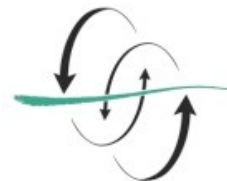


FACULTAD
DE CIENCIAS
DEL MAR



UNIVERSIDAD DE LAS PALMAS
DE GRAN CANARIA

**ANALYTICAL
PROCEDURES FOR THE
DETERMINATION OF
UV FILTERS AND
STABILIZERS.
IMPLEMENTATION IN
MICROPLASTICS.**

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Curso 2020/2021

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Trabajo Fin de Título para la obtención
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Analytical procedures for the determination of UV filters and stabilizers.
Implementation in microplastics.

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INDEX:

Abstract.....	4
1) Introduction.....	4
2) Analysis of UV filters and stabilizers in solid matrices	6
2.1) Extraction techniques.....	7
2.1.1) Soxhlet.....	7
2.1.2) Vortex extraction (VE).....	8
2.1.3) Ultrasonic extraction (USE)	9
2.1.4) Microwave assisted extraction (MAE)	10
2.1.5) Pressurized liquid extraction (PLE).....	11
2.1.6) Matrix solid phase dispersion (MSPD)	13
2.1.7) Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS)	14
2.2) Determination techniques.....	15
3) Possibilities of implementation in microplastics	18
4) Conclusions.....	19
Bibliography.....	20
Annex I.....	32

ABSTRACT

Microplastic contamination is already a worldwide problem to which the issue of adsorbed contaminants must be added. These substances can cause physical, chemical and biological internal damage and negative impacts on the metabolism of organisms. An increase in the investigation on the topic of adsorbed contaminants on microplastics is needed to developed techniques that can effectively extract them, especially emerging contaminants, since there is not much literature on the subject matter. Among these emerging contaminants, there are personal care products, hydrophobic and with a high affinity for plastic surfaces, which are divided into disinfectants, synthetic fragrances, parabens, UV protection compounds and antioxidants. In this work, different techniques used for the extraction of UV filters and stabilizers from environmental solid samples, like Soxhlet, Vortex extraction (VE), Ultrasonic extraction (USE), Microwave assisted extraction (MAE), Pressurized liquid extraction (PLE), Matrix solid phase dispersion (MSPD) and Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS), are compared. They are then discussed regarding their application to microplastic matrices. After comparing the advantages and disadvantages of each one, we determined that USE and MSPD are the ones that seem to be the overall better suited for this end. Both techniques can be implemented for the different types of microplastic polymers since neither is temperature dependent and both present high recoveries in the available literature, but further research for MSPD is needed.

1) INTRODUCTION

Every year the global plastic usage increases and it is currently considered one of the most commonly found pollutants in the ocean (Moore, 2008). To the problematic of plastic contamination, the issue of different types of toxic contaminants being adsorbed on them should be added. Plastics and specially microplastic (less than 5 mm of diameter) have a large sorption surface, are easily ingested by aquatic organisms and can move up trophic levels fast, migrate through body tissues and cause a wide variety of negative effects on biota themselves (Peng et al., 2020; Andrady, 2011). Moreover, the adsorbed toxic components can cause negative issues in marine organisms such as blockage and damage in digestive organs, inflammation, reduced reproduction, impacts on the metabolism, damages via physical, chemical and biological toxicities to different organs, and other negative impacts (Peng et al., 2020). If two different types of toxic components exist, they can compete for the available plastic surface depending on their hydrophobicity and molar ratio or stack up creating a joint toxicity (Ho & Leung, 2019).

As they are buoyant, these contaminants can be transported to distant places (Rani et al., 2017, Peng et al., 2020). Then, the microplastic weathering and degradation processes can release the contaminants into the ocean (Rani et al., 2017).

Among the pollutants that can be adsorbed and transported by microplastics, two groups can be distinguished, priority and emerging compounds. Priority pollutants are compounds included in the legislation that are being monitored because it has been established that they represent a risk to the aquatic environment due to their toxic nature (Wille et al., 2012). The most commonly found compounds are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and the insecticide DDT (Antunes et al., 2013; Frías et al., 2010), along with hexachlorocyclohexanes, chlorinated benzenes, organophosphate esters, brominated flame retardants, hexabromocyclododecanes, nonylphenols, phthalic acid esters, polybrominated diphenyl ethers and bisphenol A (Ogata et al., 2009; Lee et al., 2018; Zhang et al., 2018). Emerging contaminants are newly discovered chemicals of anthropogenic origin (Wille et al., 2012), which are not regulated, and they are being released into water sources (Bolong et al., 2009). Some of the most relevant emerging pollutants are pharmaceuticals, hormones, detergents, organophosphorus flame retardants, nanoparticles, pesticides and personal care products (Camacho et al., 2019; Geissen et al., 2015).

Within this kind of pollutants, personal care products (PCPs) are a type of chemicals of emerging concern which are continuously being introduced in the ocean after being used (Montesdeoca-Esponda et al., 2014). Due to the hydrophobic nature of a considerable number of PCPs, they have a high affinity for the solid surface of microplastics (Wille et al., 2012), making them excellent vectors for the transmission of hydrophobic organic chemicals to marine organisms (Koelmans et al., 2016). The most common PCPs can be divided into disinfectants, synthetic fragrances, parabens, UV compounds and antioxidants.

UV filters (UVFs) and UV light stabilizers (UVLSs) are used in sunscreens and other cosmetics to prevent the damage from sunlight. They comprise many different organic compounds, most lipophilic with conjugated aromatic rings. They are quite persistent, stable against biotic degradation, and bioaccumulate in marine organisms (Montesdeoca-Esponda et al., 2014). Cinnamate derivatives are the most commonly used UV filters (Wang, 2016). Other important substances are para-aminobenzoic acid (PABA), triazine, ensulizole, octinoxate, benzophenones, octisalate, camphor and benzotriazole derivatives (Russak & Riegel, 2012; Apel, 2019). UVFs and UVLSs can have adverse effects like causing an increase in the viral and marine bacterioplankton abundance and contributing to coral bleaching (Paredes et al., 2014; Danovaro & Corinaldesi, 2008). Other negative consequences are cytotoxic and developmental effects, as well as hormonal and endocrine disruption (Balázs et al., 2016; Paredes et al., 2014).

Because they are used in sunscreens among other PCPs, the concentration of UVFs and UVLSs found in coastal environment is proportional to the amount of tourism in beaches (Camacho et al., 2019), with a higher concentration in the summer season (Cadena-Aizaga et al., 2019).

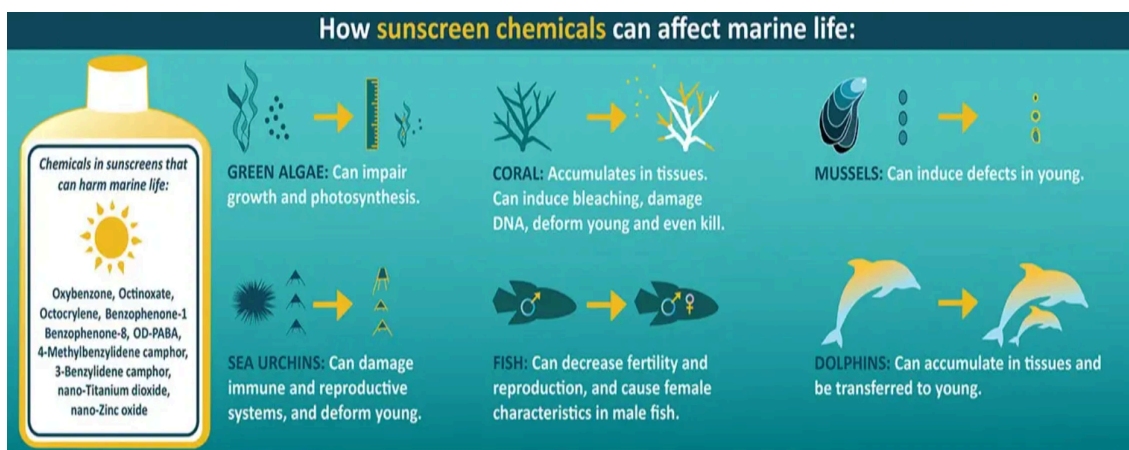


Fig 1: Effects of UV compounds on marine organisms

As has been established, microplastics are widely distributed in seawater and they are considered as a contamination vector due to their capacity to transport organic pollutants around the planet. For this reason, it is necessary to have a methodology that can allow us to monitor the presence of these adsorbed compounds on microplastics.

Different techniques exist for the separation of these contaminants from different matrices. Solid matrices represent a special challenge due to the low concentrations of pollutants in the environment and the matrix effects due to the strong union between compound and sample. They usually require pre-treatments, post-cleanup processes and preconcentration steps, which can be significantly time-consuming (Cadena-Aizaga et al., 2019, Montesdeoca-Esponda et al., 2013). However, available literature about the extraction of organic compounds in microplastics is scarce (Zhang et al., 2018; Lee et al., 2018; Frias et al., 2010; Llorca et al., 2020). To the best of our knowledge, only a small amount of works has been published about the extraction of UVFs and UVLSs compounds from this matrix, using mostly traditional techniques like liquid-solid extraction (Rani et al., 2017; Camacho et al., 2019, Ho & Leung, 2019). Other traditional techniques, like Soxhlet or ultrasonic extraction, that are commonly used for solid samples, tend to be time-consuming and wasteful (Montesdeoca-Esponda et al, 2018). Therefore, there is a need for quicker and more cost-effective methodologies for the extraction of pollutants from this matrix.

This work aims to be a revision about the different available methods for the determination of UVFs and UVLSs in different solid matrices, which has been critically discussed as alternatives that could be adapted to analyze microplastic samples.

2) ANALYSIS OF UVFs AND UVLSs IN SOLID MATRICES

The determination of organic pollutants from complex environmental solid samples (e.g., sediments, organisms) requires the implementation of an extraction technique to isolate the target analytes from the matrix. Different conventional methods like Soxhlet or ultrasound-assisted extraction offer good results and therefore are still employed, but they normally require a large volume of organic solvents and an additional evaporation step. Newer on-line techniques can improve analysis via automatization, speeding up the process, and by lower solvent waste (Montesdeoca-Esponda et al., 2018). They offer a high sample analysis frequency, allowing to analyze more samples per hour than traditional techniques.

Some of these techniques include matrix solid phase dispersion and QuEChERS procedures, which both save costs and offer the unification of extraction and purification in a single step (Montesdeoca-Esponda et al., 2013).

In the following sections, the most relevant extraction techniques employed for solid samples are summarized and their application in the determination of UVFs and UVLSs are critically revised. The characteristics of the different procedures for the extraction of UVFs and UVLSs from solid environmental samples discussed in this section can be found in Annex I.

2.1) EXTRACTION TECHNIQUES

2.1.1) Soxhlet

Soxhlet extraction is a traditional, well-established technique. The extraction program consists of a number of cycles, each of them containing several steps: (1) the sample is placed in the thimble, (2) the solvent is heated to reflux, and evaporates from the distillation flask, condensing in the refrigerant area and dropping on the sample, (3) after the extraction solvent reaches the siphon height, the content is aspirated back into the distillation flask, where the solute is separated from the solvent, (4) the solute is left in the flask and the solvent is reused for another cycle (Fig 2) (Chemat et al., 2017; Zygler et al., 2012).

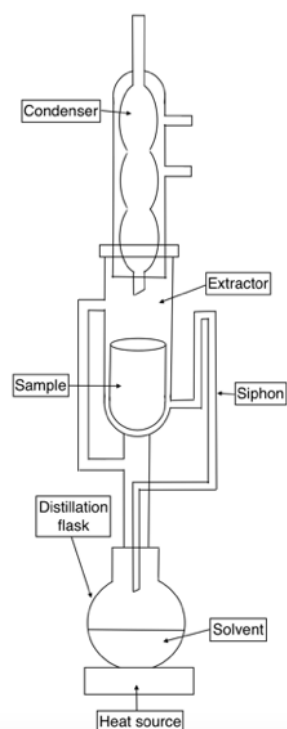


Fig 2: Soxhlet system (own elaboration). Fig 3: Soxhlet extractors (Kasalab S.A.S)

Soxhlet extraction is time consuming, labor intensive and requires the use of large volumes of organic solvents but presents a high extraction efficiency (Albero et al., 2015; Montesdeoca-Esponda et al., 2014). This technique is commonly used for extraction of analytes from biota samples, although preconcentration and clean-up steps are needed (Gago-Ferrero, Díaz-Cruz & Barceló, 2011). It has been widely employed to extract different organic compounds, especially PAHs and PCBs, from solid matrices (Zuloaga et al., 2012). Nakata et al. (2009, 2010 and 2012) also used it to extract UVLSs from organic matrices, obtained very high recoveries (93-122%, 110-114% and 110-122%, respectively) using a mix of dichloromethane and hexane. The extraction time for Nakata et al. (2009 and 2012) was high, 5 hours, while the other work does not specify duration.

2.1.2) Vortex extraction (VE)

In Vortex Extraction, a tube containing the mixture of the sample and the solvent solution is vigorously shaken and the supernatant is taken and further treated (Fig 4) (Tarazona, Chisvert & Salvador, 2014). Vortex extraction makes use of a low amount of solvent and is environmentally friendly. It can be combined to DDLME to minimize solvent use (Tarazona, Chisvert & Salvador, 2014). It is also cost-effective (Martin et al., 2017) and easy to use (Jiménez-Díaz et al., 2013).

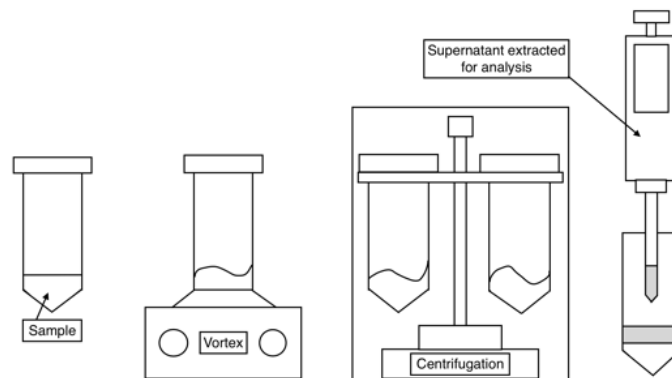


Fig 4: VE system (own elaboration)

Different authors reported diverse efficiency values depending on the analyzed compounds. Tsui et al. (2017) applied VE to extract UVFs from sediment and coral tissues and skeleton. An acetone and n-hexane mix was used as the organic solvent, obtaining recoveries ranging from 58 to 81% for the sediment and from 61 to 86 % for the coral tissues and skeleton. Vila et al. (2018) utilized this technique employing ethyl acetate to extract UVFs from sand with recoveries from 86 to 121%. Martin et al. (2017) extracted UVLSs from holothurian using acetonitrile, obtaining a recovery range of 80 to 110%.

2.1.3) Ultrasonic extraction (USE)

Ultrasonic Extraction (USE), also known as Ultrasound-assisted extraction (UAE), is often used for the extraction of analytes from solid samples. The sample, with the solvent, is immersed in an ultrasonic bath, the high temperatures and pressures applied causing cavitation bubbles which produce physical and/or chemical effects on the medium (Fig 5) (Rostagno & Prado, 2013). Cavitation leads to higher analyte solubility and solvent diffusivity by increasing the polarity of the solid sample (Bendicho et al., 2012). The ultrasound allows a greater penetration of solvent into solid matrices, providing a better mass transfer and sample-extraction efficiency (Albero et al., 2015).

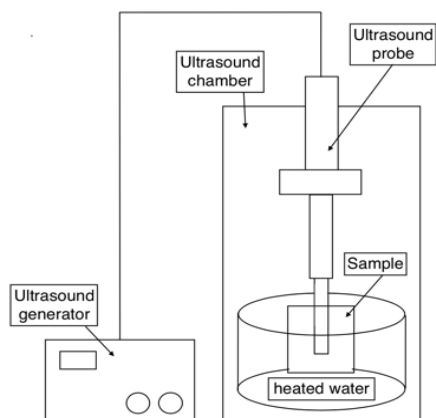


Fig 5: Ultrasound-assisted extraction mechanism (own elaboration)



Fig 6: Ultrasound-assisted extractor (Petigny et al., 2013)

USE is a conventional extraction technique that can often be combined with newer techniques to make the most of its advantages and minimize its disadvantages. USE is fast, has a high reproducibility and generates a final product of high purity with less solvent consumption than Soxhlet (Chemat et al., 2017). This technique is considered environmentally safe, fast, and cheap. It also allows fewer opportunities for sample contamination. USE is not easily automated and is not suitable for volatile analytes. It also usually requires centrifugation and concentration steps before injection to avoid degradation of the organic analytes (Montesdeoca-Esponda et al., 2014). A clean-up step is needed for complex matrices (Albero et al., 2015) and a pre-treatment of the matrix is recommended to improve extraction efficiency (Chemat et al., 2017). Jimenez-Díaz et al. (2013) obtained similar recoveries for USE and VE and deemed VE easier to use.

In sediment, Peng et al. (2017) obtained very disparate recoveries (55-118%) when extracting UVLSs, and Sanchez-Brunete et al. (2011) obtained high ones (90-104%) for UVFs. This technique has been used with efficient results in solid samples in combination with Solid Phase Extraction (SPE) as purification step, yielding acceptable precision and recoveries ($87 \pm 33\%$), but not as high as the ones obtained using other techniques (Fabunmi et al., 2020).

2.1.4) Microwave assisted extraction (MAE)

Microwave Assisted Extraction (MAE) involves using microwave radiation to heat a solid sample and a solvent in a closed vessel under controlled temperature and pressure conditions (Fig 7) (Camel, 2001). Temperature is an important factor in the extraction; high temperatures improve diffusion rates and speed up the extraction (Vilaplana et al., 2009).

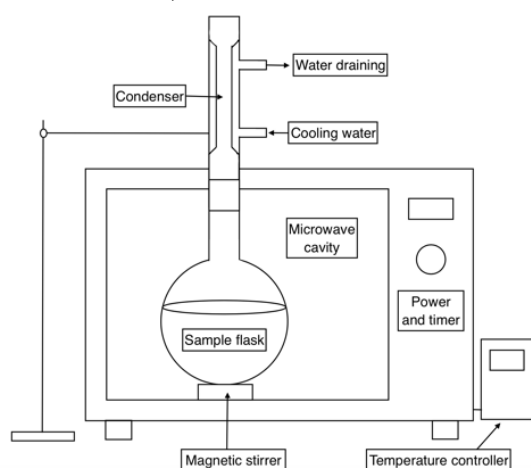


Fig 7: Microwave assisted extraction method (own elaboration) Fig 8: MAE system (ATS Scientific)

It has short extraction times, makes use of a small amount of solvent and allows several analytes to be extracted at the same time, but it is not suited for automation and in most cases, an additional clean-up step has been needed prior to the analysis (Kim, Choi & Chung, 2012; Montesdeoca-Esponda et al., 2014). Mixed polar/non-polar solvents have higher recovery rates due to a greater affinity to the analytes and matrix swelling effect (Vilaplana et al., 2009). A variation of MAE is “focused Microwave-Assisted Soxhlet Extraction” (FMASE), which presents the advantages of MAE and Soxhlet with less extraction time, less solvent waste and the possibility of automation (Montesdeoca-Esponda et al., 2014).

Amine et al. (2012) applied MAE to extract UVFs from coastal sediments subjected to riverine input. An acetone and heptane mix was used as organic solvent, obtaining recoveries ranging from 97 to 115%. Kotnik et al. (2014) employed this technique with the help of an acetone and hexane mix as organic solvent to extract UVFs from lake sediments in high activity areas. Obtained recoveries ranged from 80 to 99%. Bachelot et al. (2012) and Gomez et al. (2012) utilized this technique to extract UVFs from mussel tissues, once again with an acetone and heptane mix as extraction solvent. The former obtained recoveries ranged from 89 to 116% and the latter from 89 to 101%. Montesdeoca-Esponda et al. (2013b) applied MAE to extract UVLSs from sewage sludges and marine sediments in areas close to shore with recoveries ranging from 50.1 to 55.7 %. Acetonitrile was chosen as the organic solvent.

Pacheco-Juárez et al. (2019) applied methanol to extract UVLSs from seaweed, obtaining recoveries ranging from 49.8 to 92.3%.

Moreover, MAE has also been used with high effectiveness to extract a wide variety of additives (antioxidants, stabilizers, plasticizers) from polymer matrices like polyethylene (both high and low density), polypropylene (PP), poly(vinyl chloride) (PVC) and polydimethyl siloxane (PDMS) (Vilaplana et al., 2009; Ramos et al., 2015).

2.1.5) Pressurized liquid extraction (PLE)

In pressurized liquid extraction (PLE) pressure is applied at temperatures higher than the boiling point of the employed solvent (Fig 9). This combination of increased temperature and pressure leads to higher analyte solubility by decreasing the viscosity and a breaking of analyte-matrix interactions (Gago-Ferrero et al., 2012; Viñas et al., 2014).

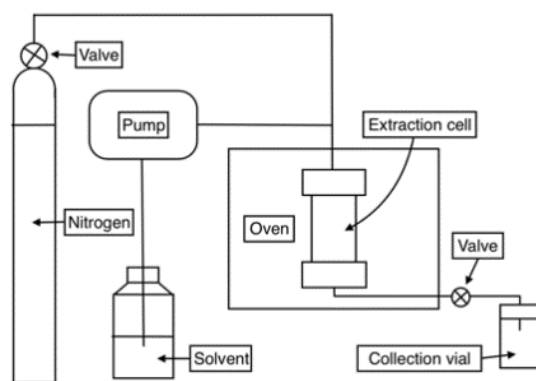


Fig 9: Pressurized liquid extraction method (own elaboration) Fig 10: PLE system (J316)

It presents several advantages over other extraction techniques like better reproducibility, less solvent consumption and faster sample pre-treatment (Gago-Ferrero et al., 2012; Viñas et al., 2014). PLE can be automated and extract in one step fast and efficiently, removing interfering species and allowing in-cell purification (Gago-Ferrero et al., 2011). This technique produces cleaner extracts than Soxhlet and UAE, with reduced background noise during analyte determination, but selectivity is not as high, and dilution of analytes occurs after a certain number of cycles. It is also an expensive technique (Montesdeoca-Esponda et al., 2014). PLE is commonly used for sludgy matrices (Gago-Ferrero et al., 2011). Sediment samples are also often extracted with PLE (Gago-Ferrero et al., 2011; Gago-Ferrero et al., 2012).

Many authors used this technique for the extraction of pollutants, but it doesn't seem to yield the best results in either sediment or organic matrices. Some works obtained very disparate recoveries. Pintado-Herrera et al. (2017) used dichloromethane to extract several different UVFs from coastal sediment, with recoveries from as low as 53 to a high of 134 %. Molins-Delgado et al. (2018) employed a mixture of dichloromethane and ethyl acetate to extract UVFs from fish fillet, obtaining recoveries from 42 to 107%. Gago-Ferrero et al. (2011) applied PLE to extract eight different UVFs from riverbed sediment samples. Methanol and methanol/water mix were used as organic solvents and obtained recoveries ranged from 58% 125%. Other authors obtained overall low recoveries. Tsui et al. (2015) utilized this technique to extract several UVFs from harbor sediments of two different high activity industrial and recreational areas. A methanol and ethyl acetate mix was chosen as solvent and recoveries ranging from 75 to 100% were obtained. Combi et al. (2016) employed dichloromethane to extract BP3, OC and EHMC from ocean basin with recoveries from 70 to 100%. Volpe et al. (2017) applied PLE for sediment from harbor and estuary areas with a high anthropogenic impact by using an ethyl acetate and hexane mix. The obtained recoveries ranged from 66 to 102%. Emnet et al. (2015) employed this technique to extract different UVFs from clam tissues. A water and isopropanol mix was chosen as extractant, obtaining low recoveries, from 53.0 to 67.4%.

Selective pressurized liquid extraction (SPLE) is a faster and cheaper alternative to PLE by simplifying the sample preparation. This can be achieved by binding the clean-up and the extraction step together, reducing time consumption (Björklund et al., 2006; Gago-Ferrero et al., 2012). Just like with PLE, authors have overall obtained a very wide range of recoveries using this technique. Baron et al. (2013), Langford et al. (2015) and Peng et al. (2017) all utilized SPLE to extract UVFs from sediment from riverine, estuary and coastal bay discharge areas, using methanol, dichloromethane and hexane mix and methanol as solvents, respectively. They obtained a wide range of recoveries; Baron et al. (2013) from 85 to 125%, Langford et al. (2015) from 72 to 102% and Peng et al. (2017) from 55 to 118%.

2.1.6) Matrix solid phase dispersion (MSPD)

In matrix solid phase dispersion (MSPD), a selected sorbent is used to disperse the sample over the surface of the bonded-phase support material, creating a mixed phase that allows target analyte isolation (Łozowicka et al., 2012). The sample is then compacted into a polypropylene syringe and analytes are recovered with the help of a small volume of a suitable organic solvent (Fig 11) (Montesdeoca-Esponda et al., 2013). MSPD permits complete fractionation of the sample matrix components, isolating components from the sample (Łozowicka et al., 2012).

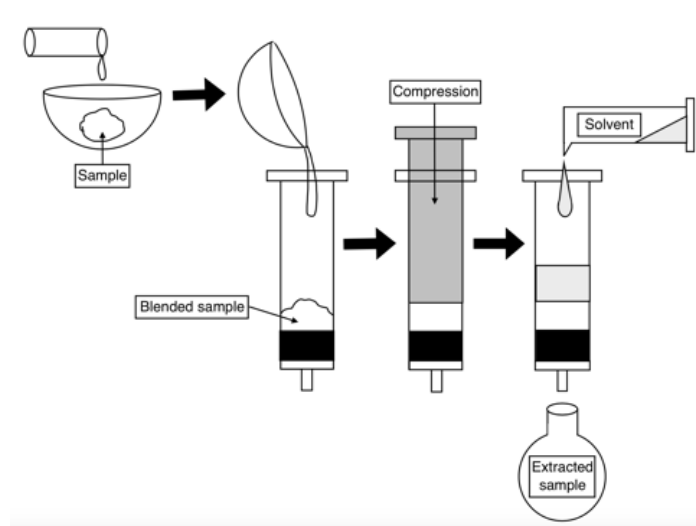


Fig 11: MSPD (own elaboration)

This technique is low cost, uses little volume of organic solvent, has mild extraction conditions and extraction and purification can be combined (Carpinteiro et al., 2012). MSPD is environmentally safe due to the small amount of utilized solvent. It is also simpler to utilize than traditional extraction techniques that need to disrupt solid sample architecture to liquify it for liquid chromatography since it directly merges the sample with the bonded-phase (Barker et al., 2007; Vela-Soria et al., 2014).

Negreira et al. (2013) applied MSPD to extract UVFs from fish fillet and mussel tissues. Acetonitrile was used as organic solvent, obtaining recoveries ranging from 84 to 106% for the fish fillet and 70 to 112 % for the mussel tissues. Tsai et al. (2014) employed this technique to extract UVFs from striped bass, cod and salmon fillet, using acetonitrile as the organic solvent, with recoveries from 83 to 98% for the striped bass fillet, 75 to 88% for the cod fillet and 77 to 96% for the salmon fillet. Vidal-Liñán et al. (2017) utilized acetonitrile to extract UVFs from mussel tissues, obtaining a recovery range from 90 to 110%. Vela-Soria et al. (2014) employed MSPD to extract UVLSs from placental tissue. Ethyl acetate was the organic solvent of choice and the recoveries ranged from 97 to 106%.

2.1.7) Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS)

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) technique consists of the extraction of a solid sample in a liquid media. The sample is vortexed and centrifuged, then the solvent is introduced, and the mix is vortexed and centrifuged once again. The supernatant is then taken for analysis (Fig 12) (Bueno et al., 2013). After extraction, a dispersive solid phase extraction is used to eliminate a great number of matrix interferences (Rejczak & Tuzimski, 2015).

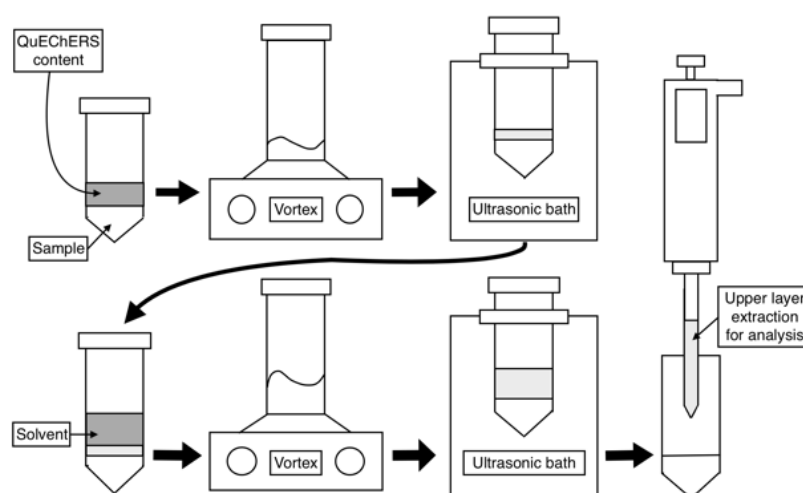


Fig 12: QuEChERS steps (own elaboration)

QuEChERS was originally introduced for pesticides and is commonly used for extraction from marine organisms (Picot-Groz et al., 2014). It is still a manual technique, not yet automated. It can obtain good recovery rates for a great variety of analytes in a short amount of time. It is also cost-effective (Rejczak & Tuzimski, 2015) and consumes a low volume of organic solvent. Extraction and purification steps are needed in order to decrease matrix effect (Picot-Groz et al., 2014). Cunha et al. (2012) uses Dispersive Liquid-Liquid Microextraction (DLLME) after QuEChERS to obtain a better enrichment factor. This technique is robust and suitable for complex samples (Viñas et al., 2014). Solid matrices require adding water to the sample to weaken analyte-matrix interactions (Rejczak & Tuzimski, 2015).

Picot-Groz et al. (2014) applied QuEChERS to extract different UVFs from mussel tissues. Acetonitrile was used as the organic solvent, obtaining recoveries ranging from 90 to 126%. Cunha et al. (2015) employed this technique with fish fillet. The chosen organic solvent was a deionized water and acetonitrile mix and the recoveries ranged from 59 to 115%. Ramos et al. (2019) used QuEChERS with acetonitrile as the organic solvent to extract several UVFs from sewage sludge. The obtained recoveries were from 86 to 122%.

2.2) DETERMINATION TECHNIQUES

After extraction and cleanup, liquid or gas chromatographic methods are mainly used to separate and determine the different emerging pollutants. These methods are combined with different detection systems to be sensitive and selective enough for a correct determination (Ramos et al., 2015). Mass spectrometry (MS) is the preferred detection system due to its high sensitivity and selectivity (Montesdeoca-Esponda et al., 2014), since it can help overcome matrix effect (Sánchez-Brunete et al., 2011).

Liquid chromatography (LC) uses a liquid as mobile phase, while gas chromatography (GC) uses a gas (McNair et al., 2019). GC is adequate for analytes with high volatility and thermal stability. Some UVFs and UVLSs present a high polarity and/or are thermally sensitive, and therefore they need a prior derivatization step to reduce the polarity of the analyte (Pietrogrande et al., 2007; Ramos et al., 2015).

LC (Fig 13) coupled with tandem mass spectrometry (LC-MS/MS), allows to determine a big range of compounds (Gago-Ferrero et al., 2012). Most of UVFs and UVLSs are non-volatile compounds, so LC is commonly used for these analytes (Ramos et al., 2015). Both benzotriazole ultraviolet stabilizers (BUVSs) and benzophenone families of UVFs and UVLSs have been determined using LC-MS in a sediment matrix with the found problematic of matrix effect (Montesdeoca-Esponda et al., 2014).

Ultra-high-performance liquid chromatography (UHPLC) reduces analysis time and solvent usage and improves selectivity and sensitivity compared to traditional LC analysis (Gago-Ferrero et al., 2012). UHPLC is practical to use since it requires less solvent and is quite fast, sensitive and offers both a better resolution and a reduction of matrix effects during MS detection (Ramos et al., 2015).

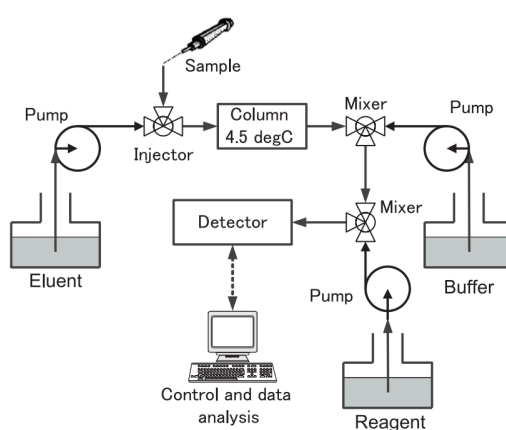


Fig 13: LC system (Hatakeyama, & Akatsuka, 2014)

3) POSSIBILITIES OF IMPLEMENTATION IN MICROPLASTICS

Although the literature regarding the extraction of pollutants from microplastics is not large, there are some examples about the extraction of organic compounds, mainly priority contaminants. Llorca et al. (2020) employed Soxhlet with a n-hexane and dichloromethane solvent mix to extract polychlorinated biphenyls (PCBs) from microplastics. Zhang et al. (2018) also utilized Soxhlet with dichloromethane to extract organophosphorus esters and phthalates, obtaining recoveries from 88 to 103%. Lee et al. (2018) employed Vortex extraction to determine six different hydrophobic organic chemicals (HOC) from microplastics with hexane as organic solvent. Frias (2010) utilized a hexane and acetone mix as the solvent to extract several PAHs, PCBs and DDTs from microplastics with the help of accelerated solvent extraction (ASE).

Among the techniques discussed in the previous section, in this section it will be discussed which of them could potentially be implemented for the extraction of UVFs and UVLSs from microplastics. Aside from the individual advantages and disadvantages that each individual method presents, when working with plastic matrices, temperature is an important factor to take into account. If the temperature applied is too high, the polymer might dissolve or collapse (Vilaplana et al., 2008) so it has to be controlled to avoid the polymer melting (Garrido-López & Tena, 2005). The melting temperature (T_m) can vary depending on the size of the plastic, as well as other variables (Shin et al., 2007). Not many authors delve into the T_m of the different types of microplastics, and those who do obtain different results. In Table 1 we present the melting temperature values from some of these works. The lower values for most of the plastic types are just slightly above 100 °C, so it could be argued that all extraction techniques are technically valid as long as the 100 °C threshold is not crossed.

Table 1: Melting temperature of different types of microplastic material.

Plastic type	T_m	Source
Polyethylene (high or low density) (PE)	102-135 °C/446 °C	Liu et al. (2019)/Dümichen et al. (2017)
Polypropylene (PP)	170 °C/310 °C	
Polystyrene (PS)	103 °C/385 °C	
Polyethylene terephthalate (PET)	404 °C	
Polyamide (PA)	103 °C/394 °C	
Polyvinyl Chloride (PVC)	230-340 °C	Mkhabela, Mishra & Mbianda (2011)
Polymethyl methacrylate (PMMA)	101 °C	Liu et al. (2019)

Regarding the extraction of UVFs and UVLSs, despite the variety of available methodologies from solid matrices, not many works are devoted to microplastic matrices. One of these works is that of Rani et al. (2017), in which several UVLSs were extracted by USE from plastic debris (PE, PP, PET, PC, and acrylic/styrene) found near the coast of Geoje, South Korea. Dichloromethane (4 mL) was the chosen extraction solvent and recoveries for the UVLSs UV 326, UV 327, UV 328, and UV 320 were 116, 96, 88, and 115%, respectively. Extraction time was 30 minutes and the found concentration of UVLSs varied from 0.003 to 82 $\mu\text{g/g}$. Camacho et al. (2019) also took PE and PP samples from beach sediment in different areas from the Canary Islands. Several types of components were extracted, among them the UVFs 2 ethylhexyl 4 dimethylaminobenzoate (EDP), 2-Ethylhexyl p-methoxycinnamate (2EHMC), Holosalate (HS), 3-benzylidenecamphor (BC3) and 4-methylbenzylidene camphor (4MBC). Liquid-solid extraction employing 5 mL of a cyclohexane and ethyl acetate mix as solvent was the utilized extraction technique with a total duration of more than 72 hours. No recovery data was presented. UVF concentration ranged from 0.9 to 2285.8 $\mu\text{g}\cdot\text{g}^{-1}$. Ho & Leung (2019) used vortex extraction with 50 μL methanol to determine benzophenone-3 (BP3), 4MBC, ethylhexyl methoxycinnamate (EHMC) and Octocrylene (OC) from PE and PS plastic matrices that had been artificially added to seawater. Once again, no recovery data was presented. Among the studied techniques, those that have yielded higher recoveries for the extraction of UVLSs and UVFs in past studies are Soxhlet, USE, MAE and MSPD.

Soxhlet is time consuming, labor intensive, requires large solvent volumes, needed pre-concentration and clean-up steps efficiency (Albero et al., 2015; Gago-Ferrero et al., 2011). Therefore, it is not a good option to extract UVFs and UVLSs from microplastic samples.

USE usually performs best between 40 and 60 $^{\circ}\text{C}$ (Zhou et al., 2019; Shirsath, Sonawane & Gogate, 2012; Altemimi et al., 2016; Bimakr et al., 2017), which means that it could be used for any type of plastic. USE presents high enough recoveries, but not as high as other techniques. It is fast, cheap, with high reproducibility and low solvent consumption and safe, but it is not easily automated, and a clean-up step is needed for complex matrices (Chemat et al., 2017; Montesdeoca-Esponda et al., 2014).

USE can be combined with Supercritical fluid extraction (SFE) to eliminate the clean-up step (Chemat et al., 2017). To the best of our knowledge, SFE has not been previously applied in the extraction of UVSs and UVLSs. In this technique, pressure and temperature are above critical values creating a supercritical fluid with values between gas and liquid (Camel et al., 2001). Since SFE preconcentrates the analytes, is clean, simple and safe, and has higher yields, it could be a possible technique to be applied in microplastic samples. Moreover, it can use both polar and non-polar solvents, allowing the extraction of a wide variety of products. Although SFE presents the disadvantage of the equipment being expensive (Arias et al., 2009; Chemat et al., 2017), is a valuable alternative if it is available at lab.

MAE is faster and consumes less organic solvent, but it is not suited for automation and a clean-up step is needed (Kim, Choi & Chung, 2012). Some authors reported better results for this technique than for USE, but it would work better for some plastic types than others. MAE usually performs at 125-140 °C (Arias et al., 2009), so it would not be an adequate choice for PE, PS, PA or PMMA microplastics types, but could be utilized for PP, PET and PVC plastics.

MSPD has the most advantages versus disadvantages since it is low cost, small solvent consumption, environmentally safe and easy to use (Carpinteiro et al., 2012). MSPD doesn't use heat so it could be applied for any type of plastic, but no literature that delves in its application on plastic was found.

Those revised extraction techniques with lower or disparate recoveries are PLE and SPLE, QuEChERS and VE. PLE has a good reproducibility, low solvent consumption, fast pre-treatment, can be automated, presents reduced background noise and is already commonly used as an extraction technique (Gago-Ferrero et al., 2012; Viñas et al., 2014), but it is also expensive and has a low selectivity and low overall efficiency. SPLE takes away the need for an additional clean-up step, but recoveries are still disparate depending on the characteristics of the analytes. PLE utilizes temperatures between 100 °C (Gago-Ferrero, 2012; Combi, 2016; Molins-Delgado, 2018) and 160 °C (Volpe, 2017; Tsui, 2015). Therefore, only if the choice of temperature is 100 °C, PLE could be theoretically used for all types of plastic.

QuEChERS is fast, cheap, has a low solvent consumption and is suitable for complex matrices (Rejczak & Tuzimski, 2015), but it is not yet automated, and extraction and purification steps are needed (Picot-Groz et al., 2014). It is not temperature dependent so it could be used for any type of plastic. Since this technique is employed to reduce matrix interference, which are common in plastic matrices, it could be useful for extraction from these matrices (Aghvami et al., 2018).

VE has a low solvent consumption, is environmentally friendly, cheap and has good extraction efficiencies (Martin, 2017; Jimenez-Díaz, 2013). As VE doesn't use heat, it could be applied for any type of plastic, but not enough literature exists on its effectiveness on plastic matrices.

Table 2: Comparison of all mentioned techniques, their adequacy for plastic matrices and their recoveries

Technique	Temperature is adequate for all plastic types	High recoveries
Soxhlet	✓	✓
Vortex extraction (VE)	✓	X
Ultrasonic extraction (USE)	✓	✓
Microwave assisted extraction (MAE)	X	✓
Pressurized liquid extraction (PLE)	✓	X
Matrix solid phase dispersion (MSPD)	✓	✓
Quick, Easy, Effective, Rugged and Safe (QuEChERS)	✓	X

4) CONCLUSIONS

To the microplastic contamination problem we must add the issue of adsorbed contaminants on them. These adsorbed contaminants can stack up and cause physical, chemical and biological internal damage and negative impacts on the metabolism of organisms.

Contaminants are also released into the ocean after the microplastic weathers. Therefore, it is necessary to procure extraction techniques that allow to extract UVFs and UVLSs from microplastics as successfully as possible for a correct quantification and classification of these adsorbed pollutants.

After comparing the advantages and disadvantages of each extraction technique, as well as their effectiveness on plastic matrices, we can conclude that USE and MSPD are the ones that seem to be the overall better suited for the extraction of UVFs and UVLSs from microplastic surfaces, but further research for MSPD is needed. USE could be combined with a preconcentration/clean-up technique like SFE to decrease the amount of labor needed.

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ANNEX I. Procedures used for the extraction of UVFs and UVSs from solid environmental samples.

Compound	Matrix	Extraction technique	LOD (ng·g ⁻¹ dw)	LOQ(ng·g ⁻¹ dw)	Eluent/extraction agent	Recovery (%)	Reference
4MBC	Holothuria	Soxhlet	-	-	Dichloromethane and hexane mix	93	Nakata et al. (2009)
UV-320						114	
UV-326						122	
UV-327						114	
UV-328						110	
UV-320	Porpoise blubber	Soxhlet	-	-	Dichloromethane and hexane mix	114 ± 12	Nakata et al. (2010)
UV-327						114 ± 14	
UV-328						110 ± 8.8	
UV-320	Mussel tissues	Soxhlet	-	-	Dichloromethane and hexane mix	114 ± 12	Nakata et al. (2012)
UV-326						122 ± 11	
UV-327						114 ± 14	
UV-328						110 ± 8.8	
BP3	Sand	VE	0.041	0.140	Acetone	106	Tarazona et al. (2014)
IMC			0.041	0.140		86	
4MBC			0.029	0.096		92	
OC			0.035	0.117		95	
EHMC			0.018	0.061		82	
OD-PABA			0.046	0.150		84	
EHS			0.038	0.130		80	
HMS			0.053	0.180		9	
BP3			Sediment	VE + SPE		0.43	
4MBC	0.09				58		
OC	0.09				76		

EHMC			7.55			76	
OD-PABA			0.16			63	
BP3	Sand	VE	-	3.2	Ethyl acetate	86-121	Vila et al. (2018)
IMC				0.42		96-106	
4MBC				4.9		99-100	
OC				0.33		103-112	
EHMC				1.6		100-112	
OD-PABA				0.30		90-106	
EHS				0.16		92-103	
HMS				2.3		91-95	
BP	Holothuria	VE	-	48.9	Acetonitrile	98-110	Martín et al. (2017)
BP2				21.4		86-111	
BP3				25.1		86-100	
BP6				25.2		80-101	
BP8				45.8		88-100	
4HB				24.8		98-103	
BP3	Coral	VE	0.50	-	Acetone and n-hexane mix	86	Tsui et al. (2017)
4MBC tissues			0.11			83	
OC and			0.12			65	
EHMC skeleton			7.06			64	
OD-PABA			0.22			61	
BP3	Soil,	USE	-	0.003-0.5	Methanol	55-118	Peng et al. (2017)
4MBC Sediment							
OC							
EHMC							
OD-PABA							
AVO							
UV-531							

UV-P							
UV-329							
UV-326							
UV-234							
UV-328							
UV-327							
4HB	Sediment	USE	0.07-0.23	0.23-0.76	Ethyl acetate and methanol mix	90-104	Sanchez-Brunete et al. (2011)
DHB			0.10-0.21	0.33-0.70			
HMB			0.10-0.28	0.33-0.90			
DHMB			0.07-0.14	0.23-0.46			
DHDMB			0.09-0.15	0.30-0.50			
EHS			0.08-0.11	0.26-0.36			
HMS			0.07-0.12	0.23-0.40			
BP3	Fish fillet	USE	-	0.08	Methanol	88.3-102.0,	Peng et al. (2015)
4MBC				0.2		86.0-102.4,	
OC				0.1		97.8-115.6,	
EHMC				10		98.3-109.5,	
OD-PABA				0.005		85.5-102.3,	
BM-DBM				1		41.1-82.8	
BP3	Fish belly	USE	-	-	Methanol	93.6	Peng et al. (2015)
4MBC						80.8	
OC						87.9	
EHMC						81.1	
OD-PABA						64.2	
BM-DBM						58.4	
4MBC	Dolphin	USE	1.50-25	1.90-75	Dichloromethane and hexane mix	60-115	Alonso et al. (2015)
OC	liver						
EHMC							

OD-PABA							
BP3	Fish fillet	USE	-	0.003-1.0	Dichloromethane and ethyl acetate mix	70-120	Peng et al. (2017b)
4MBC							
OC							
EHMC							
OD-PABA							
BM-DBM							
BP3	Fish	UAE + SPE	0.28	1.38	Aqueous acetic acid and methanol mix	87.2 ± 33.4	Fabunmi et al. (2020)
UV-P	Seaweed	MAE	4.98	7.38	Methanol	50-74	Pacheco-Juárez et al. (2019)
UV-326			4.58	15.3		57-89	
UV-327			2.60	8.66		67-92	
UV-328			1.79	5.96		63-87	
UV-329			3.14	10.5		61-91	
UV-360			2.25	7.49		64-70	
4DHB	Sediment	PLE	2.8	9.3	Methanol and methanol/water mix	80-125 (58 DBH)	Gago-Ferrero et al. (2011)
4HB			2.4	8.0			
DBH			15.5	52			
BP3			0.8	2.7			
4MBC			8.0	27			
OC			2.2	7.3			
EHMC			1.6	5.3			
OD-PABA			0.5	0.8			
BP3	Sediment	PLE	0.71	-	Methanol and ethyl acetate mix	83	Tsui et al. (2015)
IMC			2.10			82	
4MBC			7.33			91	
OC			0.58			89	
EHMC			0.51			100	

OD-PABA			0.61			94	
EHS			4.26			84	
HMS			7.55			75	
BM-DBM			3.94			78	
BP3	Sediment	PLE	0.003- 0.54	-	Dichloromethane	70-100	Combi et al. (2016)
OC							
EHMC							
BP3	Sediment	PLE	0.009	0.029	Dichloromethane	61-91	Pintado-Herrera et al.
4MBC			0.221	0.737		53-91	(2016)
OC			0.024	0.080		92-120	
EHMC			0.039	0.129		86-134	
OD-PABA			0.408	1.361		85-138	
EHS			0.065	0.216		68-94	
HMS			0.022	0.073		70-130	
BP3	Sediment	PLE	0.009	0.029	Dichloromethane	61-91	Pintado-Herrera et al.
4MBC			0.221	0.737		53-91	(2017)
OC			0.024	0.080		92-120	
EHMC			0.039	0.129		86-134	
EHS			0.065	0.216		68-94	
HMS			0.022	0.073		70-130	
4MBC	Sediment	PLE	-	0.00036	Ethyl acetate and hexane mix	74-102	Volpe et al. (2017)
OD-PABA				0.00040		66-77	
OC	Dolphin liver	PLE	23	75	Dichloromethane and hexane mix	x	Gago-Ferrero et al. (2013c)
BP3	Clam	PLE	-	6.6	Water and isopropanol mix	124	Emnet et al. (2015)
4MBC	tissues			8.0		119	
EHMC				4.8		95	

BP				2.0		124	
BP3	Fish fillet	PLE	0.93	3.20	Ethyl acetate and dichloromethane mix	107	Molins-Delgado et al. (2018)
4MBC			0.39	1.30		95	
OC			0.39	1.30		75	
EHMC			0.33	1.10		66	
OD-PABA			1.77	5.90		42	
BP3	Fish tissues	SPLE	-	20	Dichloromethane and hexane mix	75	Langford et al. (2015)
OC				20		75	
EHMC				30		85	
OD-PABA				20		51	
BP3	Sediment	SPLE	0.4	1.3	Methanol	125	Baron et al. (2013)
4MBC			1.1	3.6		89	
OC			9.9	33		85	
EHMC			4.1	14		90	
OD-PABA			0.7	2.5		120	
BP3	Sediment	SPLE	5	10	Dichloromethane and hexane mix	72	Langford et al. (2015)
OC			7	5		102	
EHMC			-	5		98	
OD-PABA			4	4		81	
BP3	Fish fillet	MSPD	9	28	Acetonitrile	97-99	Negreira et al. (2013)
IMC			3	10		97-104	
4MBC			4	12		97-101	
OC			1	4		99-106	
EHMC			2	6		94-98	
OD-PABA			4	12		86-96	
EHS			6	18		70-76	
HMS			9	28		84-93	

BP3	Mussel	MSPD	-	-	Acetonitrile	89-96	Negreira et al. (2013)
IMC	tissues					94-107	
4MBC						90-101	
OC						96-112	
EHMC						97-111	
OD-PABA						70-101	
EHS						80-97	
HMS						80-85	
BP3	Striped	MSPD	0.03	0.1	Acetonitrile	90	Tsai et al. (2014)
EHS	bass fillet		0.02	0.05		84	
HMS			0.02	0.05		98	
BP3	Cod fillet	MSPD	-	-	Acetonitrile	75	Tsai et al. (2014)
EHS						88	
HMS						76	
BP3	Salmon	MSPD	-	-	Acetonitrile	96	Tsai et al. (2014)
EHS	fillet					77	
HMS						78	
BP3	Mussel	MSPD	-	0.2-3	Acetonitrile	90-110	Vidal-Liñán et al. (2017)
BP4	tissues						
4MBC							
OC							
OD-PABA							
EHS							
EHS	Cosmetics	MSPD	-	-	Acetone	109 ± 11	Celeiro et al. (2019)
BS						110 ± 3	
HMS						109 ± 6	
BP3						106 ± 6	
IMC						98.4 ± 5.8	
4MBC						97.9 ± 6.7	

MA						106 ± 5	
ETO						97.9 ± 7.3	
EH-PABA						99.0 ± 4.3	
2EHMC						99.5 ± 4.1	
OC						104 ± 4	
BMDM						111 ± 2	
DHHB						108 ± 3	
DRT						98.7 ± 2.3	
BP	Placental	MSPD	0.1	0.3	Ethyl acetate	97-104	Vela-Soria et al.
BP2	tissue		0.1	0.3		100-104	(2014)
BP3			0.1	0.2		100-104	
BP6			0.1	0.4		97-103	
BP8			0.1	0.4		103-106	
OC	Mussel	QuEChERS	5	5	Acetonitrile	99-126	Picot Groz et al.
EHMC	tissues		1	5		93-106	(2014)
OD-PABA			2.5	0		90-93	
BP3	Fish fillet	QuEChERS	3	20	Deionized water and acetonitrile	72-83	Cunha et al. (2015)
IMC			6	20		89-95	
4MBC			2	5		79-86	
OC			23	100		75-76	
EHMC			3	20		93-115	
OD-PABA			2	5		69-79	
EHS			2	5		83-91	
HMS			6	20		76-82	
DHHB			-	-		59-62	
BP3	Fish fillet	QuEChERS	0.5	2	Deionized water and acetonitrile	72-77	Cunha et al. (2018)
IMC			1	5		68-77	
4MBC			2	5		57-88	

OC			3	10		77-79	
EHMC			0.5	1		90-107	
OD-PABA			2	5		61	
EHS			2	5		70-82	
HMS			2	5		92-108	
DHHB			7	20		82	
BP	Sludge	QuEChERS	26	86	Acetonitrile and acetonitrile	100 ± 2	Ramos et al. (2019)
4MBC			59	196		88 ± 8	
EDP			31	102		86 ± 3	
EHMC			5	18		122 ± 3	
OC			6	19		94 ± 2	
DTS			2	7		118 ± 2	

Homosalate (HS), 4,4'-Dihydroxybenzophenone (4DHB), 4-hydroxybenzophenone (4HB), 2,4-dihydroxybenzophenone (DBH), benzophenone (BP), benzophenone-2 (BP2), benzophenone-3 (BP3), benzophenone-4 (BP4), benzophenone-6 (BP6), benzophenone-8 (BP8), methylbenzylidene camphor (MBC), 4-methylbenzylidene camphor (4MBC), octocrylene (OC), ethylhexyl methoxycinnamate (EHMC), 2-Ethylhexyl p-methoxycinnamate (2EHMC), Ethyl-PABA (Et-PABA), ethylhexyl dimethyl PABA (OD-PABA), 2,2' -Dihydroxy-4-methoxybenzophenone (DHMB), 2,2- dihydroxy-4,4-dimethoxybenzophenone (DHDMB), 2-hydroxy-4-methoxybenzophenone (HMB), ethylhexyl salicylate (EHS), 3,3,5- trimethylcyclohexyl salicylate (HMS), methylene bis-benzotriazolyl tetramethylbutylphenol (MBP), isoamyl p-methoxycinnamate (IMC), diethylamino hydroxybenzoyl hexyl benzoate (DHHB), butyl methoxydibenzoylmethane (BM-DBM), 3-benzylidenecamphor (BC3), 2 ethylhexyl 4 dimethylaminobenzoate (EDP), drometrizole trisiloxane (DTS), 2-Ethylhexyl salicylate (ES), Benzyl salicylate (BS), Methyl anthranilate (MA), Etocrylene (ETO), Ethylhexyl-p-aminobenzoic acid (EH-PABA), Avobenzone (BMDM), Drometrizole trisiloxane (DRT)

Liquid-solid (LS), microwaved assisted extraction (MAE), dispersive liquid-liquid microextraction (DLLME), vortex extraction (VE), pressurized liquid extraction (PLE), selective pressurized liquid extraction (SPLE), ultrasonic-assisted extraction (USE), Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS), matrix solid phase dispersion (MSPD), Headspace Sorptive Extraction (HSSE), accelerated solvent extraction (ASE), solid phase microextraction (SPME), ultrasound-assisted extraction (UAE).