/MS method for the investigation of BP-1, BP-2, BP-3, BP-8, 4-HBP, and 4,4′-DHBP in fish collected from the Evrotas River in Greece [45]. Biota samplings were conducted following the recommended guidelines on chemical monitoring from the Directive 2000/60/EC [46]. Biota samples were analyzed according to the method by Gago-Ferrero et al. [47]. BP-2 was detected in all fish samples, ranging from 11.8 to 41.9 ng/g dw. BP3 was detected in 50% of the fish samples at low concentrations (from <LOQ to 1.8 ng/g dw).

The HPLC-MS analysis of Horricks et al. investigated BP-3 presence in the invasive Pacific lionfish (Pterois volitans), collected in the nearshore waters of Grenada, West Indies [49]. LODs and LOQs of the method were not reported. Percent recovery was reported between 107–121%. Residues of BP-3 were detected in 24% of lionfish muscle at an average concentration of 1.46 μg/kg.

A microwave-assisted extraction (MAE), followed by LC-MS/MS, was applied to the analysis of BP-3, and other UVFs, in macrophytes (seaweeds and seagrass) collected from three different beaches on the Gran Canaria Island (Spain) [64]. Determination was performed by an UHPLC system equipped with a C18 column (50 × 2.1 mm, 1.7 μm) and a MS/MS detector in PI. The extraction

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recoveries range was 51.8–65.4%. Intraday and interday precision ranged between 2.66% and 10.44%. BP-3 presented the lowest frequencies (16–25%) between the investigated UVFs.

2.2. Dibenzoyl methane derivatives

Dibenzoyl methane derivatives are substituted diketones with characteristics of UVA filters (enol form). The keto form is responsible for high photoisomerization, resulting in a significant loss of protective power. These compounds have exceptionally high molar extinction coefficients but low photostability [35]. Structurally like BPs, the avobenzone (AVO) is a long-wave UVF, which easily dissociate into oxygen-free radicals and derivatives and may damage proteins and DNA. Due to its high Log Kow (4.51), AVO could affect aquatic organisms at lower concentrations [65]. Its allowed concentration is limited to 5% by the EU legislation [32]. In sunscreen formulations, AVO is used in the enol form, with excellent UVA absorption but easily isomerizes to the di-keto form, losing effectiveness [66].

2.2.1. Environmental and biota marine matrices

In two distinguished studies of Cadena-Aizaga et al., the presence of AVO in seawater [55], and in macrophytes (seaweeds and seagrass) [64], was investigated from three different beaches on the Gran Canaria Island (Spain). Analytical methods have been already described in *2.1.1.* and *2.1.2.* paragraphs. The average recoveries were 85% and 60% in seawater and macrophytes, respectively. Intraday and interday precision were always below the 15%. The detection frequency of AVO in the summer period in seawater was of 56% with a maximum concentration of 88.9 μg/L [55]. In macrophytes, AVO was detected in 85% of samples (maximum concentration of 3663 ng/g dw)[64].

AVO was also investigated in seawater and sediments along the coast of Mahdia (Tunisia), by Fenni et al. [57]. The SPE-LC-MS/MS method is reported in *2.1.1.* paragraph. MS/MS detection was performed in PI mode. Over a period of 6 months, AVO was detected both in seawater and in sediment samples, showing its widespread occurrence in all investigated locations and seasons. Average concentrations in seawater and sediments were 16.3 ng/L and 17.6 ng/g dw, respectively.

Mokh et al. reported a SPE-LC-MS/MS method for determination of AVO in swimming pool water (see *2.1.1.* paragraph for detailed description) [60]. Satisfactory method performance for AVO was reported with high recovery (98%) and RSD for repeatability values below 15%. The method showed a LOD suitable for environmental assessment studies.

More recently, Brown et al. tested a SPE-LC-MS/MS for AVO analysis in pool water. MS/MS detection was performed in PI [61]. The performance of validated method resulted in excellent accuracy (97 %), with good LOD and LOQ.

Seyer et al. investigated the interaction of two plant species (*Lemna gibba and Cyperus alternifolius*), commonly found near lakes, with three UVFs widely used in sunscreens, including AVO [67]. The parent compound and its transformation products found within the plants tissue were characterized employing HPLC coupled to a quadrupole time-of- flight mass spectrometer (QTOF-MS). Chromatographic separation was carried out on C18 column (50×4.6 mm, 2.7 μm) with a mobile phase consisted of water and ACN with 0.1% formic acid. For AVO several transformation products resulting from hydroxylation, demethylation and oxidation of the parent molecule have been investigated. Furthermore, a kinetic study on the uptake and biotransformation of UVFs was conducted over a period of 216 h, revealing that they were mostly present in their parent form and only to a smaller part converted into transformation products.

2.3. Benzotriazoles

Benzotriazoles (BTs) are a class of compounds characterized by a phenolic group attached to the benzotriazole structure. They absorb the full spectrum of UV light and are widely used in personal care and plastic products. Like BPs, in the last decades, also BTs have been accused of being endocrine disruptors and, due to their potentially hazardous effects, they caught more attention of the scientific community.

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Although their toxicological effects are still poorly clear, many countries have set limits on the consumption of BTs. For example, the Japanese Government banned the production, use, and import of UV-320 since 2007 [68].

2.3.1. Environmental matrices

Wang et al. (2018) proponed a SPE- HPLC-UV method for the determination of six BTs UVFs in water and cosmetic samples [69]. The six BTs (UV-P, UV-234, UV-326, UV-327, UV-328, and UV-329) were separated with a C18 column (150×4.6 mm, 5 μm) in isocratic elution with a mobile phase comprising methanol/water (95/5). The UV detector was set at 340 nm. Under the optimized conditions, the method showed a wide linear range from 20.0 to 1000 μg/L for all compounds with good correlation coefficients, and acceptable reproducibility (RSDs < 6.5% for intra-day, RSDs < 8.1% for inter-day). Satisfactory recoveries ranged from 89 to 105%.

Díaz-Cruz et al. (2019) investigated the presence of 1HBT, UV-P, MeBT, DMeBT, TBHPBT, UV-326, UV-327, UV-328, and UV-329 by SPE-LC-MS/MS in river water and sediments from the Evrotas River in Greece [45]. The method has been already described in detail in *2.1.1.* paragraph. In river water, MeBT was the most frequently detected BT (in 88% of the samples), with a maximum concentration of 784.7 ng/L. In sediments, none BTs compound was determined.

The study of Cadena-Aizaga et al. (2022) analyzed the occurrence of two BTs (DTS, UV-360) in seawater and wastewater [55]. The SPE-LC-MS/MS method has been already described in detail in *2.1.1.* paragraph. The extraction recovery range was 56.5-91.3% for DTS, while for UV-360 it was very low (20.0-43.8%). Intraday and interday precision were below 15%. DTS was detected with different detection frequencies on seawater (28%) and wastewater samples (67-100%). In seawater samples, UV-360 showed a low frequency of detection (6%), which was much more variable in wastewater (17-83%), depending on the sampling date, and an input load range of 1207–2637 μg/d/1000 inhabitants.

MeBT and UV-P were investigated, among others UVFs, in seawater and sediment along the coasts of center East Tunisia by Fenni et al. [57]. The used SPE-LC-MS/MS method was previously validated by Gago-Ferrero et al. [47,58]. MeBT was found at similar concentrations in seawater (15.2-34.6 ng/L) and in sediment samples (8.7-24.9 ng/g dw). UVP was detected in nearly all analyzed water samples at similar levels as MeBT, but it was not detected in sediment samples. Highest detected concentrations for MeBT and UVP in seawater were 34.6 ng/L and 50.9 ng/L, respectively.

Five BTs (UV-P, UV-234, UV-327, UV-328, and UV-329) were investigated by Yu et al. in environmental specimens, including sediment, and river water samples [70]. A core-shell magnetic material beta-cyclodextrin-based, was first synthesized for the extraction by SPE from complex environmental matrices. The chromatographic separation process was accomplished by using a C18 column (150 ×4.6 mm, 5 μm) with a mobile phase consisting of water and ACN. The organic UVFs were detected by a UV detector at the wavelength of 210 nm. Under the optimized conditions, the linear ranges were 5.0–500 ng/mL for all BTs with regression coefficients > 0.9984. Precision and accuracy were satisfactory with RSD values below 10% and recoveries in the range of 84.2–109%.

2.3.2. Biota marine matrices

The already cited study of Díaz-Cruz et al. reported also the monitoring of 1HBT, UV-P, MeBT, DMeBT, TBHPBT, UV-326, UV-327, UV-328, and UV-329 in fish collected from the Evrotas River in Greece [45]. Fish sampling was conducted following the recommended guidelines on chemical monitoring from the Directive 2000/60/EC [46]. The analytical SPE-LC-MS/MS method is that reported by Gago-Ferrero et al. [47]. An interesting outcome regards the ubiquitous accumulation of MeBT in all analyzed fish samples, with a range concentration from 3.5 to 6.2 ng/g dw. Although this compound is enough polar (log Kow 1.89), its high acidic dissociation constant (pKa 8.7) prevents its anionic form at the river water pH (7–8.2), and thus it can be adsorbed and bioaccumulated.

A recent study of Cadena-Aizaga et al., reported a MAE-LC-MS/MS method for the analysis of different organic UVFs, including DTS and UV-360, in seaweeds and seagrass collected from Gran Canaria Island (Spain) [64]. The chromatographic conditions have been already described in detail in

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2.1.2. paragraph. The average extraction recoveries for DTS and UV-360 were 49.2% and 95.5%, respectively. Satisfactory intraday and interday precision were reported in a range from 2.78% and 8.39%. DTS concentrations measured in macrophytes samples ranged from 4.63 to 663 ng/g dw (detection frequency 57%) *versus* UV-360 concentrations between 9.46 and 969 ng/g dw (detection frequency 37%).

2.4. Cinnamates

Cinnamates possess high molar absorption coefficients and are heavily used sunscreen ingredients, present in over 90% of sun care products. Ethylhexyl methoxycinnamate (EMC) is currently the most popular organic UVF, with good UV absorption, safety, solubility in oils, and insolubility in water, so that it is suitable for its use in most waterproof sunscreen formulations [35].

2.4.1. Environmental and biota marine matrices

Díaz-Cruz et al. investigated the presence of EMC in river water, sediments and fish from the Evrotas River in Greece [45]. The SPE-LC-MS/MS method has been already described in detail in *2.1.1.* paragraph. LOQs range for EMC were 0.2-6 ng/L in river water, 0.02-0.2 ng/g dw in sediments and 0.33-5.91 ng/g dw in fish. The EMC was not found in either water, sediment, and fish samples.

EMC was also monitored in seawater and lionfish (Pterois volitans) samples from the nearshore waters of Grenada, West Indies [49]. LODs and LOQs of the method were not shown, whereas a percent recovery between 107–121% was reported. Horricks et al. found EMC residues in 20% of seawater samples at an average concentration of 0.008 μg/L. No EMC was detected in any lionfish samples.

Força-Lima et al. reported an HPLC-DAD method for the determination of EMC in swimming pool waters [48]. The analytical method has been already described in *2.1.1.* paragraph. The extraction recovery percentages ranged from 90.4% to 116.0%.

The HPLC-UV method of Votani et al. included, among various UVFs, also the determination of EMC and IMC from soils and sediments [62]. The on-line extraction exhibited recovery lower than 40% for EMC, and around 60% for IMC.

IMC was also investigated by Cadena-Aizaga et al. in two different studies, in seawater [55], and in macrophytes [64], collected from Gran Canaria Island (Spain). Analytical methods have been already described in *2.1.1.* and *2.1.2.* paragraphs. The average recoveries were 97.3% and 63.0% in seawater and macrophytes, respectively. Intraday and interday precision were always below to 15%. The detected maximum concentration was 4.27 μg/L in seawater [55] and 186 ng/g dw in macrophytes [64].

In 2021, Fisch et al. investigated EMC in the coastal waters of the Delta Pearl River (China) [56]. LC-MS/MS method (described in detail in *2.1.1.* paragraph) showed satisfactory LOD and LOQ values. Mean recovery percentage for EMC was not determined. No EMC residue was found in any samples.

In the study of Fenni et al., EMC was monitored in seawater and sediments along the coast of Mahdia (Tunisia) [57]. The detailed description of SPE-LC-MS/MS method was reported in *2.1.1.* paragraph. Over a period of 6 months, AVO was detected both in seawater and in sediment samples, showing its widespread occurrence in all investigated locations and seasons. Between UVFs investigated in this study, EMC was the compound with highest average concentrations in both seawater (296 ng/L) and sediment (4.8 ng/g dw).

Brown et al. investigated the presence of EMC in pool water by SPE-LC-MS/MS method, using PI mode detection [61]. The method performances resulted in good accuracy (86 %), with satisfactory LOD and LOQ values.

2.5. Salicylates

Salicylate esters such as ethylhexyl (EHS) and homosalate (HMS) are among the most common UVFs currently used in sunscreen preparations. They are ortho-disubstituted compounds, which

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allow the formation of internal hydrogen bonds and therefore decrease the ability of electrons to interact with other ingredients or biological substrates [35]. Therefore, they have excellent safety characteristics, and, although they are relatively weak UV absorbers, they are often incorporated into cosmetic formulations. They are often found in association with benzophenones, of which they favor solubilization in cosmetic formulations.

2.5.1. Environmental and biota marine matrices

Two distinguished HPLC-UV methods for the analysis of EHS, and HMS in swimming pool water, and in sediments were reported by Força-Lima et al. [48], and Votani et al. [62], respectively. Two different wavelengths were used: 204 nm [48] and 285 nm [62]. LODs and LOQs in water were in order of μg/L for both analytes; in sediments, only a linearity range (0.25–25 μg/g) was reported. Average recoveries from pool water were 105.4% (EHS), and 103.5% (HMS).

Another HPLC-UV method for EHS analysis from sediment and river water samples is that reported by Yu et al. [70]. The UV detector was set at the wavelength of 210 nm. Under the optimized conditions, low LODs and LOQs were reported. Precision and accuracy were very satisfactory with RSDs below 10% and an average recovery of 99.9%.

HMS was instead monitored by Cadena-Aizaga et al. in seawater [55], and in macrophytes [64] using SPE-LC-MS/MS method. The average recoveries were 95.0% and 42.7% in seawater and macrophytes, respectively. Intraday and interday precision were always below 13.5%. The detected maximum concentration was 39.8 μg/L in seawater [55] and 8128 ng/g dw in macrophytes [64].

Finally, Brown et al. investigated the presence of EHS, and HMS in pool water by SPE-LC-MS/MS method, using PI mode detection [61]. The method performances resulted in good accuracy (recovery range 80-112%), with valuable LODs and LOQs.

The presence of EHS was also studied in two aquatic plant species, *Lemna gibba and Cyperus alternifolius*, by Seyer et al. [67]. In this study, parent drug and eventual biotransformation products, found within the plant tissue, were characterized employing an LC-QTOF-MS method. It was demonstrated that only a smaller part of EHS was converted into transformation products. The maximum concentration found in the plant material was 2 μg/g.

2.6. Crylenes

Octocrylene (OCR) is the main representative of this class of UVFs. It absorbs mainly UVB radiation and short UVA wavelengths, and it is used to either provide an appropriate sun protection factor in sunscreen products or to protect cosmetic formulations from UV radiation. Like other chemical UVFs, also OCR was incriminated to potentially induce adverse effects on the endocrine system in addition to having allergic and/or photoallergic potential. Its safety profile is constantly under assessment by the European Chemical Agency (ECHA). The available data show that octocrylene can be considered as safe when used at a concentration up to 10%.

2.6.1. Environmental and biota marine matrices

From examined literature emerges that the predominant analytical technology used for analysis of OCR is LC-MS/MS. Only an HPLC-UV method for its determination from soils and sediments was reported [62]. The OLE extraction permitted recovery higher than 85%. LOD and LOQ values were not reported, while the linearity range was 0.25–25 μg/g. Details of all analytical methods were reported in previous paragraphs.

A total of five LC-MS-MS methods for OCR detection in environmental and biota marine matrices were found.

Diaz-Cruz et al. [45] analyzed it in river water, sediments and fish. In sediment samples, OCR was ubiquitous with a concentration of 0.1-0.7 ng/g dw. It was not detected in any water and fish samples.

OCR widespread was also studied in two aquatic plant species, *Lemna gibba and Cyperus alternifolius*, by Seyer et al. [67]. In this study, parent drug and eventual biotransformation products,

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found within the plant tissue, were characterized employing an LC-QTOF-MS method. It was demonstrated that only a smaller part of OCR was converted into hydroxylated transformation products.

The SPE-LC-MS/MS method of Cadena-Aizaga et al. was used to monitor OCR in seawater [55], and macrophytes [64]. The average recoveries in seawater and macrophytes were 86.7% and 69.2%, respectively. Intraday and interday precision were always below 15%. The detected maximum concentration was 171.0 μg/L in seawater [55] and 19,369 ng/g dw in macrophytes [64].

Fisch et al. used a SPE-LC-MS-MS method for investigating the presence of OCR in the coastal waters of the Delta Pearl River (China) [56]. Under the optimized conditions, the method showed good LOD and LOQ values, but a very low recovery percentage (16%). The OCR was detected with a detection frequency of 100% at a mean concentration of 33.9 ng/L.

Finally, the LC-MS/MS method of Brown et al. for the determination of OCR in swimming pool water, showed satisfactory method performances with good recovery (75%), and valuable LOD and LOQ [61].

2.7. p-Aminobenzoic acid (PABA) derivatives

PABA was introduced in the 1970s as a UVB filter. It has been shown to cause allergic dermatitis and photosensitivity. For these reasons, it is less used nowadays. Another concern is related to a probable thyroid-disrupting activity related to its long-term effect. Its derivatives are thus used as alternatives, but their safety is still debated [71]. The most commonly used Padimate O (ODPABA) is an efficient UVB filter PABA derivative that seems to cause less hypersensitivity reactions than its congener [71]. However, ODPABA seems to act as a weak endocrine disruptor [72].This endocrine disruptive potential is also reported for EtPABA which is another PABA derivative [73]. Due to its hazardous potential, PABA use is actually banned in both Canada and the European Union [27,28], while the FDA limited its use to a maximum concentration of 15%. FDA also limited ODPABA use to a maximum concentration of 8% [29].

2.7.1. Environmental and biota marine matrices

EtPABA and ODPABA were investigated in river water, sediments and fish from the Evrotas River (Greece), by Diaz-Cruz et al. [45]. The validated SPE-LC-MS/MS method (described in detail in *2.1.1.* paragraph) provided very good LOQs ranges for all three different matrices. In sediment and fish samples, EtPABA, and ODPABA concentrations were below their respective limits of quantification or were not detected. In water, EtPABA was one of the most frequently detected (in 88% of the collected samples) with a maximum concentration of 955.8 ng/L, whereas ODPABA was measured (38%) at lower concentrations, with a maximum value of 25.1 ng/L.

Fenni et al., monitored EtPABA in seawater and sediments along the coast of Mahdia (Tunisia) [57]. The SPE-LC-MS/MS method was described in detail in *2.1.1.* paragraph. EtPABA was detected in all water samples with concentrations in the range 7.3–37.7 ng/L, but it was absent in the respective sediment samples.

Two HPLC-UV method for the determination of ODPABA in sediments [62], and in river water samples [70] were reported. The method of Votani et al. exhibited extraction recoveries from 59 to 117% [62]. LOD and LOQ values were not reported, while the linearity range was 0.25–25 μg/g. Yu et al. reported LOD and LOQ of 1.3 and 4.0 ng/mL, respectively. Precision and accuracy were very satisfactory with RSDs below 10% and an average recovery of 98%.

2.8. Camphor derivatives

Camphor derivatives are bicyclic compounds with high extinction coefficients. The 4-Methylbenzylidene camphor (4-MBC) is the most used agent of this class. It protects in the UVB range (290-320 nm) with a peak absorbance at 301 nm. It is legally approved both in the EU and Australia up to 4%, however, it is not approved in the US [35] and in Japan. Because of information on potential

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genotoxicity as endocrine disruptor, a re-evaluation of the maximum permitted concentration of 4-MBC by the EU is underway.

2.8.1. Environmental and biota marine matrices

Several authors used a LC-MS/MS method for 4-MBC detection in environmental and biota marine specimens. Details of analytical methods have been already described in *2.1.1.* and *2.1.2.* paragraphs.

Diaz-Cruz et al. [45] monitored 4-MBC in river water, sediments and fish, obtaining the highest concentration of 4MBC in sediment samples (1400.4 ng/g dw). 4-MBC was present in more than half of water samples (56%) with a concentration of 63.7 ng/L, whereas in fish it was determined to a lower extent in all the analyzed species.

4-MBC was also monitored in seawater and lionfish (Pterois volitans) samples from the nearshore waters of Grenada, West Indies [49]. LODs and LOQs of the method were not shown, whereas a percent recovery between 107–121% was reported. Horricks et al. found it in 12% of lionfish samples at an average concentration of 2.11µg/kg, whereas no 4-MBC was detected in seawater.

Cadena-Aizaga et al., investigated its presence in seawater [55] and in macrophytes [64]. The average recoveries were 97.9% and 87.4% in seawater and macrophytes, respectively. Intraday and interday precision were always below to 15%. The detected maximum concentration was 17.5 µg/L in seawater [55] and 237 ng/g dw in macrophytes [64].

Fisch et al. used a SPE-LC-MS-MS method for the investigation of the presence of 4-MBC in the coastal waters of the Delta Pearl River (China) [56]. Under the optimized conditions, the method showed good LOD and LOQ values, but a very low recovery percentage (26%). The 4-MBC was not detected in any investigated samples.

The LC-MS/MS method of Fenni et al. for the determination of 4-MBC in seawater and sediments, reported valuable LOD and LOQ values [57]. 4-MBC was absent in seawater samples, but present in sediments, ranging from <LOQ to 17.10 ng/g dw.

Instead, only two HPLC-UV methods for the analysis of 4-MBC were reported for swimming pool water [48], and sediments [62], respectively. LODs and LOQs in water were in order of µg/L, whereas they were not reported for sediments. The extraction recovery percentages from water ranged from 79.3 to 98.4%.

2.9. Triazine derivatives

Triazines are an important class of UVFs whose occurrence in environment and human exposure still needs to be investigated. The basic structure of this class of UVFs consists in a heterocyclic 1,3,5-triazine group, which gives high photostability, absorption efficiency, and a broad-spectrum UV protection. The most representative compounds of triazine UVFs include ethylhexyl triazone (EHT), bis-ethylhexyloxyphenol methoxyphenyl triazine (BEMT), and diethylhexyl butamido triazone (DBT).

2.9.1. Environmental and biota marine matrices

EHT, BEMT, and BDT were monitored in swimming pool water using a SPE-LC-MS/MS method (see *2.1.1.* paragraph for detailed description) [60]. Satisfactory method performances were reported for all the three UVFs with high recoveries (81-97%), good LODs, and RSD values below 20%.

3. Results and Discussion

In this review, we summarized recent reports on liquid chromatographic methods used to analyze organic UVFs in environmental and marine biota matrices (Table 2).

Nowadays, their accurate determination is a high topic concern along the Scientific Community. In fact, UVFs contamination may derive from different sources considering their wide use in personal

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care products, plastics, paints and textile industries as well as preventing agents in many industrial, commercial and food products [75,76].

According to the different composition of the matrices, several extraction procedures were developed to isolate the analyte of interest that can be, in this way, determined with a high sensitivity.

Most of the studies reported in this review used a SPE procedure, sometimes modified according to the chemical structure of the UVF to be determined [45,50,51,55,60,61,69,70]. Other authors developed alternative extraction techniques using a semipermeable membrane device for the simultaneous extraction of different UVFs classes [48]. Another innovative extraction method consisted in an on-line extraction that allowed to extract the analytes from sediments without additional sample pretreatment [62]. A microwave-assisted extraction was instead used for the investigation of several UVFs in macrophytes (seaweeds and seagrass) [64].

Table 2. Chromatographic methods for the analysis of organic UVFs.

Class	UVF	Detection	Matrices	LOD	LOQ	Ref.
BENZOPHENONES	BP	HPLC-UV	pool water	0.2 µg/L	0.7 µg/L	[48]
	BP-1	LC-MS/MS	river water, sediment,	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			pool water	/	0.05 µg/L	[50]
			river water	0.9 µg/L	3.0 µg/L	[51]
			river water	0.01-1.7 ng/L	0.02- 2.4 ng/L	[56]
			seawater, sediment	0.3-10 ng/L	1.0-33.3 ng/L	[57]
			fish	/	0.33-5.91 ng/g dw	[45]
	BP-2	LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			river water	0.01-1.7 ng/L	0.02- 2.4 ng/L	[56]
			seawater, sediment	0.3-10 ng/L	1.0-33.3 ng/L	[57]
			fish	/	0.33-5.91 ng/g dw	[45]
	BP-3	HPLC-UV	pool water	0.2 µg/L	0.7 µg/L	[48]
		LC-MS/MS	soil, sediment	/	/	[62]
			river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			seawater	/	/	[49]
			seawater, wastewater	11.9- 29.1 ng/L	39.8-97.1 ng/L	[55]
			river water	0.01-1.7 ng/L	0.02- 2.4 ng/L	[56]
			seawater, sediment	0.3-10 ng/L	1.0-33.3 ng/L	[57]
			pool water	0.31 µg/L	1.0 µg/L	[61]
			fish	/	0.33-5.91 ng/g dw	[45]
			seawater, lionfish	/	/	[49]
			seaweeds and seagrass	22.81 ng/L	76.05 ng/L	[64]
	BP-4	LC-MS/MS	river water	0.01-1.7 ng/L	0.02- 2.4 ng/L	[56]
			seawater, sediment	0.3-10 ng/L	1.0-33.3 ng/L	[57]
			pool water	12.5 ng/L	/	[60]
			pool water	1.7 ng/L	5.8 ng/L	[61]
	BP-8	LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			seawater, sediment	0.3-10 ng/L	1.0-33.3 ng/L	[57]
			pool water	0.15 µg/L	0.49 µg/L	[61]
			fish	/	0.33-5.91 ng/g dw	[45]
	4-HBP	LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			pool water	/	0.01 µg/L	[50]
			seawater, sediment	0.3-10 ng/L	1.0-33.3 ng/L	[57]
			fish	/	0.33-5.91 ng/g dw	[45]

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	4,4′-DHBP	LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			pool water	/	0.01 μg/L	[50]
			river water	0.01-1.7 ng/L	0.02- 2.4 ng/L	[56]
			seawater, sediment	0.3-10 ng/L	1.0-33.3 ng/L	[57]
			fish	/	0.33-5.91 ng/g dw	[45]
DIBENZOYL METHANE DERIVATIVES	AVO	LC-MS/MS	seawater	10.8 ng/L	35.9 ng/L	[55]
		LC-QTOF-MS	seaweeds and seagrass	40.43 ng/L	134.77 ng/L	[64]
			seawater, sediment	0.93 ng/L, 0.51 ng/g dw	3.09 ng/L, 1.69 ng/g dw	[57]
			pool water	2.5 ng/L	/	[60]
			pool water	1.1 ng/L	3.6 ng/L	[61]
			marine plants	/	/	[67]
BENZOTRIAZOLES	1HBT	LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
	MeBT	LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
			seawater, sediment	0.73 ng/L	2.42 ng/L	[57]
	DMeBT	LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
	TBHPBT	LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
	UV-P	HPLC-UV	water	0.02-0.08 μg/L	0.07-0.26 μg/L	[69]
		LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
			seawater, sediment	1.03 ng/L	3.42 ng/L	[57]
			river water	0.12-1.4 μg/L	0.46–4.6 μg/L	[70]
	DTS	LC-MS/MS	seawater	12.1 ng/L	40.4 ng/L	[55]
			seaweeds and seagrass	6.84 ng/L	22.79 ng/L	[64]
	UV-234	HPLC-UV	water	0.02-0.08 μg/L	0.07-0.26 μg/L	[69]
			river water	0.12-1.4 μg/L	0.46–4.6 μg/L	[70]
	UV-326	HPLC-UV	water	0.02-0.08 μg/L	0.07-0.26 μg/L	[69]
		LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
	UV-327	HPLC-UV	water	0.02-0.08 μg/L	0.07-0.26 μg/L	[69]
		LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
			river water	0.12-1.4 μg/L	0.46–4.6 μg/L	[70]
	UV-328	HPLC-UV	water	0.02-0.08 μg/L	0.07-0.26 μg/L	[69]
		LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
			river water	0.12-1.4 μg/L	0.46–4.6 μg/L	[70]
	UV-329	HPLC-UV	water	0.02-0.08 μg/L	0.07-0.26 μg/L	[69]
		LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
			river water	0.12-1.4 μg/L	0.46–4.6 μg/L	[70]
	UV-360	LC-MS/MS	seawater	36.4 ng/L	121.3 ng/L	[55]
			seaweeds and seagrass	140.34 ng/L	467.81 ng/L	[64]

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CYNNAMATES	EMC	HPLC-UV	pool water	13 µg/L	44 µg/L	[48]
		LC-MS/MS	soil, sediment	/	/	[62]
			river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
			seawater, lionfish	/	/	[49]
			river water	16.1 ng/L	48.8 ng/L	[56]
			seawater, sediments	1.71 ng/L, 1.43 ng/g dw	5.69 ng/L, 4.78 ng/g dw	[57]
			pool water	1.0 ng/L	3.4 ng/L	[61]
	IMC	HPLC-UV	soil, sediment	/	/	[62]
			seawater	13.7 ng/L	45.6 ng/L	[55]
			seaweeds and seagrass	16.30 ng/L	54.35 ng/L	[64]
SALYCILATES	EHS	HPLC-UV	pool water	0.4 µg/L	1.4 µg/L	[48]
		LC-MS/MS	sediment	/	/	[62]
		LC-QTOF-MS	river water	0.80 µg/L	2.6 µg/L	[70]
			pool water	0.33 ng/L	1.1 ng/L	[61]
			marine plants	/	/	[67]
	HMS	HPLC-UV	pool water	0.9 µg/L	3.2 µg/L	[48]
		LC-MS/MS	sediment	/	/	[62]
			seawater	11.3 ng/L	37.7 ng/L	[55]
			seaweeds and seagrass	11.4 ng/L	38.0 ng/L	[64]
			pool water	0.74 ng/L	2.5 ng/L	[61]
CRYLENES	OCR	HPLC-UV	sediment	/	/	[62]
		LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
		LC-QTOF-MS	fish	/	0.33-5.91 ng/g dw	[45]
			seawater	12.7 ng/L	42.4 ng/L	[55]
			seaweeds and seagrass	20.8 ng/L	69.2 ng/L	[64]
			river water	1.3 ng/L	3.9 ng/L	[56]
			pool water	2.0 ng/L	6.7 ng/L	[61]
			marine plants	/	/	[67]
PABA DERIVATES	EtPABA	LC-MS/MS	river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
			seawater, sediments	1.71 ng/L, 1.43 ng/g dw	5.69 ng/L, 4.78 ng/g dw	[57]
	ODPABA	HPLC-UV	soil, sediment	1.3 µg/L	4.0 µg/L	[62]
		LC-MS/MS	river water	/	/	[70]
			river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
CHAMPHOR DERIVATIVES	4-MBC	HPLC-UV	pool water	0.4 µg/L	1.4 µg/L	[48]
		LC-MS/MS	sediment	/	/	[62]
			river water, sediment	/	0.2-6 ng/L, 0.02-0.2 ng/g dw	[45]
			fish	/	0.33-5.91 ng/g dw	[45]
			seawater, lionfish	/	/	[49]
			seawater	12.9 ng/L	43.1 ng/L	[55]
			seaweeds and seagrass	51.41 ng/L	171.35 ng/L	[64]
			river water	1.0 ng/L	1.6 ng/L	[56]
			seawater, sediments	0.40 ng/L, 1.19 ng/g dw	1.32 ng/L, 3.97 ng/g dw	[57]
TRIAZINES	BEMT	LC-MS/MS	pool water	50 ng/L	/	[60]
	BDT	LC-MS/MS	pool water	50 ng/L	/	[60]

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EHT	LC-MS/MS	pool water	50 ng/L	/	[60]

Often, the complexity of the matrix makes it difficult to develop multi-residue methods able to identify and quantify several analytes with the minimum sample manipulation, and in a reduced time without compromising separation and resolution efficiency [77].

For the determination of organic UVFs in investigated matrices, the chromatographic separation was generally performed on reverse phase C18 columns, except for two studies that used a C8 column [50,60].

Most of the studies reported in this review, quantified UVFs using liquid chromatography coupled with a MS/MS detector; alternatively, the UV detector is used by several authors (Table 2). Generally, LC-MS/MS methods showed limits of sensitivity better than UV detection (ng/L *vs* µg/L) for the same analytes.

MS/MS detection was generally performed in PI mode with few exceptions; for instance, between BPs, solely the aromatic sulfonic acid BP-4, being a very strong acid, was ionized under NI mode by all authors [56,57,61], except for Mokh et al. [60]. In this case, the PI mode resulted in worse detection limits, as it can see in Table 2.

The most used mobile phase for compounds analyzed in PI mode has been found to be water and methanol (both with 0.1% formic acid). Several authors preferred the mixture of water/ACN that, having lower viscosity than water/methanol, reduces the pressure problems mostly frequent in LC [45,48,60,61,67,70]. Usually, mobile phase additives like formic and acetic acids, ammonium formate and ammonium acetate are used in LC-MS methods, where they can improve analyte ionization. Nevertheless, Mokh et al. reported that the signal intensities were better without additives for all tested compounds [60]. Comparing literature data in Table 2, LOD values reported by Mokh et al. are slightly higher than other methods for the same matrix, except for AVO, where, instead, it seems more sensitive.

In conclusion, the high number of studies reported in the last five years employing different chromatographic techniques for the determination of UVFs in environmental and marine biota matrices, shows that there is a constant effort of the scientific community to develop increasingly sensitive methods. This trend is certainly related to the high concern for their ubiquitous presence, that poses a serious treat for the entire ecosystem.

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